Mathematical Modeling of Facilitated Transport of Eu(III) ion by CMPO in Modified diluents as Extractant

Rohit Kumar, Pankaj Kandwal

Department of Chemistry, National Institute of Technology, Uttarakhand, Srinagar (Garhwal) – 246174, India

Corresponding Author’s Email: pankaj.kandwal@nituk.ac.in ; rks71477@gmail.com

Abstract

A simplified model has been developed to model the pertraction of Eu(III) through the flat-sheet supported liquid membrane (FSSLM) impregnated with CMPO in modified diluents as extractant. The solvent extraction studies of europium were performed under different experimental conditions and some of solvent extraction (SX) data were taken from literature as required to obtain some basic parameters of mathematical modelling for the mass-transfer process. The metal ion transport through liquid membrane is facilitated by diffusion and formulation of model is, therefore, governed by law of diffusion. Effect of various parameters on transport rate of Eu(III) ion, such as ligand concentration, feed acidity, diluent composition etc., has been predicted.

(Keywords: Supported liquid membrane; Mass transfer resistances; Transport; Diffusion)

1. Introduction

Actinide partitioning of metal ions (Am, Pu, Eu U) is part of safe management of nuclear waste produced during nuclear fuel reprocessing has been challenging task for researcher all over the world and several research groups have been working in this direction and several individual schemes have been developed to achieve this purpose [1-4]. An explorative survey of the literature was conducted (Table 1) and found that most of the studies for extraction of europium using CMPO, a well-known extractant for lanthanides and actinides, requires TBP as phase modifier. TBP, being phosphorous-containing ligand [5], is environmentally not suitable. It was also found that there is a need to replace TBP with any suitable phase modifier, which should be environmentally benign. The phase modifier is fundamentally an organophilic molecule which modifies the polarity of solvent system and prevents the third-phase formation. In this connection, it was our aim to explore iso-decanol as a replacement for
TBP. Here, 0.20 M CMPO in iso-decanol and n-dodecane mixture was taken, where iso-decanol is employed as phase modifier to enhance the solubilization of the ligand-metal complex in the solvent and minimize acid co-transport. Furthermore, the solvent studies were carried out under the different experimental condition to evaluate the equilibrium constant and mass transfer resistances in aqueous phase and membrane phase.

| S. No. | Ligands Used                  | Method                  | Comments                                                                 | [Ref.] |
|-------|------------------------------|-------------------------|--------------------------------------------------------------------------|--------|
| 1     | CMPO Derivatives             | Solvent Extraction      | Extraction of Am(III) by 0.5M CMPO derivatives as extractants.            | [a]    |
| 2     | TRUEX Extractants            | SLM                     | Selective separation of Am(III), Feed: 3M HNO₃; Strip: 1M HCOOH.; Carrier: 0.25M CMPO + 0.75M TBP in decalin. | [b]    |
| 3     | TRUEX Extractants            | Counter-Current Extraction | Recovery of Actinides by 0.2M CMPO + 1.2M TBP by varying strippant conditions | [c]    |
| 4     | CMPO                         | SLM                     | Transport studies of Am(III), Feed: 3M HNO₃; Carrier: 0.1M CMPO and 0.1M CMPO + 1.2 M TBP; Strip: buffer mixture. | [d]    |
| 5     | Grafted CMPO-Moieties        | Synthesis               | Synthesized grafted CMPO moieties for actinides extraction.              | [e]    |
| 6     | TRUEX Extractants            | Solvent Extraction      | Solvent extraction studies of Eu(III) using 0.05 M of CMPO in TBP/bmimNTf₂. | [f]    |
| 7     | CMPO-Functionalized Ligand   | Solvent Extraction      | Extraction of Am³⁺ and U(VI) by 0.1 M CMPO functionalized ligands.       | [g]    |
| 8     | CMPO-Functionalized Ligand   | Synthesis and Solvent Extraction | Extraction studies of lanthanide and actinide by CMPO-functionalized ligands. | [h]    |
| 9     | CMPO-RTIL (C8mim+NTf₂)       | Extraction and Extraction Chromatography | Extraction of lanthanides and actinides and U(VI) by CMPO-RTIL (C8mim+NTf₂). | [i]    |
| 10    | CMPO                         | Solvent Extraction      | Solvent extraction studies of actinides and lanthanides by 0.2 M of CMPO in 10% iso-decanol in dodecane. | [j]    |

[a] E. P. Horwitz et al. 1983; [b] R. Chiarizia et al. 1987; [c] R. R. Chitnis et al. 1999; [d] A. K. Dinkar et al. 2009; [e] I. L. Odinets et al. 2010; [f] A Rout et al. 2011; [g] P. K. Mohapatra et al. 2013-1; [h] P. K. Mohapatra et al. 2013-2; [i] S. A. Ansari et al. 2014; [j] A. Sengupta et al. 2014.
Various techniques have been used for metal ion separation, such as solvent extraction, ion-exchange, extraction chromatography, liquid membranes, etc. Out of these, liquid membrane-based methods have been particularly attractive as they offer many advantages, viz., ease of operation, simultaneous extraction and stripping, easy scale-up, etc. A FSSLM is a polymeric support, impregnated with carrier solvent, which acts a barrier between feed solution (containing metal ions) and strip solution (where metal ion specie is concentrated). Herein this paper, a simplified model has been obtained for Eu$^{3+}$ transport through FSSLM assisted by CMPO in iso-decanol and $n$-dodecane mixture from acidic solution.

In this present work, mathematical equations are derived to model the mass transfer profiles of Eu$^{3+}$ through FSSLM. Also, the impact of various chemical parameters, such as feed acidity variation, ligand concentration variation, diluent concentration variation, etc. under the same condition have been studied with help of derived mathematical equations.

2. Experimental Methods and Materials

2.1. Radiotracers and Materials

Octyl (phenyl)-$N,N$-diisobutylcarbamoylmethyl phosphine-oxide (CMPO) is synthesized by a known method [6] at Bhabha Atomic Research Centre (BARC), Mumbai. The characterization of ligand was carried out by $^1$H-NMR, IR, and elemental analysis. Iso-decanol (~95% purity) has been purchased from Sisco labs and $n$-dodecane was purchased from Lancaster, UK. All other reagents were of AR grade and were used without any further purification. The radiotracers of $^{152,154}$Eu were obtained from the BRIT (Board of Radiation and Isotope Technology), Mumbai. The radiochemical purity of $^{152,154}$Eu was assayed by $\gamma$-ray spectrometry using HPGe detector.

![Chemical structure of Octyl(phenyl)-diisobutylcarbamoyl-methyl phosphine oxide (CMPO)](image)

Figure 1. Chemical structure of Octyl(phenyl)-diisobutylcarbamoyl-methyl phosphine oxide (CMPO)

2.2. Distribution studies
Distribution studies have been carried out by mixing equal volume of organic phase consisting of 0.20 ml CMPO in iso-decanol/n-dodecane with the same volume of aqueous phase (dilute HNO₃ solution having ¹⁵²,¹⁵⁴Eu) in stoppered glass tube at 25±0.1°C for 1 hour and then centrifuged to separate organic and aqueous phases. Aliquots of equal volumes (20μL) from organic and aqueous phases, respectively, were collected for further analysis. The radio-analysis of the samples was carried out by γ-counting using NaI(Tl) well-type counter. The distribution coefficient ($K_d$) is determined as below-

$$K_d = \frac{[\text{Metal}]_{\text{organic}}}{[\text{Metal}]_{\text{aqueous}}}$$

2.3. Mass Transport Process in Flat-Sheet Supported Liquid Membrane

Following steps are involved in mass transfer process through supported liquid membrane (particularly through Flat-sheet SLM), as also illustrated in Figure 2,

- The ion diffuses through the feed phase to the membrane.
- The metal ion makes a complex with the extractant molecule at membrane-feed interface and the complex is transferred into the membrane phase.
- The complex then diffuses through the membrane and reaches the strip-membrane interface.
- At strip-membrane interface, de-complexation of the metal-extractant complex takes place, releasing the metal ion into the strip phase.

![Illustrative diagram of the metal ion concentration profiles across various regions in the supported liquid membrane.](image)

2.4. Assumption of the model

Mathematical model was formulated based on the following assumptions;

(i) boundary layers exist on both sides (feed and strip) of the membrane,
(ii) the concentration gradients are linear,
(iii) the strip side distribution ratio is much smaller than feed side (i.e. \( K_{d,\text{strip}} \ll K_{d,\text{feed}} \)) and kinetics of stripping is very fast,

(iv) at pseudo-equilibrium, the mass-fluxes across feed phase and membrane phase are the equal,

(v) Diffusion law is followed.

2.5. Development of Mathematical Model for Europium ion Transport through Flat-Sheet SLM

In the case of a CMPO ligand, a counter anion is co-transported with metal ion to neutralize the charge on complex and the equilibrium \([9-11]\) is represented by following extraction reaction,

\[
\text{Eu}^{3+} + 3\text{NO}_3^- + 3\text{E}_{\text{org}} \leftrightarrow [\text{Eu(NO}_3)_3\text{(E)}_{3}]_{(\text{org})}
\]

where, \( E_{\text{org}} \) and \([\text{Eu(NO}_3)_3\text{(E)}_{3}]_{(\text{org})}\) denotes CMPO ligand and the metal-ligand complex, respectively; \( \text{NO}_3^- \) is counter-anion, species with subscript ‘aq’ and ‘org’ indicate those in the aqueous phase and organic phase respectively. The equilibrium constant \( (K_{\text{eq}}) \) is given by,

\[
K_{\text{eq}} = \frac{\bar{C}_{\text{f,i}}}{C_{\text{f,t}}} = \frac{K_d}{N_f^2E^2}
\]

where, \( \bar{C}_{\text{f,i}} \) denotes the extraction species \([\text{Eu(NO}_3)_3\text{(E)}_{3}]_{(\text{org})}\) in the organic phase of the feed membrane interface and \( C_{\text{f,i}} \) represents the Eu(III) concentration in the aqueous phase while \( E \) is the concentration of unbound ligand in the organic phase; \( N_f \) represents the effective concentration of counter anion in the feed solution and distribution ratio \( (K_d) \) is defined as,

\[
\text{Distribution ratio, } (K_d) = \frac{[\text{Eu(NO}_3)_3\text{(E)}_{3}]_{(\text{org})}}{\text{Eu}^{3+}_{(\text{ag})}} = \frac{\bar{C}_{\text{f,i}}}{C_{\text{f,i}}}
\]

Assuming that the flux \((J_a)\) at the aqueous feed side passing through the membrane having flux \((J_o)\) for Eu(III) ion can be obtained with help of the Fick’s first law of diffusion [Fig. 1],

\[
J = -D \frac{dc}{dx}
\]

Using eq. (3)

\[
J_a = \frac{D_{\text{aq}}}{d_{\text{aq}}} (C_{\text{f,t}} - C_{\text{f,i}})
\]

\[
J_o = \frac{D_{\text{org}}}{d_{\text{org}}} (\bar{C}_{\text{f,i}} - \bar{C}_{\text{s,j}})
\]

where, \( C_{\text{f,i}} \) is the conc. of europium ion in the feed solution while \( C_{\text{f,i}} \) denote the conc. of \([\text{Eu(NO}_3)_3\text{(E)}_{3}]_{(\text{org})}\) in the membrane phase, \( D \) represents the diffusivity and \( d \) denotes the diffusion path length.
Taking assumption (III) into consideration, equation (5) can be modified as,

\[ J_0 = \frac{D_{org}}{d_{org}} C_{f,i} \]

\[ J_0 = \frac{D_{org}}{d_{org}} (C_{f,i} K_d) \]

Because, \( K_d = \frac{C_{f,i}}{C_{f,i}} \)

\[ J_0 \frac{d_{org}}{D_{org} K_d} = C_{f,i} \]

(6)

Rearranging eq. (6) and adding to eq. (8)

\[ C_{f,t} = J_a \frac{d_{aq}}{D_{aq}} + J_o \frac{d_{org}}{D_{org} K_d} \]

From assumption (IV), \( J_a = J_o = J \)

\[ C_{f,t} = J \left[ \frac{d_{aq}}{D_{aq}} + \frac{d_{org}}{D_{org} K_d} \right] \]

\( \therefore d_{org} = d_m \cdot \tau \)

\[ C_{f,t} = J \left[ \frac{d_{aq}}{D_{aq}} + \frac{d_m \tau}{D_{org} K_d} \right] \]

We know that

\[ R_o = \frac{d_m \cdot \tau}{D_{org}} \text{ and } R_a = \frac{d_{aq}}{D_{org}} \]

where, Tortuosity (\( \tau \)) > 1 and \( R = 1/k \) denotes the mass-transfer resistance of the respective layer, assuming that carrier in the membrane is not saturated with Eu(III) ion then by the definition of \( K_d = \frac{C_{f,i}}{C_{f,i}} \) the flux expression for Eu(III) can be written as,

\[ J = \frac{C_{f,t} K_d}{R_o + K_d R_a} \]

(7)

where, \( R_o \) and \( R_a \) are the mass transfer resistances in organic phase membrane and feed-membrane interface, respectively.

\[ J = P \cdot C_{f,t} \]

(8)

Comparing eq. 7 and eq. 8,

Permeability \( (P) = \frac{K_d}{R_o + K_d R_a} \)

(9)

Using eq. (8) and (9), flux expression for Eu(III) can be rewritten as

\[ Q \cdot J = -V \frac{dC_{f,t}}{dt} \]

\[ J = -\frac{V dC_{f,t}}{Q \cdot dt} = \frac{C_{f,t} K_d}{R_o + K_d R_a} \]

\[ \frac{dC_{f,t}}{dt} = -\frac{Q}{V} \frac{C_{f,t} K_d}{R_o + K_d R_a} \]

(10)
where, $Q$ denotes the effective surface area of the membrane and $V$ is the volume of the aqueous feed solution.

Considering three molecules of CMPO ligand is combined with one molecule of Europium, forms the metal-carrier complex. Considering the mass-balance of ligand inside the membrane phase, we can write,

$$E_{\text{free}} + 3C_{\text{f,l}} = E_T$$

(11)

where, $E$ denotes the free carrier concentration and $E_T$ indicates the initial ligand concentration inside the membrane, the solving eq. (2), (9), (10) & (11)

$$\frac{3C_{\text{f,t}}K_d}{R_o + K_d R_a} + \left[ \frac{K_d}{[N_f K_{eq}]} \right]^{1/3} - E_T = 0$$

(12)

To maintain the electrical neutrality, considering the stoichiometry of the metal-ligand complex, the total concentration of NO$_3^-$ in feed can be expressed in order of reducing the concentration of Eu(III) ion in feed, then

$$N_f = [N_{f,0} - 3(C_{f,0} - C_{f,t})]$$

where, $N_{f,0}$ denotes initial conc. of anion in the bulk phase and $C_{f,0}$ represents initial concentrations of europium ion, respectively, putting the value of $N_f$ in eq. (12).

$$\frac{3R_o C_{\text{f,t}} K_d}{R_o + K_d R_a} + \left[ \frac{K_d}{[N_{f,0} - 3(C_{f,0} - C_{f,t})]} \right]^{1/3} - E_T = 0$$

(13)

Now, rearranging eq. (13), then

$$\frac{3R_o C_{\text{f,t}} K_d}{R_o + K_d R_a} + \left[ \frac{K_d^{1/3}}{[N_{f,0} - 3(C_{f,0} - C_{f,t})]^{1/3}} \right]^{2/3} - E_T = 0$$

(14)

Eq. (14) is differentiated with respect to time ($t$) and then coupled with equation (10). This procedure obtained two differential equations in the form of $dC_{f,t}/dt$ and $dK_d/dt$, which are solved simultaneously using Runge-Kutta 4th order numerical methods as implemented in MATLAB.

### 2.6. Determination of Mass Transfer Resistances

The permeability ($P$) of species through the flat-sheet SLM is determined by plotting the graph, $\ln \left( \frac{C_{f,t}}{C_{f,0}} \right)$ vs time ($t$) with help of following formula as [7,8],

$$-\ln \left( \frac{C_{f,t}}{C_{f,0}} \right) = \left( \frac{Q}{2} \right) \times P \times t$$

(15)

where, $C_{f,0}$ and $C_{f,t}$ are the metal ion concentration in the feed at $t = 0$ and time $t$ respectively, $V$ is the total feed volume (ml), $Q$ is the surface area of membrane (3.14 cm$^2$), $P$ is the permeability (cm/s) of metal ion.
The experimental measurement of mass-transfer resistance (R_a and R_o) was done by plotting 1/P versus 1/K_d, which is linearly filled as per the following relation,

\[ \frac{1}{P} = R_a + \frac{R_o}{K_d} \]  

(16)

From the graph so obtained experimentally, a linear fitting of the data can obtain the value of R_a = 95 s/cm and R_o = 10000 s/cm, which can be used as input for further calculations.

3. Results and Discussion

3.1. Ligand Concentration Variation

The effect of ligand (CMPO) concentration was examined in the concentration range of 0.1 M-0.4 M. It was observed that with increasing the carrier concentration, the rate of Eu(III) ion transport increased. Due to increasing carrier concentration in the membrane which results in distribution ratio of metal ion at the feed-membrane interface (Table 2) and hence extraction of metal ion increases. This results in increased Eu(III) ion transport in feed at higher ligand concentration. (Figure 3)

Table 2: Experimental value of Distribution ratio (K_d) of Eu(III) at varying ligand concentration; Aqueous phase: 3M HNO_3; Organic phase: 0.10-0.40 M CMPO in 10 % isodecanol/n-dodecanol.

| [CMPO], M | K_d, Eu(III) |
|-----------|--------------|
| 0.10      | 0.21         |
| 0.20      | 4.80         |
| 0.30      | 20.43        |
| 0.40      | 37.25        |

For the prediction of the model, the observed trend can easily be explained by looking at equation (10). An increased concentration of ligand led to higher distribution ratio value (K_d) for europium, which in turn makes the right-side of equation 10 more negative. Hence, the metal concentration reduces with a much faster rate at higher ligand concentration.
3.2. Feed Acidity Variation

Increasing the feed acidity increases the nitrate ion concentration, which enhances the extraction of metal ion (as shown in Table 3). Therefore, it is expected that the increases the concentration of counter anion will increase the transport rate. Hence, the experiments of europium transport were carried out at a different concentration of nitric acid in feed and keeping the other parameters constant. The simulation results are illustrated in Figure 4 and it can be observed that with continuously increasing the feed acidity, increases the rate of Eu(III) transport from the feed solution. The denominator in equation 10 is mainly governed by the mass transfer resistance in an organic membrane ($R_o$) because the product $K_d$, $R_a << R_o$. Hence, at higher acidity of feed phase, the rate of europium transport increased according to equation 10, the model predicts the outcomes of transport rate of europium as shown in figure 4. It must be noted here that increasing the feed acidity also increases the H$^+$ ion in the feed side. This also affects the acid transport from the feed to the strip side, which is expected to inhibit the stripping efficiency and therefore, some off-results are expected in the later part of simulated curve when compared with the experimental data.

Figure 3: Simulation of Eu(III) transport at different ligand concentration. Feed: 3M HNO3, Strip: distilled water, Ligand: 0.1-0.4 M CMPO in 10% iso-decanol/ n-dodecane.
Figure 4: Feed acidity variation study. Feed: 0.5-6 M HNO₃, Strip: distilled water, Ligand: 0.2M CMPO + 10 % isodecanol/n-dodecane.

Table 3: Distribution ratio ($K_d$) of Eu(III) at varying nitric acid concentration; Organic Phase: 0.2M CMPO in 10 % isodecanol/n-dodecane.

| [HNO₃], M | $K_d$, Eu(III) |
|-----------|---------------|
| 0.5       | 1.21          |
| 1         | 2.60          |
| 2         | 4.25          |
| 3         | 5.85          |
| 4         | 7.50          |
| 6         | 8.50          |

*The data of Distribution ratio ($K_d$) of Am/Eu(III) at varying nitric acid concentration taken from the literature [12-13].

3.3. Diluent Concentration Variation

TRUEX is a well-known process, in which tributylphosphate (TBP) is used as phase modifiers to enhance the solubility of metal-ligand complex species in the solvent to inhibit the third phase formation. TBP, being phosphorous-containing ligand, is environmentally not suitable. It is needed that alternative phase modifiers be explored. Therefore, it was thought to explore iso-decanol as a replacement of TBP in the present work. 0.2M CMPO in a diluent mixture of 10% iso-decanol and n-dodecane as a carrier was used to prevent third phase formation, and minimize acid co-transport [12-14]. Although the solubility of metal-ligand
complex species in solvent increases with increasing % of iso-decanol concentration, it was found that the distribution ratio of metal ion by ligand was decreased [13], which influence the rate of europium transport in feed. As results, the transport of Eu(III) was decreased with increasing percentage (%) of isodecanol in CMPO ligand. (figure 5)

Figure 5: Diluent concentration variation study. Feed: 3M HNO₃, Strip: distilled water, Ligand: 0.2M CMPO + 5-30 % iso-decanol/n-dodecane.

Table 4: Distribution ratio ($K_d$) of Eu(III) with 0.2 M CMPO at varying (%) diluent concentration; Aqueous phase: 3M HNO₃

| Ligand            | iso-decanol (%) | $K_d$, Eu(III) |
|-------------------|-----------------|----------------|
| 0.2 M CMPO in     | 5               | 11.5           |
| modified diluents | 10              | 4.8            |
|                   | 30              | 0.8            |

*Some of data of Distribution ratio ($K_d$) of Am/Eu(III) at varying diluent concentration taken from the literature [12-13].

4. Conclusion

In the present work, mathematical model is developed for the transport of europium metal ion through membrane with CMPO ligand. The model predicts suitable experimental conditions for efficient transport of Eu(III) from FSSLM and our previous results have shown the applicability of the model for the system. Nevertheless, further extensive validation of the model on different systems is required to apply the model on unknown systems. In future
work, an extensive study on the applicability of the model will be carried out and suitable modifications will be made to correctly represent the mass transfer process.

Acknowledgement

The author RK thanks Dr. Seraj Ansari for experimental guidance and support. Authors PK and RK also thank Dr. P. K. Mohapatra, Head, Actinide Chemistry Section, BARC Mumbai for providing the experimental facilities at Radiochemistry Division, BARC Mumbai. The authors also thank Director, NIT Uttarakhand for financial and administrative support.

References

[1] OECD Nuclear Energy Agency. Actinide and Fission Product Partitioning and Transmutation: Status and Assessment Report. OECD Nuclear Energy Agency, 1999.

[2] Mathur, J. N., M. S. Murali, and K. L. Nash. "Actinide partitioning—a review." Solvent extraction and ion exchange 19, no. 3 (2001): 357-390.

[3] Ansari, Seraj A., Priyanath Pathak, Prasanta K. Mohapatra, and Vijay K. Manchanda. "Chemistry of diglycolamides: promising extractants for actinide partitioning." Chemical reviews 112, no. 3 (2012): 1751-1772.

[4] Ravi, Jammu, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan, and PR Vasudeva Rao. "Tuning the diglycolamides for modifier-free minor actinide partitioning." Journal of Radioanalytical and Nuclear Chemistry 295, no. 2 (2013): 1283-1292.

[5] Chitnis, R. R., Wattal, P. K., Ramanujam, A., Dhami, P. S., Gopalakrishanan, V., Bauri, A. K., & Banerji, A. (1999). Recovery of actinides extracted by Truex solvent from high level waste using complexing agents. Journal of radioanalytical and nuclear chemistry, 240(3), 721-726.

[6] Izatt RM, Lamb JD, Bruening RL (1988) Comparison of bulk, emulsion, thin sheet supported, and hollow fiber supported liquid membranes in macrocycle-mediated cation separations. Sep Sci Technol. 23: 1645-1658.

[7] Ansari, Seraj A., Prasanta K. Mohapatra, and Vijay K. Manchanda. "Recovery of actinides and lanthanides from high-level waste using hollow-fiber supported liquid membrane with TODGA as the carrier." Industrial & engineering chemistry research 48, no. 18 (2009): 8605-8612.

[8] Danesi, P. R. "Permeation of metal ions through hollow-fiber supported liquid membranes: concentration equations for once-through and recycling module arrangements." Solvent Extraction and Ion Exchange 2, no. 1 (1984): 115-120.
[9] Belair, S., Labet, A., Mariet, C., & Dannus, P. (2005). Modeling of the extraction of nitric acid and neodymium nitrate from aqueous solutions over a wide range of activities by CMPO. *Solvent extraction and ion exchange*, 23(4), 481-499.

[10] Nakashima, K., Kubota, F., Maruyama, T., & Goto, M. (2003). Ionic liquids as a novel solvent for lanthanide extraction. *Analytical Sciences*, 19(8), 1097-1098.

[11] Danesi, P. R. (1984). Separation of metal species by supported liquid membranes. *Separation Science and Technology*, 19(11-12), 857-894.

[12] Sengupta, Arijit, M. S. Murali, and P. K. Mohapatra. "Studies on evaluation of modified TRUEX solvent for the partitioning of minor actinides." *Journal of Radioanalytical and Nuclear Chemistry* 302, no. 3 (2014): 1195-1199.

[13] Sengupta, Arijit, and M. S. Murali. "Effect of phase modifiers TBP and iso-decanol on the extraction and complexation of Eu$^{3+}$ with CMPO." *Separation Science and Technology* 51, no. 13 (2016): 2153-2163.

[14] Sengupta, Arijit, M. S. Murali, S. K. Thulasidas, and P. K. Mohapatra. "Solvent system containing CMPO as the extractant in a diluent mixture containing n-dodecane and isodecanol for actinide partitioning runs." *Hydrometallurgy* 147 (2014): 228-233.