



Utilization of different crown ethers impregnated polymeric resin for treatment of low level liquid radioactive waste by column chromatography

M.F. Attallah^{a,*}, E.H. Borai^a, M.A. Hilal^a, F.A. Shehata^a, M.M. Abo-Aly^b

^a Analytical Chemistry and Control Department, Hot Laboratories and Waste Management Center, Atomic Energy Authority, Post Code 13759, Abu Zaabal, Cairo, Egypt

^b Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

ARTICLE INFO

Article history:

Received 2 February 2011

Received in revised form 2 August 2011

Accepted 4 August 2011

Available online 25 August 2011

Keywords:

Liquid radioactive waste treatment

Impregnated polymeric resin

Separation

Radionuclides

Crown ether derivatives

ABSTRACT

The main goal of this study was to find a novel impregnated resin as an alternative for the conventional resin (KY-2 and AN-31) used for low and intermediate level liquid radioactive waste treatment. Novel impregnated ion exchangers namely, poly (acrylamide-acrylic acid-acrylonitril)-N,N'-methylenedi-acrylamide-4,4'(5')di-t-butylbenzo 18 crown 6 [P(AM-AA-AN)-DAM/DtBB18C6], poly (acrylamide-acrylic acid-acrylonitril)-N,N'-methylenediacylamide-dibenzo 18 crown 6 [P(AM-AA-AN)-DAM/DB18C6], and poly (acrylamide-acrylic acid-acrylonitril)-N,N'-methylenediacylamide-18 crown 6 [P(AM-AA-AN)-DAM/18C6] were prepared and their removal efficiency of some radionuclides was investigated. Preliminary batch experiments were performed in order to study the influence of the different derivatives of 18 crown 6 on the characteristic removal performance. Separation of ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu radionuclides from low level liquid radioactive waste was investigated by using column chromatography with P(AM-AA-AN)-DAM/DtBB18C6 and metal salt solutions traced with the corresponding radionuclides. Breakthrough data was obtained in a fixed bed column at room temperature (298 K) using different bed heights and flow rates. The breakthrough capacities were found to be 94.7, 83.3, 58.7, 43.1 (mg/g) for ⁶⁰Co, ⁶⁵Zn, ¹³⁴Cs, and (¹⁵²⁺¹⁵⁴)Eu, respectively. Pre-concentration and separation of all radionuclides under study have been carried out using different concentration of nitric and/or oxalic acids.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Frequently used methods for treatment of liquid radioactive waste include chemical precipitation, evaporation, solvent extraction and ion exchange processes. Among the ion exchanger materials, impregnated polymeric resins have been used for the selective removal and separation of some radionuclides from radioactive liquid waste [1–6] as well as for the pre-concentration of metal species [7–10]. Crown ethers are effective extractants due to their ability to form stable complexes with metal ions. This property of crown ethers has led to the elaboration of new processes to extract radioactive elements from radioactive waste solutions [11–14]. Among the crown ethers, which are selective for alkali metal ions, derivatives of 21 crown 7 (21C7) have been extensively used for cesium extraction [15]. The key for the extraction is the good match between the cavity of the crown ether and the ionic radius of the metal ion. However, there are also several reports

involving the extraction of cesium by 18-membered crown ethers (18C6) [16–21].

The new cesium-selective macrocycle calix[4]arene-bis[4-(2-ethylhexyl)benzo-crown-6] (“BEHBCalixC6”) has been studied by Engel et al. The other calixcrown extractant, calix[4]arene-bis[4-tert-octyl-benzo-crown-6] (“BOBCalixC6”) was used to synthesis of this new extractant “BEHBCalixC6”. It was found that replacement of the tert-octyl alkyl chains on the benzo-crown portion of the calixcrown by 2-ethylhexyl chains improves the equilibrium solubility of the free calixcrown in aliphatic diluents, while not affecting the cesium extraction strength [3].

Development of the chromatographic partitioning of cesium and strontium utilizing two impregnated polymeric composites was also studied by Zhang et al. A novel, specific macro porous silica-based 4,4'(5')di-t-butylcyclohexano 18 crown 6 (DtBuCH18C6) chelating polymeric material was synthesized by impregnating DtBuCH18C6 molecule into Si-polymer particles that was prepared by a series of polymerization reactions. They found that, DtBuCH18C6/Si-polymer is highly selective for Sr²⁺, where as DtBuCH18C6 acts as chelating agent for Sr²⁺ [4]. In acidic HLW, Cs(I) has been separated by a novel silica-based polymeric adsorption material, Calix[4]arene-R14/SiO₂-P, which is an excellent

* Corresponding author. Tel.: +20 2 446 20 806; fax: +20 2 446 20 784.

E-mail addresses: dr.m.f.attallah@gmail.com, mohamedfathy.79@yahoo.com (M.F. Attallah).

molecular recognition reagent for Cs(I) from Sr(II) and other fission products [5].

The present work was oriented to study the effect of different derivatives of 18 crown 6 based on poly (acrylamide-acrylic acid-acrylonitrile) resin as a novel impregnated polymeric material which could be used to remove some key radionuclides from low level liquid radioactive waste.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade purity and were used without further purification. Cesium chloride and europium nitrate, were obtained from Pro-labo (England). Acrylic acid, acrylonitrile purity (99%) and cobalt chloride were obtained from Merck (Germany). Acrylamide was supplied from BDH (England), 4,4'(5')di-t-butylbenzo 18 crown 6 (DtBB18C6) were purchased from Fluka (Switzerland) while 18 Crown 6 (18C6) and dibenzo 18 Crown 6 (DB18C6) were supplied from Aldrich (USA). N,N'-methylene diacrylamide (DAM) was obtained from Aldrich (USA). Oxalic acid and sodium hydroxide were purchased from Adwic (Egypt). Nitric acid and zinc chloride were obtained from Winlab (England). A radioactive waste sample containing mixed radionuclides ^{134}Cs , ^{65}Zn , ^{60}Co and $^{152+154}\text{Eu}$ was collected from various laboratory research activities in Hot Laboratories Center, Egypt.

2.2. Synthesis of impregnated polymeric material

Poly (acrylamide-acrylic acid-acrylonitrile) N,N'-methylene diacrylamide P(AM-AA-AN)-DAM was prepared to use γ -radiation induced template copolymerization and reported in our previous work [19,20].

In order to convert the polymer from the H^+ -form to the Na^+ -form, the polymer (H^+) was soaked in 0.1 M NaOH for 24 h. The solid material was separated from the solution by decantation and dried in electric oven (at $\sim 100^\circ\text{C}$). P(AM-AA-AN)-DAM (particle size 1.0–0.5 mm) was mixed individually with different concentration of each of 18 crown 6 (18C6), dibenzo 18 crown 6 (DB18C6) and 4,4'(5')di-t-butylbenzo 18 crown 6 (D-t-BB18C6) that were dissolved in nitrobenzene and soaked overnight, decanted, then dried at $\sim 50^\circ\text{C}$ for 24 h in an electric oven. The obtained three types of impregnated polymeric ion exchangers were subsequently used for batch and/or column experiments.

2.3. Instruments

The impregnated polymers were investigated using a FT-IR spectrometer (Bomen, Hartman & Braun, and model MB-157, Canada). The sample was ground into fine powder and dried to eliminate the moisture content. Representative amount of the impregnated polymer (2.0 mg) was then mixed with (98.0 mg) of potassium bromide (KBr). The mixture was compressed into the disc of 5 mm diameter and 1 mm thickness. The IR spectra of the prepared disc was then measured and recorded.

Measurements of the gamma radioactivity of the different radionuclides in the samples were carried out using a non-destructive γ -ray spectroscopic technique with high purity germanium (HPGe) detector model 2201-Oxford (USA).

2.4. Batch experiments

Preliminary batch experiments were performed to investigate the efficiency of different crown ethers impregnated into P(AM-AA-AN)-DAM particles towards the removal of ^{134}Cs , ^{65}Zn , ^{60}Co

and $^{152+154}\text{Eu}$ radionuclides from radioactive liquid waste. Different forms of P(AM-AA-AN)-DAM such as H^+ and Na^+ were prepared to test the effect of counter ion on the removal efficiency. Furthermore, the effect of crown ether loading (10, 20 and 40%, w/v) on the polymers was studied in order to find the optimal impregnation of the polymeric resin used for the removal of radionuclides. For this, 5 mL of radioactive liquid waste (at pH 8) was mixed with 50 mg of desired impregnated polymeric materials. The mixture was contacted on the thermostatic shaker at room temperature for 24 h to attain equilibrium. The activity concentration of the radionuclides in solution was determined radiometrically using the HPGe detector. The sorption percent ($S\%$) of the impregnated ion exchange resin is calculated according to the following equation:

$$S(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final counting rates per unit volume for the radionuclide, respectively; C_0 is the initial concentration (mg/L) of metal ions used.

2.5. Column chromatography studies

Fixed bed sorption studies were conducted to evaluate the column performance for Cs, Co, Zn and Eu ions removal on P(AM-AA-AN)-DAM (Na^+)/DtBB18C6. Experiments were carried out in column of 0.8 cm inner diameter and 12.0 cm length packed with prepared P(AM-AA-AN)-DAM (Na^+)/DtBB18C6 at pH of 5.0 that was selected from our previous batch experiments [19]. Sampling of effluent was done at predetermined time intervals in order to investigate the breakthrough point. The effects of inlet eluent flow rate (1.0, 3.0 and 5.0 mL/min) and the resin bed height (2.0, 4.0, 6.0 and 8.0 cm) on the performance of the breakthrough curves for each ion were studied. The initial concentration of all inactive ions was kept at 100 mg/L. The break-through capacity ($Q_{0.5}$) of the impregnated ion exchange resin is calculated according to the following equation:

$$\text{Breakthrough capacity } (Q_{0.5}) = \frac{V_{(50\%)} \times C_0}{m} \quad (2)$$

where, $V_{(50\%)}$ is the volume to break through at 50% uptake in L and m is the weight of the impregnated polymeric material (g).

Set of experimental trials has been performed in order to elute and/or separate radionuclides that retained on the impregnated polymeric materials. In this respect different eluent reagents such as oxalic and nitric acid were used.

2.6. Characterization of real radioactive liquid waste

Two types of liquid wastes were collected. The first waste sample, including mono-radionuclide (^{137}Cs only) was collected from the storage tank in Egyptian plant for treatment of radioactive liquid waste. While the second waste sample, including mixed radionuclides ^{134}Cs , ^{65}Zn , ^{60}Co and $^{152+154}\text{Eu}$ was collected from various laboratory research activities in Hot Laboratories Center, located at Abu Zaable site, Cairo, Egypt. Characterization of liquid radioactive waste used in this work has been done in our previous work [19,22], and are reported in Table 1.

3. Results and discussion

3.1. Sorption percentage of radionuclides using different derivatives of 18 crown 6 based on polymeric resin

In order to investigate the sorption of some hazardous radionuclides from radioactive liquid waste, various types of impregnated polymeric resin were prepared based on some derivatives of 18

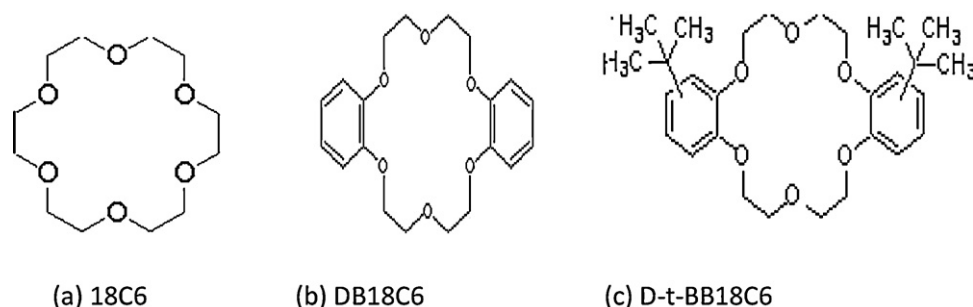


Fig. 1. Structure formula of 18 crown 6 (18C6), dibenzo 18 crown 6 (DB18C6) and 4,4'(5')di-t-butylbenzo 18 crown 6 (DtBB18C6).

Table 1
Some chemical and radiochemical properties of liquid radioactive wastes [19,22].

Name	Individual radionuclide waste	Mixed radionuclide waste
pH	8	7.5
TDS (mg/L)	1844	809
Conductivity ($\mu\text{S}/\text{cm}$)	6460	1716
Anions and cations (mg/L)		
Cl ⁻	199.0	400.0
NO ₃ ⁻	443.0	90.0
SO ₄ ²⁻	1063	200.0
PO ₄ ³⁻	40.0	75.0
Li ⁺	33.5	20.0
Na ⁺	8.50	ND
Ca ²⁺	9.0	ND
Pb ²⁺	25.0	ND
Zn ²⁺	25.0	12.5
Cu ²⁺	ND	2.50
Ni ²⁺	ND	15.0
Activity concentration (Bq/L)		
¹³⁷ Cs	25,397 ± 715	ND
¹³⁴ Cs	ND	128,549 ± 1399
⁶⁰ Co	ND	8320 ± 971
¹⁵² Eu	ND	71,921 ± 2667
¹⁵⁴ Eu	ND	9707 ± 489
⁶⁵ Zn	ND	5175 ± 200

ND: not detected.

crown 6, including 18 crown 6 (18C6), dibenzo 18 crown 6 (DB18C6) and 4,4'(5')di-t-butylbenzo 18 crown 6 (DtBB18C6) that were impregnated individually into P(AM-AA-AN)-DAM polymeric resin. Structural formula of 18C6, DB18C6 and DtBB18C6 are presented in Fig. 1.

The obtained sorption percentages have been calculated and reported in Table 2. It appeared that the P(AM-AA-AN)-DAM poly-

meric resin in the Na⁺ form was more efficient for the sorption of the radionuclides than in the H⁺ form. Significant enhancement from 9, 13.3, 33 and 56.3% to 55.1, 54, 87.6 and 88.4% was obtained for the sorption of ¹³⁷Cs, ¹³⁴Cs, ⁶⁰Co and ⁶⁵Zn, respectively. This is attributed to ion exchange process that takes place for the radionuclides with Na⁺ ions more favorably than with H⁺ ions. This characteristic behavior was reported in other investigations. In extraction chromatography, many authors activate the ion exchange resin by NaCl solution to improve the uptake percentage especially for monovalent cations [19,20,22–26]. For example, Borai et al. [24] showed this idea for the impregnated zeolite materials that used for Cs removal. Based on their results, they demonstrated that the distribution coefficients and the corresponding uptake percentages of Cs-134 are highly affected (decreases) by potassium rather than sodium ions in the waste solution. This may be due to the close similarity in ionic radii between Cs⁺ and K⁺ rather than that between Cs⁺ and Na⁺. Therefore, K⁺ ion could compete more with Cs⁺ ion during the sorption process.

This finding has a typical explanation to our results that showed significant improvement in the uptake percentage of Cs ion due to the activation of the resin with sodium rather than H⁺ form. This phenomena is clear in uni-univalent cations exchange rather than divalent cases. Therefore, interesting high uptake values for Co(II) and Zn(II) with P(AM-AA-AN)-DAM were obtained even without impregnation.

Better sorption of radionuclides on Na⁺ form was attributed to the consistence ionic radius of Na⁺ ion with the radionuclides rather than H⁺ ion [19,20,23].

Total dissolved salts and electric conductivity were found to be 1844 and 809 mg/L and 6460 and 1716 $\mu\text{S}/\text{cm}$ (as reported in Table 1) for individual ¹³⁷Cs and mixed radionuclides radioactive

Table 2
Uptake percentage of some radionuclides from LLLRW using different crown ether derivatives based on P(AM-AA-AN)-DAM ion exchanger.

Crown ether	Mono	Mixed radionuclide			
	¹³⁷ Cs	¹³⁴ Cs	⁶⁰ Co	⁶⁵ Zn	¹⁵²⁺¹⁵⁴ Eu
^a R(H ⁺)	9.0	13.3	33	56.3	63.3
R(Na ⁺)	55.1	54	87.6	88.4	42.3
R(H ⁺) + 10% 18C6	10.0	8.9	11.7	45.4	72.2
R(H ⁺) + 20% 18C6	18.8	15.1	23.2	62.5	85.8
R(H ⁺) + 40% 18C6	17.0	9.5	10.5	55.7	77.3
R(H ⁺) + 10% DB18C6	11.8	8.9	10.0	54.1	83.9
R(H ⁺) + 20% DB18C6	18.7	25.8	16.2	44.3	91.6
R(H ⁺) + 40% DB18C6	29.2	17.4	24.6	45.1	84.7
R(H ⁺) + 10% DtBB18C6	56	32.8	33.1	65.2	89
R(H ⁺) + 20% DtBB18C6	53.6	32.0	33.3	68.2	93.4
R(H ⁺) + 40% DtBB18C6	54.7	41.4	38.4	66.7	92.5
R(Na ⁺) + 10% DtBB18C6	82.7	81.6	84.7	81.1	83.8
R(Na ⁺) + 20% DtBB18C6	82.5	82.0	85.3	82.2	80.7
R(Na ⁺) + 40% DtBB18C6	83.2	82.7	86.7	82.5	84.3

Experimental condition: real waste samples, contact time 24 h at room temperature.

^a R: means resin (P(AM-AA-AN)-DAM).

Table 3
Distribution behavior of hazardous radionuclide using different crown ether.

Impregnated resin or extractant	Radionuclide	Distribution coefficient (mL/g)	References	
Impregnated resin SiO ₂ -P/DtBuCH18C6	Sr	946	Zhang et al. [30]	
	Cs	<3	Zhang et al. [30]	
	PVA/DCH18C6	Sr	30–45	Zakurdaeva et al. [31]
		Cs	457	The present work
	P(AM-AA-AN)-DAM/DtBB18C6	Co	549	The present work
		Zn	407	The present work
Eu		354	The present work	
Extractant	DB18C6			
	DAB18C6	Cs	1.8 ^a	Kumar et al. [17]
	DHB18C6	Cs	1.17 ^a	Kumar et al. [17]
	DNB18C6	Cs	0.78 ^a	Kumar et al. [17]
	DtBB18C6	Cs	0.8 ^a	Kumar et al. [17]
	DtBB18C6	Cs	3.34 ^a	Kumar et al. [17]
	BEHBCalixC6	Cs	<0.01–2.6 ^a	Mohapatra et al. [21]
	BOBCalixC6	Cs	1.78–33.4 ^a	Engle et al. [3]
	BOBCalixC6	Cs	1.22–35.3 ^a	Engle et al. [3]
	Calix[4]arene-BC6	Cs	10.32–16.35 ^a	Delmau et al. [32]
		Cs	10–40 ^a	Gorbunova et al. [33]

^a This value is distribution ratio.

Table 4
Breakthrough capacity of ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²+¹⁵⁴)Eu sorbed onto P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 at different process parameters.^a

Radionuclide	Bed height, cm	Breakthrough capacity, mg/g		
		1 mL/min	3 mL/min	5 mL/min
¹³⁴ Cs	2	–	–	11.92
	4	58.70	39.11	20.22
	6	–	–	28.01
	8	–	–	36.88
⁶⁰ Co	2	–	–	14.75
	4	94.67	59.73	25.14
	6	–	–	36.13
	8	–	–	45.02
⁶⁵ Zn	2	–	–	14.06
	4	83.34	53.10	23.00
	6	–	–	31.90
	8	–	–	40.20
⁽¹⁵²⁺¹⁵⁴⁾ Eu	2	–	–	8.69
	4	43.09	29.37	15.91
	6	–	–	22.10
	8	–	–	31.76

^a Experimental condition: real waste samples pH 5, initial concentration 100 mg/L.

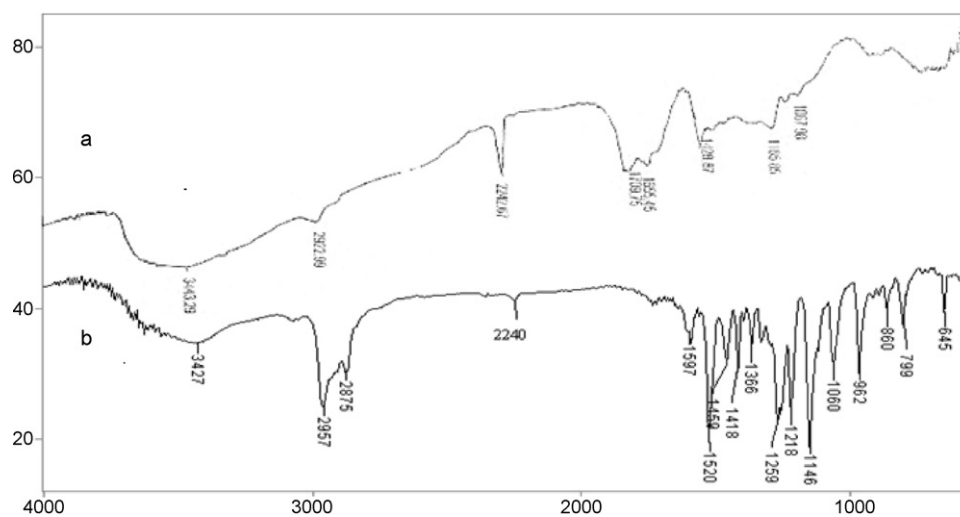


Fig. 2. Comparison of IR spectrum of (a) P(AM-AA-AN)-DAM and (b) P(AM-AA-AN)-DAM-(Dt-BB18C6) as impregnated polymeric material.

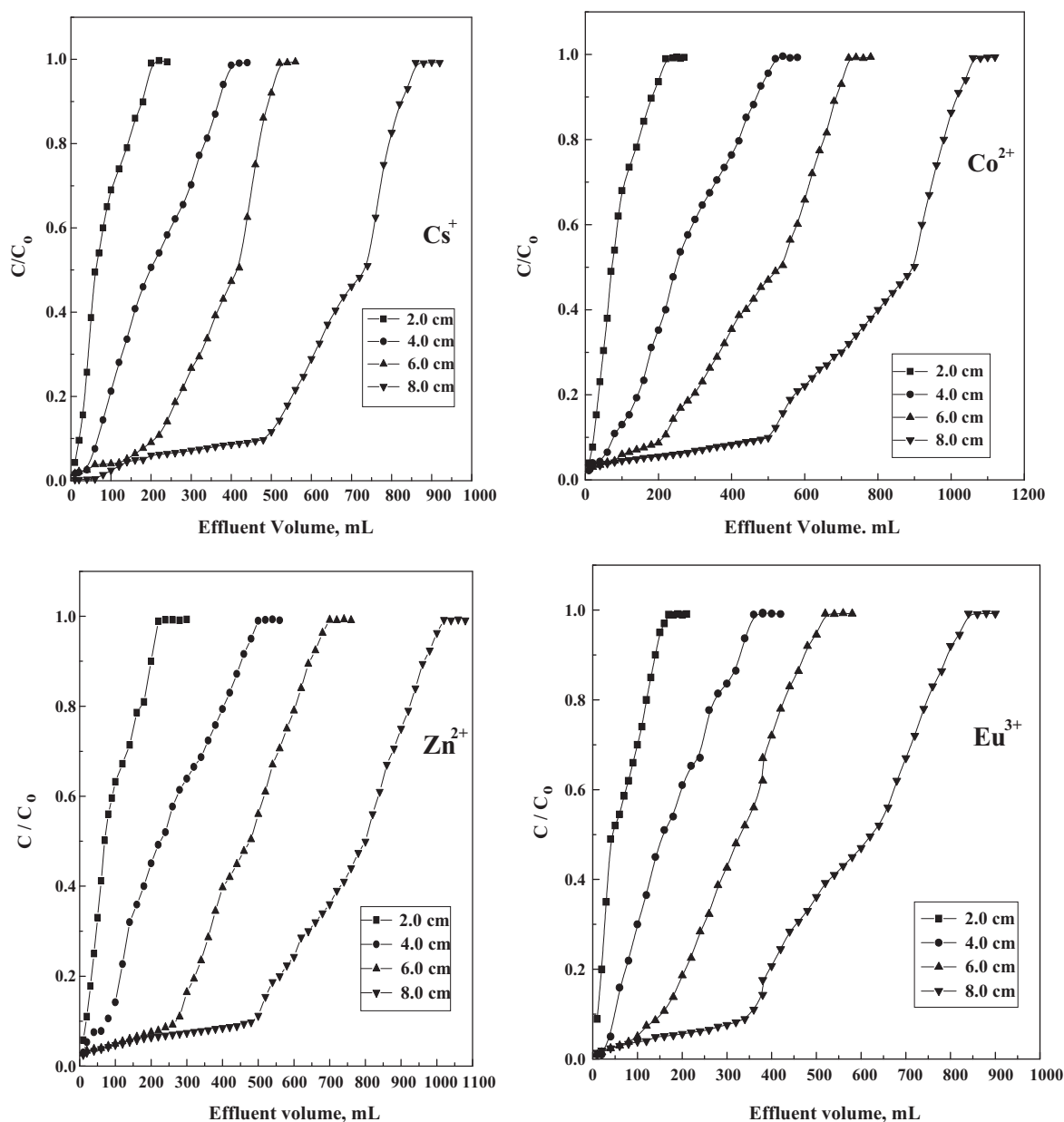


Fig. 3. Breakthrough curve of Cs⁺, Co²⁺, Zn²⁺ and Eu³⁺ sorbed onto P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 at different bed height and at 5.0 mL/min flow rate, pH 5, initial concentration (100 mg/L).

liquid wastes, respectively. Table 2, shows significant variation in the removal % of ¹³⁷Cs and ¹³⁴Cs at the same impregnated resin. This variation of results was attributed to the high TDS in the individual radioactive waste solution, leads to various exchange potentials due to the competition between non-radioactive ions and the radioactive species during sorption of radionuclides by the adsorption or ion exchange process.

Clearly, the impregnation process of both derivatives 18C6 and DB18C6 demonstrated insignificant improvement of the sorption efficiency of different radionuclides under study, except in case of (¹⁵²⁺¹⁵⁴)Eu. It was found that maximum sorption of (¹⁵²⁺¹⁵⁴)Eu reached to 85.8 and 91.6% at 20% loading of each of 18C6 and DB18C6, respectively. This may be due to their low affinity to the other radionuclides. Moreover, the impregnation of these two derivatives may be blocked the active sites in the polymeric resins, and therefore, decrease the sorption percent of radionuclides.

On the other hand, it was found that P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 gave a higher sorption percent for all radionuclides than the other derivatives of crown ether. This is likely attributed to the substituted di-tertiary butyl groups that attached to the crown ether rings. This could be probably due to the greater electron withdrawing ability of these groups when connected via the benzo group. The electron donating ability of the tertiary butyl group in DtBB18C6 has a positive inductive effect (+I) which helps in increasing the electron density on the oxygen 'O' atoms [17,19]. Moreover, ring cavity size of 18C6 is 2.6–3.2 Å [27], is large enough to allow the entry of any cation. However, the ligand is more selective for the Cs⁺. Cesium has the proper dimension (diameter ~3.40 Å) to almost fit in the ring cavity of 18C6, which favors the participation of all oxygen atoms of the macro ring cavity on the coordination, and leads to a more favorable stabilization [28]. The ionic radii of the other metals are too small comparing to the cavity of 18C6, therefore less number of oxygen atoms of 18C6 cavity coordinate with

the metal ion [28,29]. More efficient interaction between metal ions and the dipole donor (O) atoms of 18C6 may take place via ion–dipole mechanism.

The mechanism of interaction of Co(II), Zn(II) and Eu(III) with the impregnated polymeric resin may be taken place cationic exchange between Na⁺ of the carboxylic group of AA (–COONa) and metal ion. This is agree with the previous finding of interaction of polymeric materials such as P(AANa), P(AM-AA), P(AM-AANa-DAEA-HCl), P(AM-AA) with metal.

Furthermore, insignificant improvement of the sorption percentage was obtained by an increase the concentration of 18C6, DB18C6 and DtBB18C6 impregnated from 10 to 40%. The sorption percent of radionuclides using impregnated polymeric resin follows the order:

- P(AM-AA-AN)-DAM (Na⁺) / DtBB18C6
 > P(AM-AA-AN)-DAM (H⁺) / DtBB18C6
 > P(AM-AA-AN)-DAM (H⁺) / DB18C6
 > P(AM-AA-AN)-DAM (H⁺) / 18C6

Based on these results, P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 (10%) as impregnated ion exchanger was selected for the subsequent investigations. The obtained distribution coefficients of radionuclides under study have been compared with different impregnated crown ethers, derivative of crown ether and calix crown ether as extractant. It was observed the impregnated materials with different crown ether that used to remove and separate radionuclides are limited in literature. As shown in Table 3, the prepared resin (P(AM-AA-AN)-DAM/DtBB18C6) provided significantly high distribution coefficient for Cs radionuclides compared to the other derivative crown ether and calixarene.

3.2. Impregnated polymer structure

The infrared spectra of the polymeric material and impregnated polymeric material (P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6) show (Fig. 2) that there are many vibrationally absorption bands, characterized mainly to carboxylate, carboxylic, ester, ether and nitrile groups. The broad absorption band at ~3443, 3427 cm⁻¹ is characterized to stretching vibrations of CONH₂ related to amide group content in polymeric resin and impregnated polymeric material. This band was confirmed by the appearance of another band at 1520 cm⁻¹. Moreover, there is a strong absorption band at ~2922 and 2875 cm⁻¹, attributed to stretching vibrations of CH₂ group, which is confirmed by another band at 1076, 1165, and 1146 cm⁻¹. Two characteristic absorption bands at ~1428, 1418 cm⁻¹ are related to carboxylate group as well as absorption bands at ~1710, 1428, 1418, 962 cm⁻¹ are attributed to the carboxylic group. The absorption bands at 2242, 2240 cm⁻¹, are due to the nitrile group, as well as a band at 1655, 1597 cm⁻¹ are attributed to C=O bond. The new other two bands at 2957, 1366 cm⁻¹ are attributed to t-butyl in impregnated polymeric material as well as a band at 1459 cm⁻¹ is characterized to nitro-aromatic group [34–37].

The presence of the carboxylate and ester groups in P(AM-AA-AN)-DAM indicated the interaction of DAM with carboxylic groups of acrylic acid of the polymeric chain. It was found that DAM acts as a crosslinker in the polymerization of acrylamide, acrylamide–acrylic acid and acrylic acid–acrylonitrile [38,39]. This implies the presence of acrylamide, acrylic acid, acrylonitrile and ether units in the impregnated polymeric chains, as shown in Fig. 2b. The spectroscopy revealed that the resin, including DAM is linked between the polymeric chains according to the mechanism for the template copolymerization of AA-AN on P(AM) in the presence of DAM while DtBB18C6 may be linked to the polymeric chains according to hydrogen bond [19,39]. Crown ethers were providing the active

sites for sorption of metal ions beside various factional groups in the polymer support materials.

3.3. Chromatographic column studies

The operation and performance of a column are known to be influenced by it a number of parameters such as type, concentration and flow rate of the feed solution as well as column bed height. In this respect optimization of some variables is essential to evaluate the column performance.

Fixed bed column experiments were carried out to study the sorption dynamics. The shape of the breakthrough curve and the time for the breakthrough appearance are the predominant factors for determining the operation and the dynamic response of the sorption column. The general position of the breakthrough curve along the volume/time axis depends on the capacity of column with respect to bed height, the feed concentration and the flow rate [40–43]. In this concern different flow rates as well as various bed heights were tested at fixed initial ion concentration of 100 mg/L for all ions under investigation.

3.3.1. Effect of bed height

As shown in Fig. 3 (see also Table 4), the breakthrough capacity (Q_{0.5}), breakthrough time was increased with increasing bed height. The increase in the ion sorption with bed height was due to the increase of the sorbent mass in larger beds, which provide greater sorption sites for the metal ions. The obtained results are agree with the same trend by other authors [19,43–45]. Based on the obtained result it could be found that breakthrough capacity (Q_{0.5}) obeyed the following sequence at the same corresponding bed height:

Co > Zn > Cs > Eu

3.3.2. Effect of flow rate

The effect of flow rate on ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu sorption by P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 was studied by varying the flow rate for 1.0, 3.0 and 5.0 mL/min at the fixed bed height (4.0 cm) and initial concentrations (100 mg/L) for all ions under study. The plots of the breakthrough curves of ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu at various flow rates are shown in Fig. 4.

As shown from Fig. 4, an increase in flow rate reduces the effluent breakthrough volume and thereby decreases the retention time of the elements. This is due to the decrease in the residence time of the ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu within the bed at higher flow rates. Much sharper breakthrough curves for ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu sorption onto P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 were obtained at higher flow rates. The breakthrough time and the amount of total ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu sorbed also decreased with increasing flow rate, as presented in Table 4. This is attributed to the reduced contact time causing a weak distribution of the liquid inside the column, which leads to a lower diffusivity of the solute among the particle of the P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 [41].

3.4. Separation of ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu from radioactive liquid waste

Based on the previous results, removal and separation of ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu radionuclides from low level liquid radioactive waste was investigated using column containing P(AM-AA-AN)-DAM (Na⁺)/DtBB18C6 at flow rate 3.0 mL/min and 4.0 cm bed height. The loading process was carried out by passing an appropriate volume of the radioactive waste solution. Some set of an experiment were preferred for removal and separation process towards ¹³⁴Cs, ⁶⁰Co, ⁶⁵Zn and (¹⁵²⁺¹⁵⁴)Eu radionuclides using

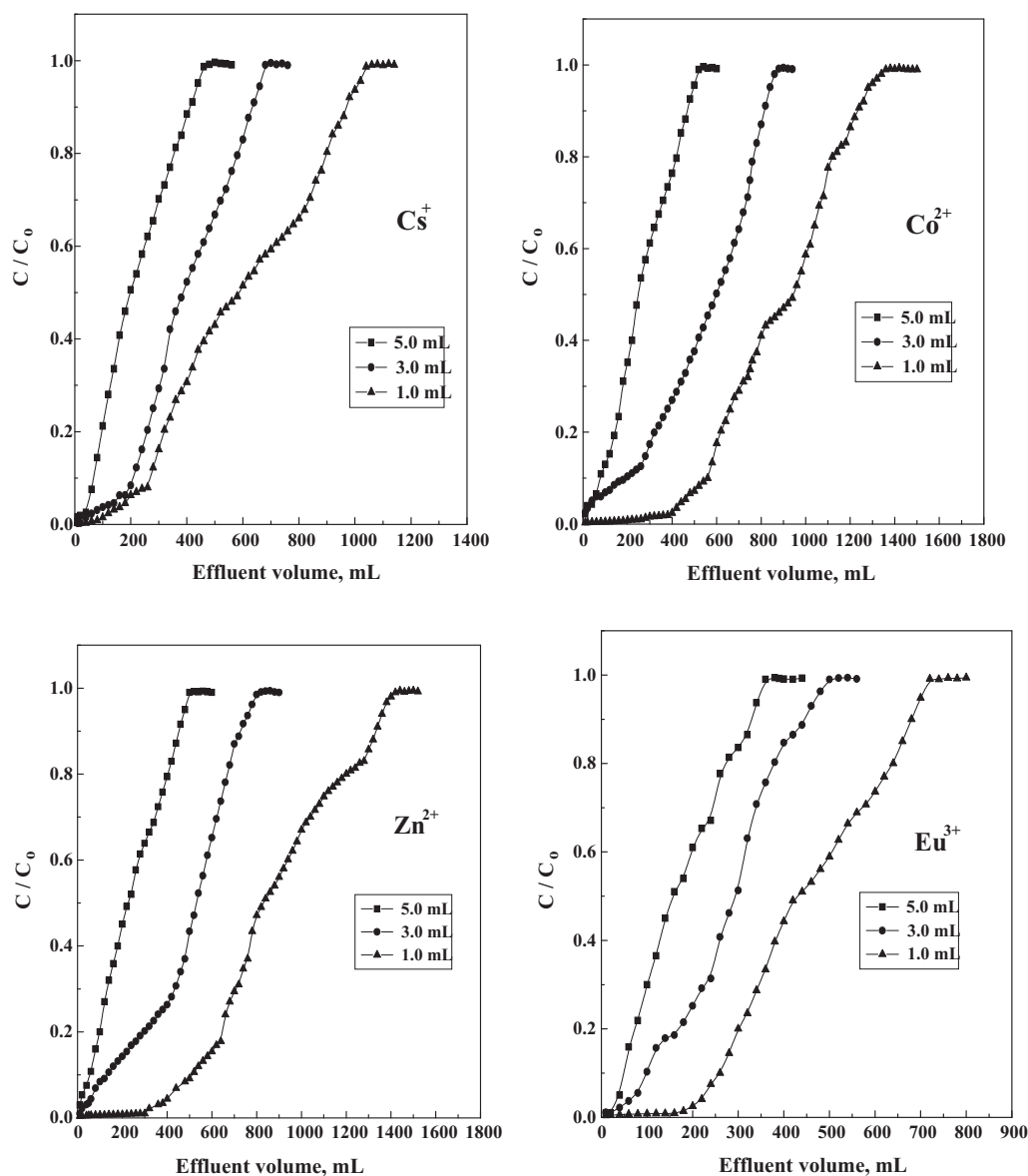


Fig. 4. Breakthrough curve of Cs^+ , Co^{2+} , Zn^{2+} and Eu^{3+} sorbed onto P(AM-AA-AN)-DAM (Na^+)/DtBB18C6 at different flow rate and at fixed bed height (4.0 cm) as well as initial concentration (100 mg/L) at pH 5.

nitric and oxalic acids as eluent reagents. Separation and removal of radionuclides under study are presented in Figs. 5–7.

Different concentrations of nitric acid such as 0.1, 0.5 mol/L, and 0.12 mol/L of oxalic acid at pH 4.5 were investigated for removal and/or separation process. As shown in Fig. 5, 0.5 M of nitric acid was used as eluent for removal and separation process. It was found that preconcentration and removal of ^{134}Cs , ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ radionuclides was done by 60 mL with recovery percent >98%, as presented in Table 5. It can be inferred that 0.5 mol/L nitric acid is a good eluent for preconcentration and removal of all radionuclides under study, but it is not capable of the separation of radionuclides from each other. The second trial was carried out using 0.1 mol/L nitric acid as eluent as shown in Fig. 6. Separation of ^{134}Cs from ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ radionuclides was obtained by 50 mL, with recovery percent 98%. No release of any other radionuclides on elution by 0.1 mol/L nitric acid took place. Therefore, higher concentration of nitric acid (0.5 mol/L) was applied to elute ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ radionuclides.

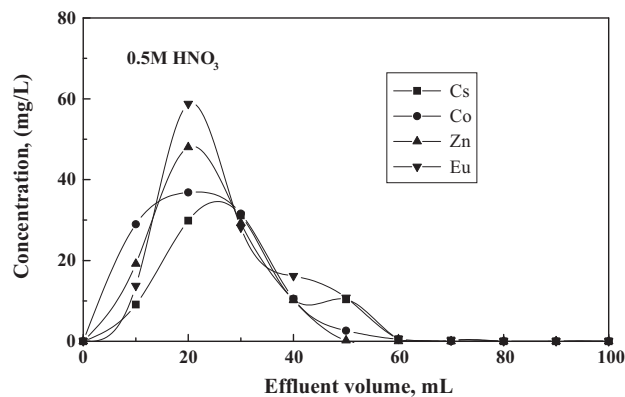


Fig. 5. Elution curves of ^{134}Cs , ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ by 0.5 mol/L nitric acid at 3.0 mL/min, 4.0 cm bed height.

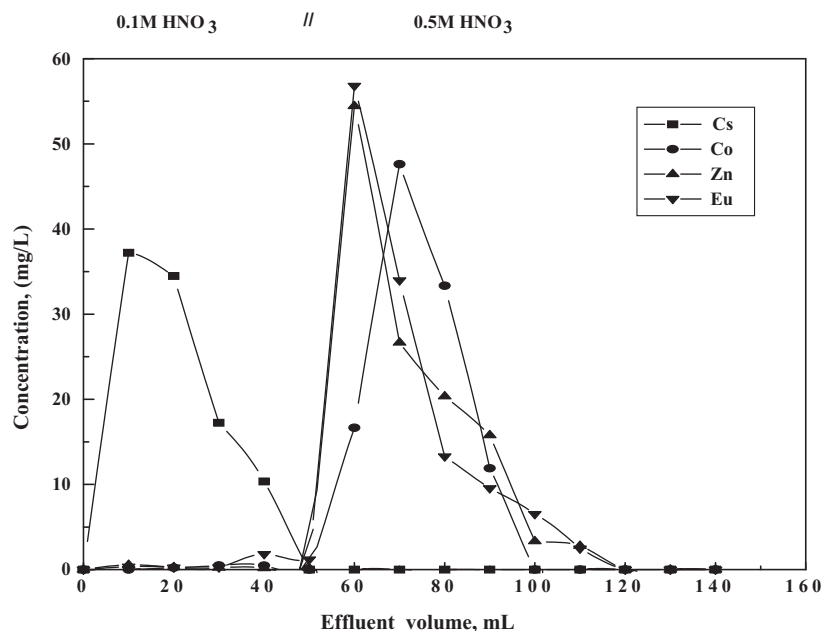


Fig. 6. Gradient separation and removal of ^{134}Cs , ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ from radioactive liquid waste using 0.1 mol/L followed by 0.5 mol/L nitric acid at 3.0 mL/min, 4.0 cm bed height.

Table 5

Recovery percent of ^{134}Cs , ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ using different eluent.

Eluent	Recovery, % Effluent volume, mL			
	^{134}Cs	^{60}Co	^{65}Zn	$(^{152+154})\text{Eu}$
0.12 M Oxalic acid (Fig. 7)	99 (60 mL)	96.8 (70 mL)	90 (80 mL)	–
0.1 M nitric acid (Fig. 6)	98.3 (50 mL)	–	–	–
0.5 M nitric acid (Fig. 6)	98.7 (50 mL)	97.6 (50 mL)	99 (60 mL)	99.5 (60 mL)

The third trial was carried out using 0.12 mol/L of oxalic acid at pH 4.5, and it appeared that 0.12 mol/L of oxalic acid is highly efficient eluent for the preconcentration of both ^{134}Cs and ^{60}Co from ^{65}Zn and $(^{152+154})\text{Eu}$ within about the first 50 mL. On the

other hand, ^{65}Zn was separated from $(^{152+154})\text{Eu}$ within the second 50 mL, while $(^{152+154})\text{Eu}$ is not eluted by oxalic acid. Then the last stage was performed for the separation of $(^{152+154})\text{Eu}$ successfully by gradient elution of 120 mL of 0.5 mol/L nitric acid as

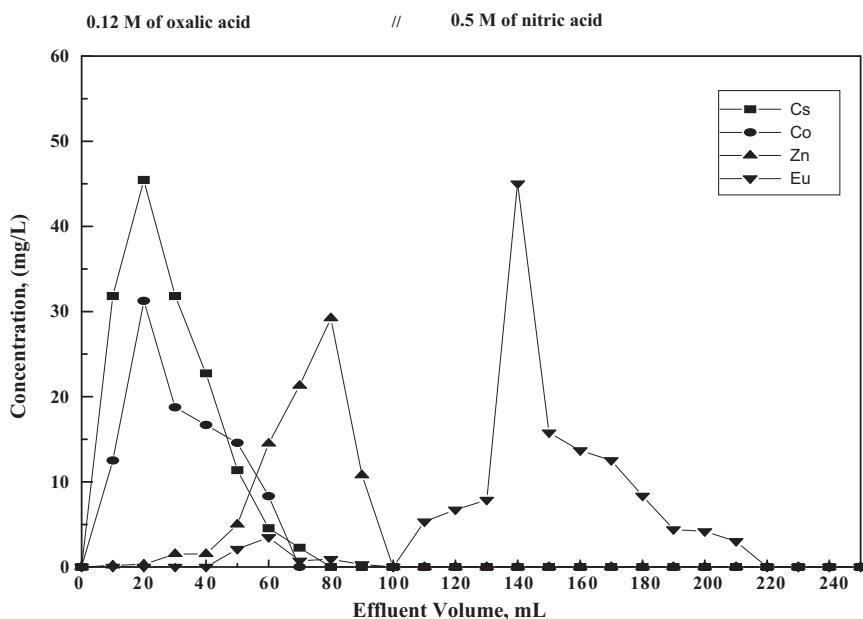


Fig. 7. Gradient separation and removal of ^{134}Cs , ^{60}Co , ^{65}Zn and $(^{152+154})\text{Eu}$ from radioactive liquid waste using 0.12 mol/L of oxalic acid at pH 4.5 followed by 0.5 mol/L nitric acid at 3.0 mL/min, 4.0 cm bed height.

depicted in Fig. 7. The recovery percent of ^{134}Cs , ^{60}Co , and ^{65}Zn were 99, 96.8, and 90% using 0.12 mol/L of oxalic acid as well as 99.5% for $(^{152} + ^{154})\text{Eu}$ using 0.5 mol/L of nitric acid, as shown in Table 5.

4. Conclusions

Impregnated polymeric materials, namely P(AM-AA-AN)-DAM/D-t-BB18C6, P(AM-AA-AN)-DAM/DB18C6 and P(AM-AA-AN)-DAM/18C6 were prepared and the removal properties for some hazardous radionuclides from radioactive liquid waste were investigated. P(AM-AA-AN)-DAM/D-t-BB18C6 exhibits promising high sorption characteristics for the removal of ^{137}Cs and other mixed radionuclides such as ^{60}Co , ^{65}Zn and $(^{152} + ^{154})\text{Eu}$. Therefore, it can be used as an alternative sorbent material to the Egyptian plant for treatment of radioactive liquid waste. Separation and removal of some hazardous fission products were successfully applied from low level liquid radioactive waste (LLRW) containing mixed radionuclides (^{134}Cs , ^{65}Zn , ^{60}Co and $^{152} + ^{154}\text{Eu}$) using extraction column chromatography packed with P(AM-AA-AN)-DAM/D-t-BB18C6. The separation process was done with high recovery by gradient elution of nitric and oxalic acids.

References

- [1] S.A. Ansari, P.N. Pathak, M. Husain, A.K. Prasad, V.S. Parmar, V.K. Manchanada, *Talanta* 68 (2006) 1273.
- [2] B.S. Shaibu, M.L.P. Reddy, A. Bhattacharyya, V.K. Manchanda, *J. Magn. Mater.* 301 (2006) 312.
- [3] N.L. Engel, P.V. Bonnesen, B.A. Tomkins, T.J. Haverlock, B.A. Moyer, *Solv. Extr. Ion Exch.* 22 (4) (2004) 611.
- [4] A. Zhang, E. Kuraoka, H. Hoshi, M. Kumagai, *J. Chromatogr. A* 1061 (2004) 175.
- [5] A. Zhang, E. Kuraoka, M. Kumagai, *Sep. Purif. Technol.* 50 (2006) 35.
- [6] A. Zhang, E. Kuraoka, M. Kumagai, *J. Chromatogr. A* 1157 (2007) 85.
- [7] T. Honjo, H. Kitayama, K. Terada, T. Kiba, *Fresenius Z. Anal. Chem.* 330 (1988) 159.
- [8] A.K. Kostad, P.Y.T. Chow, F.F. Cantwell, *Anal. Chem.* 60 (1988) 1569.
- [9] J.P. Bernal, E. Rodriguez De San Miguel, J.C. Aguilar, G. Salazar, J. De Gyves, *Sep. Sci. Technol.* 35 (10) (2000) 1661.
- [10] K.A.K. Ebraheem, M.S. Mubarak, Z.J. Yassien, F. Khalil, *Sep. Sci. Technol.* 35 (13) (2000) 2115.
- [11] I.H. Gerow, J.E. Smith Jr., M.W. Davis Jr., *Sep. Sci. Technol.* 16 (1981) 519.
- [12] K.L. Nas, *Solv. Extr. Ion Exch.* 11 (1993) 729.
- [13] V.S. Talanov, G.G. Talanova, M.G. Gorbunova, R.A. Bartsc, *J. Chem. Soc., Prekin Trans. 2* (2002) 209.
- [14] V.V. Yakshin, V.I. Zhilov, S.V. Demin, G.A. Pribylova, I.G. Tananaev, A.Y. Tsvivadze, B.F. Myasoedov, *C. R. Chim.* 10 (2007) 1020.
- [15] Y. Takeda, *Topics Curr. Chem.* 121 (1984) 1.
- [16] M.L. Dietz, E.P. Horwitz, M.P. Jensen, S. Rhoads, R.A. Bartsch, A. Palka, J. Krzykowski, *J. Nam. Solv. Extr. Ion Exch.* 14 (1996) 357.
- [17] A. Kumar, P.K. Mohapatra, V.K. Manchanda, *J. Radioanal. Nucl. Chem.* 229 (1998) 169.
- [18] Y. Kikuchi, Y. Sakamoto, *Anal. Chim. Acta* 403 (2000) 325.
- [19] M.F. Attallah, Radiochemical studies on separation and removal of some radionuclides from radioactive wastes, Ph.D. Thesis, Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt, 2009.
- [20] M.F. Attallah, E.H. Borai, K.F. Allan, *Radiochemistry* 51 (6) (2009) 622.
- [21] P.K. Mohapatra, D.S. Lakshmi, D. Mohan, V.K. Manchanda, *J. Membr. Sci.* 232 (2004) 133.
- [22] E.H. Borai, M.A. Hilal, M.F. Attallah, F.A. Shehata, *Radiochim. Acta* 96 (2008) 441.
- [23] F.A. Shehata, M.F. Attallah, E.H. Borai, M.A. Hilal, M.M. Abo-Aly, *Appl. Radiat. Isot.* 68 (2010) 239.
- [24] E.H. Borai, R. Harjula, L. Malinen, A. Paajanen, *J. Hazard. Mater.* 172 (2009) 416.
- [25] T. Siyam, M.M. Abdel-Hamid, I.M.M. El-Naggar, *Macromol. Rep. A* 32 (Suppl. 5 & 6) (1995) 871.
- [26] T. Siyam, I.M. El-Naggar, H.F. Aly, Intern. Topical Meeting on Nuclear and Hazards Waste Management Spectrum 96, 18–23 August, Seattle, Washington, 1996, p. 66.
- [27] T.M. Letcher, J.D. Mercer-Chalmers, R.L. Kay, *Pure Appl. Chem.* 66 (3) (1994) 419.
- [28] J.M. Caridade Costaa, P.M.S. Rodrigues, *Port. Electrochim. Acta* 20 (2002) 167.
- [29] H.J. Buschmann, H. Dong, E. Schollmeyer, *J. Coord. Chem.* 30 (1993) 311.
- [30] A. Zhang, Y.-Z. Wei, M. Kumagai, T. Koyama, *J. Radioanal. Nucl. Chem.* 262 (3) (2004) 739.
- [31] O.A. Zakurdaeva, S.V. Nesterov, N.A. Shmakova, G.K. Semenova, E.O. Sozontova, V.I. Feldman, *Nucl. Instr. Meth. Phys. Res. B* 265 (2007) 356.
- [32] L.H. Delmau, P.V. Bonnesen, B.A. Moyer, *Hydrometallurgy* 72 (2004) 9.
- [33] M.G. Gorbunova, P.V. Bonnesen, N.L. Engle, E. Bazelaire, L.H. Delmau, B.A. Moyer, *Tetrahedron Lett.* 44 (2003) 5397.
- [34] J.A. Dean, *Lange's Handbook of Chemistry*, thirteenth ed., McGraw-Hill Inc., USA, 1985.
- [35] B. Stuart, *Modern Infrared Spectroscopy*, John Wiley and Sons, Ltd, West Sussex, PO 19 1UD, England, 1996.
- [36] R.A. Nyquist, R.O. Kagel, *Infrared and Raman Spectra of Inorganic Compounds and Organic Salts*, Academic Press Inc, 1997.
- [37] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons Publications, New York, 1978.
- [38] K.F. Allan, T. Siyam, W.A. Sanad, 6th Arab Intern. Conf. on Polym. Sci. and Technology, 1–5 September, Sharm El Sheikh-Sinaa, Egypt, 2001, p. 121.
- [39] K.F., Allan, Gamma radiation-induced preparation of some polymeric resins and their use for the treatment of waste water, Ph.D. Thesis, Chemistry Department, Faculty of Science, Suez Canal University, Egypt, 2004.
- [40] S. Netpradit, P. Thiravetyan, S. Towprayoon, *Water Res.* 38 (2004) 71.
- [41] T.S. Singh, K.K. Pant, *Sep. Purif. Technol.* 48 (2006) 288.
- [42] E. Malkoc, Y. Nuhoglu, *J. Hazard. Mater.* 135 (2006) 328.
- [43] M. Sarkar, A.R. Sarkar, J.L. Goswami, *J. Hazard. Mater.* 149 (2007) 666.
- [44] S.S. Metwally, Ion exchange characteristics of poly-acrylamide and poly-acrylonitrile based Ce (IV) phosphate for removal and separation of some radioactive nuclides from waste solutions, Ph.D. Thesis, Chemistry Department, Faculty of Science, Ain Shams University, 2008.
- [45] A.M. El-Kamash, *J. Hazard. Mater.* 151 (2008) 432.