

Solvent extraction and separation of La(III), Nd(III), and Pr(III) from sulfate medium using PC-88A and TBP extractants

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Abstract: 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) is an established extractant for rare earth separation; however, the influence of tri-*n*-butyl phosphate (TBP) in PC-88A-based extraction of La(III), Nd(III), and Pr(III), particularly in sulfate medium, has not been previously investigated. In this study, the effects of equilibrium pH, PC-88A concentration (10-30%, v/v) and PC-88A:TBP ratio (1:1-4:1) on the distribution coefficients and separation factors of the three lanthanides were systematically examined, and the role of TBP was further investigated by slope analysis and FT-IR spectroscopy. Increasing pH and PC-88A concentration both enhanced extraction, with $D_{Nd(III)}$ and $D_{Pr(III)}$ reaching 1.39 and 1.02 at 30% PC-88A(v/v) and pH_{eq} 2.10, while $D_{La(III)}$ remained negligibly low (0.05), yielding $\beta(Nd/La)$ and $\beta(Pr/La)$ of 27.05 and 19.81, respectively. In contrast, increasing TBP concentration consistently suppressed extraction for all three lanthanides, with negative slope values of -0.97, -0.47 and -0.35 for La(III), Nd(III), and Pr(III), respectively, demonstrating that TBP acts as an antagonist rather than a synergist. FT-IR spectroscopy revealed a substantial shift in the P=O stretching band of PC-88A (from ~1198 to 1270 cm^{-1}) exclusively at the 1:1 PC-88A:TBP ratio, consistent with the antagonistic behaviour established by slope analysis. These findings suggest that controlling the PC-88A:TBP ratio offers a practical means of tuning La/Nd and La/Pr selectivity, and provides the first systematic account of TBP's antagonistic role in a PC-88A-based extraction system in sulfate medium.

Keywords: solvent extraction, PC-88A, TBP, rare earth elements, antagonistic effect, selective separation

1. Introduction

Rare earth elements (REEs), comprising the fifteen lanthanides together with scandium and yttrium, are chemically very similar due to their common electronic structure, in which the inner 4f orbital is progressively filled while the outer valence configuration remains largely unchanged. This results in a predominant trivalent state (RE^{3+}) and closely comparable ionic radii across the series, favouring their natural co-occurrence but making their mutual separation particularly difficult. Despite this similarity, individual REEs possess distinctive magnetic and electronic properties. Nd and Pr are key constituents of Nd-Fe-B permanent magnets used in electric vehicles and wind turbines, while La and Ce are widely used in Ni-MH battery alloys and petroleum-refining catalysts (Sato, 1989; Dushyanthaa et al., 2020; Alshammari, 2021).

The production of rare earth elements (REEs) as marketable products generally involves five sequential stages: beneficiation of the ore to produce a concentrate; thermal or thermochemical pretreatment followed by leaching to transfer REEs into solution; purification of the pregnant leach solution; selective separation of individual lanthanides; and recovery of the final rare earth products. Among these stages, the selective separation step represents the greatest technical challenge due to the remarkably similar physicochemical properties of the lanthanides and, consequently, has become a

major focus of rare earth processing research (Jordens et al., 2013; Xie et al., 2014; Navarro & Zhao, 2014; Sadri et al., 2017; Judge & Azimi, 2020).

Before the 1960s, ion exchange constituted the principal method employed for rare earth separation, despite its capacity to yield very high-purity products being offset by lengthy processing cycles and numerous separation stages. The industrial-scale implementation of solvent extraction emerged in the 1960s, effectively superseding ion exchange, as it enabled high-purity rare earths to be produced continuously and economically on a large scale, and it has since remained the predominant separation technology in industrial rare earth production (Sato, 1989; Xie et al., 2014; Belova, 2017).

Numerous studies have investigated solvent extraction of light rare earth elements, predominantly using acidic organophosphorus extractants either individually or in binary combinations with a second extractant. To distinguish the effect of TBP from that of the acidic extractant itself, these studies are summarised separately in Table 1, which reports systems employing a single acidic extractant, and Table 2, which reports systems in which the acidic extractant is combined with TBP.

Although the antagonistic or synergistic influence of TBP on acidic organophosphorus extractants has been examined to some extent for D2EHPA, as summarized in Tables 1 and 2, no corresponding study appears to have been undertaken for PC-88A. Moreover, research on light rare earth separation in sulfate solutions remains relatively scarce compared with the substantial literature focused on chloride and nitrate media. To address this gap, the present study systematically examines the solvent extraction of La(III), Nd(III) and Pr(III) from sulfate medium using a PC-88A–TBP extractant system. Special attention is given to elucidating the role of TBP through slope analysis and FT-IR spectroscopy, and to assessing whether its presence results in synergistic or antagonistic extraction behaviour, with a view to informing the potential development of PC-88A-based separation processes in sulfate media.

Table 1. Summary of literature studies employing PC-88A (or its structural analogues P507/HEHEHP) as a single acidic extractant for the solvent extraction of rare earth elements

Reference	Extractant(s) (tested individually)	Medium	Target Element(s)	Optimum Concentration	pH	Extraction Efficiency (%) / D	Mechanistic Note
Acharya et al., 2015	D2EHPA; PC88A	Nitrate	La	0.5 mol/L D2EHPA; 0.6 mol/L PC88A	3.0–5.5	99.8 (D2EHPA, 0.5M); 85.0 (PC88A, 0.6M)	Slopes (log D–pH): 3.0 (D2EHPA), 2.6 (PC88A); slopes (log D–log[α]): 3.28 (D2EHPA), 1.49 (PC88A); D2EHPA > PC88A for La
Safarzadeh et al., 2018	D2EHPA; PC88A; TOPO; Cyanex572	Sulfate and Chloride	Nd, Pr	10–60 mM (same range applied to all four: D2EHPA, PC88A, TOPO, Cyanex572)	2–5	Max $\beta(\text{Nd/Pr}) = 2.72$	Extraction performance order: D2EHPA > PC88A > Cyanex572 > TOPO
Battsegel et al., 2018a	D2EHPA; PC88A; TBP	Sulfate	LREE, MREE, HREE	0.6 mol/L, same concentration applied to D2EHPA, PC88A and TBP alike (initial screening); 1.8 mol/L, D2EHPA only (subsequent process optimization)	1.6–1.7	HREE >90% (1st stage); LREE >93% (2nd stage, D2EHPA)	D2EHPA most selective for HREE/LREE split; sulfate medium noted as understudied
Arellano Ruiz et al., 2020	D2EHPA; PC88A; Cyanex272	Chloride	Nd, Tb, Dy	0.8 mol/L, same concentration applied to D2EHPA, PC88A and Cyanex272 alike	4.0	Nd: 99 (D2EHPA), 64 (PC88A), 27 (Cyanex272) Dy: 98, 76; Tb: 91, 61	Extraction tendency order: D2EHPA > PC88A > Cyanex272
Zhang et al., 2014a	HEHEHP (P507); Cyanex272 (separately, then synergistic)	Chloride	Y	[HEHEHP] = [Cyanex272] = 0.1 mol/L (each tested alone at this concentration)	1.4–1.9	Max R (synergistic enhancement) = 2.94 at $X_{\text{HEHEHP}} = 0.5$	logD–pH slope ≈ 2.0 for both alone; one Y^{3+} extracted with 2 extractant molecules + 1 Cl^-
Zhang et al., 2017a	P507 (HEHEHP); P204 (D2EHPA) (separately, then synergistic)	Chloride and Sulfate (comparison)	Pr	0.02–0.10 mol/L, same range applied to P507 and P204 alike (each tested alone)	Variable	$\log K = -3.06$ (P507 alone), -0.17 (P204 alone)	Slopes ≈ 3 for both alone (pH and log[extractant]); $\text{Pr}(\text{HA})_3$; / $\text{Pr}(\text{HB})_3$ stoichiometry; Cl^- not involved (differs from sulfate medium)

2. Materials and methods

2.1. Reagents

PC-88A (Carbosynth, >95%) and TBP (Alfa Aesar, 98%) were used as the acidic extractant and neutral modifier, respectively, without further purification, and were diluted with kerosene J.T. Baker 8387 (light distillate with a low-aromatic content, always referred to as “kerosen” in the text) to the required concentrations. The synthetic solution was prepared with La_2O_3 (Sigma-Aldrich, > 99.9%), Nd_2O_3 (Sigma Aldrich-99.9%), Pr_2O_3 (Sigma-Aldrich, 99.9%), which were dissolved in H_2SO_4 (Acros organics, 96.00%) resulting in a pregnant leach-type feed solution (model PLS) containing 6380 mg/L La(III), 1400 mg/L Nd(III) and 800 mg/L Pr(III).

Table 2. Summary of literature studies employing PC-88A (or its structural analogues P507/HEHEHP) in binary or synergistic combination

Reference	Extractant 1	Extractant 2 / Additive	Medium	Target Element(s)	Synergistic / Antagonistic	Slope Analysis Result (n)	Performance (D, %E, β)	Mechanistic Note
Zhang et al., 2014a	HEHEHP (P507)	Cyanex272	Chloride	Y	Synergistic (max R=2.94 at 1:1 molar ratio)	n≈2.0 (pH); n≈2.0 (log[extractant], both alone)	R=2.94 (X _{HEHEHP} =0.5)	Extracted species: Y(HB ₂)(HA ₂) ₂ ; cation-exchange confirmed by IR; differs from single-extractant species $YCl(HA_2)_2/YCl(HB_2)_2$
Zhang et al., 2014b	HEHEHP (P507)	D2EHPA + lactic acid + citric acid (complexing agents)	Chloride	La, Ce	Synergistic (max coefficient at XHEHEHP=0.8)	-	Max β(Ce/La)=8.88; extraction capacity 53.48 g/L	FT-IR/NMR confirmed cation-exchange + P=O coordination; complexing agents further enhance selectivity
Zhang et al., 2016	P507 (HEHEHP)	Lactic acid + citric acid (complexing agents, no 2nd extractant)	Chloride	Pr, Ce	N/A (complexation-enhanced single extractant, not binary extractant synergism)	-	Extraction capacity 30.97 g/L; β(Pr,Ce)=10.48	Higher capacity/selectivity than conventional single-extractant systems; cation-exchange confirmed by IR
Zhang et al., 2017a	P507 (HEHEHP)	P204 (D2EHPA)	Chloride	Pr	Synergistic (mixed complex more stable than P507 alone, less than P204 alone)	n≈3 (pH and log[extractant] for mixture)	lgK ₁₂ =-0.25 (mixture) vs. -3.06 (P507), -0.17 (P204)	Extracted complex: Pr(HA ₂)(HB ₂) ₂ ; cation-exchange, 3H ⁺ released; K ₂ >K ₁₂ >K ₁ ordering
Chen et al., 2019	P507 (HEHEHP)	Lactic acid (complexing agent, microfluidic system)	Chloride	REEs (general)	N/A (complexation effect on single extractant, not binary extractant synergism)	-	-	Lactic acid does not participate directly in extraction reaction; cation-exchange (P-O-H) + coordination (P=O) confirmed by FT-IR/NMR/MS

2.2. Solvent extraction procedure

Extraction experiments were carried out by contacting equal volumes of the aqueous feed solution and the organic phase (A/O = 1/1). In the experiments, the initial and equilibrium pH were monitored with a pH meter (Ahlborn-Almemo 2590) and the Inlab Micro pH electrode (Mettler Toledo). The organic phase consisted of PC-88A diluted in kerosene at concentrations of 10-30% (v/v), with TBP added at PC-88A: TBP volume ratios ranging from 1:1 to 4:1. The aqueous phase pH was adjusted to the desired initial value (1-4) using dilute H₂SO₄ or NaOH before extraction. The two phases were shaken in an overhead shaker (Heidolph REAX II) for 5 min at 20 °C. For complete phase separation, the centrifugal separator (Eppendorf -5804) was used.

2.3. Analytical methods

After phase separation, the concentrations of La(III), Nd(III), and Pr(III) remaining in the aqueous (raffinate) phase were determined by inductively coupled plasma (ICP) spectrometry (PlasmaQuant PQ9000-Analytik Jena). The reproducibility of the extraction measurements was evaluated by repeating selected experiments; the relative standard deviation of the measured metal concentrations was within ±5% in all cases. The concentration in the loaded organic phase was calculated by mass balance from the difference between the feed and raffinate concentrations, resulting in %Extraction (Eq. 1). The distribution coefficient (D) for each metal ion was calculated as the ratio of its concentration in the organic phase to that in the aqueous phase (Eq. 2). The separation factors β(N(III)/La(III)), β(Pr(III)/La(III)), and β(Nd(III)/Pr(III)) were calculated as the corresponding ratios of distribution coefficients (Eq. 3). The slope analysis method was used to determine the ratio between the organic compound and the metal ion, and the exchanged protons during the extraction process, respectively. logD was plotted against pH, log[PC-88A], and log[TBP], and the experimental conditions for the other parameters were held constant. FT-IR spectroscopy was also used to characterize the unloaded and lanthanide-loaded organic phase at selected PC-88A concentrations and PC-88A:TBP ratios. Spectra were recorded using a Cary 630 FTIR Spectrometer (Agilent Technologies) equipped with a DialPath module (30 μm, 50 μm, and 100 μm path lengths).

$$\text{Extraction \%} = 100 - \left(\frac{M_o}{M_a} * 100 \right) \quad (1)$$

$$D = \frac{Mo}{Ma} \quad (2)$$

$$\beta = \frac{Da}{Db} \quad (3)$$

where Mo: total metal concentration in the organic phase, Ma: total metal concentration in the aqueous phase, D: distribution coefficient, β : separation factor, a, b: one of the REE metals under study.

3. Results and discussion

3.1. Effect of pH

Following the expectations, the extraction efficiency of La(III), Nd(III), and Pr(III) in extraction system PC-88A-TBP-kerosene/ $\text{Ln}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ (Fig. 1) increased with increasing aqueous pH_{eq} from 0.97 to 2.12, with a sharp rise observed between pH_{eq} 0.97 and 1.85, followed by a flattening trend between pH 1.85 and 2.12, for Nd(III) and Pr(III) with a maximum of 40% (Nd(III)). In contrast to this, extraction yields of La(III) remain over the whole investigated pH_{eq} range.

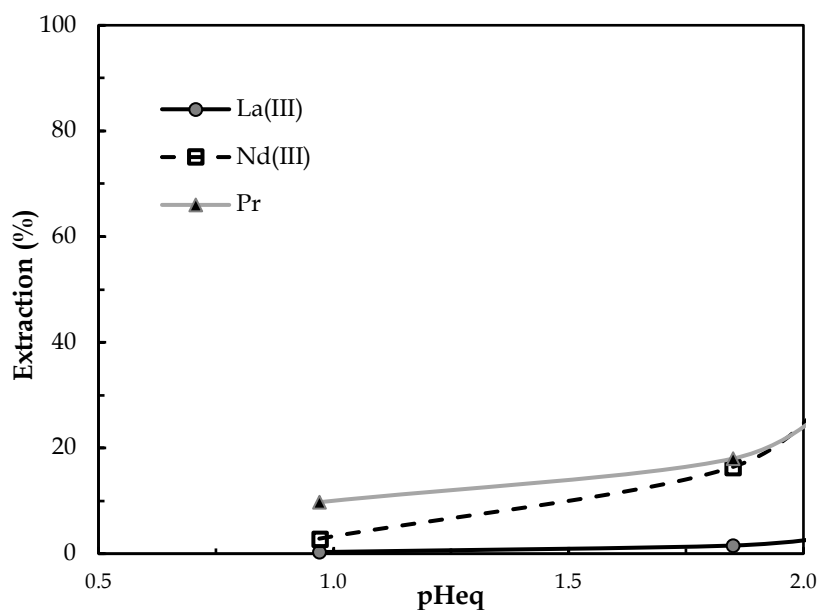


Fig. 1. Extraction efficiency of La(III), Nd(III), and Pr(III) from model PLS as a function of pH. 10% PC-88A(v/v), 5% TBP(v/v) in kerosene, A/O:1/1, 5 min, 20 °C [pH_{ini} : 1,2,3,4; H_2SO_4 medium]

Table 3 summarizes the separation factors and distribution coefficients of La(III), Nd(III), and Pr(III) at different pH values. The distribution coefficients of all three lanthanides increased progressively with equilibrium pH over the range 0.97-2.12. However, $D_{\text{Nd(III)}}$ and $D_{\text{Pr(III)}}$ increased markedly between pH_{eq} 0.97 to 2.10. The separation factors $\beta(\text{Nd/La})$ and $\beta(\text{Pr/La})$ reach a maximum near pH_{eq} 2.10 (14.55 and 12.20, respectively) before declining slightly at pH_{eq} 2.12. Notably, $\beta(\text{Pr/La})$ decreases substantially from 34.46 at pH_{eq} 0.97 to 10.95 at pH_{eq} 2.12, indicating that the La/Pr separation is most favourable under strongly acidic conditions, albeit at the expense of overall extraction efficiency, since both $D_{\text{La(III)}}$ and $D_{\text{Pr(III)}}$ remain very low at initial pH 1. Thus, these results suggest that pH_{eq} 2.10 represents a practical compromise between extraction yield and intra-lanthanide selectivity.

Table 3. The effect of equilibrium pH on distribution coefficients and separation factors

pHeq	$D_{\text{La(III)}}$	$D_{\text{Nd(III)}}$	$D_{\text{Pr(III)}}$	$\beta(\text{Nd/La})$	$\beta(\text{Pr/La})$	$\beta(\text{Nd/Pr})$
0.97	0.003	0.03	0.10	9.38	34.46	0.27
1.85	0.02	0.20	0.22	12.48	13.94	0.89
2.10	0.04	0.55	0.46	14.55	12.20	1.19
2.12	0.04	0.61	0.51	13.12	10.95	1.20

To gather information about the formed complex species in the extraction system, the dependence of $\log D$ on pH_{eq} was examined by the slope analysis method (Fig. 2). The slopes obtained for La(III), Nd(III) and Pr(III) were 0.97, 1.12 and 0.51, respectively ($R^2 \geq 0.90$), values that deviate substantially from the theoretical slope of $n=3$ expected for a classical cation-exchange reaction, a value consistently reported for single-extractant systems in chloride medium, such as the extraction of Pr(III) by P507 or P204 alone (Zhang et al., 2017a).

The observed deviation from $n=3$ can be attributed to two complementary factors. The first is the presence of the neutral modifier TBP in the organic phase which may stabilise complex species involving a lower number of acidic extractant molecules. Relatedly, the second factor is the aqueous speciation of lanthanides in sulfate media. Rare earth elements exhibit a strong affinity toward sulfate ions, forming stable complexes such as LnSO_4^+ and $[\text{Ln}(\text{SO}_4)_2]^-$ rather than existing purely as aquacomplexes of Ln^{3+} ions (Wood, 1990; Haas et al., 1995). The formation of these lower-charged species reduces the number of protons released per mole of metal extracted, further suppressing the slopes obtained from the $\log D$ vs. pH plots. This is consistent with the slope of approximately 1.85 reported for Nd^{3+} extraction using P507 alone in H_2SO_4 medium (Zhang et al., 2021), which is also lower than the theoretical value of 3.

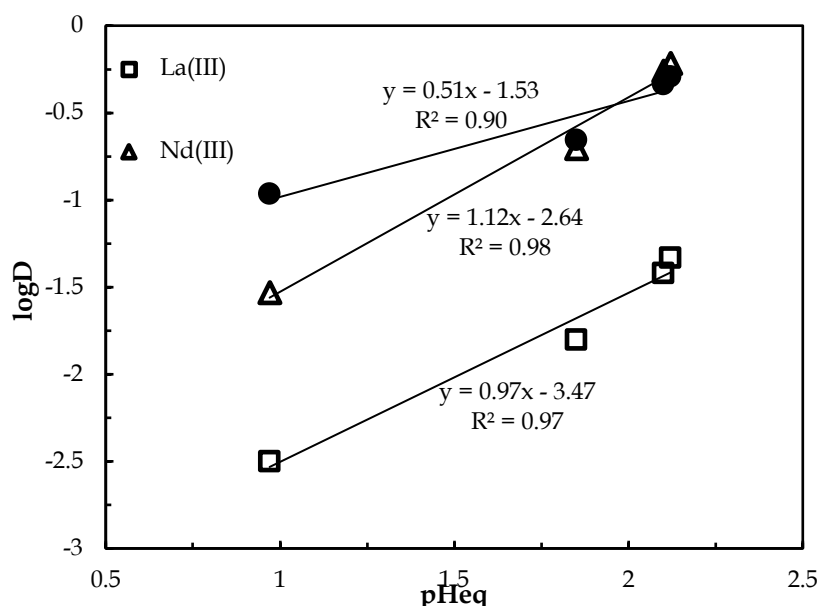


Fig. 2. Relationship between $\log D$ and pH_{eq} for the extraction of La(III), Nd(III) and Pr(III) from model PLS by 10% PC-88A (v/v), 5% TBP(v/v) in kerosene, A/O:1/1, 5 min, 20 °C [H_2SO_4 medium]

3.2. Effect of PC-88A concentration

Fig. 3 illustrates the extraction efficiencies of La(III), Nd(III), and Pr(III) as a function of PC-88A concentration (Baştürkçü et al., 2026). The Nd(III) and Pr(III) curves both show a clear upward trend across the entire concentration range, with the two profiles remaining close throughout, consistent with the relatively stable $\beta(\text{Nd}/\text{Pr})$ values reported in Table 4. By contrast, the La(III) curve remains visibly flat, showing only a marginal increase in extraction efficiency despite the threefold increase in PC-88A concentration. The pronounced divergence between the La(III) curve and those of Nd(III) and Pr(III) indicates that, at constant pH and PC-88A: TBP ratio, increasing the PC-88A concentration selectively enhances the extraction of the heavier lanthanides while exerting little influence on La(III), thereby improving the La/Nd and La/Pr separations. This can be attributed to lanthanide contraction, which favors extraction of heavier rare-earth metal ions (Sato, 1989).

Table 4 shows that the distribution coefficients of Nd(III) and Pr(III) increased substantially with PC-88A concentration, rising from 0.5837 to 1.3932 and from 0.4760 to 1.0202, respectively, as the concentration increased from 10% to 30% (v/v). In marked contrast, $D_{\text{La(III)}}$ increased only modestly, from 0.0377 to 0.0515, confirming the comparatively weak dependence of La(III) extraction on PC-88A concentration. This asymmetry is directly reflected in the separation factors: $\beta(\text{Nd}/\text{La})$ and $\beta(\text{Pr}/\text{La})$

both increased considerably with PC-88A concentration, from 15.48 to 27.05 and from 12.62 to 19.81, respectively, indicating that raising the PC-88A concentration progressively enhances the selectivity for both Nd(III) and Pr(III) over La(III). The separation factor $\beta(\text{Nd/Pr})$, however, remained largely unaffected by this parameter, increasing only slightly from 1.226 to 1.366, confirming that PC-88A concentration primarily governs the La/Nd and La/Pr separations rather than the more challenging Nd/Pr separation due to their chemical similarity. Overall, these results indicate that increasing PC-88A concentration is an effective strategy for improving both extraction efficiency for the comparatively heavier lanthanides and selectivity over La(III).

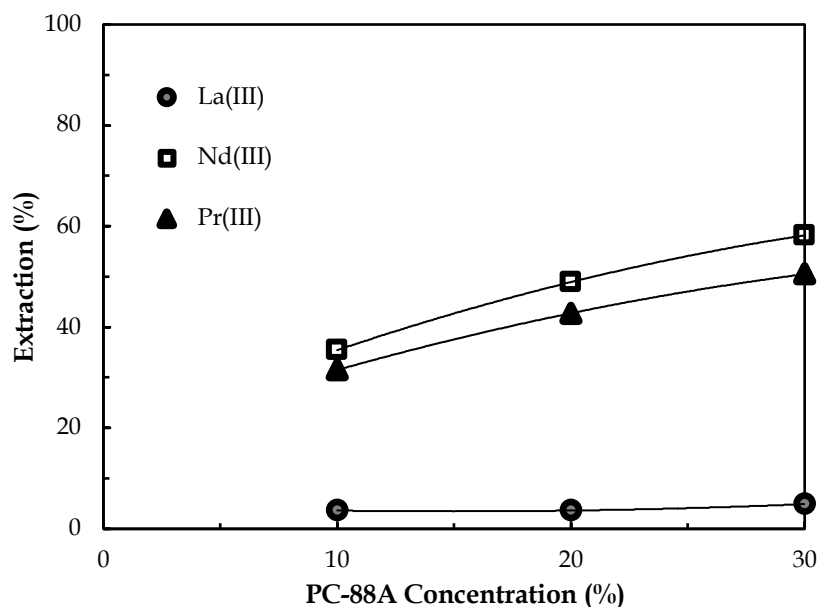


Fig. 3. Loading efficiency of La(III), Nd(III), and Pr(III) as a parameter of PC-88A concentration(%); constant parameters: PC-88A: TBP ratio: 2:1, A/O:1/1, 5 min, 20 °C, [pH_{eq}: 2.10; H₂SO₄ medium]

Table 4. Effect of PC-88A concentration on distribution coefficients and separation factors

PC-88A Concentration (%)	$D_{\text{La(III)}}$	$D_{\text{Nd(III)}}$	$D_{\text{Pr(III)}}$	$\beta(\text{Nd/La})$	$\beta(\text{Pr/La})$	$\beta(\text{Nd/Pr})$
10	0.04	0.58	0.48	15.48	12.62	1.22
20	0.04	0.96	0.75	25.41	19.80	1.28
30	0.05	1.39	1.02	27.05	19.81	1.37

The dependence of $\log D$ on $\log[\text{PC-88A}]$ was examined to determine the extractant stoichiometry of the PC-88A–lanthanide complex. The resulting plots of $(\log D - n \cdot \text{pH}_{\text{eq}})$ versus $\log[\text{PC-88A}]$ yielded slopes of 0.78 ($R^2 = 0.93$) for La(III), 1.45 ($R^2 = 0.99$) for Nd(III), and 0.99 ($R^2 = 0.99$) for Pr(III) (Figure 4). The slopes obtained for Nd(III) and Pr(III) are close to unity, indicating a positive dependence of extraction on PC-88A concentration, consistent with a cation-exchange mechanism. These values are lower than the slope of approximately 3 reported for P507 alone in chloride medium (Zhang et al., 2017a), but comparable to the slope of approximately 1.06 reported for P507 alone in H₂SO₄ medium (Zhang et al., 2021), confirming that sulfate speciation plays a significant role in decreasing the apparent extractant slope. The markedly lower slope and substantially weaker correlation obtained for La(III) are consistent with the well-established extraction order La(III) < Pr(III) < Nd(III) reported for acidic organophosphorus extractants, which reflects the lanthanide contraction (Sato, 1989): as the ionic radius decreases across the series (La(III) > Pr(III) > Nd(III)), the charge density of the metal ion increases, leading to stronger interaction with the donor groups of PC-88A and hence greater affinity for the extractant. La(III), possessing the largest ionic radius and lowest charge density among the three elements, therefore forms the weakest complex with PC-88A, resulting in an extraction that is largely

insensitive to extractant concentration over the range examined. These findings confirm that increasing PC-88A concentration is an effective strategy for enhancing both the extraction efficiency and the selectivity of Nd(III) and Pr(III) over La(III) for this model PLS, while offering limited benefit for resolving the Nd/Pr pair.

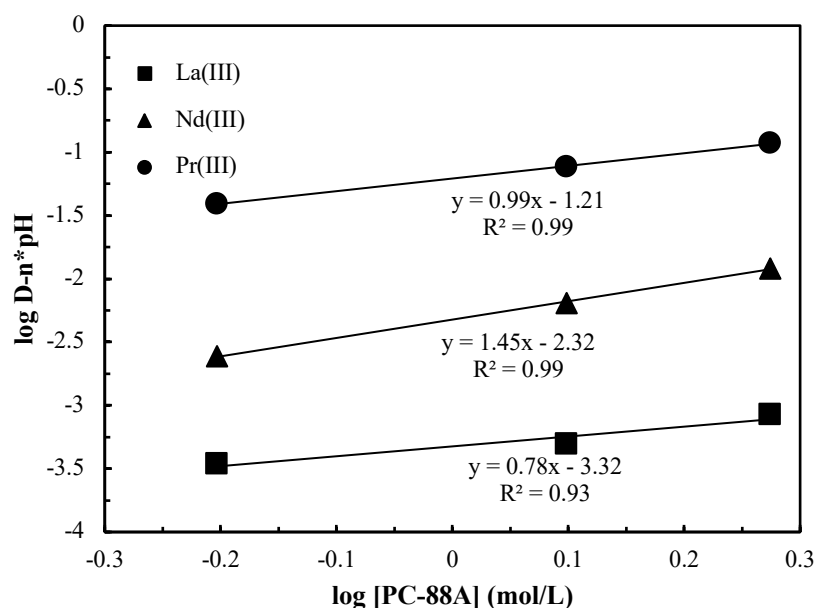


Fig. 4. Relationship between log D and log[PC-88A] for the extraction of La(III), Nd(III), and Pr(III) at PC-88A: TBP ratio: 2:1, A/O:1/1, 5 min, 20 °C, [pH_{eq}: 2.10; H₂SO₄ medium]

3.3. Effect of PC-88A: TBP ratio

With both pH_{eq}:2.10 and total PC-88A concentration (30%, v/v) held constant, the extraction efficiencies of all three lanthanides increased as the PC-88A:TBP ratio was raised from 1:1 to 4:1 (Fig. 5). As the relative TBP content decreased, extraction efficiency increased from 51% to 62% for Nd(III) and from 44% to 54% for Pr(III) (Baştürkçü et al.,2026). La(III) remained negligibly low throughout (3–9%). The antagonistic influence of TBP was most pronounced at the 1:1 ratio, where TBP content was at its highest.

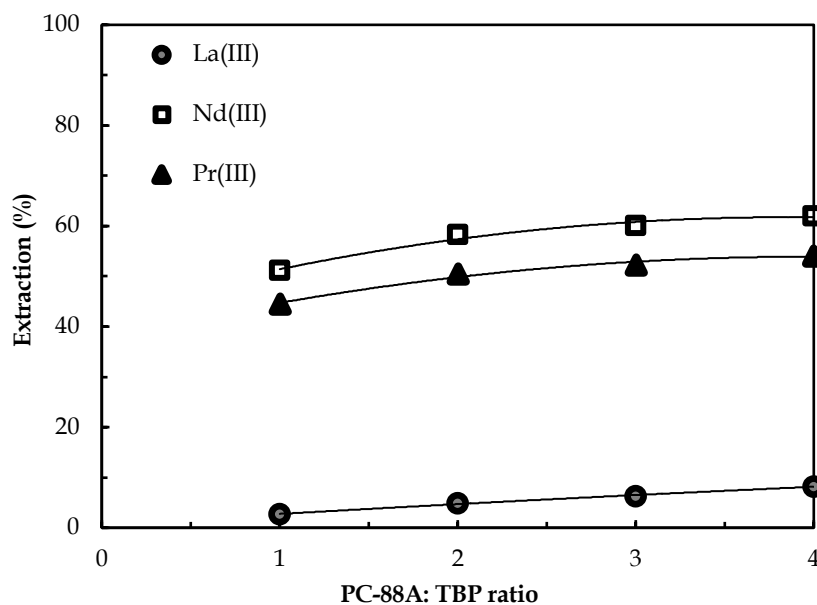


Fig. 5. Loading efficiency of La(III), Nd(III), and Pr(III) as a parameter of PC-88A:TBP ratio, constant parameters: 30% PC-88A(v/v), A/O:1/1, 5 min, 20 °C, [pH_{eq}: 2.10; H₂SO₄ medium]

Table 5 confirms that the distribution coefficients of all three lanthanides increased steadily as the PC-88A:TBP ratio increased from 1:1 to 4:1, with $D_{\text{La(III)}}$ rising from 0.0276 to 0.0895, $D_{\text{Nd(III)}}$ from 1.0468 to 1.6316, and $D_{\text{Pr(III)}}$ from 0.8018 to 1.1798. The separation factors $\beta(\text{Nd/La})$ and $\beta(\text{Pr/La})$ both decreased markedly as the PC-88A: TBP ratio increased, falling from 37.93 to 18.23 and from 29.05 to 13.18, respectively. As the relative TBP content was reduced, the La/Nd and La/Pr separations became progressively less pronounced. In contrast, $\beta(\text{Nd/Pr})$ remained essentially constant across the same range, increasing only marginally from 1.306 to 1.383, indicating that the PC-88A: TBP ratio has a negligible influence on the Nd/Pr separation due to more pronounced lanthanide contraction effects between these two neighboring REEs. Taken together, these results identify a clear trade-off inherent to this parameter: while a low PC-88A:TBP ratio favours La/Nd and La/Pr selectivity, it does so at the cost of overall extraction efficiency for all three lanthanides; conversely, a higher PC-88A: TBP ratio improves the extraction efficiency but diminishes the achievable La(III) selectivity.

To clarify the role of TBP in the extraction of La(III), Nd(III), and Pr(III), the dependence of $(\log D - n \cdot \text{pH}_{\text{eq}})$ on $\log[\text{TBP}]$ was examined. The resulting plots yielded negative slopes of -0.97 ($R^2 = 0.99$) for La(III), -0.47 ($R^2 = 0.95$) for Nd(III), and -0.35 ($R^2 = 0.97$) for Pr(III) (Figure 6), demonstrating unambiguously that increasing TBP concentration suppresses rather than enhances extraction for all three lanthanides. This behaviour is the opposite of the synergistic behaviour commonly reported for acidic extractant pairs (e.g., P204 + P507, Zhang et al., 2017a; or HEHEHP + Cyanex272, Zhang et al., 2014a), and also in marked contrast to the synergism typically reported when TBP is combined with D2EHPA (Kraikaew et al., 2005; Maslennikova & Sinegribova, 2017; Naeem et al., 2018; Desouky, 2006). The steeper slope obtained for La(III) compared with Nd(III) and Pr(III) indicates that La(III) is disproportionately more sensitive to the antagonistic effect of TBP, consistent with its inherently weaker affinity for PC-88A established in Section 3.2.

Table 5. Effect of PC-88A:TBP ratio on distribution coefficients and separation

PC-88A:TBP Ratio	$D_{\text{La(III)}}$	$D_{\text{Nd(III)}}$	$D_{\text{Pr(III)}}$	$\beta(\text{Nd/La})$	$\beta(\text{Pr/La})$	$\beta(\text{Nd/Pr})$
1:1	0.03	1.05	0.80	37.93	29.05	1.31
2:1	0.05	1.39	1.02	27.05	19.81	1.37
3:1	0.07	1.50	1.09	22.24	16.22	1.37
4:1	0.09	1.63	1.18	18.23	13.18	1.38

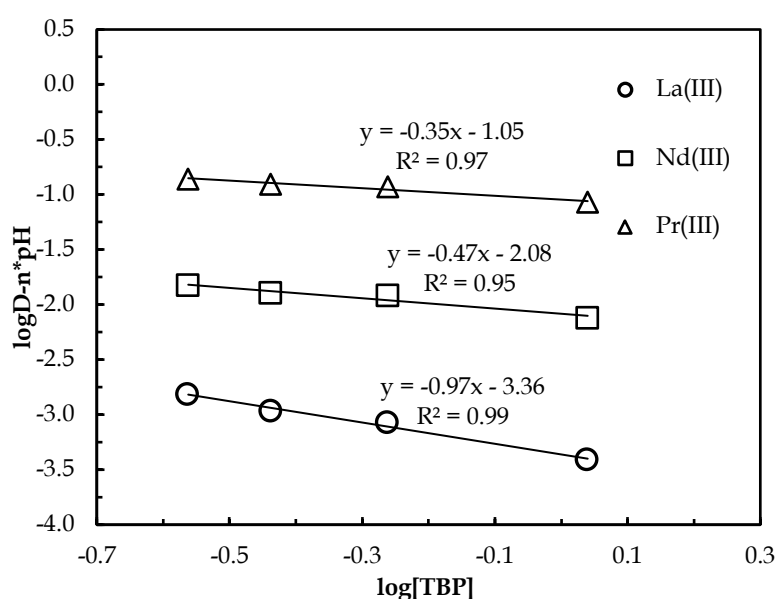


Fig. 6. Relationship between $\log D$ and $\log[\text{TBP}]$ for the extraction of La(III), Nd(III), and Pr(III) from model PLS with 30% PC-88A (v/v) in kerosene, A/O:1/1, 5 min, 20 °C, $[\text{pH}_{\text{eq}}]$ 2.10; H_2SO_4 medium]

3.4. Spectroscopic analysis

FT-IR spectroscopy was used to probe further the antagonistic role of TBP identified by slope analysis. One characteristic absorption band, is the P=O stretching vibration ($1150\text{--}1350\text{ cm}^{-1}$), which directly reports on phosphoryl-oxygen coordination to the metal centre. Reference spectra of 30% PC-88A and 30% TBP in kerosene showed well-separated P=O bands at 1197 cm^{-1} and 1285 cm^{-1} , respectively (Fig. 7), in close agreement with literature values of 1196 cm^{-1} for PC-88A (Zhang et al., 2017b) and 1282 cm^{-1} for TBP (Dashti et al., 2021) recorded at a comparable concentration and diluent. In the unloaded 1:1 PC-88A:TBP mixture, the spectrum was dominated by the TBP-derived band at 1284 cm^{-1} , with the PC-88A band appearing only as a weak shoulder near 1197 cm^{-1} in the reference spectra, indicating that the TBP P=O group governs the spectral response of the mixture prior to metal loading.

Upon lanthanide loading at the 1:1 ratio, the dominant P=O band shifted from 1284 to 1270 cm^{-1} (Table 6), a downward shift of 14 cm^{-1} accompanied by a marked reduction in band intensity (Fig. 5). Because a decrease in P=O stretching frequency reflects a weakening of the P=O bond as its oxygen lone pairs are donated to the metal centre, this shift indicates that TBP participates directly in lanthanide coordination at the 1:1 ratio, rather than acting solely as an inert phase modifier. This interpretation is consistent with related organophosphorus systems, where a red-shifted P=O band upon lanthanide loading has similarly been attributed to donation of the P=O lone-pair electrons to the metal centre and confirmed as evidence of a cation-exchange coordination mechanism (Zhang et al., 2014a; Zhang et al., 2014b; Zhang et al., 2017b).

As the PC-88A:TBP ratio was increased from 1:1 to 2:1, 3:1 and 4:1, the P=O band of the loaded organic phase reverted to 1197 , 1198 and 1198 cm^{-1} , respectively (Table 6, Figure 8), essentially coincident with the band position of pure PC-88A. This progressive return to the PC-88A-dominated spectral signature as TBP content decreases mirrors the condition dependence of the antagonistic effect established by slope analysis, where the TBP-induced suppression of La(III) extraction was itself most pronounced at the 1:1 ratio. The P-O-C band, associated with the alkyl-oxygen linkage that presumably does not participate in metal coordination, remained essentially unchanged across all four loaded conditions ($1029\text{--}1031\text{ cm}^{-1}$), supporting the conclusion that the observed spectral perturbation is localised to the phosphoryl (P=O) coordination site rather than reflecting a general solvation or dilution effect.

Taken together, these spectroscopic observations corroborate the antagonistic role of TBP inferred from the distribution data and slope analysis, indicating that this behaviour originates from a direct, ratio-dependent interaction between the TBP phosphoryl oxygen and the extracted lanthanide species, most pronounced when TBP is present in equimolar proportion to PC-88A.

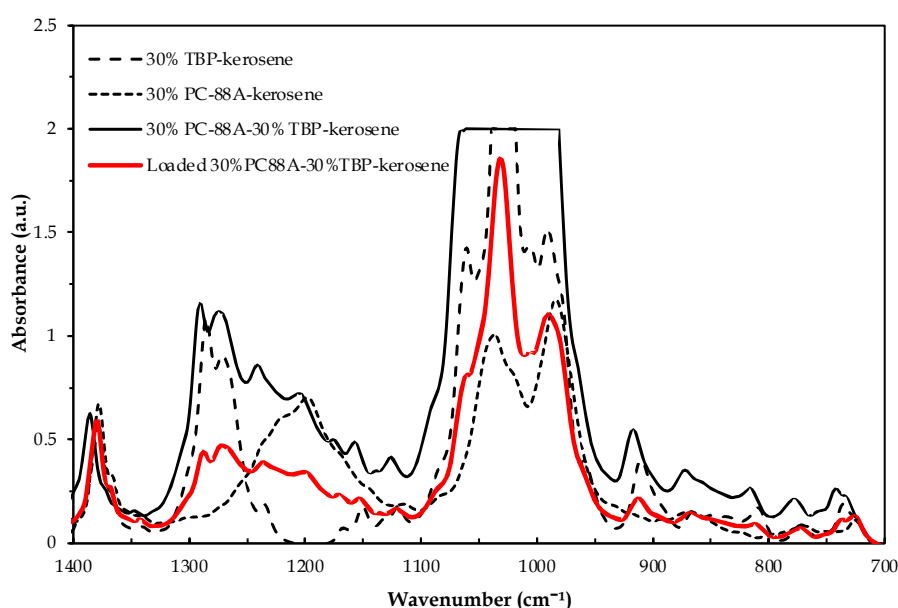


Fig. 7. Reference and loaded FT-IR spectra: 30% TBP-kerosene, 30% PC-88A-kerosene, unloaded 30% PC-88A + 30% TBP-kerosene, and loaded 30% PC-88A + 30% TBP-kerosene organic phase

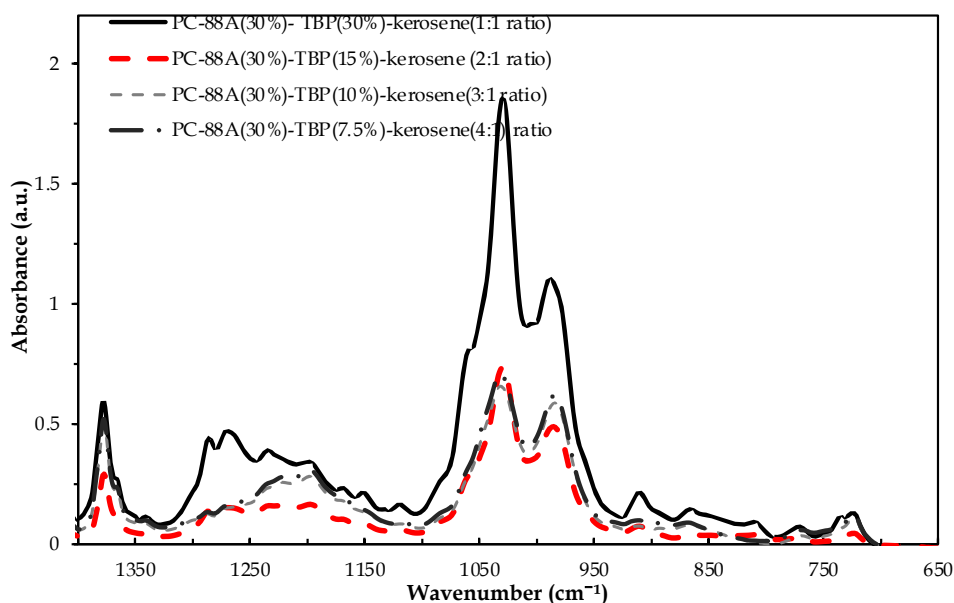


Fig. 8. FT-IR spectra of the loaded organic phases at varying PC-88A:TBP ratio

Table 6. FT-IR band assignments for reference (unloaded) and lanthanide-loaded organic phases at varying PC-88A:TBP ratio

Conditions	Phase	P=O (cm ⁻¹)	P-O-C (cm ⁻¹)
TBP 30%, kerosene	Unloaded	1285.0	n.d. ^a
PC-88A 30%, kerosene	Unloaded	1197.4	1036.2
PC-88A 30% + TBP 30%, kerosene	Unloaded	1284.1	n.d. ^a
PC-88A 30%, ratio 1:1	Loaded	1270.1	1029.7
PC-88A 30%, ratio 2:1	Loaded	1197.4	1029.7
PC-88A 30%, ratio 3:1	Loaded	1198.3	1031.5
PC-88A 30%, ratio 4:1	Loaded	1198.3	1031.5

^a P-O-C band not reported due to detector saturation (absorbance ≥ 2.0) in the 950–1070 cm⁻¹ region for this sample

4. Conclusions

This study provides the first systematic investigation of the solvent extraction of La(III), Nd(III), and Pr(III) from a sulfate medium using PC-88A combined with TBP, with particular emphasis on elucidating the role of TBP in this system.

The results showed that PC-88A concentration and pH are the primary drivers of extraction efficiency and La/Nd, La/Pr selectivity. By contrast, TBP acts as an antagonist, contrary to its synergistic behaviour in D2EHPA-based systems, disproportionately suppressing La(III) extraction. This asymmetric sensitivity of La(III) to TBP is the key finding of this work, reflected in $\beta(\text{Nd/La})$ and $\beta(\text{Pr/La})$ values ranging from 37.93 to 18.23 and from 29.05 to 13.18, respectively, as the PC-88A:TBP ratio was varied from 1:1 to 4:1. On the other hand, $\beta(\text{Nd/Pr})$ remained essentially unaffected throughout, identifying the Nd/Pr pair as the most challenging separation in this system.

The negative TBP slopes obtained for all three lanthanides, most pronounced for La(III), point to a systematic and element-specific antagonistic influence that intensifies with TBP concentration. The corroborating shift in the PC-88A P=O band observed by FT-IR under the same high-TBP conditions

suggests that this influence operates at the molecular level of the extractant, rather than through a simple dilution effect.

Future work should focus on applying complementary techniques such as NMR and mass spectrometry to more rigorously establish the nature of the interaction between TBP and PC-88A during metal loading. The Nd/Pr separation, which remained largely unaffected by all parameters studied, warrants further investigation through alternative extractant systems or process conditions.

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References

- ACHARYA, S., MISHRA, S., MISRA, P.K., 2015. *Studies on extraction and separation of La(III) with D2EHPA and PC88A in petrofin*. Hydrometallurgy, 156, 12–16. <https://doi.org/10.1016/j.hydromet.2015.05.005>
- ALSHAMMARI, M.S., 2021. *Solvent extraction of cerium from various solutions by organophosphorus-based extractants: a review*. Desalination and Water Treatment, 218, 345–351. <https://doi.org/10.5004/dwt.2021.26974>
- ARELLANO RUIZ, V.C., KUCHI, R., PARHI, P.K., LEE, J.-Y., JYOTHI, R.K., 2020. *Environmentally friendly comprehensive hydrometallurgical method development for neodymium recovery from mixed rare earth aqueous solutions using organo-phosphorus derivatives*. Scientific Reports, 10, 16911. <https://doi.org/10.1038/s41598-020-74041-9>
- BAŞTÜRKÇÜ, E., 2026. *Selective extraction of lanthanum, neodymium and praseodymium from synthetic leach solution using pc-88a/tbp system*. In: Baştürkçü, E., Pural, Y.E., Üçerler Çamur, Z. (Eds.), 20th Balkan Mineral Processing Congress Proceedings Book. Turkish Mining Development Foundation, pp. 549–555.
- BATTSENGEL, A., BATNASAN, A., HAGA, K., SHIBAYAMA, A., 2018. *Selective separation of light and heavy rare earth elements from the pregnant leach solution of apatite ore with D2EHPA*. Journal of Minerals and Materials Characterization and Engineering, 6, 517–530. <https://doi.org/10.4236/jmmce.2018.65037>
- BATTSENGEL, A., BATNASAN, A., NARANKHUU, A., HAGA, K., WATANABE, Y., SHIBAYAMA, A., 2018. *Recovery of light and heavy rare earth elements from apatite ore using sulphuric acid leaching, solvent extraction and precipitation*. Hydrometallurgy, 179, 100–109. <https://doi.org/10.1016/j.hydromet.2018.05.024>
- BELOVA, V.V., 2017. *Development of solvent extraction methods for recovering rare earth metals*. Theoretical Foundations of Chemical Engineering, 51(4), 599–609. <https://doi.org/10.1134/S004057951605002X>
- CHEN, K., HE, Y., SRINIVASAKANNAN, C., LI, S., YIN, S., PENG, J., GUO, S., ZHANG, L., 2019. *Characterization of the interaction of rare earth elements with P507 in a microfluidic extraction system using spectroscopic analysis*. Chemical Engineering Journal, 356, 453–460. <https://doi.org/10.1016/j.cej.2018.09.039>
- DASHTI, S., SADRI, F., SHAKIBANIA, S., RASHCHI, F., GHAHREMAN, A., 2021. *Separation and solvent extraction of rare earth elements (Pr, Nd, Sm, Eu, Tb, and Er) using TBP and Cyanex 572 from a chloride medium*. Minerals Engineering, 161, 106694. <https://doi.org/10.1016/j.mineng.2020.106694>
- DESOUKY, O.A.E., 2006. *Liquid-liquid extraction of rare earth elements from sulfuric acid solutions [Doctoral dissertation, University of Leeds]*.
- DUSHYANTHA, N., BATAPOLA, N., ILANKOON, I.M.S.K., ROHITHA, S., PREMASIRI, R., ABEYSINGHE, B., RATNAYAKE, N., DISSANAYAKE, K., 2020. *The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production*. Ore Geology Reviews, 122, 103521. <https://doi.org/10.1016/J.OREGEOREV.2020.103521>
- HAAS, J.R., SHOCK, E.L., SASSANI, D.C., 1995. *Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the REE at high temperatures and pressures*. Geochimica et Cosmochimica Acta, 59(21), 4329–4350.
- JORDENS, A., CHENG, Y.P., WATERS, K.E., 2013. *A review of the beneficiation of rare earth element bearing minerals*. Minerals Engineering, 41, 97–114. <https://doi.org/10.1016/j.mineng.2012.10.017>
- JUDGE, W.D., AZIMI, G., 2020. *Recent progress in impurity removal during rare earth element processing: A review*. Hydrometallurgy, 196, 105435.
- KRAIKAWE, J., SRINUTTRAKUL, W., CHAYAVADHANAKUR, C., 2005. *Solvent extraction study of rare earths from nitrate medium by the mixtures of TBP and D2EHPA in kerosene*. Journal of Metals, Materials and Minerals, 15(2), 89–95.

- MASLENNIKOVA, L.S., SINEGRIBOVA, O.A., 2017. Extraction of Gd, Tb, and Dy from nitrate media with a mixture of technical di-2-ethylhexyl phosphoric acid and tributylphosphate. *Theoretical Foundations of Chemical Engineering*, 51(5), 850–857. <https://doi.org/10.1134/S0040579517050153>
- NAEEM, A.T., KASHI, E., SALEHI, M.A., HABIBPOUR, R., 2018. Extraction and separation of La(III), Pr(III) and Nd(III) using binary mixture of D2EHPA with Cyanex272, TOPO, and TBP extractants. *Metallurgical Research & Technology*, 115(6), 612. <https://doi.org/10.1051/metal/2018043>
- NAVARRO, J., ZHAO, F., 2014. Life-cycle assessment of the production of rare-earth elements for energy applications: a review. *Frontiers in Energy Research*, 2, 45. <https://doi.org/10.3389/fenrg.2014.00045>
- SADRI, F., NAZARI, A.M., GHAHREMAN, A., 2017. A review on the cracking, baking and leaching processes of rare earth element concentrates. *Journal of Rare Earths*, 35(8). [https://doi.org/10.1016/S1002-0721\(17\)60971-2](https://doi.org/10.1016/S1002-0721(17)60971-2)
- SAFARZADEH, M.S., AGARWAL, V., HAYES, L., 2018. New insights into the separation of Nd from Pr in hydrochloric and sulfuric acid solutions. *Polyhedron*, 153, 82–87. <https://doi.org/10.1016/j.poly.2018.06.050>
- SATO, T., 1989. Liquid–liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorous compounds. *Hydrometallurgy*, 22, 121–140.
- WOOD, S.A., 1990. The aqueous geochemistry of the rare-earth elements and yttrium. 2. Theoretical predictions of speciation in hydrothermal solutions to 350 °C at saturation water vapor pressure. *Chemical Geology*, 88(1-2), 99–125.
- XIE, F., ZHANG, T.A., DREISINGER, D., DOYLE, F., 2014. A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering*, 56, 10–28. <https://doi.org/10.1016/J.MINENG.2013.10.021>
- ZHANG, C., WANG, L., HUANG, X., DONG, J., LONG, Z., ZHANG, Y., 2014. Yttrium extraction from chloride solution with a synergistic system of 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester and bis(2,4,4-trimethylpentyl) phosphinic acid. *Hydrometallurgy*, 147–148, 7–12. <https://doi.org/10.1016/j.hydromet.2014.04.008>
- ZHANG, F., WANG, A., ZHOU, F., DAL, J., WU, W., 2017a. Behavior of a synergistic system in the extraction of Pr(III) from chloride medium using di-2-ethylhexyl phosphoric acid and 2-ethylhexylphosphonic mono-2-ethylhexyl ester. *Separation Science and Technology*, 52(6), 1015–1021. <https://doi.org/10.1080/01496395.2017.1281301>
- ZHANG, F., DAL, J., WANG, A., WU, W., 2017b. Investigation of the synergistic extraction behavior between cerium (III) and two acidic organophosphorus extractants using FT-IR, NMR and mass spectrometry. *Inorganica Chimica Acta*, 466, 333–342. <https://doi.org/10.1016/j.ica.2017.06.016>
- ZHANG, F., WU, W., BIAN, X., ZENG, W., 2014b. Synergistic extraction and separation of lanthanum (III) and cerium (III) using a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester and di-2-ethylhexyl phosphoric acid in the presence of two complexing agents containing lactic acid and citric acid. *Hydrometallurgy*, 149, 238–243. <https://doi.org/10.1016/j.hydromet.2014.09.002>
- ZHANG, F., WU, W., DAL, J., BIAN, X., 2016. Extraction and separation of Pr(III)/Ce(III) from chloride medium by 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester in the presence of two complexing agents. *Separation Science and Technology*, 51(5), 778–783. <https://doi.org/10.1080/01496395.2015.1130061>
- ZHANG, H., ZHAO, L., ZHENG, X., LIU, D., FENG, Z., ZHANG, Y., HUANG, X., 2021. Extraction mechanism and separation behaviors of low-concentration Nd³⁺ and Al³⁺ in P507-H₂SO₄ system. *Journal of Rare Earths*. <https://doi.org/10.1016/j.jre.2021.04.011>
- ZHANG, W., FENG, D., XIE, X., TONG, X., DU, Y., CAO, Y., 2022. Solvent extraction and separation of light rare earths from chloride media using HDEHP-P350 system. *Journal of Rare Earths*, 40(2), 328–337. <https://doi.org/10.1016/j.jre.2021.05.003>