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Research Article

Synthesis, investigation of the structure and physico-chemical properties of modified solid-phase extractants (SPE) based on N,N,N',N'-tetraoctyldiglycolamide (TODGA)

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Abstract

The paper presents the results of the development of modified solid-phase extractants (SPE) based on N,N,N',N'-tetraoctyl diglycolamide (TODGA) intended for the selective extraction of americium-241 from nitric acid solutions of liquid radioactive waste. (LRW). The structural and physico-chemical properties of synthesized materials, including granulometric composition, porosity, and stability in nitric acid media, have been studied. The developed SPEs are stable in nitric acid solutions and meet the size requirements for use in industrial sorption columns. The results obtained can be used as a basis for creating technological schemes for the processing of LRW based on synthesized experimental modified samples of SPE TODGA, in particular for the isolation of minor actinides, including americium-241.

Keywords

sorption materials, polystyrene matrices, TODGA, solid-phase extractants, modification, physico-chemical characteristics, granulometric composition, IR spectroscopy

Introduction

To date, the primary technologies for liquid radioactive waste (LRW) treatment include ion exchange, chemical precipitation, membrane methods (reverse osmosis, ultrafiltration), electrodialysis, evaporation, and sorption techniques. These technologies have their own advantages and disadvantages. For instance, ion exchange achieves high efficiency for low-level waste with high regeneration of ion-exchange materials. However, this technology exhibits low selectivity in multicomponent solutions due to resin degradation in acidic media, as well as limited capacity for actinides (IAEA 1994; Rahman 2011).

Chemical precipitation, which involves adding reagents (hydroxides, carbonates) to convert radionuclides into insoluble forms, generates significant amounts of secondary waste while demonstrating low efficiency for trace components such as actinides (including americium and plutonium) (Valsala et al. 2010; Nilchi et al. 2012). Membrane technologies face challenges such as membrane fouling, high energy consumption, and limited radiation resistance (Zakrzewska-Trznadel et al. 2001; Ambashta and Sillanpää 2012; Zakrzewska-Trznadel 2013).

In addition to these "conventional technologies," modern or hybrid LRW treatment methods are being developed. For example, nanosized sorbents (metal oxides, carbon nanotubes) such as TiO_2 and Fe_3O_4 functionalized with ligands are being explored. These nanosorbents exhibit high specific surface area and rapid kinetics. However, they suffer from significant drawbacks, including difficulties in nanoparticle separation from process solutions and a tendency to aggregate in acidic media (Stockmann et al. 2011; Khalaf et al. 2019; Wang et al. 2020). Furthermore, they demonstrate low chemical stability in nitric acid solutions and high cost of synthesis.

Another area of development involves extraction resins, such as those based on tributyl phosphate or carbamoylmethylphosphine oxide (e.g., octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide). Nevertheless, these materials also face challenges, including extractant leaching during prolonged use and limited selectivity toward americium and other trivalent actinides in the presence of lanthanides (Lyzlova et al. 2022).

In summary, the key challenges in modern LRW treatment methods include:

- Low selectivity toward minor actinides (Am, Cm) in the presence of macrocomponents (Fe, Al, lanthanides);
- Extractant leaching from the matrix, leading to solution contamination and the need for frequent sorbent replacement;
- Instability in aggressive environments (high HNO_3 concentrations, radiolysis).

Sorption methods remain the most widely used technology for low- and intermediate-level LRW treatment due to their high selectivity, enabling the recovery of target radionuclides (Wei et al. 1998; Egorin and Avramenko 2012; Suresh et al. 2013; Milyutin et al. 2015; Milyutin et al. 2017; Rae et al. 2019; Lyzlova et al. 2022; Vidanov et al. 2023). A promising approach for the selective recovery of trivalent actinides and lanthanides from nitric acid LRW solutions is solid-phase extractants (SPE) incorporating specialized ligands (Sasaki and Tachimori 2002; Ansari et al. 2005; Horwitz et al. 2005; Mokhodoeva et al. 2011; Ansari 2012; Klochkova et al. 2019; Savelev and Rachkov 2024), which provide high selectivity and stability under extreme environmental conditions. SPEs combine the advantages of liquid-liquid extraction and solid-phase sorption.

Currently, the most promising ligands for the recovery of trivalent actinides and lanthanides from nitric acid solutions are diglycolamides, particularly N,N,N',N'-tetraoctyldiglycolamide (TODGA) (Sasaki et al. 2001), which exhibits high solubility in aliphatic hydrocarbons and demonstrates high distribution coefficients (Sasaki and Tachimori 2002).

The use of the TODGA extractant enhances radionuclide recovery and improves purification efficiency (Sasaki et al. 2001). Furthermore, the application of SPEs with TODGA immobilized in a porous matrix facilitates the formation of complexes with trivalent ions (Am^{3+} or Eu^{3+}) through coordination with oxygen atoms in the diglycolamide groups (U.S. Patent and Trade Patent No. 9,051,629, 9 June, 2015).

The innovativeness of SPE TODGA can be assessed by comparing its efficiency, stability and applicability with silica-based resins (Zhang et al. 2005); (Zhang et al. 2005); (Zhang et al. 2007); (Zhang A W. Y., Chromatographic separation of strontium (II) from a nitric acid solution containing some typically simulated elements by a novel silica-based TODGA impregnated polymeric composite in the MAREC process, 2005) and TODGA-based membranes (Ansari et al. 2006; Modolo et al. 2007; Ansari et al. 2009; Magnusson et al. 2009; Panja et al. 2009; Raut and Mohapatra 2013; Milyutin et al. 2015). Silica-based resins with TODGA have a high specific surface area, which provides good capacity for actinide/lanthanide extraction; selectivity is comparable to SPE, but leaching of TODGA in acidic environments (e.g., > 1 M HNO_3) reduces long-term efficiency. Also, this material is prone to degradation in strongly acidic/alkaline conditions, which limits the possibility of reuse, which is especially important in the processing of liquid radioactive waste. In addition, TODGA leachability remains an unsolved problem, especially in continuous flow systems. However, the fast kinetics due to the porous structure are suitable for column chromatography. TODGA-based membranes have lower extraction capacity compared to resins, and selectivity depends on the membrane design. Membrane fouling and TODGA leaching are also a big problem, which leads to a reduction in service life. In addition, the membranes are sensitive to organic solvents and extreme pH values. In turn, the use of membranes is characterized by slow mass transfer and high wear during long-term operation, but they are energy efficient for large-scale processes. Therefore, they are more suitable for industrial separation of rare earth elements and it is necessary to select a compromise solution between stability and productivity. If we compare SPE TODGA with the above options, we have the following advantages: improved TODGA retention due to covalent bonding or modification of the polymer matrix (e.g. polystyrene-divinylbenzene), which increases resistance to acids; high capacity comparable to silicon-based resins, and better selectivity in nitric acid environments; excellent chemical/mechanical stability under acidic conditions; minimal leaching due to strong interaction with the carrier at faster kinetics than membranes, comparable to silica-based resins. In addition, the use of SPE TODGA allows for a somewhat simplified design of sorption columns, which reduces operating costs. Therefore, the use of SPE allows for the elimination of key gaps in TODGA-based materials, namely, compared to silica-based resins - eliminate vulnerability to acids and leaching, which allows use in aggressive nuclear waste, compared to membranes - provide higher productivity and simple regeneration, avoiding clogging. This makes the use of modified SPE a universal solution for separations requiring durability, high capacity and resistance to acids, combining the accuracy of laboratory methods with industrial practicality. The need for this development is due to the following factors:

- insufficient selectivity of ion-exchange resins and extraction systems to Am^{3+} in the presence of lanthanides;
- leaching of the extractant from the sorbent in acidic environments;
- instability of materials under conditions of high concentrations of HNO_3 and radiation exposure;
- impossibility of using finely dispersed SPE in industrial sorption equipment.

Due to this, SPE TODGA has the following advantages over other technologies for the selective extraction of trivalent actinides:

- TODGA selectively binds Am^{3+} even in the presence of lanthanides and other metals. In a study, the separation coefficient of Am/Eu reaches 10–15 in 3M HNO_3 (Ansari et al. 2012);
- • covalent fixation of TODGA in the matrix (e.g., through modification with nitrile groups) reduces extractant losses. TODGA leaching does not exceed 2% after 10 sorption-desorption cycles (Modolo et al. 2007);
- • the polymer matrix is resistant to 4–6 M HNO_3, which allows its use in LRW processing technology (Modolo et al. 2007; Magnusson et al. 2009).

Building upon the successful application of TODGA for selective americium-241 recovery from LRW processing streams within the “Proryv” project, the objective was set to develop, synthesize, and investigate experimental modified samples of SPE TODGA. These materials are designed for selective extraction of americium-241 and other trivalent actinides from nitric acid LRW solutions, enabling the return of fissile materials to the nuclear fuel cycle while reducing the hazard class of disposed LRW.

In the context of the set goal, the data on the selectivity of experimental modified samples of SPE TODGA were previously conducted and published (Klochkova et al. 2019; Savelev and Rachkov 2024). In the article (Savelev and Rachkov 2024), the main attention is paid to the effect of salting out ($NaNO_3$) on the sorption of Am-241 and U, demonstrating that the maximum distribution coefficient on the synthesized sample for Am-241 reaches 3045 at 100 g/l $NaNO_3$, while for U it is 59. This confirms that the selectivity of TODGA to Am^{3+} is significantly higher than to macrocomponents such as U. In the article (Klochkova et al. 2019), Table 2 shows the distribution coefficients for Am and U, as well as the Am/U separation coefficient. For example, for the synthesized sample, the maximum distribution coefficient of Am-241 reaches 1875, the distribution coefficient of U reaches 58, the Am/U separation coefficient is 32, while the separation coefficient of the industrial sample is two times lower (15). This confirms that the experimental modified samples of SPE TODGA effectively separate Am and U, which indirectly indicates their potential for the selective extraction of Am^{3+} in the presence of other elements. However, this article did not consider in detail the process of synthesis and study of the experimental modified samples of SPE TODGA.

The purpose of this study is to synthesize and conduct a comprehensive investigation of experimental modified samples of SPE TODGA, focusing on elucidating their structural characteristics, evaluating their chemical stability in aggressive media, and assessing their potential applicability in actinide separation processes.

Materials and methods

To synthesize experimental modified samples of SPE TODGA with different composition of the polymer matrix, the path of modification of the base polystyrene matrix with various functional groups was chosen. It is assumed that this leads to the fact that TODGA will be fixed in the matrix not only due to physical adsorption in micropores on polystyrene, but also due to covalent or coordination bonds with the functional groups of the matrix. Additional fixation of TODGA in the matrix can lead to a decrease in the extractant leaching and an improvement in the performance characteristics of the synthesized SPEs. In addition, modification of the matrix composition and its intermediate treatment can affect the diffusion rate of the target components and, accordingly, the kinetic characteristics of ion-exchange processes. Industrial samples with a TODGA content of 40 wt% in the polystyrene matrix served as a reference for the synthesis of experimental modified samples. The authors of the study were provided with these samples as part of the “Proryv” project assignment. These samples or their analogs were used in many research works on the extraction of americium and other actinides or their chemical analogs, as well as in industry (Milyutin et al. 2015; Klochkova et al. 2019; Milyutin et al. 2021; Milyutin et al. 2022; Savelev and Rachkov 2024).

When developing the requirements for experimental modified samples and, accordingly, developing the synthesis conditions, industrial samples of SPE with the following characteristics served as a reference: matrix – polystyrene; TODGA content in SPE – 40% wt%; main purpose – extraction of rare earth elements and americium-241; application environment – nitric acid solutions; exchange capacity – 0.8 mg-eq/g; desorption – ammonium carbonate and 0.01M HNO_3; humidity – no more than 35%; appearance – spherical grains of regular shape from white to light beige color; dispersion of the working fraction > 90% – 0.4–1.25 mm; capacity for rare earth elements (Nd^{3+}) – 0.74 mg-eq/g; specific volume – 2.48 ml/g. The following main starting reagents are used for the synthesis of SPE: technical styrene, chemical formula – $CH_2{=}CHC_6H_5$, inhibitor – tert-butylpyrocatechol, boiling point – 145.2 °C, density – 0.906 g/cm^3; technical divinylbenzene

(64% wt%), chemical formula – $(CH_2=CH)_2C_6H_4$, inhibitor – tert-butylpyrocatechol, total content of unsaturated compounds 99% wt%, density – 0.907 g/cm^3; acrylonitrile, chemical formula – $CH_2=CH\text{-}CN$, boiling point – 77 °C, density – 0.806 g/cm^3; Methyl methacrylate, chemical formula – $CH_2=CHC(O)OCH_3$, density – 0.942 g/cm^3; refractive index nD^{20}=1.414; 2.5-methylvinylpyridine, chemical formula – $C_5H_3N(CH_3)CH=CH_2$, the content of the main substance is not less than 95% wt%, refractive index nD^{20}=1; benzoyl peroxide, chemical formula – $(C_6H_5COO)_2$, melting point – 107 °C; density – 1.3340 g/cm^3; hydroxyethyl cellulose; methacrylic acid with a mass content for the main substance of 99.5%, the mass fraction of impurities is not more than ≤ 0.4%.

The synthesis experimental modified samples of SPE were carried out in laboratory copolymerizers with a volume of 0.1 to 0.5 liters, shown in Figs 1, 2. The process temperature was maintained using a water or glycerol bath; the temperature of the heat carrier was regulated by a two-point thermostat with an accuracy of ± 0.5 °C. Operations not related to copolymerization were carried out in 3- and 4-neck round-bottomed flasks with a volume of 0.1 to 0.5 liters, heated with a liquid bath. Polyethylsiloxane was used as a heat carrier. Separation of the liquid phase and washing of the copolymers were carried out on glass-ceramic Schott filters with a volume of up to 0.1 liter. Drying of the copolymers for intermediate operations and analysis was carried out in a vacuum drying cabinet with an accuracy of maintaining the temperature of ± 0.2 °C.

For the synthesis of experimental modified samples of SPE, TODGA was used, created in laboratory conditions, the structure of which is shown in Fig. 3, with the following characteristics - a light yellow liquid, chemical formula - $C_{36}H_{72}N_2O_3$, crystallizes at 8 °C, boiling point - 400 °C, the content of the main component is more than 95%.

The method for obtaining SPEs consists of the following operations: preparation of a suspension medium; preparation of a polymerization mixture; carrying out copolymerization; washing and sieving of SPEs.

To synthesize SPEs, a measured amount of an aqueous dispersion medium containing an emulsion stabilizer and providing the required viscosity is loaded into a glass copolymerizer reactor (Fig. 1) equipped with a thermometer, reflux condenser, dropping funnel, and frame stirrer. A polymerization mixture consisting of a mixture of monomers, an extractant, and a polymerization initiator (benzoyl peroxide) is prepared separately. The stirrer rotation speed is set to the required value to obtain the optimal droplet size when dispersing the organic phase and granules of the future copolymer. The dispersion medium is heated to the required temperature and the polymerization mixture is slowly introduced. An exposure is made to “break” the organic layer and form droplets of the required size. In suspension copolymerization, the quality of the copolymer depends on such synthesis conditions as the temperature regime, the amount of polymerization initiator, the composition of the suspension medium, and the polymerization mixture. The copolymer granules must be of the correct spherical shape and have an optimal pore structure. The copolymer must not contain aggregates of stuck granules. The temperature-time profile of the process, the exact composition of the polymerization mixture, and the brand of the emulsion stabilizer are not given in this work. After the polymerization process

Figure 1. Laboratory copolymerization reactor.

Figure 2. Granular copolymerization.

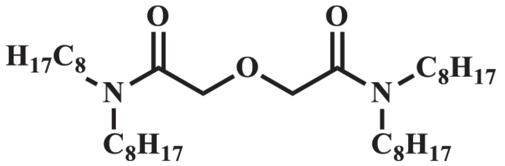

Figure 3. Structure of TODGA.

is complete, the reaction mass is cooled, the mother liquor is filtered, and the SPEs are washed with distilled water. The copolymer is unloaded and dispersed into fractions.

The polymer matrix of SPEs is analyzed using standard methods and in accordance with the requirements for general-purpose sorbents, as well as the specific requirements used in heavy metal hydrometallurgy. When analyzing SPEs and polymer matrices, the following physicochemical characteristics were mainly determined: granulometric composition; humidity (%); specific volume (cm^3/g); swelling coefficient (ml/ml); specific surface area of the matrix (m^2/g); matrix porosity (%); matrix density, true and apparent (g/cm^3); mechanical strength to abrasion and impact (%); functional composition of the copolymer; exchange capacity, including: - total static exchange capacity (mg-eq/g, mg-eq/ml); - capacity for cation-exchange and anion-exchange groups; - capacity for strongly basic and weakly basic groups.

For a correct technological comparison of the synthesized experimental modified samples with the industrial sample, an experimental series of SPEs was manufactured with a TODGA content of 40% wt% in all samples.

The composition of the base matrix (highly porous polystyrene) is the same in all synthesized samples; the cross-linking of divinylbenzene, the content of styrene, ethylstyrene and other components of the polymerization mixture corresponds to the industrial analogs indicated earlier. The base polymer matrix was modified through the incorporation of weakly acidic (carboxyl) cation-exchange groups, weakly basic anion-exchange groups, and nitrile functionalities in various combinations. In nearly all samples, the modifying monomer content was maintained at 10 wt.%. This value was selected empirically, as higher concentrations of hydrophilic solvated functional groups in the matrix were found to induce changes in specific volume (so-called "breathing effects") upon variation of solution acidity and composition.

Such dimensional instability is undesirable as it may lead to extractant losses during matrix contraction. Furthermore, in describing the matrix composition, all component contents are reported relative to the total monomer mass, excluding the contribution from TODGA.

Based on the analysis of data presented in the following sources (Tachimori et al. 2002; Iqbal et al. 2010; Gujar et al. 2012; Galán et al. 2015; Chen et al. 2023), the following were selected as the most promising modifying monomers: methacrylic acid ($CH_2{=}C(CH_3){-}COOH$); 2.5-methylvinylpyridine ($CH_2{=}CH{-}C_5H_3N{-}CH_3$); acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$). When styrene is copolymerized with methacrylic acid, the high-capacity carboxyl cation exchanger (SG-1) is formed in the matrix. When styrene is copolymerized with 2.5-methylvinylpyridine, the weakly basic anion exchanger (VP-1P) is formed in the matrix, which has shown good results in work with LRW. If necessary, SPE with 2.5-methylvinylpyridine is easily alkylated to VP-1P. SPEs with polyacrylonitrile is produced with 10 and 40 wt% in the matrix. Polyacrylonitrile hydrolyzes when interacting with nitric acid to form a carboxyl group (working solutions can contain up to 7 M nitric acid). At 20 °C, the degree of hydrolysis is 4–6%. At 110 °C – up to 95%. In this work, to exclude losses of TODGA, SPEs hydrolysis was carried out at 70 °C, the degree of hydrolysis was about 25–30%. As a result, the matrix with polyacrylonitrile, depending on its initial content (10–40%) and hydrolysis temperature (20–70 °C), contained 0.005–12% of carboxyl groups and 9–40% wt% (up to 50% mol) of acrylonitrile groups. The nitrile nitrogen of these electroneutral groups can also form coordination bonds with the TODGA molecule and affect the strength of the bond between the extractant and the polymer matrix and the extraction properties of SPE.

The synthesis of SPEs based on styrene copolymers involves the polymerization of styrene, divinylbenzene, and ethylstyrene monomers, initiated by benzoyl peroxide. The chemical reaction can be represented by the following equation (1):

$$(C_6H_5COO)_2 + mCH_2{=}CHC_6H_5 + n(CH_2{=}CH)_2C_6H_4 + p(CH_2{=}CH)(C_2H_5)C_6H_4 \rightarrow [CH_2CHC_6H_5]m[(CH_2CH)_2C_6H_4]n[(CH_2CH)(C_2H_5)C_6H_5]p \tag{1}$$

The copolymerization reactions of acrylonitrile (2), methacrylic acid (3), and 2.5-methylvinylpyridine (4) with divinylbenzene can be represented by the following equations:

$$mCH_2{=}CH{-}C{\equiv}N + nC_6H_4(CH_2{=}CH)_2 \rightarrow [-CH_2{-}CH{-}C{\equiv}N]m[C_6H_4(CH{-}CH_2{-})_2]n \tag{2}$$

$$mCH_2{=}C(CH_3)COOH + nC_6H_4(CH_2{=}CH)_2 \rightarrow [-CH_2{-}C(CH_3)COOH]m[C_6H_4(CH{-}CH_2{-})_2]n \tag{3}$$

$$mC_5H_3N(CH_3)CH{=}CH_2 + nC_6H_4(CH_2{=}CH)_2 \rightarrow [-C_5H_3N(CH_3)CH{-}CH_2{-}]m[C_6H_4(CH{-}CH_2{-})_2]n \tag{4}$$

Followed by hydrolysis of the nitrile group:

$$[-CH_2{-}CH{-}C{\equiv}N]m[C_6H_4(CH{-}CH_2{-})_2]n + HNO_3 \rightarrow [-CH_2{-}CHCOOH]m[C_6H_4(CH{-}CH_2{-})_2]n \tag{5}$$

where *m*, *n*, *p* are coefficients determining the number of monomer units in the polymer chain; $C_6H_4(CH_2{=}CH)_2$ is divinylbenzene, a crosslinking agent that creates transverse bonds between polymer chains; HNO_3 is nitric acid, used for the hydrolysis of the nitrile group (−C≡N) into a carboxyl group (−COOH).

The purpose of varying the experimental conditions in this work was to study the influence of the nature and concentration of modifying comonomers, as well as the conditions of subsequent hydrolysis (for nitrile-containing samples), on the properties of the polymer matrix and the final SPE, under standardized conditions for carrying out the main reaction of suspension copolymerization.

To determine the properties of the matrix of the obtained SPE TODGA extractant, multiple washings with acetone were performed, followed by vacuum drying at 80 °C. Based on the coloration of the acetone extract portions, it was clearly evident that the extractant was difficult to remove from the samples containing nitrile acrylic acid that had undergone hydrolysis at 70 °C. The exchange capacity and total porosity of the washed matrix samples were determined. The polymer matrices were then studied using infrared (IR) spectroscopy, with a targeted search for residual characteristic bands of TODGA (e.g., the C=O band at ~1647 cm^{-1} or C-O-C at ~1123 cm^{-1}). The IR spectrum of the polymer serves as a unique identifier, allowing not only the characterization of its composition but also reliable future identification. In all studied samples after multiple washings, no presence of TODGA in the matrix was detected. The specific surface area and porometric characteristics of the samples were also determined using an automatic specific surface area and pore size analyzer. To assess the concentration ratio of TODGA and styrene-divinylbenzene matrix in the sorbent phase, the optical densities of the absorption bands of TODGA and the styrene-divinylbenzene matrix were calculated based on the IR spectra of the studied samples. The optical density values of the absorption bands were determined using the "baseline" method (Sasaki et al. 2001).

For IR spectroscopy studies, two samples of SPE TODGA were selected: an industrial sample and synthesized sample №1. The infrared absorption spectra of the studied samples were obtained using a Fourier-transform IR spectrometer IR Prestige-21 in the range of 4000–400 cm^{-1} and a Specord 75 IR spectrometer in the range of 3000–2800 cm^{-1}. Sample preparation was carried out using the standard alkali metal halide pellet method. The IR absorption spectra were recorded with a resolution of 2 cm^{-1}. The IR spectra of the TODGA extractant were obtained in the form of a film between silver bromide windows, as well as in a carbon tetrachloride solution using liquid cuvettes with an optical path length of 1.03 mm. The accumulation for both samples under study was 60 scans.

Results

To confirm the compliance of the industrial SPE samples, additional analyses were carried out for clarification. The results of these analyses are presented in Table 1. This table also includes the characteristics of the synthesized reference experimental sample SPE TODGA №1, produced on a polystyrene matrix without modifying additives.

Based on the description of the synthesis method presented earlier, a series of seven experimental modified samples of SPE were manufactured, the matrix composition and some characteristics of which are given in Table 2. In this table, the parameter "matrix capacity" refers to the number of introduced functional ion-exchange

Table 1. Characteristics of the industrial-grade SPEXT and the experimental sample based on a polystyrene matrix

Parameter	Industrial-grade sample	Sample № 1
Matrix	Polystyrene	Polystyrene
Content of organic phase in the matrix, %	42	42
Including TODGA, %	40	40
Moisture content, %	29	18
Swelling coefficient	1.03	1.08
Density (apparent), g/mL	0.416	0.594
Specific volume, mL/g	2.49	1.82
Granulometric composition, mm:		
0.2–0.315	1.3	0.0
0.315–0.4	9.5	0.0
0.4–0.5	24.3	0.4
0.5–0.63	39.2	0.2
0.63–0.8	24.3	12.1
0.8–1.0	0.4	27.7
1.0–1.25	0.5	41.3
1.25–1.4	0.5	18.3
1.4–1.6	0.0	0.0
Uniformity coefficient	1.468	1.465
Effective grain diameter, mm	0.39	0.79
Specific surface area of the matrix, cm²/g	59.19	83.24
External surface area of granules, cm²/mL	12.54	6.79

Table 2. Composition of experimental modified SPEXTs with 40 wt.% TODGA content

Sample, №	Monomer used for modification	Monomer content in the matrix, wt%	Matrix functionality	Matrix capacity, mg-equiv/g	Acrylonitrile		Structural parameters of the polymer matrix in SPEXTs		Hydrolysis temperature, °C
					Degree of conversion, %	Polymer content, wt%	Porosity, %	Specific surface area, m^2/g	
1	–	–	Neutral	–	–	–	54.3	83.2	–
2	2.5-Methylvinylpyridine	10	Anion exchanger	0.57	–	–	48.4	65.4	–
3	Methacrylic Acid	10	Cation exchanger	1.35	–	–	33.8	87.0	25
4	Acrylonitrile	10	Cation exchanger	0.045	6	9.4	51.5	55.8	25
5	Acrylonitrile	10	Cation exchanger	0.15	21	8.1	50.9	57.2	70
6	Acrylonitrile	40	Cation exchanger	0.13	5	38	51.8	12.7	25
7	Acrylonitrile	40	Cation exchanger	0.72	25	30	57.7	11.8	70

groups, and the parameter "degree of conversion" was estimated based on the determined cation-exchange capacity that appeared as a result of the conversion of nitrile groups (-CN) to carboxyl (-COOH) during hydrolysis.

The obtained SPEs are spherical opaque granules from white to light yellow in color, with a moisture content of 15–30%, the grain size of the working fraction in an air-dry state is 0.4–1.25 mm, and the mass fraction of the working fraction is at least 95%. Samples with 2.5-methylvinylpyridine and methacrylic acid have a shiny, smooth surface of the granules, while the other samples are matte (as in sample №1). Micrographs of some samples are shown in Figs 4–6.

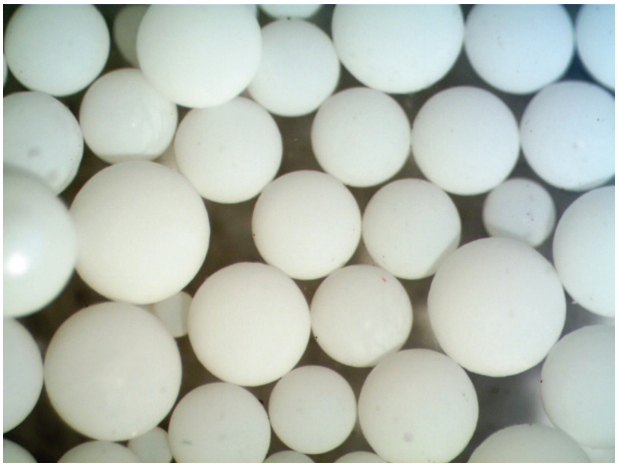

Figure 4. Sample №1 (Polystyrene matrix + 40 wt% TODGA).

Infrared absorption spectra of sorbents are shown in Figs 7, 8. Absorption in 4 frequency ranges is determined by the absorption of aromatic compounds.

The IR spectrum of the styrene divinylbenzene matrix and TODGA are shown in Figs 9, 10, respectively. X-ray structural studies and infrared absorption spectra studies convincingly show that the amides have a ketone structure.

In the spectral region of 3000–3100 cm^{-1}, the stretching vibrations of aromatic C–H groups are observed. The stretching vibrations of aromatic C–C bonds appear in the region of 1480–1620 cm^{-1}. In the regions of 1225–950 cm^{-1} and 1000–650 cm^{-1}, in-plane and out-of-plane

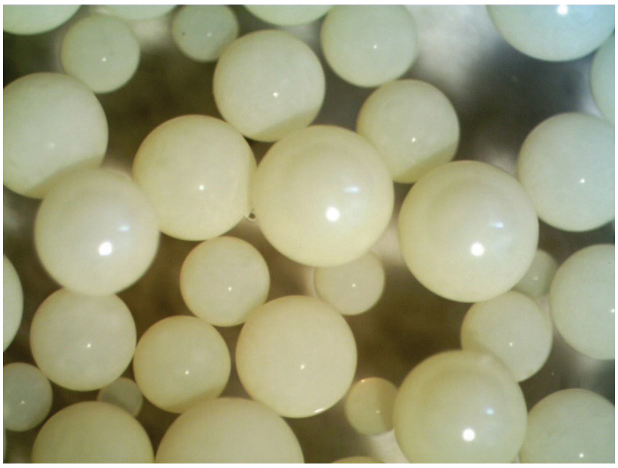

Figure 5. Sample №3 (Polystyrene matrix + 10 wt% methacrylic acid + 40 wt% TODGA).

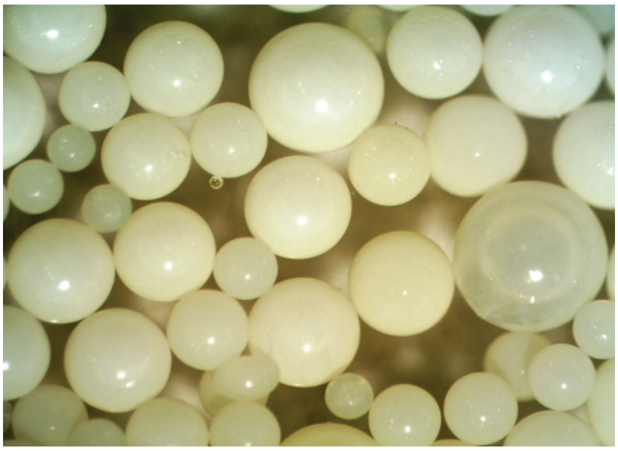

Figure 6. Sample №3 (Polystyrene matrix + 10 wt% methacrylic acid + 40 wt% TODGA) after treatment with 45% HNO_3 at 25 °C.

deformation vibrations of C–H bonds are detected. Table 3 presents the absorption frequencies in the IR spectra of all studied SPEs and the IR spectrum of the styrene-divinylbenzene matrix.

Thus, the IR spectra of Sample №1 and the industrial sample contain absorption bands corresponding to both the styrene-divinylbenzene matrix and the TODGA extractant. As indicated in Table 3 and noted earlier, the

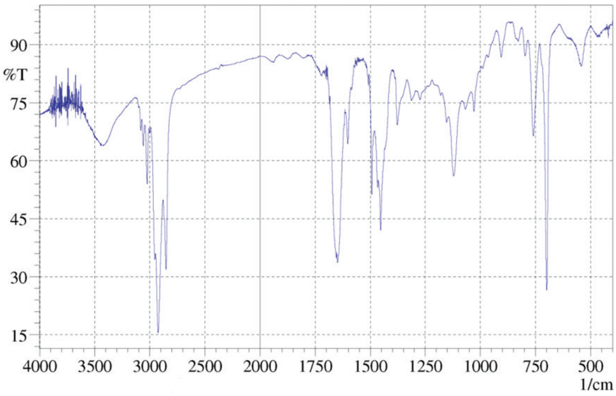

Figure 7. IR spectrum of sample №1 (tablet in potassium bromide). x-axis – wave number, cm^{-1}; y-axis – absorption intensity, %.

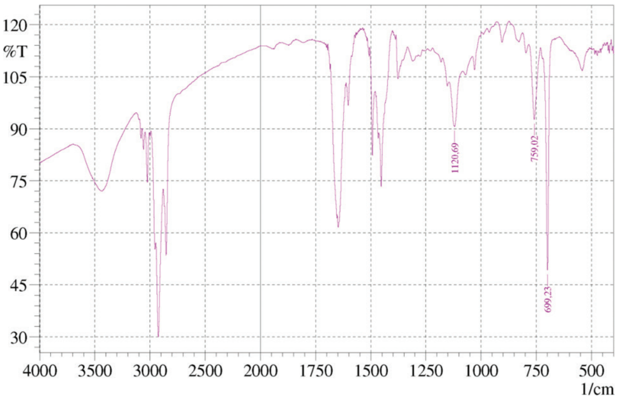

Figure 8. IR spectrum of an industrial sample (tablet in potassium bromide). x-axis – wave number, cm^{-1}; y-axis – absorption intensity, %.

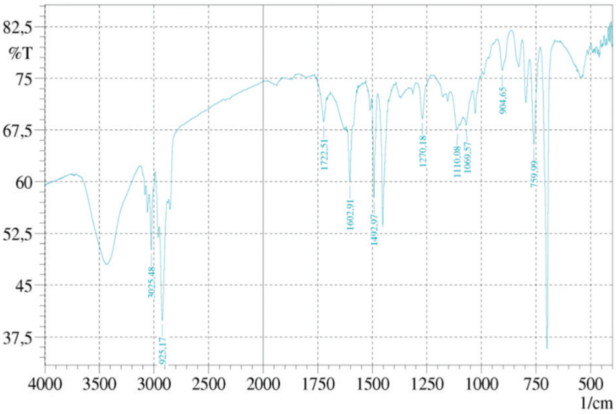

Figure 9. IR spectrum of a sample of styrene divinylbenzene matrix (tablet in potassium bromide). x-axis – wave number, cm^{-1}; y-axis – absorption intensity, %.

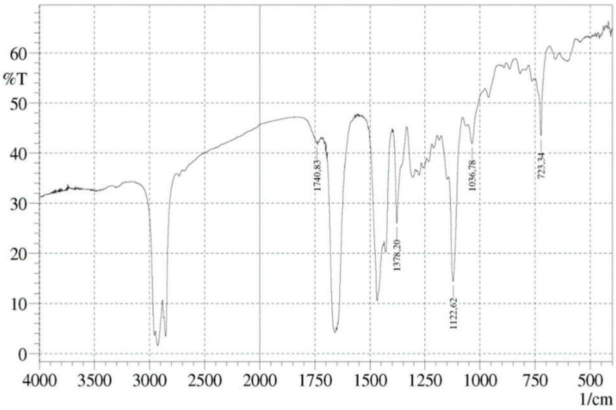

Figure 10. IR spectrum of TODGA (film, silver bromide window). x-axis – wave number, cm^{-1}; y-axis – absorption intensity, %.

characteristic intense band at 1647 cm^{-1} unambiguously corresponds to the stretching vibrations of the carbonyl group (C=O) in the amide bond of TODGA (the "Amide I" band). The bands in the 2800–3000 cm^{-1} region are attributed to C–H stretching vibrations in the alkyl chains of TODGA and, to a lesser extent, the matrix, while the band near 1123 cm^{-1} arises from the C–O–C ether bond stretching vibrations in TODGA.

The intensity ratios D_{1647}/D_{3025} and D_{1121}/D_{3025} were determined, with values ranging within 3.32–3.52 and 1.26–1.42, respectively.

Discussion

More than 90% of the granular composition of the industrial sample of SPE is in the range of 0.3–0.8 mm, with the declared 0.4–1.25 mm; accordingly, these SPEs have a granule size that is half as large.

In the course of refining the composition of the industrial sample of SPEs, the main differences between the synthesized experimental sample of SPE were established: TODGA with a purity of more than 95% was used for the synthesis of experimental samples of SPEs, while technical TODGA of lower purity was used in the industrial sample of SPE, this assumption was established during the analysis of the kinetic parameters of americium-241 sorption in the article (Klochkova et al. 2019); also, during the synthesis of all experimental samples of SPEs, the granulometric composition was the same and constituted the upper limit in the range of 1.25–1.4 mm. The granulometric characteristics of the industrial sample of SPE indicate that they were manufactured for preparative or analytical purposes. These SPE are not suitable for use in industrial sorption equipment. The need to use large-grained SPE for industrial purposes is due to the fact that standard sorption equipment, for which sorbents and SPE are manufactured, is designed to use drainage nets or spatula grids with a cell (slot) of 0.4 mm. To eliminate sorbent losses and reduce hydrodynamic resistance, the optimal granule size should be more than 0.8 mm. Otherwise, the granules block the openings in the outlet devices, and to maintain the required flow rate of solutions, the working pressure in the sorption column must be increased significantly, which is especially unacceptable when working with LRW. In this case, sorbent losses also increase. Thus, when using such SPE in production, up to 10–15% of the ion-exchange material would be immediately and irretrievably lost. Or a change in the design of the sorption columns would be required. In this case, the experimental synthesized samples have

Table 3. Main absorption bands in the IR spectra of the studied samples

Sample name				Assignment of IR bands
Sample №1	**Industrial-grade sample**	**Matrix**	**TODGA**	
Wavenumber, cm^{-1}				
3082	3082	3082		
3061	3061	3061		Stretching vibrations of C–H groups in the aromatic ring
3025	3025	3025		
2925*	2929*	2925	2929*	Asymmetric stretching vibration of C–H_2 groups
2856	2856	2856	2856	Symmetric stretching vibration of C–H_2 groups
1647*	1647*		1647*	Stretching vibrations of C=O groups in TODGA
1602	1602	1603		
1493	1493	1493		Pulsation vibrations of the hydrocarbon skeleton in the aromatic ring
1473	1473	1473		
1454	1454			
1125	1122		1123	Stretching vibrations of C–O groups in TODGA
760	759	760		Out-of-plane deformation vibrations of C–H groups in the aromatic ring
699*	699*	704*		

Note: * – Very strong.

a twice larger granule size, an effective grain diameter, and a twice smaller contact surface “solution-SPE”. All these factors should lead to the fact that the kinetics of the extraction equilibrium for the synthesized experimental modified samples should be approximately 2 times lower than for the industrial SPE samples under consideration. This must be taken into account when comparing the kinetic and capacity characteristics (Klochkova et al. 2019; Savelev et al. 2024).

The differences in the surface of the studied samples can be explained by several probable factors based on the sample composition and general principles of polymer chemistry and physics:

1) Surface gloss is directly related to its smoothness at the micro level. Shiny/smooth surfaces (samples №2 and №3) have less roughness, which leads to specular reflection of light, while matte surfaces (samples №1, №4–7) scatter light diffusely due to greater microroughness. This difference in morphology may be due to the influence of the modifying monomer on the process of granule formation during suspension copolymerization;
2) Methacrylic acid (sample №3) and 2.5-methylvinylpyridine (sample №2) introduce relatively polar groups (carboxyl and pyridine, respectively) into the initially hydrophobic polystyrene matrix. Acrylic acid nitrile (samples №4–7) introduces a less polar nitrile group, part of which is then hydrolyzed to a carboxyl group. It is possible that the presence of methacrylic acid and 2.5-methylvinylpyridine at the early stages of polymerization or upon subsequent introduction of TODGA contributes to the formation of a more ordered or less rough surface structure of the granule;
3) Data on the porosity of the matrices (Table 2) show that sample №3 (glossy) has the lowest porosity (33.8%), and sample №2 (glossy) has an intermediate porosity (48.4%). Matte samples №1 (base) and №4–7 generally have higher porosity (50.9–57.7%). Although a direct correlation between total porosity and surface gloss is possible, it is also necessary to consider the nature of the surface porosity and its subsurface layer structure, which may differ, which affects the appearance. For example, the lower total porosity of sample №3 may correlate with a denser and smoother surface;
4) Different compatibility of the modifying monomers with styrene, divinylbenzene and the polymerization medium (including the stabilizer) may affect the thermodynamics and kinetics of phase separation during the formation and curing of the polymer granules. This, in turn, may lead to differences in the final surface morphology.

Comparison of the positions of the main bands of TODGA in pure form and as part of SPE (sample №1 and industrial sample) shows insignificant frequency shifts (for example, for C–O vibrations the shift is 2−3 cm^{-1}), or their absence (for C=O vibrations the frequency of 1647 cm^{-1} is preserved). This may indicate that the immobilization of TODGA in the polystyrene matrix occurs mainly due to physical retention in pores and weak van der Waals interactions, which do not lead to a significant redistribution of the electron density in the key functional groups (C=O, C–O–C) of TODGA, recorded by IR spectroscopy. A small shift of the band of out-of-plane deformation vibrations of C–H of the aromatic ring of the matrix from 704 cm^{-1} to 699 cm^{-1} in the presence of TODGA may be associated with a change in the local environment of the benzene rings when the pores are filled with the extractant. The absorption band of the stretching vibrations of carbonyl groups observed in the IR spectra of sample №1 and the industrial sample has a frequency of about 1647 cm^{-1} (the “Amide I” band).

In addition to the intense band at about 1647 cm^{-1}, the IR spectra of the sorbents show intense absorption in the range of 2800–3000 cm^{-1}, which is characteristic of the absorption of stretching vibrations of methyl and methylene groups and has a high intensity in the IR spectrum of TODGA, as well as an absorption band of stretching vibrations of the C–O groups of TODGA.

Thus, the IR spectra of sample №1 and the industrial sample include absorption bands of the styrene-divinylbenzene matrix and absorption bands of the TODGA extractant.

TODGA is highly soluble in carbon tetrachloride, which makes it possible to quantitatively analyze TODGA by the IR absorption spectrum in carbon tetrachloride solutions. The bands at 1647 and 1121 cm^{-1}, free from overlapping lines of the styrene divinyl benzene matrix, can be used as analytical absorption bands. The main purpose of using these intensity ratios is to characterize the relative content of the active component (TODGA extractant) in relation to the inert carrier (polymer matrix). In IR spectroscopy of solid samples, the absolute band intensities can vary greatly due to factors unrelated to concentration (e.g. tablet thickness and homogeneity, particle size). Using the ratio of the band intensity of the analyte (TODGA) to the matrix band intensity (which is assumed to be relatively constant in the sample) allows us to level out these variations. The matrix band (3025 cm^{-1}) acts as an “internal standard”. This is a standard technique in quantitative and semi-quantitative IR spectroscopy to obtain more reliable and reproducible results that reflect the ratio of components. The goal of the work was to synthesize SPE samples with a TODGA content of 40% by weight.

The calculated intensity ratios serve as confirmation that TODGA is indeed present in the matrix in significant quantities. These data are part of the general characteristics of the synthesized materials. They confirm that the extractant was successfully introduced into the matrix and that its relative quantity corresponds to expectations. This is important for further study of the sorption properties, since it is the quantity of TODGA that determines the capacity and efficiency of SPE.

Conclusions

The paper presents the results of the development of experimental modified samples of SPE TODGA intended for the selective extraction of americium-241 from nitric acid solutions of LRW.

- The polymer matrix, based on styrene and divinylbenzene, was modified with functional groups (methacrylic acid, 2.5-methylvinylpyridine, acrylonitrile) to enhance the extractant’s stability and reduce its leaching.
- The synthesized SPE samples were characterized by their granulometric composition (0.4–1.25 mm), porosity (33.8–57.7%), specific surface area (11.8–87.0 m^2/g), and exchange capacity (up to 0.72 meq/g).
- It was established that coarse-grained samples (0.8–1.25 mm) are preferable for industrial applications due to their compatibility with standard equipment. The industrial samples used for comparison possessed a smaller granule size (main fraction 0.3–0.8 mm), rendering them less suitable for industrial equipment without modifications.
- The experimental modified samples, synthesized using higher purity TODGA (>95%), potentially exhibited superior characteristics compared to the industrial samples prepared from technical-grade TODGA.
- The most promising modification option is the introduction of nitrile groups (acrylonitrile) into the polymer matrix followed by hydrolysis at 70 °C (sample №7), which enhances the binding of TODGA to the matrix due to coordination interactions and is confirmed by the results of IR spectroscopy and acetone leaching tests.
- Samples containing methacrylic acid and 2.5-methylvinylpyridine displayed smooth, glossy surfaces, whereas those with acrylonitrile and the base polystyrene sample were matte, likely attributable to differences in porosity and surface morphology.
- IR spectroscopy confirmed the presence of both the polymer matrix and TODGA in the synthesized and industrial SPE samples. Minor shifts or the absence of shifts in the characteristic TODGA band frequencies indicate that immobilization primarily occurs through physical retention within pores and weak interactions. The intensity ratios of TODGA bands to matrix bands affirmed the successful incorporation of the extractant in the expected quantities.

The results obtained can be used as a basis for creating technological schemes for the processing of LRW based on synthesized experimental modified samples of SPE TODGA, in particular for the isolation of minor actinides, including americium-241.

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