

Separation of Gadolinium(III) from Samarium(III) using Emulsion Liquid Membrane Method and The Application of Experimental Design for its Selection Parameters

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This study aimed to study the parameters, which affect the separation of gadolinium(III) from samarium(III) and determine extraction efficiency (%E) and stripping efficiency (%S). Parameter selection was made to design experiment using two-level factorial based on response concentration of gadolinium(III) maximum and samarium(III) minimum. A simulation sample of a mixture of gadolinium(III) and samarium(III) was mixed with an emulsion prepared from a mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) or tributylphosphate (TBP) ligands extractant, surfactant and the internal phase. Then the extraction and stripping results were analyzed using ICP-AES. The results for %E and %S separation of gadolinium(III) from samarium(III) were 72.48% and 48.46%, respectively.

Keywords: Emulsions liquid membrane, Gadolinium, Samarium, Di-2-ethylhexyl phosphoric acid, Tributylphosphate.

INTRODUCTION

The unique physical and chemical properties of rare earth elements (REEs) generate many benefits for industrial and technological advances. Thus, REEs are known as “industrial vitamins” and “gold industry 2045” [1]. One of the REEs, gadolinium, is widely used as a material for making contrast compounds in the diagnostic method using magnetic resonance imaging (MRI) [2]. The Ministry of Energy and Mineral Resources (KESDM) stated that REEs is widely distributed globally [3], where China leads in the most REEs production of 20,000 tons per year, while Indonesia produces 3,000 tons per year. Many countries are also competing to separate and refine REEs for production. Separation and purification of individual REEs are not easy to achieve due to the similarity in their chemical and physical properties, especially the adjacent REEs [4].

Several methods for separating rare earth elements (REEs) include extraction, chromatography, ion exchange resin, multi-level crystallization and precipitation are reported in the literature [5-7]. Conventional solvent extraction is widely used in the separation of REEs since the recovery using this separation technique is relatively high [8]. However, according to Tasaki *et al.* [9], solvent extraction has several drawbacks for example,

high chemical consumption, especially in solvents and extractants. They are also less environmentally friendly and the high cost involvement [10], therefore another more practical and alternative method for REEs separation, namely the liquid membrane method was developed. One of the liquid membrane methods is the emulsion liquid membrane (ELM), which has several advantages, like requires less organic solvents, high selectivity, high separation factor, the solvent used is reusable which can support green chemical issues and high mass transfer rates [11].

In ELM method, the ligands uses as extractants. Thus, the extractants used in this study are D2EHPA and TBP ligands. The two ligands are an organophosphorus group suitable for separating lanthanides [10]. The separation of Gd(III) from Sm(III) is based on the many benefits of Gd(III) and pure Gd(III) conditions on the market are often found to be mixed with Sm(III) in high concentrations because the physical and chemical properties between Gd-Sm are very similar to the difference of one atomic number. This study used an experimental design with a two-level factorial method for parameter selection. The purpose of using this method is to plan all possible experiments from an early stage and determine the most influential parameters in separating Gd(III) from Sm(III) so that the number of experiments that must be carried out is small [12].

The selection of parameters that affect the separation of Gd(III) from Sm(III) was carried out to produce high %E and %S. From the literature, parameters that affect the REES separation by ELM vary widely. In this study, the parameters to be selected in the Gd(III) extraction from Sm(III) by ELM are internal phase concentration and external phase concentration based on the REEs diffusion process from the internal and external phases. Surfactant concentration, ligand concentration, emulsion stirring speed, extraction stirring speed, extraction time was based on the REEs mass transfer rate. The type of ligand parameter is based on selecting the best ligand in the separation, namely between di-2-ethylhexyl phosphoric acid (D2EHPA), tributylphosphate (TBP) ligands. The responses chosen in the study were the maximum concentration of Gd(III) and minimum Sm(III) concerning the separation objective of separating Gd(III) from Sm(III).

EXPERIMENTAL

The materials used in this research were samarium oxide, gadolinium chloride, *n*-hexane, Span-80 (sorbitanmonooleate), di-2-ethylhexyl phosphoric acid (D2EHPA), tributylphosphate (TBP) (99.9%) and nitric acid were precured from Sigma-Aldrich, USA.

Preparation of experimental design: Span-80 concentration variance of 2.5 and 4.5% (v/v), 0.1 and 0.3% (v/v) D2EHPA or TBP ligands were dissolved with *n*-hexane up to 25 mL in a measuring cylinder. Transferred it to a beaker and stirred with an ultratorax stirrer with a speed variation of 6000 or 10000 rpm (according to the experimental design) for 5 min. Furthermore, 25 mL of nitric acid solution was added as the internal acid phase slowly with various concentrations of 0.5 or 2.5 M (according to the experimental design), while continuing to stir for 50 min until a milky white emulsion formed.

Extraction of samarium(III) and gadolinium(III): Gd(III) and Sm(III) 1000 mg/L solutions were diluted to 25

and 75 mg/L, respectively in 50 mL of nitric acid solution with various concentrations of 3.0 or 6.0 M (according to experimental design), then stirred with a magnetic stirrer with a variation of speed of 200 or 500 rpm for a variation of the stirring time of 10 or 30 min. The solution [Gd(III)-Sm(III) emulsion] was transferred to a separating funnel. After two phases have been formed, the external water phase was separated from the membrane phase. The membrane phase was awaited again until complete demulsification occurs until two phases were formed, namely the internal water phase at the bottom and the membrane phase at the top. The internal water phase was separated again by the membrane phase and finally the volume was measured.

Detection method: Solution analysis was carried out after the demulsification process. The solutions measured were the external water phase and the internal water phase, then the Gd(III) and Sm(III) concentrations were measured using ICP-AES, respectively.

RESULTS AND DISCUSSION

Experimental design results parameter selection used two level factorial: The two-level factorial model experimental design is a first-order design, which functions to select the parameters that affect the response [13]. In this study, the parameters selected in the extraction process Gd(III) from Sm(III) using a ELM were internal phase concentration, surfactant concentration, ligand concentration, external phase concentration, speed of stirring for emulsion production and extraction, type of ligand and time to extract. The selection of parameters in the separation of Gd(III) from Sm(III) using two factorial levels aims to determine each parameter's effect both individually and the interaction between parameters on the response. In Table-1, all the parameters were selected with various levels and the targeted response using a two-level factorial design in the process of separating Gd(III) from Sm(III) by ELM.

TABLE-1
SELECTION DESIGN PARAMETERS FOR SEPARATION OF Gd(III) FROM Sm(III)

Parameters								Response	
C. Internal phase (M)	C. Surfactant (%)	C. Ligand (%)	V. Emulsion Stirring (rpm)	C. External phase (M)	V. Extraction Stirring (rpm)	T. Extraction (min)	Type of Ligand	C. Gd	C. Sm
2.5	4.5	0.3	6000	6	200	10	-1	7.091	24.877
2.5	2.5	0.3	6000	3	500	10	1	9.391	26.404
0.5	4.5	0.3	10000	3	500	10	-1	10.858	23.492
2.5	4.5	0.1	10000	3	200	10	1	11.103	26.118
0.5	2.5	0.3	10000	6	200	10	1	7.528	23.589
0.5	2.5	0.1	10000	3	500	30	1	10.689	28.239
2.5	4.5	0.1	6000	3	500	30	-1	7.836	28.389
0.5	4.5	0.1	10000	6	200	30	-1	8.885	24.841
0.5	4.5	0.1	6000	6	500	10	1	7.808	19.966
2.5	2.5	0.1	10000	6	500	10	-1	8.686	26.202
0.5	2.5	0.3	6000	6	500	30	-1	8.563	24.326
2.5	2.5	0.1	6000	6	200	30	1	6.386	17.659
0.5	4.5	0.3	6000	3	200	30	1	9.651	22.882
2.5	4.5	0.3	10000	6	500	30	1	8.775	25.274
2.5	2.5	0.3	10000	3	200	30	-1	17.2	39.413
0.5	2.5	0.1	6000	3	200	10	-1	9.346	28.246

Results of two-level factorial selection: The parameter selection in the extraction of liquid emulsion membranes was carried out based on a two-level factorial design with variance (ANOVA) in the data processing. Based on the results of design data processing, the selected parameters can significantly affect the response of the maximum extracted Gd(III) concentration and the concentration of Sm(III), which is still extracted (minimum). In contrast, unselected parameters do not have a significant effect on the desired response.

Parameters which significantly affect the response to maximum Gd(III) and minimum Sm(III) concentrations are internal phase concentration, surfactant concentration, ligand concentration, emulsion stirring speed, external phase concentration, extraction stirring speed, types of ligand parameters. Fig. 1 shows the relationship between all parameters in response to the maximum Gd(III) and minimum Sm(III) concentrations.

A relationship line which decreases or increases with increasing concentration, speed and time of all parameters, shows that these parameters significantly affect.

Internal phase concentration parameters: Each selected parameter was tested at various conditions/levels. The internal phase was carried out at an acidic pH because it ultimately extracts the dissolved metal ions in an acidic atmosphere. The internal phase concentration is not as high as the external phase concentration, this prevents the breakthrough of the external phase to the internal phase. The acid solution used is HNO_3 . In research conducted by Hasan *et al.* [14] HNO_3 as an internal phase can produce %S for Gd(III) by 90% compared to HCl , which can only produce 85% S and H_2SO_4 of 83% S in the same concentration. This is because HNO_3 acts as an oxidizing agent that can break down the REEs and ligand bonds enter the internal phase.

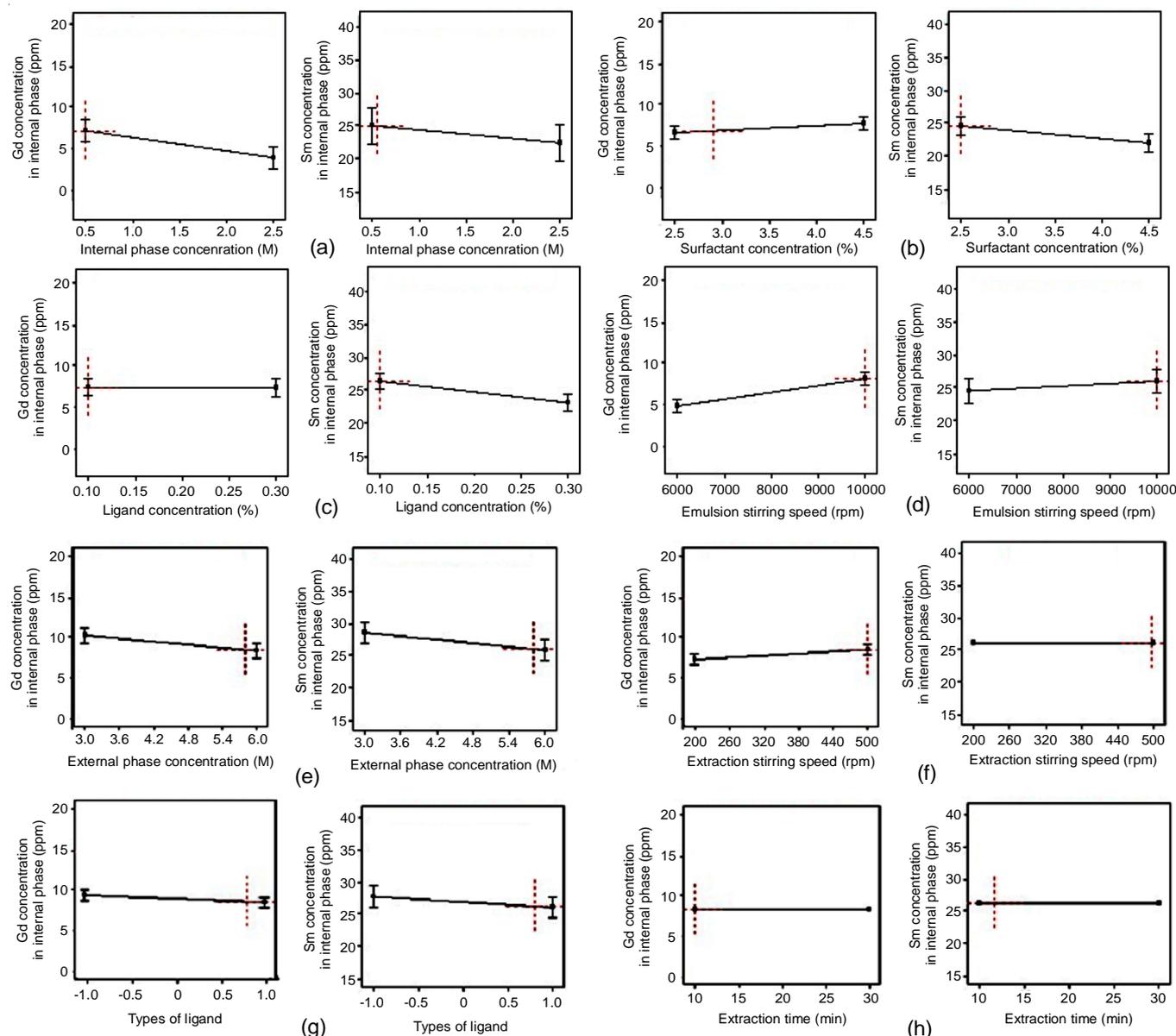


Fig. 1. Relationship between (a) the internal phase concentration, (b) surfactant concentration, (c) ligand concentration, (d) emulsion stirring speed, (e) external phase concentration, (f) extraction stirring speed, (g) types of ligand, (h) extraction time parameters to the response of Gd(III) maximum and Sm(III) minimum concentration

In Fig. 2a, internal phase concentration is between the range of 0.5-2.5 M, resulting in the optimal design prediction at a concentration of 0.5 M. At a concentration of 0.5 M, it can produce a maximum concentration of Gd(III) and minimum concentration of Sm(III). These results are the same as the research conducted by Davoodi-Nasab *et al.* [2].

Effect of surfactant concentration: The addition of surfactant was carried out to stabilize the emulsion and reduce the surface tension between the membrane and external water phases. The smaller the surfactant concentration, the decrease in surface tension will not be significant. However, if the surfactant addition is too high, this will cause an increase the viscosity of the emulsion so that it can slow down the complex diffusion. In the membrane phase, because the membrane is too thick.

The surfactant used is Span-80 because according to Hasan *et al.* [14] reported the effect of various types of surfactants on the stability of emulsion liquid membrane, Span-80 showed the highest stability in the prepared emulsion membrane. Span-80 is biodegradable and has a hydrophilic-lipophylic balance (HLB) value of 4.3. Surfactants in the HLB 4-6 range are suitable for emulsifying water in oil [15]. The surfactant concentration parameter used is at the level range of 2.5-4.5%. The optimal design prediction result for surfactant concentration is shown in Fig. 2b.

Effect of ligand concentration: The ligand greatly influence the extraction performance to a certain level of concentration. The smaller the ligand concentration as a carrier, the less likely the reaction to form a ligand complex with metal will result in the metal being extracted not maximally. In contrast, if ligands addition is too high, this will cause an increase the viscosity of the emulsion so that it can slow down the diffusion of the complex in the membrane phase and causes metal ion complexes with ligands to be very stable in the membrane phase. As a result, the complexation process is challenging to occur at the membrane phase interface and the stripping phase. The ligand concentration parameter used is at the 0.1-0.3% level limit. From the selected level range, the optimal design prediction result is 0.1% as shown in Fig. 2c.

Effect of emulsion speed stirring: The emulsion stirring speed affects the stability of the membrane. In this study, the stirring speed selection was carried out in the range of 6000 rpm to 10000 rpm. The higher the stirring speed when making

the emulsion, the smaller the formation of liquid emulsion granules in the membrane. Consequently, the membrane is more stable because it will be challenging to form larger emulsion particles. However, if the emulsion speed is very high, the emulsion granules in the membrane will be smaller so that the space for the stripping process is getting smaller and causes the stripping process to be less effective. Fig. 2d shows the emulsion stirring speed according to the optimal design prediction, which is at 10000 rpm.

Effect of external phase concentration: The acid concentration in the external phase is relatively reduce the surface tension between the external and the membrane phase. The contact between the external phase that contains metal ions and ligands on the membrane is more due to the complex formation reaction between ligands and metal ions. According to Handini *et al.* [16], at a relatively high acidity concentration of ± 6 M, the reaction that occurs is the formation of a complex, while at a low concentration of ± 0.5 M, the reaction occurs is ion exchange. The optimal design prediction result for external phase concentration is 5.8 M (Fig. 2e).

Effect of extraction speed stirring : The optimum stirring speed can increase the Gd(III) extraction rate because it will increase the interface area. The extraction stirring speed parameter was carried out at the 200-500 rpm level limit. The optimal design prediction result for the extraction stirring speed is shown in Fig. 2f at 500 rpm.

Types of ligands: Types of ligands used in parameter selection were D2EHPA (symbol +1 in the selected design) or TBP (symbol -1 in the selected design). The ligands must show a particular affinity for one component to obtain high selectivity [17]. Among the two ligands, the most selective choice of the target metal ion as an electron acceptor is Gd(III) from Sm(III), which will form complexes with ligands covalently coordinating. Based on previous studies [2,10], the extraction of rare earth metals uses these two ligands with a large enough extraction yield, this is done by the selection of two types of ligands. The two selected ligands belong to the organophosphorus group, which has a phosphoryl group (P=O), so that it has the character of a strong electron donor.

Based on the design prediction results in Fig. 2g, the corresponding ligand is D2EHPA. According to Handini *et al.* [16], D2EHPA is an acidic solvent so that is relatively low acidity conditions, the feed can take better REEs than TBP, which tends

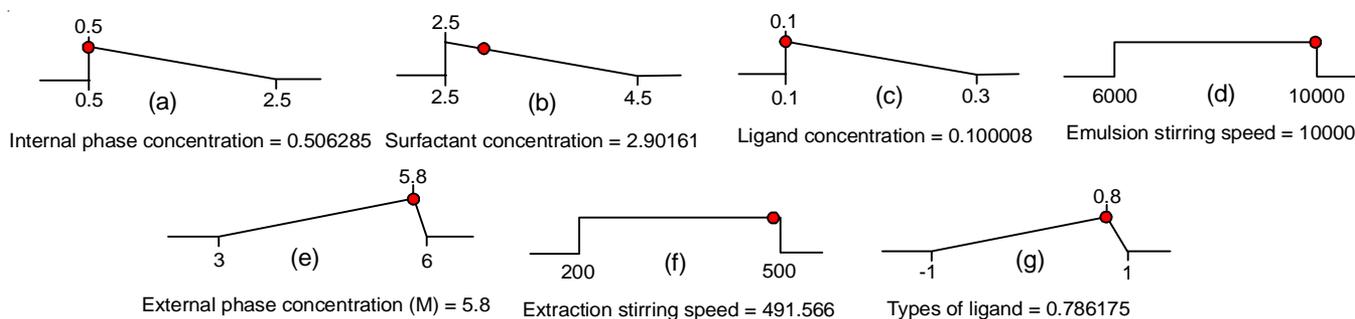


Fig. 2. Optimal design prediction result (red dot) for (a) the internal phase concentration, (b) surfactant concentration, (c) ligand concentration, (d) emulsion stirring speed, (e) external phase concentration, (f) extraction stirring speed, (g) types of ligand, (h) extraction time parameters

to be alkaline. D2EHPA ligands are selective for Gd(III) and Sm(III), but based on the study of Anggraeni *et al.* [18], the stability constant of the Gd-D2EHPA complex is more excellent than Sm D2EHPA in terms of %E, so it can be said that D2EHPA is more selective towards Gd(III).

Effect of extraction time: According to Handini *et al.* [16], after achieving equilibrium, the amount of extracted REEs will remain and the extraction time does not affect anymore. Although the extraction time parameter is not selected, this time is used to optimize other parameters. Relatively good conditions are selected at 10 min based on optimal design predictions.

This parameter selection is based on ANOVA-based data processing, selected by selecting the optimum conditions for each parameter both individually and by the interaction between parameters. The optimum condition is seen from the prediction of the model displayed in the design by showing a significant *p* value, this shows that the design made is by an error rate of below 5% ($p < 5$). The processing results based on ANOVA, are shown in Tables 2 and 3.

The response to the maximum Gd(III) concentration based on ANOVA is obtained by a predictive design model with a *p* value of 0.0103 (Table-2). Thus, the predictive design model is significant. Similar to Table-3, the response to the minimum

Sm(III) concentration based on ANOVA obtained a significant predictive design model with a *p* value of 0.0074.

The design model is made must be known for its linearity because it can determine the relationship between the predicted data and the actual data. Fig. 3a-b show the linearity graph of the suitability between the expected extraction results and the actual results for the extracted response of Gd(III) concentration with the resulting correlation coefficient (*r*) of 0.9219 and the concentration of Sm(III), which is extracted with a value of $r = 0.9308$, which meet the acceptable criteria, namely 0.9 [19].

Extraction results of emulsion liquid membrane based on two-level factorial selection: A liquid emulsion membrane separates a mixture of metal ions and compounds on an extraction basis. However, in this method, the extraction process and the extraction process were carried out one step at a time. In liquid membranes, the separation principle is determined by the membrane itself and the carrier molecules' specific properties that remain in the membrane [17]. In this study, two carrier molecules were selected, namely D2EHPA or TBP using a two-level factorial design.

Based on the response from the selected parameters, namely the maximum Gd(III) concentration and the minimum Sm(III) concentration, the optimal design prediction for each

TABLE-2
PREDICTION TABLE FOR PARAMETER SELECTION WITH RESPONSE OF
Gd(III) MAXIMUM CONCENTRATION BASED ON ANOVA

Source	Sum of the total squares	Degrees of freedom	Average square	F-Value	P-Value Prob > F
Model	85.13	9	9.46	7.87	0.0103
C	4.32	1	4.32	3.60	0.1066
D	19.47	1	19.47	16.21	0.0069
E	31.23	1	31.23	25.98	0.0022
H	3.18	1	3.18	2.65	0.1549
AB	3.93	1	3.93	3.27	0.1204
AC	4.59	1	4.59	3.82	0.0983
AD	9.72	1	9.72	8.08	0.0294
AE	2.92	1	2.92	2.43	0.1702
AF	5.76	1	5.76	4.79	0.0711
Residual	7.21	6	1.20	–	–

Information: A = Internal phase concentration, B = Surfactant concentration, C = Ligand concentration, D = Emulsion stirring speed, E = External phase concentration, F = Extraction stirring speed, G = Extraction time, H = Types of ligand.

TABLE-3
PREDICTION TABLE FOR PARAMETER SELECTION WITH RESPONSE OF
Sm(III) MAXIMUM CONCENTRATION BASED ON ANOVA

Source	Sum of the total squares	Degrees of freedom	Average square	F-Value	P-Value Prob > F
Model	304.65	9	33.85	8.96	0.0074
A	21.98	1	21.98	5.82	0.0524
B	20.79	1	20.79	5.50	0.0574
D	37.27	1	37.27	9.87	0.0200
E	83.03	1	83.03	21.98	0.0034
H	54.96	1	54.96	14.55	0.0088
AC	37.83	1	37.83	10.01	0.0195
AD	13.94	1	13.94	3.69	0.1031
AE	16.35	1	16.35	4.33	0.0827
AH	18.48	1	18.48	4.89	0.0690
Residual	22.67	6	3.78	–	–

Information: A = Internal phase concentration, B = Surfactant concentration, C = Ligand concentration, D = Emulsion stirring speed, E = External phase concentration, F = Extraction stirring speed, G = Extraction time, H = Types of ligand.

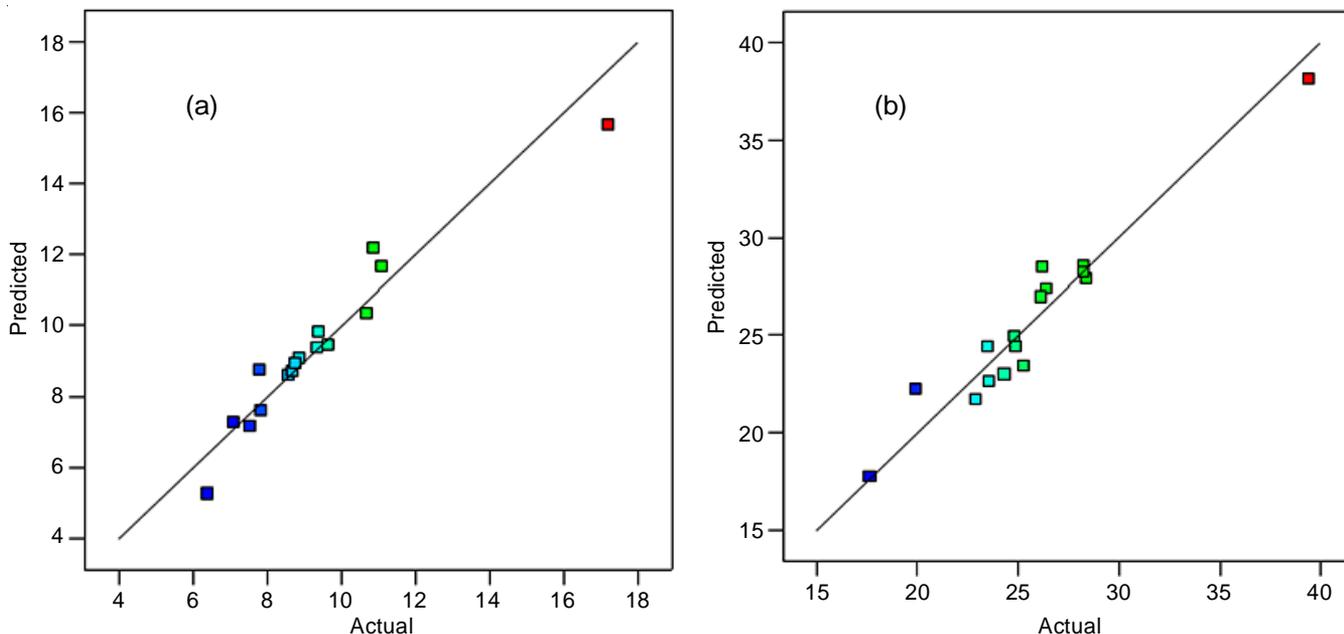


Fig. 3. Linearity between the predicted and the actual for responses of (a) Gd(III) maximum and (b) Sm(III) minimum concentration

selected parameter to achieve the response is internal phase concentration of 0.5 M; external phase concentration 5.8 M; surfactant concentration 2.9%; ligand concentration 0.1%; the type of ligand used is D2EHPA; emulsion stirring speed 10,000 rpm; the extraction stirring speed is 500 rpm and the extraction time is 10 min.

Effect of maximum Gd(II) concentration: The liquid membrane extraction process was carried out based on optimal design predictions resulting in a concentration of Gd(III) in internal phase, which is 8.7781 ppm, while in external phase is 6.88059 ppm with an initial concentration of Gd(III) before extraction of 25 ppm (Fig. 4).

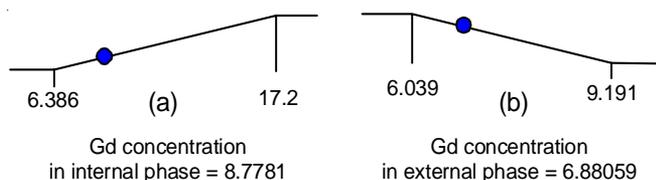


Fig. 4. Concentration of Gd(III) is obtained in (a) the internal phase and (b) the external phase

The success of an extraction can be determined by the extraction efficiency (%E) and stripping efficiency (%S) values of the extraction carried out with the selected optimal design prediction parameters. Based on the measurement data, it was found to be 72.48 %E and 48.46 %S. Based on the organic phase calculation, still Gd(III) which forms complexes with ligands left in the organic phase. So there is a need for multi-level stripping and optimizing the stripping conditions because these results still use the optimum conditions prediction based on selection.

Effect of minimum Sm(III) concentration: Based on the liquid membrane extraction process, the optimal design predictions in internal phase concentration of Sm(III) resulted

the value of 25.5424 ppm and for the external phase is 46.2317 ppm, having an initial concentration Sm(III) before extraction of 75 ppm (Fig. 5). Thus, the %E and %S obtained were 38.36% and 86.76%, this still needs to be re-optimized because it uses the optimum conditions for software prediction. The concentration of Sm(III) extracted was less than the concentration of Gd(III). Therefore, the separation of Gd(III) from Sm(III) was successful.

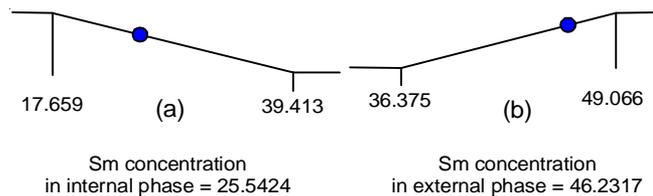


Fig. 5. Sm(III) concentration is obtained in (a) the internal phase, (b) the external phase

Conclusion

The parameters that have a significant effect on the response to the maximum Gd(III) and the minimum Sm(III) concentration for the separation of Gd(III) from Sm(III) with liquid emulsion membranes using D2EHPA or TBP extractants are internal and external acid phase, surfactant concentrations, type and concentration of ligand, stirring rate extraction and stirring rate emulsion. The extraction (%E) and stripping efficiency (%S) separation of Gd(III) from Sm(III) by liquid emulsion membrane method using D2EHPA extractant, respectively, namely 72.48 and 48.46% for Gd(III) and 38.36 and 88.79% for Sm(III), meanwhile %E and %S for the separation of Gd(III) from Sm(III) using TBP ligands were not selected according to the experimental design results. The separation was successful, but re-stripping had to be done because the %S yield was relatively low.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. H. Yuan, W. Hong, Y. Zhou, B. Pu, A. Gong, T. Xu, Q. Yang, F. Li, L. Qiu, W. Zhang and Y. Liu, *J. Rare Earths*, **36**, 642 (2018); <https://doi.org/10.1016/j.jre.2018.01.011>
2. P. Davoodi-Nasab, A. Rahbar-Kelishami, J. Safdari and H. Abolghasemi, *J. Mol. Liq.*, **262**, 97 (2018); <https://doi.org/10.1016/j.molliq.2018.04.062>
3. KESDM, Kajian Potensi Mineral Ikutan pada Pertambangan Timah. Pusat Data dan Teknologi Informasi Energi dan Sumber Daya Mineral, Jakarta, Indonesia (2017).
4. M. Anitha, D.N. Ambare, D.K. Singh, H. Singh and P.K. Mohapatra, *Chem. Eng. Res. Des.*, **98**, 89 (2015); <https://doi.org/10.1016/j.cherd.2015.04.011>
5. V. Baliram, *Geosci. Front.*, **10**, 1285 (2019); <https://doi.org/10.1016/j.gsf.2018.12.005>
6. A.C. García, M. Latifi, A. Amini and J. Chaouki, *Metals*, **10**, 1524 (2020); <https://doi.org/10.3390/met10111524>
7. Y. Hu, J. Florek, D. Larivière, F.-G. Fontaine and F. Kleitz, *The Chem. Record*, **18**, 1261 (2018); <https://doi.org/10.1002/tcr.201800012>
8. S. Suren, T. Wongsawa, U. Pancharoen, T. Prapasawat and A.W. Lothongkum, *Chem. Eng. J.*, **191**, 503 (2012); <https://doi.org/10.1016/j.cej.2012.03.010>
9. T. Tasaki, T. Oshima and Y. Baba, *Ind. Eng. Chem. Res.*, **46**, 5715 (2007); <https://doi.org/10.1021/ie061671u>
10. S. Budiman, H.H. Bahti, A. Mutalib and A. Anggraeni, *J. Sains Kesehatan*, **1**, 510 (2018).
11. M. Raji, H. Abolghasemi, J. Safdari and A. Kargari, *Chemical Eng. Processing Process Intensif.*, **120**, 184 (2017); <https://doi.org/10.1016/j.cep.2017.06.010>
12. A.P. Panovska, J. Acevska, G. Stefkov, K. Brezovska, R. Petkovska and A. Dimitrovska, *J. Chromatogr. Sci.*, **54**, 103 (2015); <https://doi.org/10.1093/chromsci/bmv123>
13. T. Jiapeng, L. Yiting and Z. Li, *Prep. Biochem. Biotechnol.*, **44**, 90 (2014); <https://doi.org/10.1080/10826068.2013.833111>
14. M.A. Hasan, R.F. Aglan and S.A. El-Reefy, *J. Hazard. Mater.*, **166**, 1076 (2009); <https://doi.org/10.1016/j.jhazmat.2008.12.010>
15. M.G. Kassem, A.M.M. Ahmed, H.H. Abdel-Rahman and A.H. Moustafa, *Energy Reports.*, **5**, 221 (2019); <https://doi.org/10.1016/j.egyr.2019.01.009>
16. T. Handini, B. Ehb and S. Sukmajaya, *IPTEK Nuklir*, **20**, 49 (2017); <https://doi.org/10.17146/gnd.2017.20.1.3072>
17. M. Mulder. Basic Principles of Membrane Technology, Springer: Dordrecht (1997).
18. A. Anggraeni, B. Mutalib, P. Primadhini and H.H. Bahti, *Chim. Nat. Acta*, **3**, 80 (2015); <https://doi.org/10.24198/cna.v3.n2.9197>
19. J.C. Miller and J.N. Miller, Statistic and Chemometrics for Analytical Chemistry, In: Handbook of Pharmaceutical Analysis by HPLC, Purdue Pharma: New York (2005).