

Separation of ¹⁵²⁺¹⁵⁴Eu, ⁹⁰Sr from radioactive waste effluent using liquid–liquid extraction by polyglycerol phthalate

M. F. Attallah¹ \cdot S. E. Rizk² \cdot S. A. Shady³

Received: 5 October 2017/Revised: 30 November 2017/Accepted: 4 December 2017/Published online: 30 April 2018 © Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Chinese Nuclear Society, Science Press China and Springer Nature Singapore Pte Ltd. 2018

Abstract A new polyglycerol phthalate extractant was prepared and characterized using Fourier transform infrared spectroscopy, proton nuclear magnetic resonance (¹H NMR) spectroscopy, and thermogravimetric analysis. A preliminary study of the extraction of long-lived (⁹⁰Sr and ¹⁵²⁺¹⁵⁴Eu) and short-lived (⁹⁰Y) radionuclides by polyglycerol phthalate was performed. The influence of different diluents, concentration of the acid, type of acid, and various interfering ions was explored. The stripping of ¹⁵²⁺¹⁵⁴Eu radionuclide was studied by using different acid solutions, and it was found that sulfuric acid was the ideal acid for this purpose. Furthermore, ¹⁵²⁺¹⁵⁴Eu was extracted from the fission products (⁹⁰Sr) and the extraction% of ⁹⁰Sr was found to improve in the presence of interfering ions.

Keywords Liquid–liquid extraction · Long-lived radioisotopes · Polyglycerol phthalate · Nuclear waste

☑ M. F. Attallah dr.m.f.attallah@gmail.com; Mohamed.attallah@eaea.org.eg

- ¹ Analytical Chemistry and Control Department, Hot Laboratories Center, Atomic Energy Authority of Egypt, Abu Zaabal, Cairo 13759, Egypt
- ² Chemistry of Nuclear Fuel Department, Hot Laboratories Center, Atomic Energy Authority of Egypt, Abu Zaabal, Cairo 13759, Egypt
- ³ Technology of Nuclear Fuel Department, Hot Laboratories Center, Atomic Energy Authority of Egypt, Abu Zaabal, Cairo 13759, Egypt

1 Introduction

Glycerol is the by-product of the esterification of vegetable oils and is also produced during the preparation of bio-diesel. It has been utilized in diverse fields such as cosmetics, pharmaceutical industry, and for the manufacturing of resins. Its demand has also increased owing to its use in dental care (tooth paste) and food industry [1, 2]. Alkyd resins are typically produced by the polyesterification of a polybasic acid with a polyhydric alcohol, which may be modified with fatty acids or drying oil [3–5].

The wide spectrum of properties of all alkyd resins is broadened by their use with a variety of reactive chemicals and other resinous materials. In fact, alkyd resins have the distinction of participating in more of what might be termed as "polymeric mergers" than any other single class of resins [3]. This feature has been utilized for different applications such as in furniture and architectural coatings, product finishes, and automotive refinishing primers. Polyesters of multi-functional phenols and phthalic acid are also used for the production of gas separation membranes with good selectivity coefficients [2]. In addition, several new materials have been produced by using polyesters synthesized by reacting glycerol and phthalic acid for their use in desalination membranes and as modifiers for polyurethane foams.

To the best of our knowledge, there are only a limited number of reports that describe the application of alkyd resins for the extraction and separation of radioisotopes from radioactive waste effluents. It is common knowledge that a large number of radionuclides are generated in nuclear reactors and ultimately end up in their waste effluents. The radioactive effluents are monitored carefully, and significant efforts are undertaken to avoid the release of the effluent radionuclides into the environment. Consequently, there is a continuous search for processes and technologies in the research community for the safe and efficient treatment and conditioning of liquid radioactive waste. It is well known that the 152 Eu ($t_{1/2} = 13.5$ years), ¹⁵⁴Eu ($t_{1/2} = 8.6$ years), and ⁹⁰Sr ($t_{1/2} = 28.8$ years) radionuclides are the major fission products in the nuclear waste solution. Their separation from the liquid waste is crucial from the viewpoint of human and environmental protection. Solid phase extraction, including ion exchange and adsorption [6–9], precipitation [10], membrane technique [11], and solvent extraction [12] are some of the techniques that have been reported for the removal of radionuclides from the radioactive liquid waste. Previously, Clark et al. have studied the adsorption of europium onto sandy soil [13]. Extraction of Am(III) and Eu(III) from the NO₃⁻, ClO_4^- , SCN^- , and $NO_3^- + ClO_4^-$ media with trioctylphosphine oxide (TOPO) in xylene has also been investigated [14]. Calix [4] arene phosphine oxides have been used for the extraction of Am(III) and Eu(III) from their nitric acid solution [15]. The sorptive removal of Sr^{2+} and I⁻ from an aqueous solution has been carried out using nanofibers of sodium niobate. In this report, it was shown that sodium niobate, with its negatively charged layers and readily exchangeable sodium ions between the lavers, could efficiently remove radioactive Sr^{2+} [16]. The removal of radioisotopes such as ⁶⁰Co, ⁹⁰Sr, and ¹³⁷Cs has been performed with plasticized membranes using organophosphorus acid compounds (di-ethyl-hexyl phosphoric acid (DEHPA), Cyanex 272, Cyanex 301, and Cyanex 302) [17].

The application of polyglycerol phthalate alkyd resin for the extraction of U(VI), Th(IV), and Eu(III) was studied by Shady and Abou-Mesalam [18]. The extraction percentages of the ions U(VI), Th(IV), and Eu(III) using the alkyd resin were found to be 25.8, 22.3, and 0.06%, respectively. In the present work, we have modified the previously reported synthetic method of the alkyd resin of polyglycerol phthalate. The modified method is based on the addition of 10% of toluene di-isocyanate, which improved the extraction properties of the resin toward the radionuclides to be utilized the polyglycerol phthalate as solvent extractant. The polyglycerol phthalate resin was characterized using FTIR, ¹H NMR, and thermogravimetric analyses (TGA). Thus, a novel application of alkyd materials as an organic extractant has been explored. The distribution coefficient and extraction percentages of the radioelements ¹⁵²⁺¹⁵⁴Eu, ⁹⁰Sr, and ⁹⁰Y from aqueous media were determined. The influence of different parameters on the extraction process and separation factor in the extraction system was studied. A method of separation of the radioisotopes under study (152+154 Eu and 90 Sr) was also developed. Furthermore, the effect of the concentrations of mineral acids and ammonia on the stripping of $^{152+154}$ Eu has been investigated.

2 Experiments

2.1 Chemicals and reagents

All chemicals were of analytical grade and used as received without further purification. Sunflower oil and tall fatty acid were obtained from El-Naser for Oils and Soap Company at Cairo, Egypt. Phthalic anhydride and pentaerythritol were procured from BDH and Merck, respectively. Glycerol was purchased from de Haen. HCl, HNO₃, and H₂SO₄ were acquired from Prolabo, and hydrogen peroxide was purchased from Merck. The radioactive tracers ¹⁵²⁺¹⁵⁴Eu and ⁹⁰Sr were obtained from the second Egyptian Nuclear Reactor (ERR-2) and Amersham, respectively.

2.2 Synthesis and characterization

2.2.1 Polycondensation process

It is common knowledge that polyesters are produced by a reaction between an alcohol and an acid, as shown below:

$RCOOH + HOR' \leftrightarrow RCOOR' + H_2O$

Furthermore, the structure of the reaction products depends on the ratio and concentration of the monomers [19]. In practice, a monobasic acid is added to the reaction to modify the product by blocking some of hydroxyl groups of glycerol. This results in a soluble resin instead of an invisible cross-linked mass that would have been produced if all the hydroxyl groups had reacted with phthalic acid.

2.2.2 Synthesis of the extractant

Polyglycerol phthalate was synthesized by a condensation reaction between phthalic anhydride and glycerol mixed with pentaerythritol, as reported previously [18, 20]. In a three-neck flask, 50% of sunflower oil was added to a mixture of 3 g of tall oil fatty acid, 10% glycerol, 7% pentaerythritol, and 2 g of lead oxide as a catalyst. The mixture was then heated to 250 °C. The formation of monoglycerides was detected by the addition of methanol to the test sample (2:1 volume ratio). A clear solution indicated the successful formation of monoglycerides. Subsequently, the temperature was lowered to 180 °C and the flask was connected with a separator and a Rad condenser using an azeotropic mixture. Next, 10% of toluene di-isocyanate, 45 g of glycerol, and 30% of phthalic anhydride were added. The mixture was heated again at 250 °C with xylene as an azeotropic mixture up to a viscosity of 2 poise and an acid value of ~ 8 to 10. The acid value and viscosity were measured at 25 °C [18, 20] according to the protocol in ASTM D1980-87 and ASTM D1545-89, respectively. There are a number of calculations that must be done before starting the above-mentioned reaction from the view point of safety in the laboratory and economic evaluation. The safety factor (*S*) and yield (*Y*) of the reaction were determined to be 1.14 and 89%, respectively. Based on these calculations, the yield of the product was considered to be good and it was also concluded that this reaction could be safely performed in the laboratory.

2.2.3 Characterization of the synthetic extractant

The synthetic extractant was characterized by different methods. The IR spectrum of the sample under study was obtained using an FTIR spectrometer (4100 Jasco, Japan). The IR spectrum of polyglycerol phthalate sample was scanned over the wavenumber range of 400–4000 cm⁻¹. The ¹H NMR spectrum was recorded on a Varian Mercury VX-300 NMR spectrometer at 300 MHz in dimethyl sulphoxide (DMSO) as the solvent. TGA and differential thermal analysis (DTA) curves of the synthetic extractant were obtained by heating the sample at a rate of 15 °C min⁻¹ using a Shimadzu DTA-50 thermal analyzer.

2.3 Extraction experiments

Batch experiments were carried out by shaking equal volumes of the synthetic extractant with the aqueous phase containing the desired radioisotope under study for 2 h in stoppered glass bottles using a thermostat shaking water bath adjusted at a temperature of 25 ± 1 °C. Aliquots from both phases were analyzed after phase separation by centrifugation, and the distribution ratio was calculated. The activity of 152+154Eu in aqueous and organic phase was measured using a high-resolution (7.5%) NaI(Tl) scintillation detector (Model 802-3X3, Canberra, USA). Radiotracers of ⁹⁰Sr and/or ⁹⁰Y were measured using a liquid scintillation counter (TRI-CARB model, 2700TR series, PerkinElmer). In an extraction experiment, ⁹⁰Y was separated from its parent ⁹⁰Sr (under equilibrium conditions) following a reported method [21]. The distribution ratio (D) was calculated as the ratio of the concentration of the radionuclide ions in the organic phase to that in the aqueous phase. In other words, D was calculated by dividing the counts per minute in the organic phase over that of the aqueous phase.

$$D = (C_{\rm O}/C_{\rm A}),\tag{1}$$

where $C_{\rm O}$ and $C_{\rm A}$ are the net counts in the organic and

aqueous phase, respectively, after extraction. The percentage extraction (% E) was calculated using the following relation:

$$\% E = 100D / (D+1). \tag{2}$$

Stripping experiments were carried out by shaking 10 mL of the organic phase loaded with the extracted radionuclide and 10 mL of the aqueous stripping solution under study. The activity concentration of the radionuclide in the aqueous phase was determined, and the stripping percent (%Strip) was calculated using the following relation:

$$\% \text{Strip} = (C_{\text{S}}/C_{\text{O}}) \times 100, \tag{3}$$

where $C_{\rm S}$ refers to the concentration of the stripped radionuclide in the aqueous phase after stripping.

3 Results and discussion

3.1 Characterization of the synthetic extractant

IR spectroscopy was used for the characterization of the molecular structure of the modified polyglycerol phthalate (Fig. 1). The absorption due to the $-CH_2$ and -CH groups of the esterified and unreacted glycerol appears as twin peaks at 2925 and 2855 cm⁻¹, which are typically associated with the C–H stretching of aliphatic compounds. The C–H stretching frequency of the benzene ring of phthalic acid was identified by the absorption at 3007 cm⁻¹. The absence of an absorption peak at 1711 cm⁻¹ (assigned to – COOH dimers) indicated that the esterification reaction was almost complete. The absorption between 3300 and 3000 cm⁻¹ was attributed to adsorbed water and unreacted –OH groups of glycerol. The aromatic C=C stretching of phthalic acid was identified at 1600 cm⁻¹, while the C=O stretching of the esterified phthalic acid was observed near



Fig. 1 IR spectrum of polyglycerol phthalate

1737 cm⁻¹. The band near 1070 cm⁻¹ corresponded to a CH₂ group in a primary alcohol (CH₂–OH), and those near 1458 and 1535 cm⁻¹ were assigned to CH₂ group vibration [22–24]. The bands in the range of 3331-2800 cm⁻¹ were attributed to the N–H stretching [20, 22] and that observed at 1225 cm⁻¹ corresponded to the NHC=O group [22]. The reaction between –NCO and –OH is confirmed [20] and indicated the successful synthesis of polyglycerol phthalate.

TGA and DTA curves of the polyglycerol phthalate extractant are illustrated in Fig. 2. The TGA curve indicates that the loss of weight upon heating occurred in three stages. The first weight loss of 34.77% took place over the temperature range of 20-209 °C and corresponded to the loss of water from the synthetic extractant. The second weight loss of 11.5% was observed from 210 to 329 °C. In the third stage, a complete decomposition, i.e., 99% weight loss, of the synthetic polyglycerol phthalate extractant occurred at ~ 450 °C. The DTA curve shows that the endothermic peak observed at 105 °C was due to the removal of free water molecules and that at 267 °C could be attributed to the dehydration of interstitial water molecules, which were the by-products of the condensation reaction of -OH groups [6]. The endothermic peak at 436 °C was attributed to CO₂ gas release as a result of the decarboxylation of polyester molecules and the complete decomposition of the synthetic polyglycerol phthalate.

The NMR spectrum provides valuable information about the number of chemically distinct types of protons in an organic molecule. The area under each peak is proportional to the number of hydrogens generating that peak. Thus, the NMR spectrum can not only distinguish how many different types of protons a molecule has, but it can also reveal how many of each different type are contained within the molecule. There are a number of different types of protons of the synthetic polyglycerol phthalate resin. The peaks of NMR are listed in Fig. 3. The peak at



Fig. 2 Thermal analysis of polyglycerol phthalate



Fig. 3 ¹H NMR spectrum of synthetic polyglycerol phthalate

2.0 ppm, which integrated for three protons, corresponded to the methyl protons. Aromatic protons characteristically resonate in the range of 7-8 ppm. The aromatic CH-OCOR moiety was identified by the peaks in the range of 6.8-7.5 ppm, while the peaks corresponding to the aliphatic CH-OCOR moiety appeared at 3.3 and 5.18 ppm. In addition, the peak at 5.1 ppm was characteristic of a free alkyl-OH group that was left unreacted during the polymerization reaction. The peaks in the range of 2.0-2.5 ppm are assigned to the aliphatic CH-COOR protons. The chemical shifts of CH₃ groups and the CH₂ and CH groups of the modified polyglycerol phthalate were observed at 0.78-1.02 ppm and 1.1-1.8 ppm, respectively. The peaks at 2.1 and 7.8 ppm could be assigned to the NH-CO proton [22]. Chemical shifts in ¹H NMR spectra are usually reported relative to the peak position of tetramethylsilane (TMS) added to the sample as an internal reference. Typical chemical shift of DMSO as a solvent is 1.39 ppm. No peaks were observed in the range of 10-13 ppm, which indicated that the resin was devoid of COOH moieties (i.e., it was acid-free). Thus, the IR and ¹H NMR spectra confirmed the formation of the polyglycerol phthalate extractant.

3.2 Extraction study of ¹⁵²⁺¹⁵⁴Eu and ⁹⁰Sr using polyglycerol phthalate

The effect of different parameters on the extraction of $^{152+154}$ Eu(III), 90 Sr(II), and 90 Y(III) ions with polyglycerol phthalate was investigated to gain an insight into the extraction mechanism.

3.2.1 Influence of pH

The effect of different pH, which was varied in the range of 1–7.5, on the extraction of Eu(III), Sr(II), and Y(III) by polyglycerol phthalate was studied by dissolving the ions and the resin in white spirit in the ratio of 1:2. The obtained data indicated that the increase in the pH of the solution led to an increase in the metal extraction up to its maximum at pH 4 and then remained constant with a further increase in pH, as shown in Fig. 4a. The results are presented in Fig. 4b, implying that one proton is probably liberated during the extraction of all investigated metal ions. The unreacted OH and/or COOH groups on the synthetic resin might be involved in the extraction of the radioisotopes by ion exchange.

These results also demonstrate the improvement in the extraction of Eu(III) using synthetic polyglycerol phthalate as compared to the previous study [18], wherein extraction percentages of 5.8, 22.3, and 0.06% have been reported for U(VI), Th(IV), and Eu(III) ions, respectively. Therefore, the significant enhancement in the extraction of Eu(III) in this study might be attributed to the modification of the prepared material by toluene di-isocyanate. It is revealed not only that the new NH functional group replaced the radioactive ions with H^+ , but that the lone pair of electrons on the nitrogen (a donor atom) also increased the possibility of extraction of the radioisotope.



3.2.2 Influence of the extractant-to-diluent ratio

The effect of the extractant–diluent ratio on the extraction of $^{152+154}$ Eu(III) was studied by varying this ratio from 0:1 to 2:1, and the results are shown in Fig. 5. The results indicated that the extraction percentage increased with the increasing amount of the extractant and reached its maximum at a value of 0.3:1. The extraction percentage remained constant with a further increase in the extractantto-diluent ratio.

3.2.3 Influence of different diluents

The effect of diluents on the extraction of ¹⁵²⁺¹⁵⁴Eu(III) with organic-to-aqueous (O:A) phase ratio = 1 and extractant-diluent = 0.3:1 was investigated by using several different aromatic and aliphatic diluents such as methyl isobutyl ketone (MIBK), toluene, chloroform, kerosene, white spirit, and o-xylene. The obtained results shown in Fig. 6 indicate that the extraction of Eu was quite high when chloroform, toluene, and o-xylene were used as diluents. The extraction ability of the diluents decreased in the following order: chloroform > xylene \ge toluene > white spirit > kerosene > MIBK. This trend can be attributed to the dipole moment (μ) and dielectric constants of the diluents, as summarized in Table 1. The dipole moment is an indicator of solvent polarity, and a high dipole moment corresponded to the high extraction% of Eu(III) for all diluents except MIBK. The lowest E% achieved by using MIBK was explained by the highest dielectric constant of this diluent. Owing to its



Fig. 4 Effect of pH on the extraction of ${}^{152+154}$ Eu(III), 90 Sr(II), and 90 Y(III) at phase ratio (O/A) = 1. Shaking time = 2 h, polyglycerol phthalate:toluene = 0.3:1, temperature = 25 ± 1 °C

Fig. 5 Effect of extractant concentration on the extraction of $^{152+154}\text{Eu}(\text{III})$ from aqueous solution at O/A = 1. Shaking time = 2 h at 25 \pm 1 °C



Fig. 6 Effect of different diluents on $^{152+154}$ Eu(III) extraction at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:diluent = 0.3:1, $25 \pm 1 \text{ °C}$

 Table 1 Physical properties of aliphatic and aromatic diluent on extraction of Eu(III)

Diluent	3	μ	%E
Chloroform	4.81	1.04	70.14
O-Xylene	2.56	0.62	67.96
Toluene	2.38	0.375	67.53
White spirit	NR	NR	53.77
Kerosene	2.002	0	49.12
MIBK	13.11	2.8	23.63

%*E* extraction percentage of Eu(III); μ dipole moment; ε dielectric constant; *NR* not reported

economic advantage and lower toxicity than chloroform, toluene was selected as the preferred diluent for all further experiments.

3.3 Application on simulated radioactive waste

3.3.1 Influence of feed acidity

The effect of acidity on the extraction of $^{152+154}$ Eu and 90 Sr/ 90 Y using polyglycerol phthalate was studied by using different concentrations of different acids (HNO₃ and HCl) as shown in Figs. 7 and 8. The obtained results indicated that the increase in the acidity decreased the extraction of the investigated metals. It was also evident that the extraction of 90 Sr/ 90 Y was extremely low in comparison with that of $^{152+154}$ Eu. Thus, this method is a very promising strategy to conduct an efficient separation between $^{152+154}$ Eu and 90 Sr/ 90 Y.



Fig. 7 Effect of acid concentration on the extraction of $^{152+154}$ Eu(III) at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:-toluene = 0.3:1, 25 ± 1 °C



Fig. 8 Effect of acid concentration on the extraction of 90 Sr/ 90 Y at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:toluene = 0.3:1, 25 ± 1 °C

3.3.2 Influence of interfering cations

The influence of foreign cations on the extraction of $^{152+154}$ Eu(III) with polyglycerol phthalate was investigated by using different concentrations of NaNO₃, KNO₃, and CaNO₃ solutions (Fig. 9). It was found that the extraction of $^{152+154}$ Eu(III) with polyglycerol phthalate increased in the presence of calcium and sodium cations and decreased in the presence of potassium cations. It is well known that the different cations in an aqueous solution compete for interaction with the extractant and the radii of hydration are K⁺ < Na⁺ < Ca²⁺, respectively [25, 26]. As indicated by the competition principle, K⁺ has a higher tendency for complexation with the extractant and blocks its functional groups, leading to a reduced extraction of $^{152+154}$ Eu(III). The same behavior was also observed in the case of the extraction of 90 Sr, as shown in Fig. 10.





Fig. 9 Effect of cation concentration on the extraction of $^{152+154}$ Eu(III) at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:toluene = 0.3:1, 25 ± 1 °C



Fig. 10 Effect of cation concentration on the extraction of 90 Sr/ 90 Y at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:toluene = 0.3:1, 25 ± 1 °C

3.3.3 Separation between $^{125+154}Eu$ and $^{90}Sr/^{90}Y$

The feasibility of ${}^{152+154}$ Eu(III) separating from 90 Sr(II)/ 90 Y(III) can be evaluated in terms of the separation factor (SF), which is given for ${}^{152+154}$ Eu(III) and 90 Sr(II) by the following expression:

$$SF_{(Eu/Sr)} = D_{Eu}/D_{Sr}.$$
(4)

The variation of the SF as a function of the acid concentration and foreign ions at a constant extractant concentration is given in Figs. 11 and 12. The results indicated that the SF increased with the decreasing acid concentration. It is predicted that the optimum conditions for the maximum separation of $^{152+154}$ Eu(III) from 90 Sr(II) using polyglycerol phthalate require 3 M nitric acid solution. The extraction and separation of $^{152+154}$ Eu and 90 Sr with



Fig. 11 Effect of acid concentration on the separation factor (SF = D_{Eu}/D_{Sr}) at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:toluene = 0.3:1, 25 ± 1 °C



Fig. 12 Effect of cation concentration on the separation factor (SF = D_{Eu}/D_{Sr}) at O/A = 1. Shaking time = 2 h, polyglycerol phthalate:toluene = 0.3:1, 25 ± 1 °C

polyglycerol phthalate are acidity dependent. The cation concentration was varied in the range of 5-100 mg/L, and it was found that the separation was more facile in the presence of Ca²⁺. The separation factor had a maximum value of 59 and 45 in case of 50 mg/L Ca⁺² and 3 M nitric acid, respectively.

In order to verify the above-mentioned prediction for the separation of $^{152+154}$ Eu and 90 Sr, a mixture consisting of 50 mg/L of each Eu³⁺ and Sr²⁺ was extracted using polyglycerol phthalate from either 3 M HCl and/or 3 M HNO₃ acid solutions and 5 mg/L of Na⁺ or Ca²⁺. A comparison between the E% of Eu³⁺ and Sr²⁺ from

individual and mixed solutions is presented in Table 2. The experimental results obtained revealed that a separation between the two ions could be achieved in the presence of the acids and interfering cation solutions, albeit to a lesser extent than that predicted previously from Figs. 11 and 12. This trend may be related to the interference caused by the existence of the two metals in the same simulated solution, which affected the extraction equilibrium and consequently the value of SF (Eu/Sr). Furthermore, the decrease in the SF was due to the co-extraction of Sr²⁺.

3.3.4 Stripping study of ¹⁵²⁺¹⁵⁴Eu from loaded organic phase

The stripping of $^{152+154}$ Eu was investigated using different concentrations of H₂SO₄, HCl, HNO₃, NH₃OH, H₂O₂, oxalic acid, and water. Thus, the most suitable agent was identified for stripping this radionuclide from the loaded extractant in a toluene solution. The relationship between the stripping agent concentration and the stripping percentage of $^{152+154}$ Eu from the organic phase is given in Table 3. Generally, it is difficult to attain a complete stripping of the Eu radioisotope. In our work, the extractant was able to hold the radioisotope very well, which is considered as a good result from the viewpoint of environmental safety. The tabulated data indicate that sulfuric acid was able to strip Eu(III) from the loaded extractant successfully and was more efficient than the other reagents.

4 Conclusion and outlook

A new organic extractant based on polyglycerol phthalate was prepared by the addition of toluene di-isocyanate during the synthetic process. Characterization using FTIR and ¹H NMR confirmed the successful synthesis of a modified polyglycerol phthalate. The extraction of longlived radionuclides, ¹⁵²⁺¹⁵⁴Eu and ⁹⁰Sr, by the modified polyglycerol phthalate was studied. The radionuclide extraction selectivity of the extractant in the aqueous solution of the radionuclides and in the pH range of 1–7.5

Table 2 Percentage extraction of Eu^{3+} and Sr^{2+} from individual and mixed solutions

Media	Mixed solutions (Eu + Sr)		Individual solutions	
	Eu ³⁺	Sr ²⁺	⁹⁰ Eu	⁹⁰ Sr
5 mg/L Na ⁺	56.7	3.4	82.84	35.04
5 mg/L Ca ²⁺	59.9	6.3	94.44	34.38
3 M HCl	38.9	1.02	40.57	2.75
3 M HNO ₃	63.0	1.5	57.1	2.81

Table 3 Stripping of ¹⁵²⁺¹⁵⁴Eu by different reagents

Reagents	0.01 M	0.1 M	1 M	3 M
HNO ₃	30.45	25.80	29.62	37.86
HCl	59.79	20.36	21.85	9.33
H_2SO_4	34.71	38.63	67.41	40.49
NH ₃ OH	52.32	49.54	33.70	25.67
$H_2C_2O_4$	44.61	42.90	39.8	NR
H ₂ O ₂ (10%)	16.06			
Distilled water	17.80			

NR not reported

decreased in the order of ${}^{152+154}$ Eu > 90 Sr > 90 Y. The separation of ${}^{152+154}$ Eu from 90 Sr was achieved by using 3 M HNO₃ solution. The extraction% value of 90 Sr was also determined in the presence of Na⁺ or Ca²⁺ as interfering ions. It was concluded that the newly synthesized modified polyglycerol phthalate extractant was very promising for the extraction of radioisotopes. Nevertheless, this material can be further improved in terms of increasing the extraction percentage of the radioisotopes. This may be achieved by decreasing the viscosity and incorporating other features to generate an economic and efficient extractant, as compared to the known highly expensive extractants.

References

- J.F. Stumbe, B. Brunchmann, Hyperbranched polyesters based on adipic acid and glycerol. Macromol. Rapid Commun. 25, 921–924 (2004). https://doi.org/10.1002/marc.200300298
- E. Bucio, J.C.I. Lara-Estevez, F.A. Ruiz-Trevino et al., Synthesis and characterization of new polyesters derived from diphenols and aromatic diacids chlorides. Polym. Bull. 56, 163–170 (2006). https://doi.org/10.1007/s00289-005-0487-x
- H.J. Lanson, Chemistry and technology of alkyd and saturated reactive polyester resins, in *Applied Polymer Science*, Tess, R., et al., ACS symposium series (American Chemical Society, Washington, DC, 1985), pp. 1181–1204. 0097-6156/85/0285-1181\$07.00/0 © 1985
- O.D. Ekpa, I.O. Isaac, Kinetic studies on polyesterification of unsaturated oils and diacids in alcoholysis process. Res. J. Appl. Sci. 4, 125–128 (2009). http://medwelljournals.com/abstract/ ?doi=rjasci.2009.125.128
- E.U. Ikhuoria, A.I. Aigbodion, F.E. Okieimen, Enhancing the quality of alkyd resins using methyl ethers of rubber seed oil. Trop. J. Pharm. Res. 3, 311–317 (2004). https://doi.org/10.4314/ tjpr.v3i1.14615
- M.F. Attallah, K.F. Allan, M.R. Mahmoud, Synthesis of poly (Acrylic Acid-Maleic Acid)SiO₂/Al₂O₃ as novel composite material for cesium removal from acidic solutions. J. Radioanal. Nucl. Chem. **307**, 1231–1241 (2016). https://doi.org/10.1007/ s10967-015-4349-1
- 7. M.M. Hamed, M.F. Attallah, S.S. Metwally, Simultaneous solid phase extraction of cobalt, strontium and cesium from liquid

radioactive waste using microcrystalline naphthalene. Radiochim. Acta **102**, 1017–1024 (2014). https://doi.org/10.1515/ract-2013-2200

- M.F. Attallah, E.H. Borai, M.A. Hilal et al., Utilization of different crown ethers impregnated polymeric resin for treatment of low level liquid radioactive waste by column chromatography. J. Hazard. Mater. **195**, 73–81 (2011). https://doi.org/10.1016/j. jhazmat.2011.08.007
- E.M. El Afifi, M.F. Attallah, E.H. Borai, Utilization of natural hematite as reactive barrier for immobilization of radionuclides from radioactive liquid waste. J. Environ. Radioact. 151, 156–165 (2016). https://doi.org/10.1016/j.jenvrad.2015.10.001
- V.V. Milyutin, S.V. Mikheev, V.M. Gelis et al., Coprecipitation of microamounts of cesium with precipitates of transition metal ferrocyanides in alkaline solutions. Radiochemistry 51, 295–297 (2009). https://doi.org/10.1134/S106636220903014X
- P. Kandwal, P.K. Mohapatra, S.A. Ansari et al., Selective caesium transport using hollow fibre-supported liquid membrane containing calix[4]arene-bis-naphthocrown-6 as the carrier extractant. Radiochim. Acta 98, 493–498 (2010). https://doi.org/ 10.1524/ract.2010.1750
- Y. Dai, A. Zhang, Extraction equilibrium and thermodynamics of cesium with a new derivative of calix[4]biscrown. J. Radioanal. Nucl. Chem. **302**, 575–581 (2014). https://doi.org/10.1007/ s10967-014-3287-7
- S.B. Clark, A.L. Bryce, A.D. Lueking et al., Factors affecting trivalent f-element adsorption to an acidic sandy soil. in Adsorption of Metals by Geomedia. Variables, Mechanisms, and Model Applications, ed. by E.A. Jenne (Academic Press, San Diego, 1998), pp. 149–164
- 14. G. Suresh, M.S. Murali, J.N. Mathur, Thermodynamics of extraction of Am(III) and Eu(III) from different anionic media with Tri-n-octylphosphine oxide. Radiochim. Acta **91**, 127–134 (2003). https://doi.org/10.1524/ract.91.3.127.19983
- M.D. Karavan, I.V. Smirnov, S.R. Kleshnina et al., Micelle mediated extraction of americium and europium by calix[4]arene phosphine oxides from nitric acid media. J. Radioanal. Nucl. Chem. **311**, 599–609 (2017). https://doi.org/10.1007/s10967-016-5096-7

- W. Mu, Q. Yu, X. Li et al., Niobate nanofibers for simultaneous adsorptive removal of radioactive strontium and iodine from aqueous solution. J. Alloys Compd. 693, 550–557 (2017). https:// doi.org/10.1016/j.jallcom.2016.09.200
- C.A. Kozlowski, J. Kozlowska, W. Pellowski et al., Separation of cobalt-60, strontium-90, and cesium-137 radioisotopes by competitive transport across polymer inclusion membranes with organophosphorous acids. Desalination **198**, 141 (2006). https:// doi.org/10.1016/j.desal.2006.02.005
- S.A. Shady, M.M Abou-Mesalam, in *7th Arab international conference on polymer science and technology*, 5–9 October, Hurghada, Egypt (2003)
- D.H. Guimarães, M.D.M. Brioude, R.D.P. Fiúza et al., Synthesis and characterization of polyesters derived from glycerol and phthalic acid. Mater. Res. 10, 257–260 (2007)
- E.A. Ismail, A.M. Motawie, E.M. Sadek, Synthesis and characterization of polyurethane coatings based on soybean oil-polyester polyols. Egypt. J. Pet. 20, 1–8 (2011). https://doi.org/10. 1016/j.ejpe.2011.06.009
- M.S. Mansur, A. Mushtaq, Separation of yttrium-90 from strontium-90 via colloid formation. J. Radioanal. Nucl. Chem. 288, 337–340 (2011). https://doi.org/10.1007/s10967-011-1015-0
- E. Pretsch, P. Buhlmann, C. Affolter, *Structure determination of organic compounds: tables of spectral data*, 3rd edn. (Berlin: Springer, 2000). ISBN 3-540-67815-8
- N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to infrared and Raman spectroscopy*, 3rd edn. (Academic press, Inc., New York, 1990)
- F. Guo-dong, H. Yun, X. Bin et al., Synthesis and characterization plasticizer epoxy acetyl polyglycerol ester. J. For. Prod. Ind. 3, 100–105 (2014)
- F. Esmadi, J. Simm, Sorption of cobalt(II) by amorphous ferric hydroxide. Colloids Surf. A 104, 265–270 (1995). https://doi.org/ 10.1016/0927-7757(95)03289-4
- D. Xu, X. Tan, C. Chen et al., Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes. J. Hazard. Mater. 154, 407 (2008). https://doi.org/10.1016/j.jhazmat.2007. 10.059