Research Article

Open Access

Studies on the Radiation Stability of Several Polymeric Flat Sheets used for Actinide Ion Separation from Radioactive Feeds

Mohapatra PK[1]*, Raut DR[1], Shah JG[2] and Bhardwaj YK[3]

[1]*Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*
[2]*Process Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*
[3]*Radiation Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*

Abstract

Radiolytic stability of polymeric flat sheet membranes was evaluated from surface morphology (SEM), contact angle and porosity data. The flat sheets made from PES (polyether sulfone), PP (polypropylene), PC (polycarbonate) and PVDF (polyvinylidenefluoride) were irradiated to varying extent using a ^{60}Co gamma ray source and the physical characterization of the membranes was carried out using various techniques mentioned above. Subsequently, the transport efficiency of the irradiated flat sheets was evaluated by studying the mass transfer of Am^{3+} from a feed containing 3 M HNO_3 in to a receiver phase containing 0.01 M HNO_3 as the strippant while 0.1 M TODGA (*N,N,N',N'*-tetraoctyldiglycolamide) +0.5 M DHOA (di-*n*-hexyloctanamide) in *n*-dodecane was used as the carrier extractant. Out of the flat sheet membranes, PC membranes were found to be more promising and transport studies were carried out using PC membranes up to an absorbed dose of 50 MRad which suggested very good transport of Am^{3+} without any deterioration of the membrane.

Keywords: Polymeric membranes; Radiolytic degradation; Transport; Liquid membrane

Introduction

Membrane based separation methods have been used for the remediation of industrial waste water emanating from a large number of industries [1-6]. The major challenge in such studies has been the membrane fouling which arises due to a large number of suspended particles. In view of the high efficiency of the membrane based separation systems, attempts are made, of late, to employ them in the nuclear industry for radioactive waste streams as well. The radioactive wastes are categorized as low, medium and high level wastes depending on their radioactivity content. Though low level wastes have been treated by membrane based separation methods at large scales [7], it is really a challenge to employ membrane separations to high level wastes. This is due to the large amount of radiation dose prevailing in the high level waste mainly due to the high beta gamma containing isotopes such as ^{137}Cs and ^{90}Sr [8]. Secondly, most of the membrane based separation methods employ polymeric membranes which are highly susceptible to radiolytic degradation [9]. Radioactive waste management is one of the major challenges of the nuclear power program [10] and there are reports on the application of membrane based separation methods for the separation of actinide and fission product nuclides from radioactive wastes [11]. Though low level wastes have been treated using polymeric membranes, the latter can be reused and recycled for a significantly long period of time due to the low dose rates (<microcuries per litre of the waste solution) of these wastes. On the other hand, high level waste processing can be done using radiation resistant polymers.

There are limited numbers of reports available in the literature on the radiolytic stability of polymeric membranes. Development of radiation resistant membranes has become important due to the growing interest in membrane based separation methods for radioactive waste water treatment. Also, though commercial membranes are available for gas separation, applications in food processing industries, etc. till recently, there was no need for applying membrane based separation methods for radionuclide separations. Therefore, there is a need to investigate the radiation stability of polymeric membranes. The radiation stability of polysulphonic acid cation exchange membranes was reported by

Ramachandhran and Mishra [12] up to 18.7 MRad absorbed dose. Recently, the authors have reported the transport efficiencies of several polymeric membranes after exposing those to an absorbed dose of 20 M Rad [13]. Though a vague idea was obtained, it was required to carry out a systematic study involving physical characterization of the irradiated membranes as well as metal ion transport. This would enable one to get a direct correlation of the properties such as surface morphology (the surface area has a very relevant role in metal ion transport), hydrophobicity (hydrophobic membranes can retain the organic carrier molecule and solvent for a long time, thereby enhancing the membrane stability), pore size (the pore size may get damaged by exposure to radiation) and tensile strength (overall reusability may be affected if the membranes are damaged) with the metal ion transport over a wide range of absorbed dose.

The authors have used common polymeric membranes like PS (polysulphone), PP (polypropylene), PC (polycarbonate) and PVDF (polyvinylidenefluoride) in the present study. The mass transfer studies were carried out by obtaining the transport behaviour of Am^{3+} using TODGA (*N,N,N'N'*-tetraoctyl diglycolamide) as the carrier and DHOA (di-*n*-hexyloctanamide) as the modifier. Distilled water was used as the receiver phase in the transport studies. The radiation stability of the polymeric membranes was also evaluated after irradiating them to 50 MRad in a ^{60}Co gamma ray chamber.

*Corresponding author: Mohapatra PK, Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India, Tel: +91-22-25594576; Fax: +91-25505151; E-mail: mpatra@barc.gov.in

Experimental

Materials

PES, PC and PP membranes (with close to 100% polymer content) were prepared at CSMCRI, Bhavnagar while the PVDF membranes were prepared at Desalination Division, BARC. The flat sheet polymeric membranes were irradiated using a ^{60}Co irradiator at a dose rate of 3.54 KGy/h. *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and DHOA (di-*n*-hexyloctanamide) were synthesized by reported methods and were used after ascertaining their purities by NMR and HPLC [14,15]. *n*-Dodecane (purity: 99%), procured from Lancaster, UK, was used as obtained. All other reagents were of AR grade and were used without further purification. ^{241}Am tracer was taken from a laboratory stock after checking its radiochemical purity [16]. ^{241}Am was assayed radiometrically by gamma ray counting using NaI(Tl) scintillation counter (Para Electronics) interphased with a multi-channel analyzer (ECIL, India). Counting statistics errors were minimized (<1%) by obtaining at least 10,000 counts.

Membrane characterization

SEM images were obtained for surface morphology analysis using a Stereoscan 100 Cambridge model operating at 15/25 kV with a magnification of 50-70X at a working distance of 15 mm at a tilt angle of 45°. The images were obtained after giving a 15 nm coating of gold using a Balzer's coating unit (model: CEA 30). The flat sheet membrane sample was analyzed for contact angle by mounting them on glass plates. The contact angles of the samples were measured by the sessile drop technique using image analysis software. Usually, a drop of MilliQ water (conductivity 0.05 µS.cm^{-1}), was allowed to fall on the flat sheet membrane samples using a software-controlled syringe. An image sequence was obtained through a CCD camera of a goniometer (GBX instruments, France) interfaced with an image capture software (Windrop^{++}, GBX instruments).

The porometer (Porolux 1000 model, Benelux Scientific, Belgium) operated in standard pressure range of 0-35 bar with flow rates up to 200 liters per minute. The sample holder diameter was 10 mm, and data acquisition and analysis was carried out using LabView software supplied by the manufacturer. The "Porefil" solution (γ=16 dyne/cm, vapour pressure=3 mm Hg at 298 K) supplied by Benelux Scientific, Belgium was used as a wetting liquid for capillary flow porometry as it is non-toxic inert fluorocarbon wetting fluid having zero contact angle in membrane or Cos θ=1. Mean flow pore size was calculated from the pressure at which the wet flow was half of the dry flow. The portions of plot of wet run from the point where the first flow of gas was observed up to the point where it meets the dry run plot were used for determining pore size distributions.

Transport studies

Transport of Am^{3+} was monitored using standard procedure reported earlier [17], in which the flat sheet membranes (irradiated as well as pristine membranes) were mounted in between the flanges of a two-compartment Pyrex glass cell for subsequent transport studies. Each compartment of the transport cell has 20 mL capacity and was filled with the feed (3 M HNO$_3$) and the receiver (0.01 M HNO$_3$) solutions. The flat sheet membranes were soaked overnight in the carrier solution (0.1 M TODGA + 0.5 DHOA in *n*-dodecane) and appeared completely wet before the transport studies. The cumulative % transport as seen from the feed side was determined by the following equation,

$$\% \ T_f \ = \ 100 \ \frac{\left(C_{f,o} - C_{f,t} \right)}{C_{f,o}} \tag{1}$$

where, $C_{f,o}$, $C_{f,t}$ and $C_{r,t}$ are the concentration of Am in the feed at 'zero' time, after time 't' and in the receiver compartment after time 't'. Am concentrations in the transport studies were about 10^{-7} M. Permeability coefficient values (P) were calculated from the effective membrane area (Q) and the feed volume (20 mL) using the following expression [18]:

$$\ln\left(C_{f,t} / C_{f,0} \right) \ = \ -\left(Q / V_f \right) Pt \tag{2}$$

The transport studies were carried out at ambient temperature (24 ± 1°C) and repeated twice. The results presented are the average of the two measurements.

Results and Discussion

Membrane characterization

Surface morphology analysis: The surface morphology analysis of the flat sheet polymeric membranes was done by taking SEM images of the membranes after exposing to gamma radiation. The flat sheets were exposed to 10, 20, 30 and 50 MRad dose and some membranes were found to disintegrate beyond a particular dose (Table 1). The SEM pictures are shown in Figure 1 for PES and PC flat sheets which were exposed to 30 MRad and 50 MRad doses, respectively. On the other hand, PP membranes were not stable even at 10 MRad absorbed dose and hence, their SEM pictures are not included in Figure 1. PVDF membranes were also irradiated and found to be stable up to an absorbed dose of 30 MRad. However, as good quality SEM pictures of irradiated PVDF membranes were not obtained, the same are not included here. As shown in the figure, the membranes appeared to be

Polymeric membrane	Irradiated up to	Observation
PP	20 MRad	Found to be brittle even after 10 MRad
PC	100 MRad	Integrity of membranes was good up to 50 Mrad. Beyond that membranes appeared brittle
PES	50 MRad	Integrity of membranes was good up to 30 Mrad. Beyond that membranes appeared brittle
PVDF	50 MRad	Integrity of membranes was good up to 30 Mrad. Beyond that membranes appeared brittle

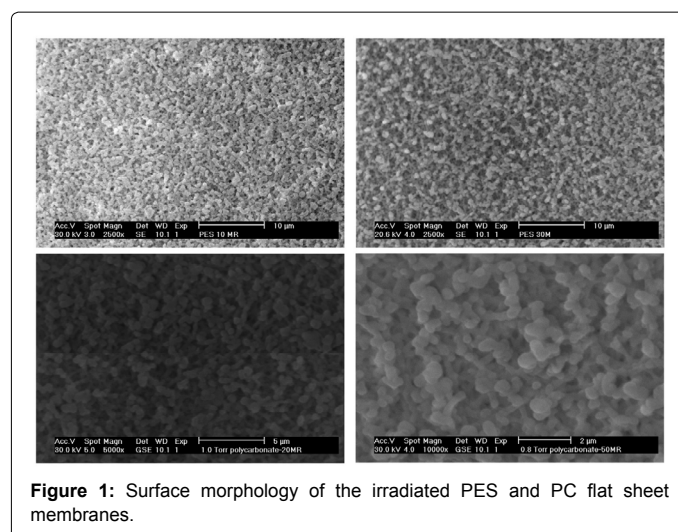**Table 1:** Summary of radiation stability data of the polymeric membranes used in this study

Figure 1: Surface morphology of the irradiated PES and PC flat sheet membranes.

uniform without any visible degradation marks. This is clear from the PES membranes irradiated at 10 MRad and 30 MRad doses and PC membranes irradiated at 20 MRad and 50 MRad absorbed doses. For better clarity, PC membrane irradiated at 50 MRad dose is magnified by a factor of two. The results suggest that PP membranes have much inferior radiation stability and hence, do not hold much promise for application.

Contact angle measurements: The membranes were usually exposed to an estimated absorbed dose up to 50 MRad. However, as some of the membranes were found to be brittle at this high absorbed dose, the data obtained at lower exposure are presented. Actual photographs of the water droplet are included in Table 2 for different membranes. The contact angle data are also presented in Figure 2 as a function of time which can give an indication about the membrane hydrophobicity. The contact angle data indicated that the hydrophobicity of the membranes decreased in the order: PVDF>PP>PC>>PES which was found to get affected with absorbed dose. PES membranes were found to be the least hydrophobic as the water drop was found to get quickly soaked in to the membrane in a few seconds and hence, the photographs are not included in Table 1. On the other hand, PP membranes were not very stable against radiation and became brittle even after exposure to 10 MRad dose (vide supra) suggesting that contact angle measurements was not possible. Out of all the membranes, PC showed better radiation stability while PVDF showed better hydrophobicity. Both the membranes also showed an enhancement in hydrophobicity with increasing absorbed dose. Furthermore, while only 4.4% change in

the contact angle was seen after about 2.5 minutes for the irradiated PVDF membranes, 12.9% change in the contact angle was seen in the same time interval for the irradiated PC membranes. Correlation of the metal ion permeability coefficients with the membrane hydrophobicity are presented below.
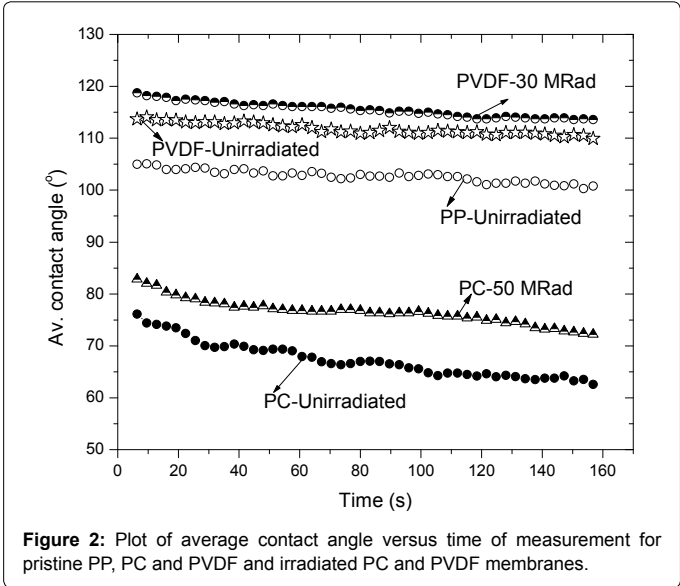

Figure 2: Plot of average contact angle versus time of measurement for pristine PP, PC and PVDF and irradiated PC and PVDF membranes.

Polymeric membrane	Photograph of the water droplet on the membrane at different time	
	Initial	**After 157 sec**
PC (pristine)		
PP (pristine)		
PVDF (pristine)		
PC (50 MRad)		
PVDF (30 MRad)		

Table 2: Contact angle measurement of the polymeric flat sheet membranes as photographed before and after irradiation.

Porosity measurements: The porosity of the membranes may get changed after exposure to radiation which may affect the transport properties. In view of this, the porosity of the polymeric membranes was measured both with the pristine membranes as well as the irradiated membranes and the data are presented in Table 3. As shown in the table, the errors in the pore size data were much less in the pristine membranes which increased after irradiation suggesting the increase in the average pore size after irradiation. This was particularly seen in case of PC and PVDF membranes while for PS membranes, the pore size did not change significantly after irradiation.

Transport studies

Figure 3 shows the % T data for Am^{3+} transport by the unirradiated PC membrane containing carrier solvent (TODGA + DHOA in *n*-dodecane) from a feed solution of 3 M HNO_3 into a receiver compartment containing 0.01 M HNO_3. The %T data are for the pristine membranes of all the four polymeric materials are given in Table 4. The %T data presented here are found to be significantly higher than those reported by us earlier with analogous membranes which were attributed to the fabric support used in the previous study which also led to large fraction of the Am^{3+} ion getting trapped in the membrane. In sharp contrast, the present study showed highly efficient Am^{3+} transport with all the four pristine membranes.

Results of the mass transfer studies using the irradiated membranes are also included in Table 4. PP membrane data are not included due to their poor radiation stability. The mass transfer data (Table 4) for the pristine membranes followed the trend: PP~PC>PES>PVDF which changed marginally to PES>PC>PVDF with the irradiated membranes. With the exception of PC, where significant difference in the Am^{3+} transport data was seen between the pristine and the irradiated membranes, the transport data obtained with the irradiated membranes of the other two membranes were very close to those obtained with the pristine membranes. As mentioned above, the mass transfer rates were found to be much higher as compared to those reported by the authors in a previous report which was attributed to the fabric support used in the membranes studied earlier [13]. Also, the data reported in the present paper are more meaningful as the hold up reported in the previous work is no longer valid [13]. In view of higher radiation stability of PC membranes, subsequent studies were carried out with PC flat sheet membranes exposed to varying amounts of absorbed gamma ray dose. As shown in Figure 3, the transport profiles were found not to deviate significantly from those obtained with the pristine PC membranes suggesting the mass transfer is not significantly affected with the absorbed dose (Table 5). Also, mass transfer studies were carried out using PP membranes which were used in most of the previously reported studies involving hollow fiber contactors [19,20] and the comparable mass transfer data (Table 5) validate PC as a suitable polymeric material for subsequent studies using hollow fiber contactors. All the above studies were carried out in duplicate and the results presented are average of the data. The errors in the mass transfer data were found to be less than ±2% and may be mainly due to non-uniformity of the membrane thickness (±2%) and counting statistics error (<1%). However, the membrane thickness variation averaged out and the counting statistics errors were minimized by long time counting.

In case of other membranes such as PES and PVDF, slight increase in the Am^{3+} transport rate was seen after 2 h with membranes exposed to 30 MRad absorbed dose. Though the membrane hydrophobicity was found to increase after exposing to radiation (Figure 2), this was not reflected clearly in their mass transport results (Table 4).

Membrane	Average pore size (µm)
PC (pristine)	0.33 ± 0.01
PC (50 MRad)	0.35 ± 0.03
PES (pristine)	0.36 ± 0.01
PES (30 MRad)	0.36 ± 0.02
PVDF (pristine)	0.25 ± 0.01
PVDF (30 MRad)	0.27 ± 0.03

Table 3: Measurement of pore size of polymeric membranes before and after irradiation. Data for PP membranes are not included as the membranes were found to be brittle even after exposure to even low doses of radiation
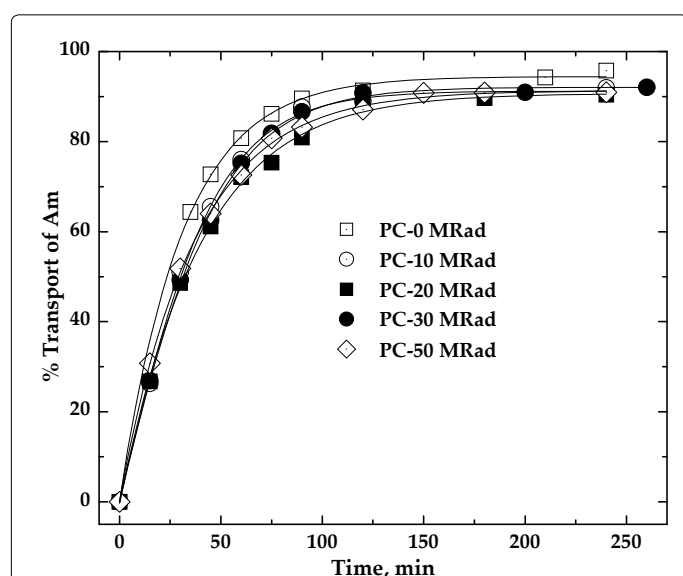

Figure 3: Am^{3+} transport data using polyethersulfone (PES) membrane filter. Feed: 3 M HNO_3; Receiver: 0.01 M HNO_3; Carrier: 0.1 M TODGA+0.5 M DHOA in *n*-dodecane.

Polymeric support	% Am transport (2 h)	
	Unirradiated[a]	Irradiated[a]
PP	92.0 ± 0.3	--[b]
PC	91.4 ± 0.2	87.1 ± 0.7[c]
PES	87.9 ± 0.3	88.2 ± 0.8[d]
PVDF	85.1 ± 0.5	86.3 ± 0.6[d]

Note: [a]Data as seen from the feed side mass balance

[b]Polymer was completely degraded to carry out any experiment

[c] Irradiated to 50 MRad

[d] Irradiated to 30 MRad

Table 4: Transport data after 2 hours with various polymeric solid supports, before and after irradiation. Feed: 3 M HNO_3; Receiver: 0.01 M HNO_3; Carrier: 0.1 M TODGA + 0.5 M DHOA in *n*-dodecane

Radiation dose (MRad)	Permeability×10^3, cm/sec	% Transport of Am (120 min)
Nil	3.548 ± 0.05	91.4 ± 0.2
10	3.645 ± 0.10	88.9 ± 0.4
20	3.004 ± 0.04	88.1 ± 0.4
30	3.200 ± 0.05	90.8 ± 0.7
50	2.992 ± 0.03	87.1 ± 0.7
PP	3.061 ± 0.07*	92.0 ± 0.2*

*Experiments were carried out with PTFE membrane (unirradiated) as support

Table 5: Comparison of Am^{3+} transport performance of PC membranes irradiated at variable doses using ^{60}Co irradiator. Feed: 3 M HNO_3; Receiver: 0.01 M HNO_3; Carrier: 0.1 M TODGA + 0.5 M DHOA in *n*-dodecane

Conclusions

The present study was taken up to evaluate the radiation stability of several polymeric membranes using their physical characterization such as surface morphology, hydrophobicity, pore size etc. and also to study mass transfer for actual application to radioactive waste processing. PP based membranes were found to be highly unstable to radiation while PES membranes were the least hydrophobic suggesting only PVDF and PC based membranes have some amount of resistance against radiation. However, in view of higher radiation resistance of PC membranes, these were further subjected to mass transfer studies which appeared to be quite satisfactory. It is proposed to prepare PC based hollow fibers for large scale mass transfer studies using radioactive solutions.

Acknowledgements

References

1. Qdaisa HA, Moussa H (2004) Removal of heavy metals from wastewater by membrane processes: a comparative study. Desalination 164: 105-110.

2. Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: A review. J Environ Manag 92: 407-e418.

3. Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arab J Chem 4: 361-377.

4. Bloecher C, Dorda J, Mavrov V, Chmiel H, Lazaridis NK, et al. (2003) Hybrid flotation—membrane filtration process for the removalof heavy metalions from wastewater. Water Research 37: 4018-4026.

5. Pancharoen U, Somboonpanya S, Chaturabul S, Lothongkum AW (2010) Selective removal of mercury as $HgCl_4^{2-}$ from natural gas well produced waterby TOA via HFSLM. J Alloys Comp 489: 72-79.

6. Saffaj N, Younssi SA, Albizane A, Messouadi A, Bouhria M, et al. (2004) Preparation and characterization of ultrafiltration membranes for toxic removal from wastewater. Desalination 168: 259-263.

7. (2004) Application of membrane technologies for liquid radioactive waste procesing. IAEA Technical Reports Series No. 431. International Atomic Energy Agency, Vienna.

8. Schulz WW, Bray LA (1987) Solvent extraction recovery of by product ^{137}Cs and ^{90}Sr from HNO_3 solutions-a technology review and assessment. Sep Sci Technol 22: 191-214.

9. Clough R, Shalaby SW (1991) Radiation Effects on Polymers, ACS Symposium Series 475, ACS, Washington D.C.

10. Choppin GR, Morgenstern A (2000) Radionuclide separation in radioactive waste disposal. J Radioanal Nucl Chem 243: 45-51.

11. Mohapatra PK, Manchanda VK (2003) Liquid membrane based separations of actinides and fission products. Indian J Chem 42A: 2925-2939.

12. Ramachandhran V, Misra B M (1986) Studies on the radiation stability of ion exchange membranes. J Appl Polym Sci 32: 5743-47.

13. Mohapatra PK, Raut DR, Ghosh AK, Reddy AVR, Manchanda VK (2013) Radiation stability of several polymeric supports used for radionuclide transport from nuclear wastes using liquid membranes. J Radioanal Nucl Chem 298: 807-811.

14. Sasaki Y, Sugo Y, Suzuki S, Tachimori S (2001) The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO_3-n-dodecane system. Solv Extr Ion Exch 19: 91-103.

15. Thiollet G, Musikas C (1989) Synthesis and use of the amide extractants. Solv Extr Ion Exch 7: 813-827.

16. Mohapatra PK (1993) PhD Thesis, University of Bombay.

17. Sriram S, Mohapatra PK, Pandey AK, Manchanda VK, Badheka LP (2000) Facilitated transport of americium(III) from nitric acid media using dimethyldibutyltetradecyl-1,3-malonamide. J Membr Sci 177: 163-171.

18. Danesi PR (1984-85) Separation of metal species by supported liquid membranes. Sep Sci Technnol 19: 857-894.

19. Kandwal P, Ansari SA, Mohapatra PK (2012) A highly efficient supported liquid membrane system for near quantitative recovery of radio-strontium from acidic feeds. Part II: Scale up and mass transfer modeling in hollow fiber configuration. J Membr Sci 406: 85-91.

20. Ansari SA, Mohapatra PK, Raut DR, Adya VC, Thulasidas SK, et al. (2008) Separation of Am(III) and trivalent lanthanides from simulated high-level waste using a hollow fiber-supported liquid membrane. Sep Purif Technol 63: 239-242.