International Journal of Engineering

Optimization of Green Technique Develop for Europium (III) Extraction by using Phosphonium Ionic Liquid and Central Composite Design Approach

M. Asadollahzadeh*, R. Torkaman, M. Torab-Mostaedi

Nuclear Fuel Cycle Research School, Nuclear Science and Technology Research Institute, Tehran, Iran

P A P E R I N F O	*A B S T R A C T*

Rare earth compounds widely used in industrial applications and new processes with green solvents are appropriate for recovering these elements. In this study, the ionic liquid application development was investigated to extract europium ions in single and binary systems. A green procedure for europium (III) extraction from aqueous chloride solution was investigated using phosphonium ionic liquid Cyphos IL 104. Comparative conditions were investigated for analyzing better results with the presence of organic extractant such as Cyanex272, D2EHPA in the batch experiments. The experiment design was carried out based on the central composite design principles to analyze the relationships between the responses and the significant parameters. The obtained data revealed that the quadratic equation has good desirability to predict the extraction percentage. Investigation of the extraction process showed that the ionic liquid Cyphos IL104 has selective power in the extraction of europium and the efficiency is higher than the organophosphorus extractants. Accordingly, optimum conditions for maximum removal of europium ions were obtained equal to 5.5, 1, 16 min, and 0.008 M for feed acidity (pH), phase ratio, time, Cyphos IL 104 concentration. Examination of binary systems of rare earth elements showed that ionic liquid had positive and negative effects on the separation factor. The high efficiency of ionic liquid in the reuse condition indicated that the system is appropriate from an economic perspective.

1. INTRODUCTION

The demand for rare earth elements due to their increasing critical applications has been increased in recent years [1]. New rules and regulations have been reported according to these elements' application types in various industries [2, 3]. Their increasing prices led to improvements in their extraction and separation from ore in their recovery from wastes in electric and electronic equipment or other industrial materials [4]. It is associated with the introduction of new routes for production [5]. For example, lanthanum nanoparticles with optical properties synthesized during the sol-gel procedure [6]. Nowadays, paths are more favorable with less environmental impact [7], and ecological processes such as electrodialysis have expanded to reduce COD of

contaminated water [8]. Solvent extraction is one of the conventional techniques in the extraction of rare earth metals. This technique is coupled with the simplicity of the system, facilitating the separation process.

Still, the high-volume of organic solvent and environmental pollutants are the disadvantages of this approach [9]. Therefore, it led to other procedures such as adsorption or liquid membranes with different types such as emulsion liquid membrane [10], supported liquid membrane, bulk liquid membrane [11], etc. Many adsorbents from simple materials in nature to complex nanocomposite materials have been described in the literature to extract these elements [1]. The supported liquid membranes with the aim of separation of rare earth elements have been reported in various studies [12]. The research work by Asadollahzadeh and co-workers [13]

Corresponding Author Institutional Email: masadollahzadeh@aeoi.org.ir (M. Asadollahzadeh)

showed that the combination of ionic liquid and organophosphorus solvents with stabilization in the supported liquid membrane was an appropriate procedure in the separation of yttrium ions. But the coefficients of separation factor in the solvent extraction technique are much higher than other methods [14]. Thus, this method by modifying the input organic matter has been investigated in many studies [15-17]. In addition to the type of organic solvent, the type of equipment is also useful in solvent extraction and the increment in the mass transfer coefficients [18-21]. It has been studied in various studies with rotating and pulsed columns for rare earth separation [22-24]. Different organic solvents of anionic, cationic, and soluble extractants have been utilized to recover rare earth elements [25, 26]. Alongside these solvents, ionic liquids as environmental green solvents have been found to have particular applications in the extraction and separation procedure of rare earth elements [27]. The separation factor of gadolinium from samarium equal to 8.47 obtained in the combination of TBP, Cyanex272, [C_6MIM][PF_6] in one contact of both phases [28]. In another work, cerium ion recovery investigated from glass polishing powder waste using the synergistic effects of imidazolium ionic liquids and TOPO and TBP [29].

Europium is one of the rare earth elements that has been received particular attention in recent years. The neutron absorbers, europium phosphors on television, fluorescent powders, and lamps are applications that are reported by the use of these ions in the industry [30]. Recently, the discussion of ionic liquids for the extraction of europium ions has been received special attention [31]. The results of the investigation with undiluted ionic liquids from the thiocyanate family [C101][SCN] showed that the four extraction steps achieved with the high efficiency for the recovery of europium on the organic/aqueous phase ratio equal to 1/10 [32]. In the study of Dai et al. [33], a homogeneous extraction technique with ionic liquids [DHbet][Tf_2N] and [THbet][Tf_2N] showed that the europium ions recovered from aqueous solution with the extraction efficiency higher than 90% during the four extraction stages. The utilization of Cyphos IL 104 was evaluated for the extraction abilities in the recovering of Eu(III) in the rotating disk column with an asymmetrical structure [34]. The percentage increase for overall mass-transfer coefficients obtained using this solvent and the higher mixing rate [34].

Examination of eight imidazolium ionic liquids as a diluent, and Octyl(phenyl)-N, N-diisobutyl carbamoyl-methylphosphine oxid (CMPO) as an extractant showed that the ligand/metal ratio in the extracted complex with ionic liquids was far higher than that of the use of n-dodecane as a diluent [35]. A combination of solvation and cation-exchange mechanisms proposed to extract europium with imidazolium ionic liquids. The

temperature was reported as a critical factor in the exothermic reaction to remove europium ions with these ionic liquids [35]. In similar results conducted by Tan and co-workers [36], the combination of 2,6-bis(5,6-diethyl-1,2,4-triazin-3-yl) pyridine (C2-BTP) and [Cnmim][NTf_2] imidazolium ionic liquid, the temperature rise was favorable for the europium extraction, and cation-exchange proposed as an extraction mechanism.

Rao et al. [37] investigated the examination of the behavior of the two extractants such as T2EHDGA, and CMPO diluted in the bis(trifluoromethylsulfonyl)imide ([N1444] [NTf_2]) ionic liquid. The europium ions' extraction revealed that the contribution of three and two molecules of two extractants under ion-exchange reactions led to the desired removal [37]. In the research conducted by Atanassova and Kurteva [38], similar results were reported from a chloride solution with a mixture of CMPO, HTTA, and [Cnmim][NTf_2]. The investigation of the separation factor of europium from gadolinium with ionic liquid [A336][P204] compared with the P204 extractant. The results showed that the higher separation factor under the same conditions provided by ionic liquid [39].

The species of Eu(OHA)$_4$(H$_2$O)$_4$(PF$_6$)$_3$ is the result of complex formation between the ionic liquid 1-alkyl-3-methylimidazolium hexafluorophosphate and 4-oxaheptanediamides extractant for the europium recovery during the ion exchange mechanism as the studies by Niu and co-workers [40].

Research conducted by Larsen and Benjamin [41] showed that with ionic liquids and a chelating agent (EDTA), the light rare earth elements separated from heavy elements with the higher separation factor. In this research, ionic liquid tricaprylmethylammonium nitrate [A336][NO_3] was used as an organic solvent, which was highly desirable in the extraction. With all the benefits of ionic liquids, the limitations such as the loss of cations in imidazolium ionic liquids, the low thermal stability of ammonium-based ionic liquids lead to an increase in the tendency towards phosphonium ionic liquids.

Limited studies have carried out on the separation of rare earth elements with phosphonium types of ionic liquids. Therefore, in this study, the phosphonium ionic liquid was investigated to extract europium from chloride solution. Extraction conditions were investigated by examining various factors such as temperature, pH, ionic liquid concentration, and acidity in the recovery rate. The results using of organic solvents such as D2EHPA and Cyanex272 were reported for comparison and conclusion.

The use of the central composite design approach for the separation of europium ions from chloride solution with phosphonium ionic liquid as a green solvent is the innovation of this study that has not been observed in the literature.

2. EXPERIMENTAL

2. 1. Reagents   In this study, the ionic liquid trihexyl (tetradecyl) phosphonium bis(2,4,4-trimethylpentyl) phosphinate with purity of higher than 90% was supplied by Sigma-Aldrich company. The organic solvents such as Cyanex272 (Solvay, 85%>) and D2EHPA (Sigma-Aldrich) were used for the preparation of the organic phase in comparison with ionic liquid. The commercial kerosene from the Iranian petroleum oil refinery was used as a diluent. The salt of europium(III) nitrate pentahydrate from Sigma-Aldrich company was used for the preparation of the aqueous phase containing Eu(III) ions for solvent extraction procedure (ion concentration equals 250 mg/L). The sulfuric, nitric, and hydrochloric acids (Merck company) were utilized to prepare acidic solutions.

2. 2. Experimental Procedure   By selecting three solvents (D2EHPA, Cyanex272, and Cyphos IL 104) to extract europium ions, the design process of the extraction experiments was performed for each solvent with the selective parameters as summarized in Table 1.

Two aqueous and organic phases were prepared for the extraction process. The aqueous phase was prepared by only europium ions as a single element or by other ions (La(III), Ce(III), Nd(III), Gd(III), Dy(III)) to investigate the behavior of different elements.

The organic phase was prepared from ionic liquid dissolution in kerosene solvent. This ionic liquid was substituted for comparing with the D2EHPA or Cyanex272 extractant. Polyethylene containers were used for two-phase contact. The amount of 10 mL of phases added to the container. The bottles were incorporated into the shaker for the mixing process.

After a specific time, the separation of two phases was performed by the decanter. The measurement of the europium ions in the aqueous phase was performed with a UV instrument (UNICO model), and arsenazo material. The concentration of ions in the aqueous phase is the criterion for the objective parameter. It is defined based on the distribution coefficient (D) as follows:

TABLE 1. Definition of independent variables and their levels in the central composite design

Independent Variables	Symbols	-α	-1	0	+1	+α
Time, min	X_1	2	6	11	16	20
Concentration of ionic liquid or extractant, M	X_2	0.001	0.003	0.006	0.008	0.01
pH of aqueous solution	X_3	1	2	3.5	5	6

$$D = \frac{[Eu(III)]_{org}}{[Eu(III)]_{aq}} \qquad (1)$$

$$\%E = \frac{D}{D + \dfrac{V_{aq}}{V_{org}}} \times 100 \qquad (2)$$

In the above equation, E, V_{aq}, and V_{org} are the extraction efficiency, the volume of the aqueous phase, and the volume of the organic phase, respectively.

3. RESULTS AND DISCUSSION

3. 1. Results from the Experimental Design Approach   In this study, the experiments were carried out based on Table 1, analyzed in three-dimensional graphs, as shown in Figures.1 to 3. The results in Figure 1 described that the ionic liquid Cyphos IL 104 at low concentrations (0.001 to 0.01 M) is highly desirable for the extraction of europium ions. This feature helps extract with the maximum extraction efficiency higher than 98% with 0.01 M Cyphos IL 104 diluted in kerosene. But, D2EHPA extractant at low concentrations showed the maximum extraction efficiency higher than 60% in 0.01 M concentration, and this parameter is below 10% by using Cyanex272 in 0.01 M value.

This figure illustrated that the enhancement in ionic or extractant liquid concentration led to the rise in the extraction rate. These results are due to more solvents for the complex formation, which is associated with an increment in the transfer of europium ions to the organic phase. But, no desirable extraction is obtained with the Cyanex272 at these concentrations. Therefore, an increase in the extraction efficiency higher than 99%, it would be necessary to increase the extraction concentration of Cyanex272 higher than 0.5 M.

The time variation showed that the D2EHPA extractant behavior is faster than the ionic liquid for the complex formation. The maximum extraction efficiency reached with the final desirability equal to 2 minutes. But, the ionic liquid contributed more slowly to the formation of the complex, and it required about ten minutes to reach the maximum ion transport to the organic phase.

The variation in pH in Figures 2 and 3 showed that the extraction behavior depends on the acidity of the aqueous solution. The D2EHPA extractant from a pH value higher than two faces fewer hydrogen ions in the aqueous solution, so the extraction reaction led to the release of more hydrogen ions. This process is associated with an increase of complex formation and, consequently, greater extraction efficiency. The oxygen in the ionic liquid tends to form a reaction with more hydrogen ions than the europium ions. This effect causes the tendency for the europium ions to be negligible when

the amount of hydrogen in the aqueous solution is high. Still, with increasing pH and the decrease in the soluble acidity, the hydrogen ions' reduction tends towards the europium ions and increases the extraction efficiency.
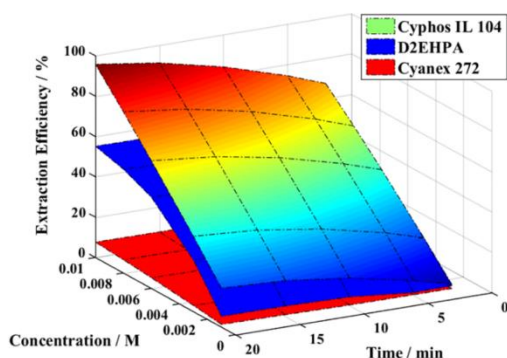

Figure 1. Response surface graphs for the extraction efficiency of Eu(III) with the effect of time, and concentration of ionic liquid or extractant (O/A ratio=1, temperature=25 ◦C, pH of aqueous phase=3.5)
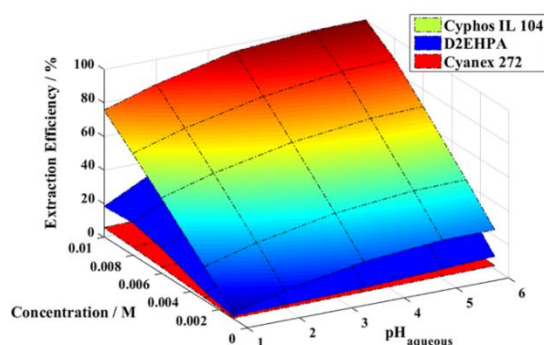

Figure 2. Response surface graphs for the extraction efficiency of Eu(III) with the effect of aqueous pH, and concentration of ionic liquid or extractant (O/A ratio=1, temperature=25 ◦C, time=20 min)
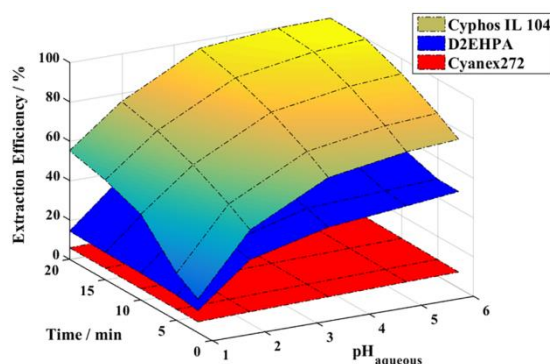

Figure 3. Response surface graphs for the extraction efficiency of Eu(III) with the effect of aqueous pH, and time (concentration of ionic liquid or extractant=0.01 M, O/A ratio=1, temperature=25 ◦C, time=20 min)

In the next step, the obtained data were evaluated using the statistical AVOVA results, as shown in Table 2. The data for F-value and p-value illustrate that the model is essential or not. This table shows that F-values equals 21.36, 14.67 for Cyphos IL 104, and D2EHPA extractant and p-value equal to 0.0001, which led the model important for the response.

The F and P values are essential for the selected model, and their significance is determined in the Design-Expert® Software for the proposed model. These values may not be meaningful in some parameters due to the interaction of the parameters. But the significance value is essential for the selected model and should be evaluated explicitly by examining other parameters (R^2 coefficient, adjusted R^2 coefficient, average absolute relative errors).

The values of R^2 for the selected model were examined by linear, quadratic, and cubic models. The high values equal to 0.9505 and 0.9260 from the quadratic model for extraction with Cyphos IL 104, and D2EHPA extractant, respectively, indicated that the model is highly accurate for predicting extraction efficiency (see Figure 4). As a result, quadratic model equations representing the extraction efficiency (Y) in the reactive condition acquired as Equations (3), and (4):

Cyphos IL104
$$Y = -34.016 + 1.953X_1 + 7268.762X_2 + 10.303X_3 + 70.536X_1X_2 + 0.008X_1X_3 + 186.048X_2X_3 - 0.050X_1^2 - 74613.069X_2^2 - 0.943X_3^2 \quad (3)$$

TABLE 2. ANOVA data for europium extraction in the reactive condition with Cyphos IL 104

Source	Sum of Squares	degree freedom	F-Value	P-Value
model	7485.83	9	21.36	<0.0001
X_1	624.12	1	16.03	0.0025
X_2	6063.74	1	155.70	<0.0001
X_3	699.92	1	17.97	<0.0017
X_1X_2	8.16	1	0.21	0.6559
X_1X_3	0.036	1	9.36×10^{-4}	0.9762
X_2X_3	4.38	1	0.11	0.7443
X_1^2	29.93	1	0.77	0.4013
X_2^2	4.11	1	0.11	0.7519
X_3^2	62.62	1	1.61	0.2335
Residual	389.44	10	-	-
Lack of Fit	383.46	5	64.18	0.0002
Pure Error	5.98	5	-	-
Cor Total	7875.27	19	-	-

$$Y = -36.788 + 0.449X_1 + 11005.221X_2 + $$
D2EHPA $$12.801X_3 + 17.896X_1X_2 + 0.241X_1X_3 + \qquad (4)$$
$$384.352X_2X_3 - 0.046X_1^2 - 684645.028X_2^2 - 1.936X_3^2$$

The average absolute relative errors equal to 7.83 and 11.29% with Equations (3) and (4) indicate that the selected model is very appropriate for the prediction of extraction efficiency.

As shown in Figure 4, this model is also applicable to the Cyanex272 extractant, but since the extraction rate is low, no proposed model reported for the extraction of Eu(III) ions with Cyanex272.

The maximum extraction efficiency was selected as the criterion in the experiments in the optimization condition. All independent variables were kept within range. The results were obtained by using Design-Expert® Software, as shown in Table 3. Besides, under optimal points, the experiments were conducted in the optimal points, and the results of extraction efficiency for Cyphos IL 104 and D2EHPA extractant were added in this Table. As can be observed in Table 3, the predicted values from models were compatible with the experimental data. The research results were reviewed at the optimal point with studies conducted by Mishra and Devi [42]. The results showed that the obtained data correspond to the conditions examined in reference [42]. The accuracy of the results compared with the data in the literature is also revealed in this study.

3. 2. Results from the Investigation of other Parameters

3. 2. 1. Synergistic Factor   This study showed that at low concentrations, Cyanex272 is not suitable for the extraction of europium ions. The synergistic effect can help to the incremental trend for the extraction of these ions. For this purpose, the combination of the extractants and the ionic liquid was investigated in this study. The critical parameter is the synergistic factor as defined by the following equation:

$$SF = \frac{D_{mix(1,2)}}{D_1 + D_2} \qquad (5)$$

The results of the study of the effect of the synergistic factor are shown in Figure 5. The results described that adding ionic liquid to the Cyanex272 extractant helps to increase the extraction rate. The SF coefficients more

significant than one showed synergistic effects between the Cyanex272 and Cyphos IL 104. Also, the addition of an ionic liquid to the D2EHPA extractant showed the formation of synergistic effects. Therefore, the extraction efficiency of europium ions improves by ionic liquid at low concentrations of the extractants. Extraction with a smaller amount of organic solvent indicated that more favorable conditions would be provided with less environmental impact in the extraction of rare earth elements.

3. 2. 2. Organic/ Aqueous Phase Ratio   The ratio of aqueous to organic phases is a parameter that affects the rate of ions extraction. The increase or decrease of the A/O ratio on the extraction of europium ions is shown in Figure 6. The results in this diagram described that large amounts of the organic phase over the aqueous phase increase the value of complexing agents caused by ionic liquids or extractant. This increase is an upward trend in the extraction of ions and their transfer to the organic phase.

3. 2. 3. Temperature Factor   The temperature behavior of the europium extraction was investigated under optimum conditions. The results of extraction with Cyphos IL 104 showed that the increase in temperature from 298.15 K with the distribution coefficient equals 778.43 led to the increment in the extraction of europium ions with a D value equal to 1386.8 at 328.15 K. This increase indicates that the extraction process is endothermic. The examination of the logarithmic graph
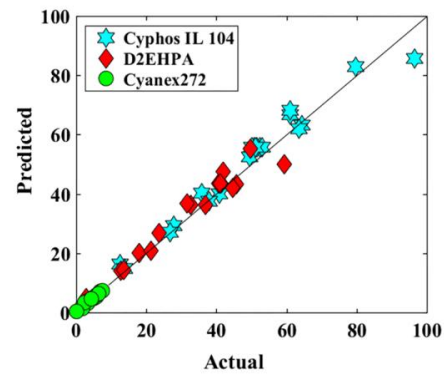

Figure 4. Diagnostic plots of the central composite design model for europium extraction (predicted value versus actual value)

TABLE 3. The optimal point for the reactive extraction of europium ions with Cyphos IL 104, and D2EHPA extractant

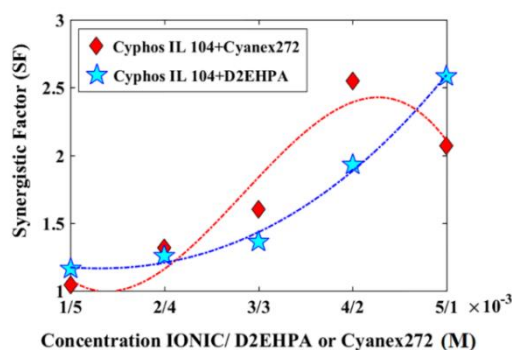| Organic Phase	Time/ min	Concentration of Solvent/ M	pH of aqueous solution	Predicted Extraction Efficiency (%)	Experimental Extraction Efficiency (%)	Deserability
Cyphos IL 104	16	0.008	5.5	87.95	86.23	1
D2EHPA	5	0.01	4.3	63.74	61.84	1

Figure 5. Synergistic effect on the extraction of Eu(III) ions by using Cyphos IL 104, Cyanex272, and D2EHPA (pH of aqueous solution=3.5, O/A ratio=1, temperature=25 ∘C, time=20 min)
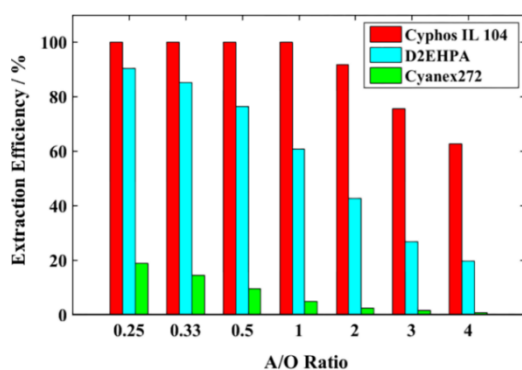

Figure 6. Effect of A/O ratio on the extraction efficiency of Eu(III) with ionic liquid Cyphos IL 104, D2EHPA, and Cyanex272 (concentration of ionic liquid or extractant=0.01 M, pH of aqueous solution=3.5, temperature=25 ∘C, time=20 min)

TABLE 4. Effect of stripping agents on the recovery of Eu(III) ions from the organic phase

Stripping Agent	Concentration / M	Ionic	DE	CYA
H_2SO_4	0.5	61.23	58.98	40.78
H_2SO_4	1	67.45	87.43	91.44
H_2SO_4	2	70.77	98.45	99.88
HCl	0.5	50.37	65.11	70.33
HCl	1	59.87	89.67	87.77
HCl	2	66.19	83.76	80.14
HNO_3	0.5	74.56	66.33	72.45
HNO_3	1	98.91	99.56	99.12
HNO_3	2	90.23	98.45	93.45

described that the stripping percent is enhanced by the acid concentration from 0.5 to 2 molar. The nitric acid in the reaction medium dramatically affects the stripping efficiency from the organic phase containing ionic liquid, D2EHPA, or Cyanex272.

3. 2. 5. Diluent Effect   The effect of diluent in the extraction of europium ions is shown in Figure 7. The extraction rate with Cyphos IL 104 is not dependent on the diluent impact. Approximately the same values for extraction efficiencies were obtained by using different diluents. In the extraction of metals with the organophosphorus extractant, a diluent with a lower dielectric constant is more appropriate. The results in Figure 7 showed that the solubility of D2EHPA in non-polar diluents is better than polar solvents. Therefore, the higher transfer for Eu(III) ions occurs in the reactive extraction with kerosene as a diluent.

3. 2. 6. Impact of other Rare-earth Ions in Aqueous Solution   Binary systems containing europium ions and other rare earth elements were investigated with the organic system containing ionic liquid under optimum conditions. The results showed that the variation in separation factor ($\beta = \dfrac{D_1}{D_2}$), were desirable in

the separation of the europium from the light elements, and the separation factor equals to 9.51, 3.98, 2.24 was obtained for binary systems of $\beta_{Eu/La}$, $\beta_{Eu/Ce}$, and $\beta_{Eu/Nd}$, respectively. But in the separation of europium from heavy rare earth elements, the ionic liquid exhibits synchronous behavior in the extraction of both elements. Therefore, a high separation factor for binary compounds $\beta_{Gd/Eu}$, and $\beta_{Dy/Eu}$ equal to 1.12, 1.34, respectively, was observed in the experimental study.

of the distribution coefficient in terms of temperature described that the reaction enthalpy was 15.35 KJ/mol. The variation of temperature by using D2EHPA extractant from 298.15 to 328.15 K showed the changing in D values in the range 1.51-1.55 that temperature factor has little effect on the extraction of europium that ambient temperature is more favorable for the reaction. A small enthalpy value of calculations was derived equally to 0.145 KJ/mol for Eu(III) extraction with D2EHPA extractant.

3. 2. 4. Stripping Aqueous Solution   The stripping of the organic solution containing D2EHPA or Cyphos IL 104 with water is impossible due to the strong ionic bonds between the ionic liquid or D2EHPA, and Eu(III) ions. Three different acidic solutions, including sulfuric, chloride, and nitric acid, were investigated for stripping study, as shown in Table 4. The present results
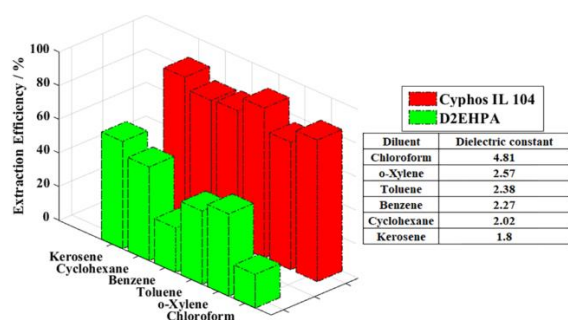
Figure 7. Role of diluents in the extraction of europium ions by using of Cyphos IL 104, and D2EHPA in the organic phase in the optimum condition

4. CONCLUSION

The development of a solvent extraction process is crucial for the extraction and separation of rare-earth metals, and attention has been shifted to the application of green solvents. In this research work, the phosphonium ionic liquid Cyphos IL 104 as a green solvent was investigated in the europium extraction from chloride solution by using the new predicted model. The extraction process was performed using the experimental design technique to minimize the number of experiments and identify the interaction effects of the critical parameters. The results showed that the ionic liquid had higher extraction efficiency compared to the D2EHPA and Cyanex272 extractant. But, the variation of E% with time and aqueous pH showed that the response rate of Cyphos IL 104 for attracting ions and transferring them to the organic phase is slower than applying the D2EHPA extractant.

The optimum conditions for maximum removal of europium ions were obtained equal to 5.5, 1, 16 min, and 0.008 M for feed acidity (pH), phase ratio, time, Cyphos IL 104 concentration. The values equal to 4.3, 1, 5 min, and 0.01 M for these parameters, respectively, were obtained by extraction procedure with D2EHPA extractant.

The Cyanex272 at low concentrations showed inferior performance, but its combination with ionic liquid due to the synergistic effect was identified as a desirable extraction system at low concentrations. The binary system of rare-earth ions with ionic liquid showed that this solvent is very suitable for the separation of light rare earth elements.

5. REFERENCES

1. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, M. "Extraction and Separation of Rare Earth Elements by Adsorption Approaches: Current Status and Future Trends", *Separation and Purification Reviews*, Article in Press (2020) DOI: 10.1080/ 15422119. 2020.1792930.

2. Gallucci, R.H. "Risk-Reduction Credit for Very Early Warning Fire Detection at Nuclear Power Plants: From FAQ to Fiction", *Civil Engineering Journal*, Vol. 5, No. 2, (2019), 309-319. DOI: 10.28991/cej-2019-03091246

3. Gallucci, R.H. "Risk-Deformed Regulation: What Went Wrong with NFPA 805", *Civil Engineering Journal*, Vol. 4, No.12, (2018), 2894-2876. DOI: 10.28991/cej-03091205

4. Torkaman, R., Safdari, J., Torab-Mostaedi, M., Moosavian, M.A., Asadollahzadeh, M. "Extraction of samarium and gadolinium from aqueous nitrate solution with D2EHPA in a pulsed disc and doughnut column", *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 48, (2015), 18-25. DOI: 10.1016/ j.jtice. 2014. 10.016.

5. Balaram, V. "Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact", *Geoscience Frontiers*, Vol. 10, No. 4, (2019), 1285-1303. DOI: 10.1016/j.gsf.2018.12.005

6. Theingi, M., Tun, K.T., and Aung, N.N. "Preparation, Characterization and Optical Property of LaFeO3 Nanoparticles via Sol-Gel Combustion Method", *SciMedicine Journal*, Vol. 1, (2019), 151-157. DOI: 10.28991/SciMedJ-2019-0103-5

7. Ali, S.H. "Social and Environmental Impact of the Rare Earth Industries", *Resources*, Vol. 3, No.1, (2014), 123-134. DOI: 10.3390/resources3010123

8. Parsa, N., Khajouei, G., Masigol, M., Hasheminejad, H., and Moheb, A. "Application of Electrodialysis Process for Reduction of Electrical Conductivity and COD of Water Contaminated By Composting Leachate", *Civil Engineering Journal*, Vol. 4, No. 5, (2018), 1034-1045. DOI: 10.28991/cej-0309154

9. Jha, M.K., Kumari, A., Panda, R., Kumar, J.R., Yoo, K., and Lee, J.Y. "Review on hydrometallurgical recovery of rare earth metals", *Hydrometallurgy*, Vol. 165, (2016), 2-26. DOI: 10.1016/ j.hydromet. 2016.01.035

10. Laguel, S., and Samar, M.H. "Removal of Europium(III) from water by emulsion liquid membrane using Cyanex 302 as a carrier", *Desalination Water Treatment*, Vol. 165, (2019), 269-280. DOI:10.5004/ dwt.2019.24551

11. Belova, V.V. "Development of solvent extraction methods for recovering rare earth metals", *Theoretical Foundation Chemical Engneering*, Vol. 51, (2017), 599-609. DOI: 10.1134/S004057951605002X

12. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, M. "Recovery of gadolinium ions based on supported ionic liquid membrane: parametric optimization via central composite design approach", *International Journal of Environmental Science and Technology*, Vol. 17, (2020) 3983-3996. DOI: 10.1007/s13762-020-02743-8

13. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, M. "Recovery of yttrium ions from fluorescent lamp waste through supported ionic liquid membrane: process optimisation via response surface methodology", *International Journal of Environmental Analytical Chemistry*, Article in Press, (2020), DOI: 10.1080/ 03067319. 2020.1763976.

14. Hidayah, N.N., and Abidin, S.Z. "The evolution of mineral processing in extraction of rare earth elements using liquid-liquid extraction: A review", *Minerals Engineering*, Vol. 121, (2018), 146-157. DOI: 10.1016/j.mineng.2018.03.018

15. Tunsua, C., Lapp, J.B., Ekberg, C., and Retegan, T. "Selective separation of yttrium and europium using Cyanex 572 for applications in fluorescent lamp waste processing", *Hydrometallurgy*, Vol. 166, (2016), 98-106. DOI: 10.1016/j.hydromet.2016.10.012.

16. Lu, X., Zhang, D., He, S., Feng, J., Reda, A.T., Liu, C., Yang, Z., Shi, L., and Li, J. "Reactive extraction of europium(III) and neodymium(III) by carboxylic acid modified calixarene derivatives: Equilibrium, thermodynamics and kineticsc",

Separation and Purification Technology, Vol. 188, (2017), 250-259. DOI: 10.1016/j.seppur.2017.07.040

17. Torkaman, R., Torab-Mostaedi, M., Asadollahzadeh, M., "Studies of Drop Behavior and Prediction of Sauter Mean Drop Diameter in Various Rotary Agitated Extraction Columns", *International Journal of Engineering, Transactions B: Applications*, Vol. 29, No. 8, (2016) 1047-1055. DOI: 10.5829/idosi.ije.2016.29.08b.03

[18. Asadollahzadeh, M., Shakib, B., Torab-Mostaedi, M., Outokesh, M. "Extraction of Molybdenum (VI) and Vanadium (V) from Nitrate Solutions Using Coupling of Acid and Solvating Extractants", *International Journal of Engineering, Transactions A: Basics*, Vol. 32, No. 10 (2019) 1366-1371. DOI: 10.5829/ije.2019.32.10a.0

19. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, "Optimization of lanthanum extraction in asymmetric rotation pilot plant column by using central composite methodology", *Geosystem Engineering*, Vol. 23, No. 2, (2020), 101-111. DOI: 10.1080/ 12269328. 2020. 1719905.

20. Torkaman, R., Asadollahzadeh, M., and Torab-Mostaedi, M. "Determination of slip and characteristic velocities in reactive extraction with experiments in the Oldshue-Rushton column and presence of samarium and gadolinium metals", *Chemical Engineering and Processing*, Vol. 111, (2017) 7-13. DOI: 10.1016/j.cep.2016.10.018

21. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, M. "Coupling minimum cross-entropy model with experimental data to determine the drop size distribution for lanthanum extraction in ARDC column", *Separation Science and Technology*, Article in Press, (2020), DOI:10.1080/01496395.2020.1754429.

[22. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, M. "Study on the feasibility of using a pilot plant Scheibel extraction column for the extraction and separation of lanthanum and cerium from aqueous solution", *Korean Journal of Chemical Engineering*, Vol. 37 (2020) 322-331. DOI: 10.1007/s11814-019-0443-3.

23. Asadollahzadeh, M., Torkaman, R., Torab-Mostaedi, and M., Moazami, F. "Estimation of Performance with the Two Truncated Probability Density Functions, Case Study: Using Mixco Column to Extract Samarium and Gadolinium", *Separation Science Technology*, Article in Press, (2020), DOI:10.1080/ 01496395. 2020.1757713.

24. Shakib, B., Torab-Mostaedi, M., Outokesh, M., and Asadollahzadeh, M. "Direct extraction of Mo(VI) from sulfate solution by synergistic extractants in the rotation column", *Chinese Journal of Chemical Engineering*, Vol. 28, No. 2, (2019), 445-455. DOI: 10.1016/ j.cjche. 2019.11.011.

25. Zhang, J., Zhao, B., and Schreiner, B. "*Separation Hydrometallurgy of Rare Earth Elements*", Springer, New York (2018).

26. Pradhan, S., Swain, N., Prusty, S., Sahu, R.K., and Mishra, S. "Role of extractants and diluents in recovery of rare earths from waste materials", *Materials Today*, Vol. 30, (2020), 239-245. DOI: 10.1016/ j.matpr. 2020.01.288

27. Wang, K., Adidharm, H., Radosz, M., Wan, P., Xu, X., Russell, C.K., Tian, H., Fan, M., and Yu, J. "Recovery of rare earth elements with ionic liquids", *Green Chemistry*, Vol. 19, (2017), 4469-4493. DOI: 10.1039/C7GC02141K

28. Asadollahzadeh, M., Torkaman, R., Torab-Mostaedi, M., Hemmati, A., and Ghaemi, A. "High performance separation of gadolinium from samarium with the imidazolium ionic liquid through selective complexation of organophosphorus extractants", *Environmental Technology & Innovation*, Vol. 19, (2020), 100979. DOI: 10.1016/j.eti.2020.100979.

29. Asadollahzadeh, M., Torkaman, R., Torab-Mostaedi, M., and Hemmati, A. "Enhancing Cerium Recovery from Leaching Solution of Glass Polishing Powder Waste Using Imidazolium Ionic Liquid", *Waste and Biomass Valorization*, Article in Press, (2020). DOI:10.1007/s12649-020-01070-w.

30. Abhilash; Akcil, A. "*Critical and Rare Earth Elements: Recovery from Secondary Resources*", CRC Press, New York, (2019).

31. Chen, J. "*Application of Ionic Liquids on Rare Earth Green Separation and Utilization*", Springer, New York, (2016).

32. Banda, R., Forte, F., Onghena, B., and Binnemans, K. "Yttrium and europium separation by solvent extraction with undiluted thiocyanate ionic liquids", *RSC Advances*, Vol. 9, (2019), 4876-4883. DOI: 10.1039/C8RA09797F

33. Dai, Y., Cao, B., Zhong, S., Xie, G., Wang, Y., Liu, Y., Zhang, Z., Liu, Y., and Cao, X. "Homogeneous liquid–liquid extraction of europium from aqueous solution with ionic liquids", *Journal of Radioanalytical Nuclear Chemistry*, Vol. 319, No. 3, (2019), 1219-1225. DOI: 10.1007/s10967-019-06419-7

34. Asadollahzadeh, M., Torkaman, R., and Torab-Mostaedi, M. "Continuous Extraction of Europium(III) by Ionic Liquid in the Rotating Disk Column with an Asymmetrical Structure Aimed at the Evaluation of Reactive Mass Transfer", *ACS Omega*, Vol.5, No.30, (2020), 18700-18709. DOI: 10.1021/acsomega.0c01636

35. Sun, T., Zhang, Y., Wu, Q., Chen, J., Xia, L., and Icon, C.X.O. (2017) "Comparative study on the extraction of trivalent americium and europium by CMPO in imidazolium-based ionic liquids and dodecane", *Solvent Extraction Ion Exchange*, Vol. 35, No. 6, (2017), 408-422. DOI: 10.1080/ 07366299. 2017.1379142

36. Tan, C., Zhang, X., Cao, S., Li, S., Guo, H., Tian, Y., Chena, D., Tian, W., Wang, L., and Qin, Z. "Solvent extraction of americium(III) and europium(III) with 2,6-bis(5,6-diethyl-1,2,4-triazin-3-yl) pyridine in ionic liquids: Experimental study and molecular dynamics simulation", *Separation Purification and Technology*, Vol. 192, (2018), 302-308. DOI: 10.1016/j.seppur.2017.09.033

37. Rao, C.V., Rout, A., and Venkatesan, K.A. "Europium(III) complexation behaviour in an alkyl ammonium ionic liquid medium containing neutral extractants", *Separation Purification and Technology*, Vol. 213, (2019), 545-552. DOI: 10.1016/ j.seppur. 2018.12.076

38. Atanassova, M., and Kurteva, V. "Synergism in the Solvent Extraction of Europium(III) with Thenoyltrifluoroacetone and CMPO in Methylimidazolium Ionic Liquids", *Journal of Solution Chemistry*, Vol. 48, No. 1, (2019), 15-30. DOI: 10.1007/s10953-019-00844-8

39. Ismail, N.A., Yunus, M.Y.M., Aziz, M.A.A., Abidin, M.A., "Comparison of optimal solvent extraction stages between P204 and [A336][P204] for the separation of europium and gadolinium", *IOP Conference Series: Materials Science and Engineering*, Kuantan, Pahang, Malaysia, 2019.

40. Niu, Y.N., Ren, P., Zhang, F., Yan, Z.Y. "Solvent extraction of Eu3+ with 4-oxaheptanediamide into ionic liquid system", *Separation Science and Technology*, Vol. 53, No. 17, (2018), 2750-2755. DOI: 10.1080/ 01496395. 2018.1471507

41. Larsson, K., Binnemans, K. "Separation of Rare Earths by Solvent Extraction with an Undiluted Nitrate Ionic Liquid", *Journal of Sustainable Metallurgy*, Vol. 3, (2016), 73-78. DOI: 10.1007/s10953-019-00844-8

42. Mishra, B.B., and Devi, N. "Solvent extraction and separation of europium (III) using a phosphonium ionic liquid and an organophosphorus extractant-A comparative study", *Journal of Molecular Liquids*, Vol. 271, (2018), 389-396. DOI: 10.1016/ j.molliq. 2018.08.160

Persian Abstract

چکیده

ترکیبات عناصر نادر خاکی به طور گسترده در کاربردهای صنعتی استفاده می‌شوند و فرآیندهای جدید با حلال‌های سبز برای بازیابی این عنصر مطلوب می‌باشند. در این مطالعه، توسعه کاربرد مایعات یونی برای استخراج یون‌های یوروپیوم از سیستم‌های تک جزئی و دوتایی مورد تحقیق قرار گرفت. فرآیند سبز برای استخراج یوروپیوم (III) از محلول کلرید آبی با مایع یونی فسفونیوم Cyphos IL 104 بررسی شد. شرایط مقایسه‌ای برای آنالیز بهتر نتایج با حضور Cyanex272 و D2EHPA در آزمایش‌های ناپیوسته بررسی شد. طراحی آزمایش‌ها بر مبنای مفاهیم طراحی مرکب مرکزی با بررسی پارامتر بین پاسخ‌ها و پارامترهای موثر انجام شد. نتایج بدست آمده از فرآیند استخراج نشان می‌دهد که معادله درجه دوم از مطلوبیت خوبی در پیش بینی درصد استخراج برخوردار است. تحقیقات فرآیند استخراج با مایع یونی Cyphos IL 104 از قدرت انتخابی بالایی در استخراج یوروپیوم برخوردار است و درصد استخراج بسیار بالاتر با حضور استخراج‌کننده‌های اورگانوفسفر است. شرایط بهینه برای ماکزیمم استخراج یوروپیوم برابر با ۵٫۵، min ۱، ۱۶ و ۰٫۰۰۸ M برای اسیدیته خوراک (pH)، نسبت فازی، زمان، غلظت Cyphos IL 104 بدست آمد. ارزیابی سیستم‌های دوتایی عناصر نادر خاکی نشان داد که مایع یونی اثرات مثبت و منفی روی فاکتور جداسازی دارد. بازده بالای مایعات یونی در شرایط استفاده مجدد نشان می‌دهد که سیستم از نقطه نظر اقتصادی مناسب است.