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Investigation of operational parameters in the separation factor of praseodymium and neodymium from model NdFeB magnet-leaching solution in the solvent extraction: Optimization by response surface methodology

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Abstract. In this study, the separations of praseodymium (Pr) and neodymium (Nd) from model NdFeB magnet-leaching solution were evaluated by two different mixtures, namely Aliquat 336/toluene (System I) and Cyanex 272/kerosene (System II). The operational parameters such as Aliquat 336 concentration (0.30–0.85 mol/L), Cyanex 272 concentration (0.23–0.57 mol/L), pH (2.0–5.0), organic to aqueous phase (O/A) ratio (1–3), and ammonium nitrate (AN) concentration (2.2–5.6 mol/L) were investigated. The impacts of the studied parameters on the separation factor were modeled, compared, and optimized by Response Surface Methodology (RSM) based on the Central Composite Design (CCD). The parameters had relatively consistent and inconsistent impacts on the extraction efficiency and selectivity of Systems I and II, respectively. According to the optimization results of the operational selectivity, System I was more fitted in which the extraction efficiencies of Pr and Nd were obtained 74.8% and 61.2%, respectively, and the separation factor was 2.10. The obtained values for Aliquat 336 concentration, O/A ratio, pH, and AN concentration were 0.85 mol/L, 1, 5.0, 3.9 mol/L, respectively. Finally, the stripping of metal ions from the loaded organic phase was effectively conducted with 0.1 M hydrochloric acid solution within a contact time of 5 minutes.

1. Introduction

Rare Earth Elements (REEs) have many applications in advanced technologies such as hybrid cars, compact fluorescent lights, wind turbines, flat-screen televisions, disc drives, mobile phones, and defense technologies due to their unique properties. They can be used individually or in combination [1,2]. Owning to the similar properties of the REEs, the separation of these elements is often a challenging task [3]. The solvent extraction process is used in many applications, either researches or industries, because it has a high capability to control the high volumes of polar liquids [4]. Praseodymium (Pr) and neodymium (Nd) are categorized as light REEs. Pr is used in the production of ceramics, glasses, and pigments, while

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Nd is employed in the production of constant magnets, catalysts, IR filters, pigments for glass, and lasers [5].

Since the extraction and separation of Pr and Nd are challenging, much effort has been made to improve the extraction process of these two elements. The separation of a mixture of Pr and Nd, called didymium, was firstly carried out through fractional crystallization of ammonium nitrate double salts [6]. The research efforts had been made to separate the Pr and Nd elements via conventional or innovative methods in the solvent extraction process. In this case, various methods such as extractants mixture [7–14], complexing agent and weak organic acid [15,16] or chelating agent [9,17], non-equilibrium extraction [18,19], ionic liquid [20], membrane [21], microchannel [22], selective striping [23], selective scrubbing [24,25], and "push and pull" impacts [26,27] have been probed. Also, several studies have applied a combination of the mentioned methods.

One of the well-known methods for solvent extraction is the use of a mixture of extractants to achieve the synergistic impact. Liu et al. studied the solvent extraction of Pr and Nd from chloride solution with a mixture of Cyanex 272 and Alamin 336. Owning to the variation in equilibrium pH, the extraction of hydrogen ions during the reaction process was attributed to Alamin 336, which ultimately led to the improvement of the extraction efficiency [7]. In the subsequent study, Liu et al. proposed a ternary mixture derived from a combination of Cyanex 272, Alamin 336, and Tributyl phosphate (TBP), which had higher extractability and higher separation factor than Cyanex 272/Alamin 336. The addition of TBP increased the hydrophobicity of the extracted species [10].

The modification of the chemical species at the aqueous phase has been identified by adding a water-soluble complexing agent as one of the effective methods to improve the metal extraction [28–30]. The most common complexing agents used in the extraction process include aminopolyacetates such as Ethylenediaminetetraacetic acid (EDTA) and Diethylenetriaminepentaacetic acid (DTPA) or weak organic acids such as citric acid, lactic acid, and acetic acid. Shaohua et al. used lactic acid to intensify the extraction efficiencies of Pr and Nd with D2EHPA. Lactic acid plays a buffering role and prevents the enhancement of acidity at the aqueous phase during the extraction process [15]. Bauer and Lindstrom investigated the separation of light REEs from Aliquat 336 in the presence of some chelating agents. The highest separation factor of Pr/Nd achieved 5.4 in the presence of DTPA [31].

Minagawa studied the selective extraction of Pr from an Nd solution with B2EHPA by a non-equilibrium extraction in the presence of DTPA. In this study, the extraction of Pr reached equilibrium before Nd and when the pH of the aqueous phase decreased, the Pr^{3+} ions reached equilibrium much earlier than Nd^{3+}. As a result, the two metal ions exhibit higher separation factors in the pre-equilibrium up to the highest value of 5 [18]. Matsuyama et al. studied the non-equilibrium extraction of Pr and Nd with Cyanex 272 in the presence of DTPA. In this case, the extraction rate of Pr was higher than Nd. As a consequence, the separation factor increased from 1.4 to about 1.9 [19].

Padhan and Sarangi studied the recovery of Pr and Nd from NdFeB magnets with bi-functional ionic liquid based on Cyanex 272 and Aliquat 336. It was proven that when ionic liquids were used even in comparison to D2EHPA, the higher extraction efficiency could be achieved. They claimed that not only hydrogen ions were not released at the aqueous phase, but they could also be extracted by the ionic extractant [20]. He et al. studied the increment of the extraction efficiencies of Pr and Nd with HEHEHP in the presence of lactic acid in a serpentine microchannel. The equilibrium time was 12 seconds in this system and the value of the separation factor was 2.23. In contrast, the equilibrium time and the separation factor of Nd/Pr for a conventional batch system were 560 seconds and 2.19, respectively [22]. Banda et al. investigated the separation of Pr and Nd from a chloride medium with saponified PC-88A and a selective scrubbing process. The maximum separation factor between Pr and Nd with PC-88A was about 1.5. Therefore, the co-extraction process of these two elements and subsequently, the selective scrubbing of Pr with a pure Nd solution were performed [24].

Besides, the simultaneous presence of other elements such as lanthanum (La) and dysprosium (Dy) was considered in the study on the extraction of Pr and Nd. La usually coexists in the leach solution from the mineral processing of REEs [12,13]; Dy was also involved in the processes of REEs recovery from NdFeB magnets with Pr and Nd [32,33]. Nakayama et al. investigated the extraction of La, Pr, and Nd using a supported liquid membrane (Gore-Tex Micro-Porous Film impregnate with PC-88A). In this regard, the impact of the DTPA presence on the permeation rate and selectivity was examined and Nd/Pr separation factor reached 2.5 [21]. Kumari et al. probed into the separation of Pr, Nd, and Dy from the leach solution of waste NdFeB magnets using Maxtral 336 in the presence of EDTA. The order of the extraction efficiency of these elements with Maxtral 336 follows Pr > Nd > Dy, while the order of the stability constants values of the complexes formed with EDTA follows Dy > Nd > Pr. The coincidence of the above points resulted in a higher separation factor with a value of 2.9 for the Pr/Nd [32].

Modeling and optimization of the operational conditions in the solvent extraction via mathematical-statistical methods help identify "How and What amount" do the influential parameters and their interactions affect the responses [34]. Taguchi's design and Response Surface Methodology (RSM) can be applied regarding this purpose [35]. Safarzadeh et al. employed the Taguchi's L16 orthogonal array to study the impact of some parameters on the separation factor of Nd/Pr. The order of the most prominent parameters in the separation factor were reported as follows: pH > extractant type > acid type > extractant concentration > the total concentration of the metal ions [35]. Some of the previous studies on the solvent extraction and separation of Pr and Nd are summarized in Table 1. The results of these studies (see Table 1) indicate that it is difficult to achieve high extraction efficiency and separation factor in the solvent extraction of Pr and Nd, simultaneously. Although the impacts of the operational parameters on the separation factor were low, these impacts should be investigated carefully due to their importance in the solvent extraction processes. On the other hand, by reviewing the reliable studies, it was found that there were no comprehensive results regarding the impacts of the operational parameters on the separation factor. Indeed, the main aim of this study is to examine this issue in detail. Aliquat 336 (A336) and Cyanex 272 (C272) are anion and cation exchangers, respectively [39,40], which have been effectively used in the solvent extraction of Pr and Nd from acidic solutions. In this regard, the separation of Pr and Nd from model NdFeB Magnet-leaching solution by two different mixtures of A336/toluene (System I) and C272/kerosene (System II) was investigated. The RSM based on the Central Composite Design (CCD) was applied to the experimental modeling and optimization of the operational parameters on the separation factor of the studied systems. The investigated parameters selected for System I include A336 concentration, pH, organic to aqueous phase (O/A) ratio, and Ammonium Nitrate (AN) concentration, while the investigated parameters for System II were selected C272 concentration, pH, and O/A ratio. At the end of this study, the striping of the loaded organic phase was conducted using hydrochloric acid (HCl) solution.

2. Experimental

2.1. Materials

Aliquat 336 (Tri-C8-10-alkylmethylammonium chloride or A336) with a purity of 95% and Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid or C272) with a purity of 90% were purchased from Merck and Sigma-Aldrich, respectively. Toluene was used as a diluent for A336 and kerosene for the dilution of C272. The experiments illustrated that the third phase would be formed after extraction using the kerosene as the diluent of A336. The aqueous phase was formed by the dissolution of a certain amount of Pr $(NO_3)_3.6H_2O$ (99.9%) and $Nd(NO_3)_3.6H_2O$ (99.9%) salts (purchased from Sigma) in a hydrochloric acid medium. HCl/NH_3 was used to adjust the initial pH of the aqueous phase.

2.2. Experimental procedure and solvent extraction theory

Two different mixtures of extractant/diluent were used to form the organic phases of A336/toluene and C272/kerosene. Based on the initial investigation, the equilibrium time for the extraction with the A336/toluene and C272/kerosene was approximately 20 and 10 minutes, respectively. The concentration of Pr and Nd in the model NdFeB magnet-leaching solution was considered to be 200 and 400 ppm, respectively [41,42]. The ammonium nitrate at the aqueous phase is also required for the extraction of Pr and Nd with A336/toluene. The contact times of 30 and 15 minutes were assumed as suitable times to achieve the equilibrium for Systems I and II, respectively. In each experiment, the aqueous and organic phases were contacted using a mechanical stirrer with a 300 rpm and then, these two phases were separated in a separatory funnel. The concentrations of Pr and Nd at the aqueous phase (before and after extraction) were measured spectrophotometrically (ICP-OES: LIBERTY-RL model of Agilent Company's (Australia)), and the metal contents at the organic phase were calculated by mass balance. The two responses of the extraction efficiency and the separation factor were measured using the obtained data. The extraction efficiency is defined as follows:

$$\%E = \frac{[M^{3+}]_{aq,0} - [M^{3+}]_{aq,eq}}{[M^{3+}]_{aq,0}} \times 100, \tag{1}$$

where $[M^{3+}]_{aq,0}$ and $[M^{3+}]_{aq,eq}$ represent the concentration of Pr/Nd in the feed and raffinate solution, respectively. The separation factor is also expressed as follows:

$$SF_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}. \tag{2}$$

This parameter is equal to the ratio of the distribution coefficient of first metal (M_1) to the second metal (M_2). The distribution coefficient is also defined as the concentration of one of metal ions at the organic phase to the concentration of the same metal ion at the aqueous phase. A336 is an anion exchanger that causes an increase in the distribution coefficient of Pr than Nd. In contrast, in the presence of C272, i.e., a cation exchanger, the values of the distribution coefficient of Nd are higher than Pr. Therefore, the ratio of the distribution coefficients of Pr to Nd ($SF_{Pr/Nd}$) is used to represent the separation factor in the extraction with A336, while Nd to Pr ($SF_{Nd/Pr}$) is used in the extraction with C272. Both definitions (i.e., $SF_{Nd/Pr}$

Table 1. Relevant studies on the extraction and separation of Pr and Nd by the solvent extraction method.

Authors	**Year**	**Extractant**	**Diluent**	**SF_{Nd-Pr}**	**Note**	**Ref.**
Bauer and Lindstrom	1971	Aliquat 336	Socal 355 L	5.4	DTPA used as a chelating agent	[31]
Lu et al.	1989	Aliquat 336	Naphta-100	–	Multi-stage process design in the presence of DTPA	[36]
Minagawa	1993	B2EHPA	Kerosene	5	Use of non-equilibrium extraction and DTPA agent	[18]
Nakayama et al.	1995	PC–88A	Kerosene	≈ 2.5	A microporous Teflon film (Gore-Tex) impregnated with PC-88A	[21]
Matsuyama et al.	1995	Cyanex 272	N-heptane	1.9	Use of non-equilibrium extraction and DTPA agent	[19]
Preston	1996	Aliquat 336	Shelsol AB	2.05	Recovery of 75% of the neodymium with a purity of 95–96% in 40 stages	[37]
Yamaguchi	1997	D2EHPA	ISOPAR M	≈ 2	Electrostatic liquid contactor used for continuous extraction process	[9]
Yin Shaohua et al.	2010	D2EHPA	Kerosene	1.57	Doubling the extraction capacity in the presence of lactic acid	[15]
Liu et al.	2014	Cyanex 272 + Alamin 336	Kerosene	1.29	Extraction efficiency increased but separation factor decreased	[7]
Liu et al.	2015	Cyanex 272+ Alamin 336+ TBP	Kerosene	1.59	pH = 5	[10]
Banda et al.	2015	saponified PC 88A	Escaid 110	1.5	Selective scrubbing process used to reach a Nd solution obtained with a purity of 99%	[24]
Batchu et al.	2015	Cyanex 301+LIX 63	Kerosene	2.07	–	[38]
Padhan and Sarangi	2017	Bif-ILs based on Aliquat 336 and Cyanex 272	Distilled kerosene	–	The extraction efficiency for the extractant concentration of 0.35 M was about 100%	[20]
Safarzadeh et al.	2018	D2EHPA	Kerosene	2.72	The optimum conditions: D2EHPA concentration of 30 mM, pH of 5 and Pr-Nd concentration equal to 30 ppm in hydrochloric acid medium	[35]
Yuan et al.	2018	HEHEHP	Sulfonated Kerosene	2.23	Use of microfluidic contactor	[22]
Kumari et al.	2019	Mextral 336	Kerosene	2.9	Iso-decanol and EDTA used as a modifier and a chelating agent, respectively.	[32]
Sun et al.	2019	PC-88A and $N_{4441}NO_3$	Dodecane	3.5	A new external push-pull extraction system suggested.	[26]

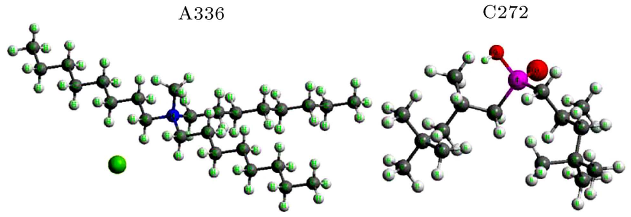


Figure 1. Three-dimensional structure formulas of A336 and C272.

and $SF_{Pr/Nd}$) for each system are used in the current study to compare the impact of the operational parameters on the separation factor. The structural formulas of A336 and C272 as the extractants are depicted in Figure 1.

A336 is a quaternary ammonium salt with the ability to extract metal ions which forms anionic complexes at the aqueous phase. The extraction of lanthanides with quaternary amine compounds exhibits proper efficiency when the extraction occurs in the concentrated electrolyte. Among the different electrolytes for extraction, the ammonium nitrate is preferred for practical applications, even though it has lower efficiency than the lithium nitrate. The high concentrations of NO_3^- ions are essential to the formation of extractable complexes such as undissociated lanthanide nitrates [43–45]. The lower extraction ability of heavier lanthanides with anion exchangers was described with an increase in the bond strength between the lanthanide ion and the hydrate shell [46]. The equilibrium reaction of the extraction of any rare-earth nitrates by a nitrate form of A336 is expressed as follows [37,45]:

$$n\overline{R_3CH_3NNO_3} + M(NO_3)_3 \Leftrightarrow \overline{(R_3CH_3NNO_3)_n.M(NO_3)_3}\ , \tag{3}$$

where M represents Pr and/or Nd, the superscripts indicates the compounds at the organic phase, and the coefficient of stoichiometric (i.e., n) is greater than one. Based on the observations of Černá et al., the apparent stoichiometric coefficient in Eq. (3) decreased with the loading of extractant and the complexes with a low amine-to-metal ratio could be formed at high metal concentrations [45]. The formation of anionic species is given below:

$$M^{3+} + 4NO_3^- \Leftrightarrow M(NO_3)_4^-\ . \tag{4}$$

The cation of the dissociated amine nitrates at the aqueous phase reacts with the $Ln(NO_3)_4^-$ species, and the formed complex is transferred to the organic phase presented in the reaction below:

$$\overline{R_3CH_3N^+NO_3^-} + M(NO_3)_4^- \Leftrightarrow \overline{R_3CH_3N^+M(NO_3)_4^-} + NO_3^-. \tag{5}$$

The formed 1:1 complex resulted from the anion-exchange reaction and it could react with another lanthanide nitrate. Then, 1:2 amine/metal complexes are formed as follows:

$$\overline{R_3CH_3N^+M(NO_3)_4^-} + M(NO_3)_3 \Leftrightarrow \overline{R_3CH_3N^+M(NO_3)_4^-.M(NO_3)_3}\ . \tag{6}$$

Also, the presence of the supporting electrolyte causes a high NO_3^- concentration and shifts Reactions (3) to (6) to the right side and then:

$$NH_4^+ + NO_3^- \Leftrightarrow NH_4NO_3. \tag{7}$$

Although some di-alkyl phosphinic acids have been investigated for REE separation, only C272 is used commercially [39,47]. Generally, in the solvent extraction of REEs with organophosphorus extractants, the use of C272 reduces the extraction efficiency but increases the selectivity [7]. The reaction of the dimeric form of C272 with the trivalent metal ions is as follows:

$$M^{3+} + 3\overline{H_2A_2} \Leftrightarrow \overline{M(HA_2)_3} + 3H^+, \tag{8}$$

where H_2A_2 represents the dimeric form of the organic acid. The reaction progress is accompanied by increasing the acidity of the aqueous phase.

2.3. Experimental design

As mentioned, the RSM based on the CCD was applied to the experimental design and mathematical-statistical modeling of the two systems. The CCD is a second-order design, and its standard second-order model for the number of p factors is in the following [48]:

$$y = \beta_0 + \sum_{i=1}^{p}\beta_i x_i + \sum_{i=1}^{p}\beta_{ii}x_i^2 + \sum_{1\leq i\leq j}\beta_{ij}x_i x_j + \varepsilon, \tag{9}$$

where x_i is the parameters and ε the residual associated with the experiments. While β_0 represents the constant term and β_i, β_{ii}, and β_{ij} represent the coefficients of the linear, quadratic, and interaction parameters, respectively.

The impacts of the dominant parameters of the A336 concentration, pH, O/A ratio, and the AN concentration in System I as well as the concentration of C272, pH, and O/A ratio in System II were modeled and optimized. The corresponding ranges of these parameters are presented in Table 2. Several errors could occur in the pH adjustment, the exact determination of material concentration at the organic and aqueous phases, and the analyses of the ions' concentration in a batch extraction process.

It should be noted that the A336 relies intensively on the presence of the concentrated electrolyte to form a suitable complex that leads to REE ion extraction. Therefore, the AN concentration as a supporting electrolyte can be considered as an additional parameter in System I.

Table 2. The parameters levels for the experimental design in Systems I and II.

Parameter	Symbol	Levels	Unit
System I			
A336 concentration	Y_1	0.30, 0.57, 0.85	mol/L
pH	Y_2	2.0, 3.5, 5.0	–
O/A ratio	Y_3	1, 2, 3	–
AN concentration	Y_4	2.2, 3.9, 5.6	mol/L
System II			
C272 concentration	Z_1	0.23, 0.40, 0.57	mol/L
pH	Z_2	2.0, 3.5, 5.0	–
O/A ratio	Z_3	1, 2, 3	–

3. Results and discussion

3.1. *Extraction of Pr and Nd with Aliquat 336 in toluene*

A total of 30 experimental runs were carried out in this study for System I. The experimental design based on CCD as well as the experimental data, predicted data, and the operating conditions are presented in Table A.1 in Appendix A. Based on the reported data, some runs (25 to 30) have the same operational conditions because of the identification of the lack-of-fit.

3.1.1. *The impact of operational parameters on extraction efficiency of System I*

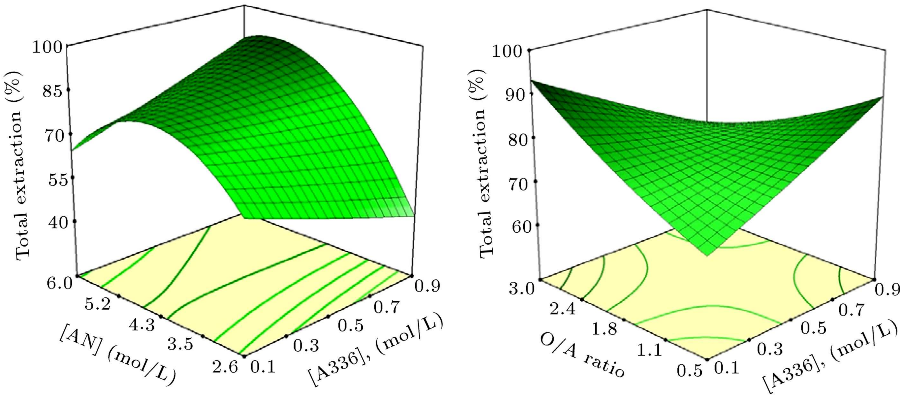
Figure 2 depicts the impact of some interaction parameters on the total extraction efficiency. Figure 2(a) shows the impact of the interaction between the A336 and AN concentrations on the extraction efficiency. It was found that the variation in the extraction efficiency by changing the A336 concentration was dependent on the levels of AN concentration, intrinsically. According to Figure 2(a), increase in the A336 concentration causes partial decrease in the extraction efficiency at low levels of AN concentration (e.g., 2.6 mol/L). However, at high levels of AN concentration (e.g., 6.0 mol/L), it causes the increase in the extraction efficiency. The reason for these different trends can be attributed to the ratio of quaternary ammonium cations ($R_3CH_3N^+$) to the nitrate ions (NO_3^-) [41]. The nitrate ions play two roles in achievement of:

1. The nitrate form of A336;
2. The concentrated electrolytes at the aqueous phase.

Figure 2(b) shows the impact of the interaction between O/A ratio and A336 concentrations on the extraction efficiency. There was a productive interaction between these parameters. At the low levels of O/A ratio (e.g., 0.5), the increase of the A336 concentration leads to increase in the extraction efficiency, while at high levels of O/A ratio (e.g., 3), it leads to decrease in the extraction efficiency. The number of quaternary ammonium salt molecules can be specified using the values of two above parameters and subsequently, the ratio of $R_3CH_3N^+$ to NO_3^- relies on this specified number. For this reason, such different trends are shown in Figure 2(b). In the present work, the pH only had a slight impact on the extraction efficiency with A336.

3.1.2. *Analysis of variance for separation factor of System I*

The analysis of variance (ANOVA) related to the separation factor of Pr/Nd in System I is presented in Table A.2 in Appendix A. The value of R^2 was obtained 0.96. Predicted-R^2 of 0.83 was properly consistent with the adjusted-R^2 of 0.93, i.e., the absolute deviation was less than 0.2. The difference between the highest (2.22) and lowest experimental data (1.39) was 0.83. The p-values higher than 0.1 and lower than 0.05 pointed out that the model parameters were insignificant and significant, respectively. According to this definition, the significant parameters were Y_1, Y_2, Y_4, $Y_1 \times Y_4$, $Y_3 \times Y_4$, and Y_4^2 in the presented model. The parameter



(a) (b)

Figure 2. The impact of interaction parameters: (a) [A336]:[AN] (with pH = 3.5 and O/A = 2) and (b) [A336]:(O/A) (with pH = 3.5 and [AN] = 3.9 mol/L) on total extraction efficiency in System I.

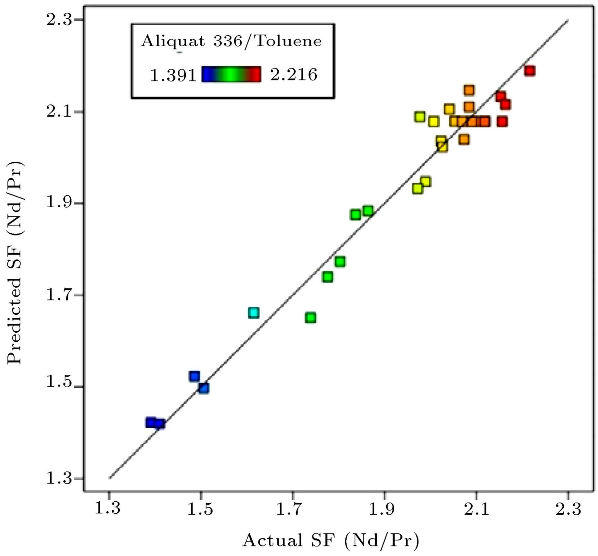


Figure 3. Actual versus predicted values for System I.

of O/A ratio was not significant, but it induced a significant impact through the interaction with the AN concentration on the separation factor. Based on the F-values, the parameters did influence the separation factor following the order [AN] > [A336] > pH > O/A and significant interaction between parameters follow the order as (O/A):[AN] > [A336]:[AN]. The predicted (from Eq. (A.1) of Appendix A) versus the actual values are depicted in Figure 3.

3.2. Extraction of Pr and Nd with Cyanex 272 in kerosene

The experimental design for System II is presented in Table B.1 in Appendix B. This design consisted of 20 runs in which some runs (i.e., 1 to 15) had different conditions. However, the other runs (i.e., 15 to 20) were related to the central point.

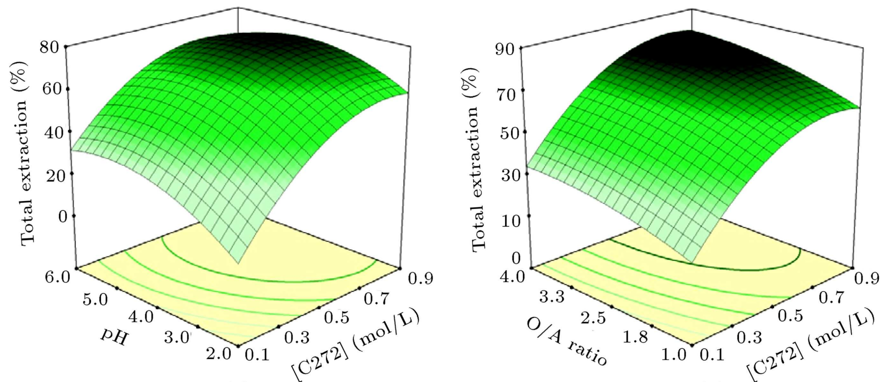
3.2.1. The impact of operational parameters on extraction efficiency of System II

Figure 4 indicates the impact of the interactions of C272 concentration with pH (Figure 4(a)) and O/A ratio (Figure 4(b)) on the total extraction efficiency. The interactive impact on the extraction efficiency was not significant in System II. The increase in the Cyanex 272 concentration and O/A ratio enhanced the number of extractant molecules that participated in the extraction reaction. Therefore, more loaded-metal ions at the organic phase and increase in the extraction efficiency were expectable. According to Eq. (8), the Pr and Nd extraction reaction with Cyanex 272 was associated with the release of hydrogen ions in the aqueous solution. On the other hand, the enhancement of pH parameter reduced the number of hydrogen ions in the aqueous solution and forwarded the extraction reaction to the right side which caused the improvement of the extraction efficiency (unlike System I where the pH parameter had slight impact on the extraction efficiency). The reason for the low efficiency of the extraction process with Cyanex 272 was related to high acid dissociation constant (pKa = 6.37) [49]. However, the extraction efficiency of Pr and Nd ions for the studied aqueous feed can be considered appropriate.

3.2.2. Analysis of variance for separation factor of System II

The ANOVA related to the separation factor of Nd/Pr in System II is presented in Table B.2 in Appendix B. The R^2, Predicted-R^2, and adjusted-R^2 values were 0.96, 0.82, and 0.91, respectively. The significant parameters of the proposed model based on the p-values were Z_1, Z_2, Z_3, and Z_2^2.

The order of parameters' impact on the separation factor of Nd/Pr was O/A > pH > [C272] with respect to the F-values. In comparison with System I, the inverse order was obtained. The interaction parameters in the proposed model were insignificant, and the most effective parameter was the interaction between the C272 concentration and pH. Figure 5 shows the predicted (from Eq. (B.1) of Appendix B) versus actual values for the separation factor of Nd/Pr.



(a) (b)

Figure 4. The impact of interaction parameters: (a) [C272]:pH (with O/A = 2) and (b) [C272]:(O/A) (with pH = 3.5) on total extraction efficiency in System II.

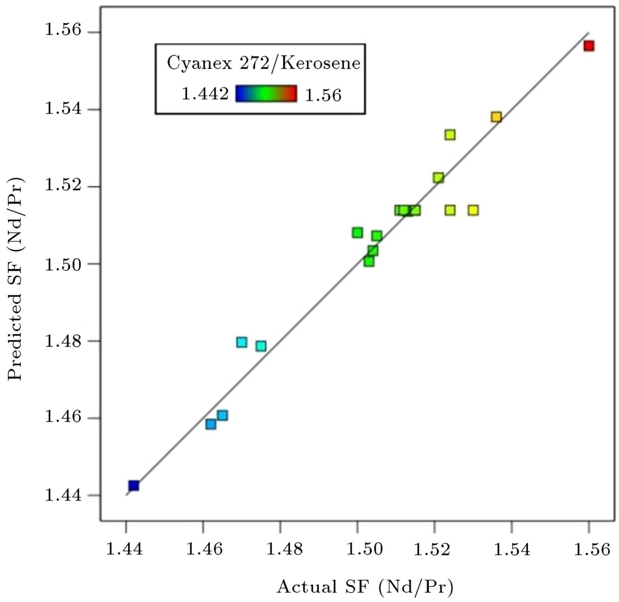


Figure 5. Actual versus predicted values for System II.

3.3. Comparison of the impact of operational parameters on the separation factor in Systems I and II

From the obtained results, the inverse order of the impact of the parameters in both systems was determined. The orders were [A336] > pH > O/A, and O/A > pH > [C272] in Systems I and II, respectively.

3.3.1. The impact of the interaction between extractant concentration and O/A ratio

The interaction between the extractant concentration and O/A ratio on the separation factor is presented in Figure 6. Figure 6(a) and (c) illustrate the interaction of the A336 and O/A ratio in System I. Figure 6(b) and (d) also show the interaction between the C272 and O/A ratio in System II. As shown in Figure 6(a) and (b), the Nd/Pr separation factor reduced by increasing the extractant concentration. However, according to Figure 6(b), the direct relationship between Cyanex 272 concentration and Nd/Pr separation was observed at a high concentration, which was also in agreement with the results of Liu et al. [7]. The O/A ratio had a direct relationship with the Nd/Pr separation factor in both systems, meaning that increasing the O/A ratio at all extractant concentrations reduced the Nd/Pr separation factor. The operational parameters of O/A ratio and extractant concentration were more effective in the performance of System I than System II. According to Figure 6(c), both Aliquat 336 and O/A ratio had a direct relationship with the Pr/Nd separation factor. According to the above, in the case of the mechanism of the metal ion extraction with Aliquat 336 at high extractant concentrations, the extracted species were formed at a smaller ratio of amine to the metal ion. Due to this direct relationship, it can be concluded that smaller molecular compounds had a relatively higher tendency to metal ions with a smaller ionic radius (i.e., Pr^{3+}).

3.3.2. The impact of the interaction between pH and O/A ratio

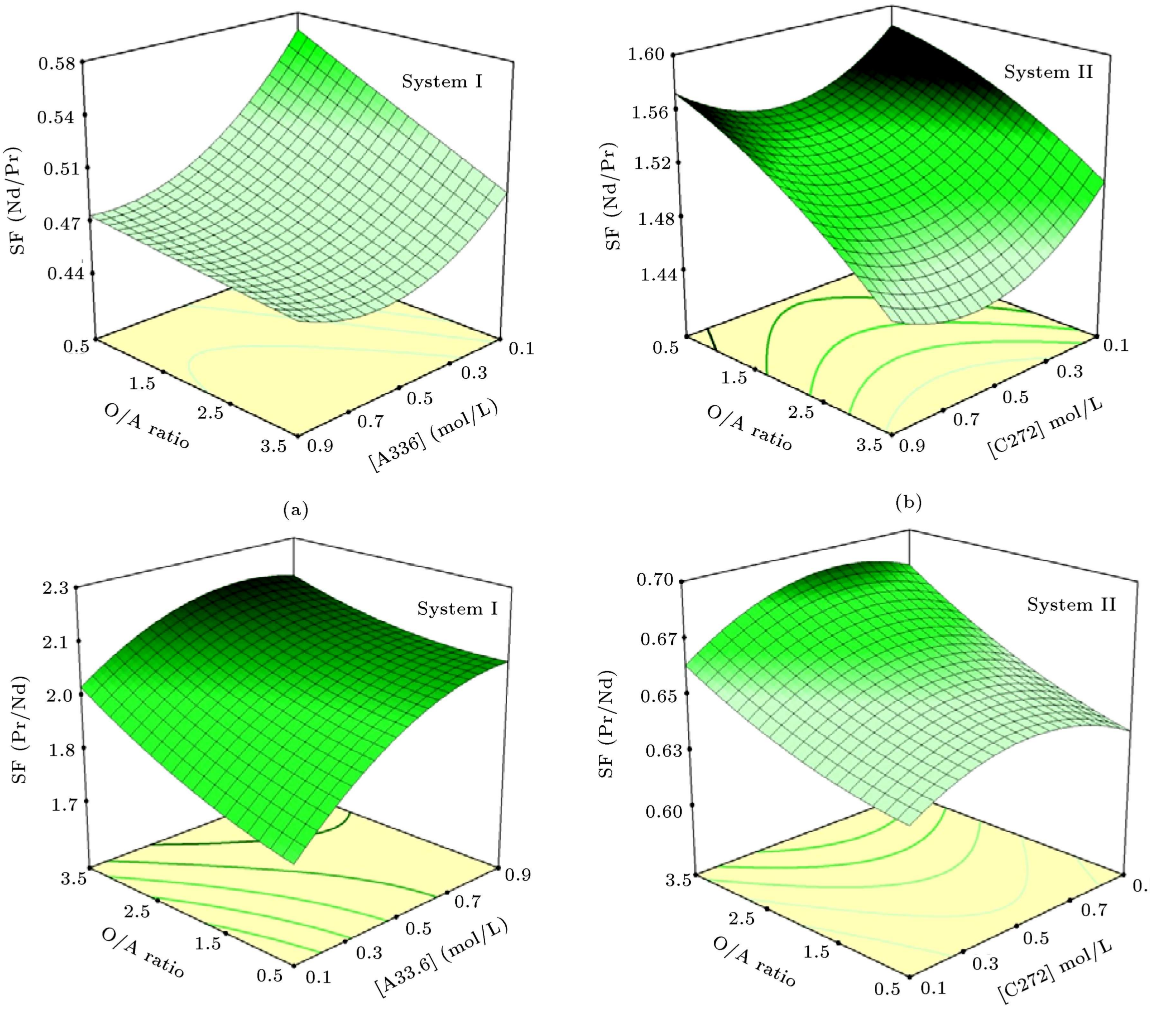
The interactive impact between pH and O/A ratio on the separation factor is depicted in Figure 7. Figure 7(a) and (c) show System I, while Figure 7(b) and (d) illustrate System II. From Figure 7(a), it can be observed that the pH impact on the separation factor of Nd/Pr was in reverse, meaning that increase in pH caused a slight decrease in the separation factor of Nd/Pr. However, the pH impact on System II was different. Based on Figure 7(b), the pH impact on the separation factor of Nd/Pr appeared as a curve with a maximum. As can be seen in Figure 7(c) and (d), increasing the O/A ratio at all pH values increased the Pr/Nd separation factor.

The impact of the operational parameters on both of the systems was low, which is the reason why it has not been considered in the researches. For example, Bauer and Lindstrom reported that the pH parameter could not affect the extraction efficiency and separation factor in the solvent extraction with Aliquat 336 [31]. Also, the impact of this parameter was ignorable in the present study. In Cerna's study, higher Aliquat 336 concentrations and concentrated electrolyte could lead to a greater separation factor of Pr/Nd [45], being in good agreement with the results obtained from the present study.

3.3.3. The impact of the interaction between extractant concentration and pH

Figure 8 shows the interactive impact between the extractant concentration and pH on the separation factor. Figure 8(a) and (c) show the interaction between the A336 concentration and pH in System I. Figure 8(b) and (d) illustrate the impact of the interaction between the concentration of C272 and pH on the separation factor in System II. According to Figure 8(a) and (b), the highest separation factor of Nd/Pr was achieved at low extractant concentrations and low pH in both of the systems, although the optimum pH of System II was not the minimum pH. As is expected, different results were obtained for the impact of the desired parameters on the separation factor of Pr/Nd (Figure 8(c) and (d)) in which the high values of separation factor of Pr/Nd were attained at a high extractant concentration and pH values in both systems.

The separation factor in the extraction process under different extractant concentrations and pH is shown in Figure 9. Figure 9 is a contour plot expression of Figure 8. Figure 9(a) and (c) show the interaction contours of the A336 concentration and pH in System I, and Figure 9(b) and (d) represent the interaction con-



(a) (b)

(c) (d)

Figure 6. Interaction between extractant concentration and O/A ratio for the separation factor: (a) $SF_{Nd/Pr}$–[A336]:(O/A), (b) $SF_{Nd/Pr}$–[C272]:(O/A), (c) $SF_{Pr/Nd}$–[A336]:(O/A), and (d) $SF_{Pr/Nd}$–[C272]:(O/A), [AN] = 5.6 mol/L.

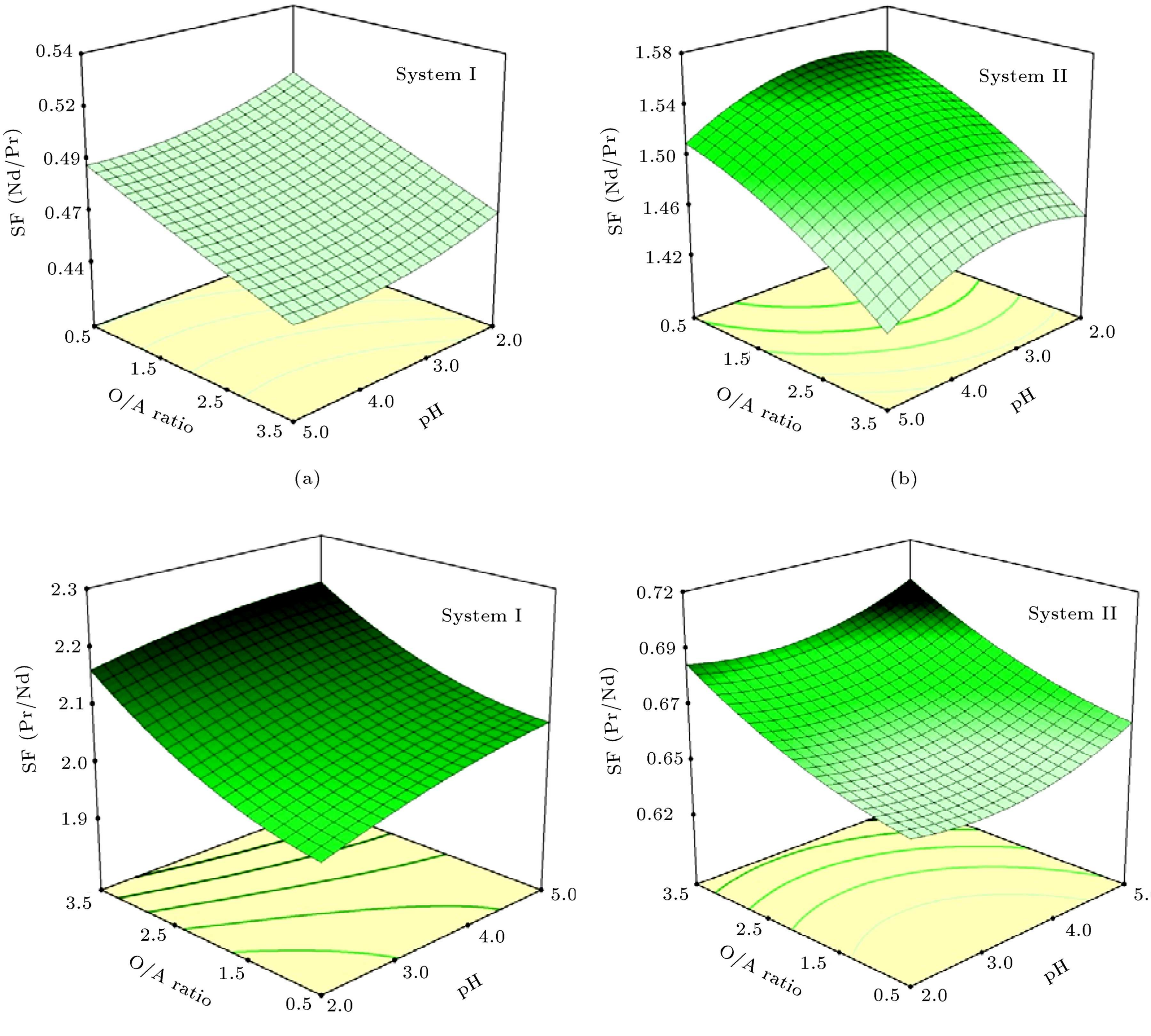
tours of the C272 concentration and pH in System II. The investigation of the studied systems demonstrated that if the operational conditions were suitably adjusted, the operational parameters of the extraction system containing the anion exchanger (System I) had a direct relationship with the extraction efficiency and selectivity. However, in the extraction system containing the cation exchanger (System II), the operational parameters had direct and indirect relationships with the extraction efficiency and selectivity, respectively. Therefore, the modification of the extraction systems containing Aliquat 336 with the aim of promoting the selectivity is associated with a lower decrease in extraction efficiency and it yields more effective results.

3.4. Optimization

Systems I and II were optimized to achieve the maximum operational selectivity [41]. The initial conditions and optimization results for both systems are presented in Table 3. The identical conditions were considered for all the parameters in both systems. The results showed that the extraction efficiencies of Pr and Nd were 74.8% and 61.2% in System I and 48.9% and 59.3% in System II, respectively. The separation factor was obtained as 2.10 and 1.54 for Systems I and II, respectively. Based on the obtained results in the present study, System I is more suitable for the extraction and separation of Pr and Nd in the studied range of the parameters.

3.5. Stripping investigations

HCl solution was used for the stripping process of the Pr and Nd ions loaded at the organic phase. In order to determine the equilibrium time and suitable concentration of the HCl, the stripping runs were conducted for recovering of organic phase. In this respect, the loaded organic phase from extraction runs was used at the center point of the related experimental design for each system (see Tables A.1 and B.1 in



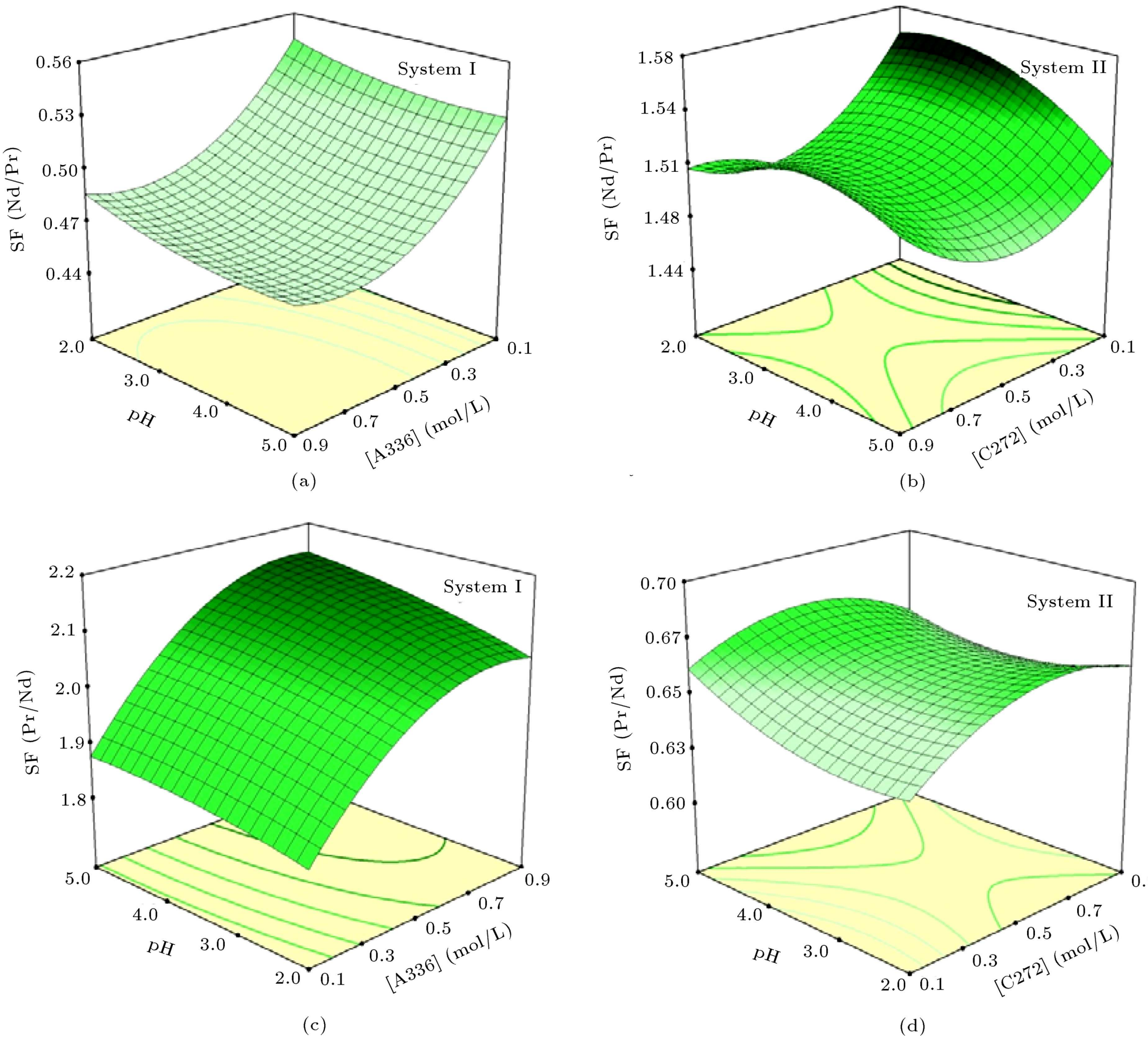
(a) (b)

(c) (d)

Figure 7. Interaction between pH and O/A ratio for the separation factor: (a) $SF_{Nd/Pr}$–pH:(O/A) in System I, (b) $SF_{Nd/Pr}$–pH:(O/A) in System II, (c) $SF_{Pr/Nd}$–pH:(O/A) in System I, and (d) $SF_{Pr/Nd}$–pH:(O/A) in System II, [AN]=5.6 mol/L.

Table 3. Initial condition and results of the numerical optimization.

Terms	**Goal**		**Parameter range**	**Optimum condition**	
	System I	**System II**		**System I**	**System II**
Extractant concentration (mol/L)	–	–	0.1–0.85	**0.85**	**0.85**
pH	–	–	2.0–5.0	**5.0**	**2.4**
O/A ratio	–	–	1–3	**1**	**1**
AN concentration (mol/L)	–	–	2.2–5.6	**3.1**	–
Pr extraction (%)	Maximize	Minimize	–	**74.8**	**48.9**
Nd extraction (%)	Minimize	Maximize	–	**61.2**	**59.3**
Separation factor	Maximize	Maximize	–	**2.10**	**1.54**
Desirability	–	–	–	**0.62**	**0.61**



(a) (b)

(c) (d)

Figure 8. Interaction between extractant concentration and pH for the separation factor of Nd and Pr: (a) $SF_{Nd/Pr}$-[A336]: pH, (b) $SF_{Nd/Pr}$–[C272]: pH, (c) $SF_{Pr/Nd}$–[A336]: pH, and (d) $SF_{Pr/Nd}$–[C272]: pH, [AN]=5.6 mol/L.

Appendices A and B). It should be noted that the ratio of the organic to aqueous phase for all the stripping runs was considered as 1:1. Figure 10(a) shows the impact of the contact time on the total stripping percentage for Systems I and II which were investigated at different contact times such as 1, 5, 10, 20, 30, and 40 minutes. Based on the available evidence, increase in the contact time leads to increase in the total stripping percentage and thus, the two systems reach equilibrium at the same time contact equal to 5 minutes. Figure 10(b) shows the impact of the concentration of HCl on the total stripping percentage for the two systems which were investigated at different concentrations of HCl such as 0.1, 0.2, 0.5, 1, and 2 mol/L. As can be seen, by increasing the concentration of the HCl, the total stripping percentage increased and even, the recovering of the organic phase for both systems could be conducted almost completely from 0.1 mol/L concentration of the HCl at the aqueous strip phase. In summary, it can be concluded that both of the systems had desirable features for the recovering of the organic phase.

4. Conclusions

The solvent extraction process was applied to the separation of Pr and Nd ions from model NdFeB magnet-leaching solution. Aliquat 336/toluene (System I) and Cyanex 272/kerosene (System II) were employed as the extractant/diluent. The response surface methodology based on central composite design was applied to experimental modeling of the operational parameters on the separation factor. The investigation of the variation of the separation factor of Pr/Nd in both systems indicated that by increasing the extractant concentration and O/A ratio, this response generally increased. From the analysis of pH value, it was concluded that the enhancement of pH caused a

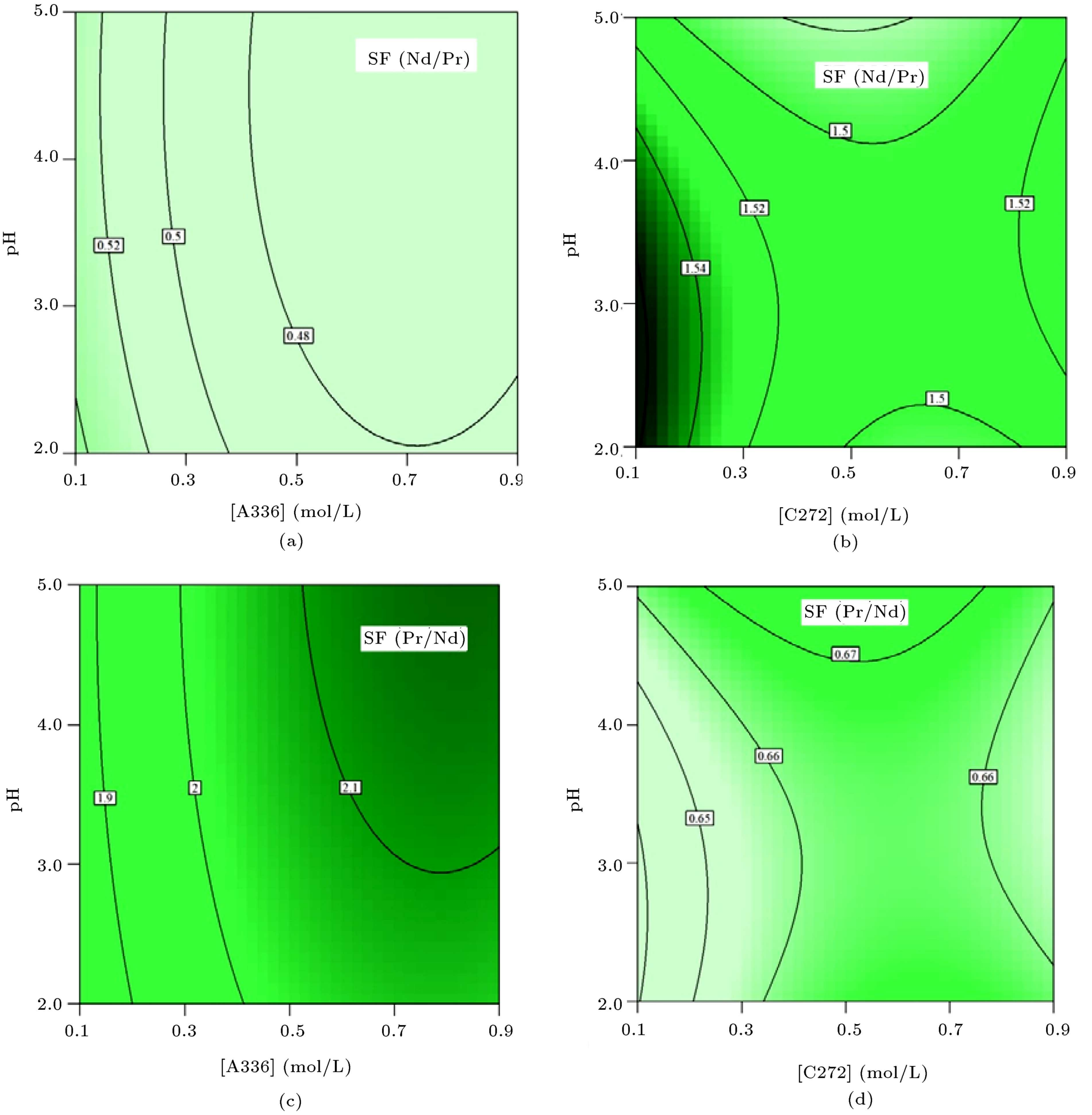


Figure 9. Contour plot of interaction between extractant concentration and pH for the separation factor of Nd and Pr: (a) $SF_{Nd/Pr}$-[A336]:pH, (b) $SF_{Nd/Pr}$-[C272]:pH, (c) $SF_{Pr/Nd}$- [A336]:pH, and (d) $SF_{Pr/Nd}$–[C272]:pH.

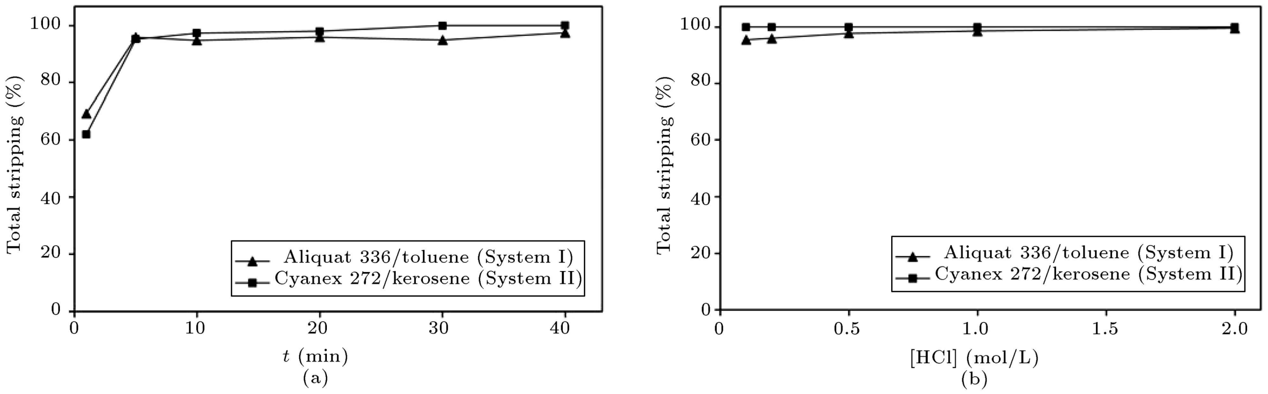


Figure 10. The impact of (a) contact time, and (b) HCl concentration on the total stripping.

slight reduction in the separation factor of Nd/Pr in System I and also, this enhancement led to a curve with the maximum point in System II. Based on the optimization results, the extraction efficiencies of Pr and Nd were 74.8% and 61.2% in System I and 48.9% and 59.3% in System II, respectively. Also, the separation factor in Systems I and II was 2.10 and 1.54, respectively. Therefore, System I was more appropriate in the studied range of parameters. The obtained values for Aliquat 336 concentration, O/A ratio, pH, and AN concentration in System I were 0.85 mol/L, 1, 5.0, and 3.9 mol/L, respectively. The suitable contact time and HCl concentration for striping Nd and Pr from loaded organic phase in both of the extraction systems were determined as 5 minute and 0.1 mol/L, respectively.

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Nomenclature

[A336]	Aliquat 336 concentration, mol/L
[AN]	Ammonium nitrate concentration, mol/L
[C272]	Cyanex 272 concentration, mol/L
$[Ln^{3+}]$	Pr/Nd concentration, ppm
E	Extraction efficiency %
p	Number of parameters
O/A	Organic to aqueous phase
SF	Separation factor
Y	Parameter in System I
Z	Parameter in System II
β	Coefficient in CCD second-order model
ε	Residual associated

Subscripts and superscripts

0	Initial
1	Extractant concentration
2	pH
3	O/A ratio
4	Ammonium nitrate concentration
eq	Equilibrium
i	Linear parameters
ii	Quadratic parameter
ij	Interaction parameters

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Appendix A

The experimental design data for System I is presented in Table (A.1):

$$\begin{aligned} SF_{Pr/Nd} &= -0.170161 + 1.37454 \times [A336] + 0.075391 \\ &\times pH - 0.078709 \times (O/A) + 0.708136 \\ &\times [AN] + 0.020606 \times [A336] \\ &\times pH - 0.069091 \times [A336] \times (O/A) - 0.088503 \\ &\times [A336] \times [AN] - 0.003917 \times pH \times (O/A) - 0.003725 \\ &\times pH \times [AN] + 0.023235 \times (O/A) \times [AN] \\ &-0.508163 \times [A336]^2 - 0.005080 \times pH^2 \\ &+0.013570 \times (O/A) - 0.072121 \times [AN]^2. \end{aligned} \tag{A.1}$$

The experimental data and predicted values are presented in Table A.1. The analysis of variance (ANOVA) related to the separation factor of Pr/Nd in System I is presented in Table A.2.

Appendix B

The predicted values for the separation factor of Nb/Pr are obtained by Eq. (B.1):

$$\begin{aligned} SF_{Nd/Pr} &= 1.56817 - 0.314555 \times [C272] + 0.043707 \\ &\times pH - 0.006062 \times (O/A) + 0.023529 \\ &\times [C272] \times pH - 0.011765 \times [C272] \\ &\times (O/A) + 0.0005 \times pH \times (O/A) \\ &+0.223341 \times [C272]^2 - 0.009131 \times pH^2 \\ &-0.005045 \times (O/A)^2. \end{aligned} \tag{B.1}$$

The experimental design for System II is presented in Table B.1, and the ANOVA related to the separation factor of Nd/Pr in System II is presented in Table B.2.

Table A.1. Experimental design based on CCD in System I.

Run no.	**Parameters**				**Response**			
	[A336] (mol/L)	**pH**	**O/A**	**[AN] (mol/L)**	E_{Pr} (%)	E_{Nd} (%)	$\mathrm{SF}_{Pr/Nd}$	
							$SF_{\mathrm{exp.}}$	$SF_{pred.}$
1	0.30	2.0	1	2.2	51.88	41.58	1.391	1.42
2	0.85	2.0	1	2.2	56.14	44.51	1.776	1.74
3	0.30	5.0	1	2.2	53.12	42.34	1.486	1.52
4	0.85	5.0	1	2.2	52.89	36.40	1.837	1.88
5	0.30	2.0	3	2.2	58.73	51.98	1.41	1.42
6	0.85	2.0	3	2.2	13.19	10.39	1.615	1.66
7	0.30	5.0	3	2.2	55.30	44.23	1.506	1.50
8	0.85	5.0	3	2.2	12.58	9.02	1.803	1.77
9	0.30	2.0	1	5.6	78.39	65.03	1.864	1.88
10	0.85	2.0	1	5.6	93.09	86.77	2.023	2.04
11	0.30	5.0	1	5.6	79.03	68.54	1.989	1.95
12	0.85	5.0	1	5.6	94.32	88.38	2.153	2.13
13	0.30	2.0	3	5.6	93.75	87.72	2.073	2.04
14	0.85	2.0	3	5.6	97.08	93.86	2.163	2.12
15	0.30	5.0	3	5.6	92.52	85.58	2.053	2.08
16	0.85	5.0	3	5.6	97.08	93.71	2.216	2.19
17	0.30	3.5	2	3.9	81.19	65.16	1.972	1.93
18	0.85	3.5	2	3.9	87.29	79.39	2.084	2.15
19	0.57	2.0	2	3.9	85.68	74.26	2.026	2.02
20	0.57	5.0	2	3.9	89.01	79.23	2.084	2.11
21	0.57	3.5	1	3.9	82.36	67.27	2.119	2.08
22	0.57	3.5	3	3.9	91.04	84.35	2.041	2.11
23	0.57	3.5	2	2.2	50.39	33.87	1.739	1.65
24	0.57	3.5	2	5.6	93.34	87.61	1.977	2.09
25	0.57	3.5	2	3.9	86.02	74.09	2.099	2.08
26	0.57	3.5	2	3.9	86.45	74.27	2.156	2.08
27	0.57	3.5	2	3.9	93.33	81.42	2.09	2.08
28	0.57	3.5	2	3.9	88.19	78.50	2.007	2.08
29	0.57	3.5	2	3.9	86.45	74.63	2.118	2.08
30	0.57	3.5	2	3.9	82.17	70.59	2.069	2.08

Table A.2. ANOVA for the response of separation factor of Pr/Nd in System I.

Source	Sum of squares	Df	Mean square	F-value	p-value
Model	1.57	14	0.1123	27.350	< 0.0001
A336 conc. (Y_1)	0.2061	1	0.2061	50.180	< 0.0001
pH (Y_2)	0.0343	1	0.0343	8.360	0.0112
O/A ratio (Y_3)	0.0033	1	0.0033	0.792	0.3875
AN conc. (Y_4)	0.8659	1	0.8659	210.850	< 0.0001
$(Y_1) \times (Y_2)$	0.0012	1	0.0012	0.281	0.6035
$(Y_1) \times (Y_3)$	0.0058	1	0.0058	1.410	0.2541
$(Y_1) \times (Y_4)$	0.0274	1	0.0274	6.670	0.0208
$(Y_2) \times (Y_3)$	0.0006	1	0.0006	0.134	0.7190
$(Y_2) \times (Y_4)$	0.0014	1	0.0014	0.352	0.5620
$(Y_3) \times (Y_4)$	0.0250	1	0.0250	6.080	0.0262
$(Y_1)^2$	0.0038	1	0.0038	0.932	0.3497
$(Y_2)^2$	0.0003	1	0.0003	0.082	0.7780
$(Y_3)^2$	0.0005	1	0.0005	0.1162	0.7379
$(Y_4)^2$	0.1126	1	0.1126	27.410	0.0001
Residual	0.0616	15	0.0041	–	–
Lack of fit	0.0491	10	0.0049	1.950	0.2381
Pure error	0.0126	5	0.0025	–	–
Cor. total	1.63	29	–	–	–
Standard deviation = 0.0641		$R^2 = 0.9623$			
Mean = 1.93		Adjusted $R^2 = 0.9271$			
Coefficient of variation = 3.32		Predicted $R^2 = 0.8319$			
Press = 0.2747		Adequate precision = 16.9758			

Table B.1. Experimental design based on CCD in System II.

Run no.	Parameters			Response			
	[C272] (mol/L)	pH	O/A	E_{Pr} (%)	E_{Nd} (%)	$SF_{Nd/Pr}$	
						$SF_{\exp.}$	$SF_{pred.}$
1	0.23	2.0	1	13.10	21.04	1.560	1.56
2	0.57	2.0	1	38.05	48.30	1.521	1.52
3	0.23	5.0	1	35.28	45.20	1.513	1.51
4	0.57	5.0	1	57.67	67.21	1.504	1.50
5	0.23	2.0	3	26.68	35.36	1.503	1.50
6	0.57	2.0	3	54.08	63.38	1.462	1.46
7	0.23	5.0	3	49.97	58.60	1.465	1.46
8	0.57	5.0	3	71.60	78.42	1.442	1.44
9	0.23	3.5	2	35.45	45.56	1.524	1.53
10	0.57	3.5	2	62.23	71.74	1.505	1.51
11	0.40	2.0	2	35.67	45.41	1.500	1.51
12	0.40	5.0	2	56.23	65.46	1.475	1.48
13	0.40	3.5	1	42.69	53.35	1.536	1.54
14	0.40	3.5	3	57.63	66.17	1.470	1.48
15	0.40	3.5	2	53.75	63.73	1.511	1.51
16	0.40	3.5	2	52.65	62.89	1.524	1.51
17	0.40	3.5	2	54.62	64.65	1.512	1.51
18	0.40	3.5	2	52.46	62.40	1.515	1.51
19	0.40	3.5	2	53.51	63.55	1.515	1.51
20	0.40	3.5	2	52.89	63.49	1.530	1.51

Table B.2. ANOVA for the response of separation factor of Nd/Pr in System II.

Source	Sum of squares	Df	Mean square	F-value	p-value
Model	0.0148	9	0.0016	23.58	< 0.0001
C272 conc. (Z_1)	0.0017	1	0.0017	24.60	0.0006
pH (Z_2)	0.0022	1	0.0022	30.98	0.0002
O/A ratio (Z_3)	0.0085	1	0.0085	122.23	< 0.0001
$(Z_1) \times (Z_2)$	0.0003	1	0.0003	4.13	0.0696
$(Z_1) \times Z_3)$	0.0000	1	0.0000	0.4587	0.5136
$(Z_2) \times (Z_3)$	4.5E–06	1	4.5E–06	0.0645	0.8047
$(Z_1)^2$	0.0001	1	0.0001	1.64	0.2289
$(Z_2)^2$	0.0012	1	0.0012	16.64	0.0022
$(Z_3)^2$	0.0001	1	0.0001	1.00	0.3401
Residual	0.0007	10	0.0001	–	–
Lack of fit	0.0004	5	0.0001	1.47	0.3423
Pure error	0.0003	5	0.0001	–	–
Cor. total	0.0155	19	–	–	–

Standard deviation = 0.0084
Mean = 1.50
Coefficient of variation = 0.5552
Press = 0.0027

$R^2 = 0.9550$
Adjusted $R^2 = 0.9145$
Predicted $R^2 = 0.8239$
Adequate precision = 19.3029

Biographies

Hesamoddin Gorzin was born in 1990, Ghaemshahr, Mazandaran. He recieved his PhD degree in 2021 from Iran University of Science and Technology (IUST), Tehran, Iran, in the field of Chemical, Petroleum and Gas Engineering. His specialty branches are hydrometallurgy and solvent extraction. He has published 5 ISI papers and 1 ISC paper in the field of metal solvent extraction.

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Alireza Hemmati was born in 1986, Tehran, Iran and spent primary, high school and higher education in this city. He obtained his PhD at Iran University of Science and Technology (IUST) and finished his thesis in 2015. He has been an active faculty member at Iran University of Science and Technology (IUST), School of Chemical, Petroleum and Gas Engineering since 2019. His research areas of interest are green chemistry, solvent extraction, and membrane technology with a 14 H–index according to Google scholar. He has published 34 ISI papers, 5 ISC papers, wrote and published 2 professional books, and translated and published 2 books in Farsi in the field of chemical engineering. He has experience in unit operation, applied mathematics for chemical engineering, plant design and economics for chemical engineers, kinetics and reactor design, and advanced heat transfer in terms of teaching. As of the moment, he directs and supervises thee dissertation of 3 PhD, 8 MA, and 12 undergraduate students. He is now an Assistant Professor at the School of Chemical Petroleum and Gas Engineering, Iran University of Science and Technology (IUST), Tehran, Iran.

Ahmad Rahbar-Kelishami was born in 1980, Tehran, Iran and spent primary, high school and higher education in this city. He achieved his PhD at the University of Tehran and finished his thesis in 2010. He has been an active faculty member at Iran's University of Science and Technology (IUST), School of Chemical, Petroleum and Gas Engineering since 2019. His specialty branches are liquid phase separation, and water/waste water treatment with a 17 H-index according to Google scholar. He has published more than 50 ISI papers, 10 ISC papers, and wrote and published one professional book in the field of chemical engineering. He has engineering experience in oil, gas and energy plant design. At the moment, he directs and supervises dissertation of 4 PhD and 12 M.A.students. He is an Associate Professor at the School of Chemical Petroleum and Gas Engineering, Iran University of Science and Technology (IUST), P.O. Box 16765-163 Tehran Iran.

Ali Maleki was born in 1980. He received his PhD in Chemistry from Shahid Beheshti University in 2009. He started his career as an Assistant Professor at the Department of Chemistry, IUST in 2010 where he is currently a Full Professor. His research interests focus on design and development of novel multicomponent reactions, organic synthesis, natural and synthetic polymers, heterocycles, pharmaceutical compounds, nanochemistry, magnetic, composite, hybrid, core/shell nanomaterials, catalysts and catalytic reactions, and medicinal and green chemistry. Professor Maleki has hundreds of ISI–JCR publications and book chapters and executed industrial and applied projects. He has been selected as a distinguished researcher of IUST within 2010–2020. He has been awarded IUPAC-CHEMRAWN VII prize for green chemistry in 2016. Dr. Maleki was ranked as being among the top 1% International Scientists in ESI (Web of Science) in 2018–2020. He had more than 20 highly cited papers in 2010–2021. His H-index is currently 50 including more than 7000 citations. He was a distinguished Professor of the Fourth Young Scientists Festival in 2020 and Iran Science Elites Federation Member (Scientific Elite Professor - Top 100 Scientists) in 2021.