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## Research Article

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# Sustainable Separation of Actinides and Rare Earth Elements Using Sorbitol-Oleic Acid Derived Bio-Based Solvents: Synthesis and Extraction Performance

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## Abstract

Building a sustainable refinement process for Th, U, and REEs requires the development of eco-friendly solvent extraction systems. This study presents the extraction performance of bio-based solvents synthesized by reacting sorbitol and oleic acid at different molar ratios, referred to as SOA2 and SOA3. Chemical properties such as acid number (AN) were measured hourly from samples taken from the synthesis reactor, which demonstrated a decreasing trend due to the transformation of carboxylic acid groups into ester groups. The chemical structures of SOA2 and SOA3 were investigated by FTIR and XPS analyses, and characteristic ester bond peaks were identified in both materials. Extraction behavior was investigated as a function of aqueous phase pH and contact time, and the results were benchmarked against conventional acidic organophosphorus extractants, Cyanex and D2EHPA. Under optimized conditions, SOA2 and SOA3 demonstrated log KD values for Th<sup>4+</sup> above 2.55, with SF<sub>Th4+/REE3+</sub> values of 411 and 1822, respectively. In contrast, Cyanex and D2EHPA exhibited higher overall extraction capacity across the investigated conditions due to stronger ligand-metal ion complexation.

**Key Words:** Bio-based solvents, Extraction, Separation, Actinides, Rare Earth Elements

## 1. Introduction

According to the Global Critical Minerals Outlook (2025), the annual global consumption of rare earth elements (REEs) is approximately 91.000 tons, and this demand is projected to increase to 150.000 tons by 2040 [1]. REEs comprises of lanthanide series with inclusion of scandium and yttrium. They are essential components in a wide range of industries, including energy storage systems, renewable energy technologies, electric motors, semiconductors, catalysts, and specialty fertilizers. The purity grade of REEs hold significant importance, as their physicochemical properties and functional performance are highly sensitive to impurities in their composition. Consequently, REEs are typically utilized at the highest purity grade in order to reveal their full technological potential [2-5].

However, due to their electronic configuration, specifically ineffective shielding of nuclear charge by the 4f orbitals in lanthanide series, the electrons in outer shell exposed to an increased effective nuclear charge resulting in a developing decrease in atomic and ionic radius, known as lanthanide contraction. Due to this effect, most lanthanides are thermodynamically stable in trivalent oxidation state and poses similar charge/ionic radius ratios. Consequently, their physicochemical properties are remarkably alike, making their individual separation challenging [6]. Furthermore, the presence of actinide ions such as  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  complicates the separation process due to their competitive extraction behavior.

Th and U as actinides, generally co-present with REEs in primary mineral resources [7]. However, most REEs are considered as neutron poisons and are undesirable in nuclear fuel materials. Adversely, because of the radioactive nature of Th and U, their presence in REEs is problematic [8, 9]. Therefore, these element groups must be separated and purified after their extraction from primary resources via chemical separation techniques.

A variety of chemical separation techniques have been employed for the separation and purification of Th, U and REEs, including selective adsorption [10-12], ion exchange [13, 14], solvent extraction [15-17] and electrochemical separation [18, 19]. Among these methods, solvent extraction holds significant advantages for its high separation efficiency and rate, operational flexibility and scalability for industrial implementation [20]. Given these features,

extensive research has been conducted to optimize solvent extraction process for the selective recovery of Th, U and REEs [21, 22].

In solvent extraction process, extractants decompose because of protonation, radiation, hydrolysis or chemical degradation during operation, resulting in a loss in their selectivity that ends their functional life cycle [23, 24]. Though, this decomposition may not be significant as all materials lose their functionality in time, the ultimate challenge is the management of spent solvents. In industrial applications, spent solvents are commonly disposed through incineration in cement plants or industrial furnaces as fuel [25]. Having the fact that most extractants are petroleum derived or synthesized from petroleum-based precursors, the end-of-life treatment contributes to CO<sub>2</sub> emissions originating from fossils and makes the metal separation process rely heavily on petroleum products. Notably, this reliance is inconsistent with the critical role of solvent extraction in supplying refined metals for clean energy and advanced technological applications. In response to this inconsistency, global environmental policies increasingly emphasize green mining and sustainable metal refining practices to support a cleaner future [26, 27].

Utilization of bio-based solvents can mitigate these problems; such solvents are typically synthesized from renewable naturally occurring chemicals including vegetable oils and carbohydrates rather than petroleum derivatives [28-30]. As a result, bio-based solvents may reduce the environmental impacts originating from solvent production, solvent extraction and end-of-life management, thereby supporting more sustainable metal separation processes. Sorbitol-oleic acid esters are bio-based compounds that can be synthesized via one-step fisher esterification in the presence of an acid catalyst [15]. They are widely integrated into detergent, cosmetics and plastics industries due to their renewable origin and favorable chemical properties. Owing to their hydrophobic nature, sorbitol-oleic acid esters can readily separate their phase from aqueous solutions without requiring diluent. Furthermore, their low toxicity and low flammability make sorbitol oleic acid esters promising candidates for use as extractants in metal separation processes [31].

The presence of -OH and =O functional groups in the chemical structure of sorbitol oleic acid esters enable interaction with Th, U, and REE ions in solution primarily through ion-dipole interactions. These interactions are inherently weaker than ion-ion interactions, which dominate in conventional acidic extractants. Common extractants used for Th, U, and REE separation, such as D2EHPA, Cyanex 272, and PC-88A, interact with metal ions through negatively charged functional groups, resulting in strong ionic coordination. In contrast, sorbitol oleic acid esters act as neutral, solvating extractants, and their extraction mechanism does not rely on ionic bonding. Instead, metal ion transfer occurs through a solvation-driven mechanism, in which the hydration shell of the metal ion is partially disrupted, and water molecules are replaced by extractant molecules [32, 33]. In this process, ion dipole interactions play a critical role in stabilizing the metal extractant complex [34]. Although these interactions are weaker than ionic interactions, this reduced interaction strength can be advantageous for the selective separation of Th, U, and REEs, as the extractant is less capable of penetrating through the strongly bound hydration shells, resulting in a selective separation between Th, U and REEs.

To comprehensively evaluate the extraction performance of sorbitol oleic acid esters, benchmarking against commercial extractants is critical. In this study, two sorbitol oleic acid esters, denoted as SOA2 and SOA3, were synthesized via Fischer esterification and utilized as extractants in solvent extraction experiments. Their chemical structures were characterized using XPS and FTIR analyses, additionally, the densities and acid numbers, were determined. The effects of aqueous phase pH (1–5) and extraction time (5–120 min) on the  $K_D$  and SF were systematically investigated. For comparison purposes, the extraction data of Cyanex 272 and D2EHPA obtained under identical experimental conditions in our previous study [15] were used as benchmark references. These datasets were re-plotted to enable direct comparison with SOA2 and SOA3. Through this comparative evaluation, the extraction behavior, selectivity, and relative separation performance of the bio-based esters were assessed against established commercial extractants.

## **2. Materials, Instrumentation and Experimental Methods**

### **2.1 Materials**

The chemicals used in the study were either analytical or chemical grade and employed in all experiments without purification. Sorbitol (powder) was purchased from ZAG, and oleic acid was purchased from AFG Bioscience, both were used in the synthesis of SOA2 and SOA3. Potassium hydroxide, phenol phthalein, methanol, and n-heptane were purchased from Sigma and used in titrimetric acid number determination. Cyanex 272 was supplied by Cytec Inc. LME Group Ltd. Co and D2EHPA was obtained from Sigma. Cerium nitrate hexahydrate, lanthanum nitrate hexahydrate, praseodymium nitrate hexahydrate, samarium nitrate hexahydrate, europium nitrate hexahydrate, gadolinium nitrate hexahydrate, thorium nitrate pentahydrate, and uranyl nitrate hexahydrate were purchased from Sigma and used to prepare the aqueous phase. Sulfuric acid was purchased from Merck and used for the pH adjustments of the aqueous phase and acidic catalyst for the esterification reaction. Ultrapure water (resistivity 18.2 MΩcm, TOC level 1–5 ppb) was prepared by the Millipore model water purification system.

## 2.2 Instrumentation

The molecular structures of SOA2 and SOA3 were characterized using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, PerkinElmer Spectrum II) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The pH of the aqueous solutions was monitored using a Mettler Toledo Seven Compact S210 pH meter. Metal ion concentrations in the aqueous phases were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima DV 2000).  $K_D$  and SF values were calculated based on the measured metal concentrations.

## 2.3 Synthesis SOA2 and SOA3

SOA2 and SOA3 were synthesized through Fischer esterification between sorbitol and oleic acid in the presence of  $H_2SO_4$  as an acidic catalyst. The molar ratio of sorbitol to oleic acid was 1:2 for SOA2 and 1:3 for SOA3. The synthesis procedure was as follows; oleic acid was placed into a glass reactor and 0.25 mL of concentrated  $H_2SO_4$  was added dropwise. The reaction mixture was then heated to 60 °C, after which sorbitol was gradually added to the medium. The temperature then increased to 200 °C and maintained throughout the reaction. Samples were taken from the reaction medium at 60 min intervals for acid number determination, and the reaction was

continued until the acid number stabilized. The synthesized solvent was then cooled to ambient temperature and filtered to remove unreacted sorbitol particles. SOA2 and SOA3 were used directly as extractants in subsequent solvent extraction experiments [35]. A schematic presentation of the synthesis setup is adopted and inserted in Figure 1.

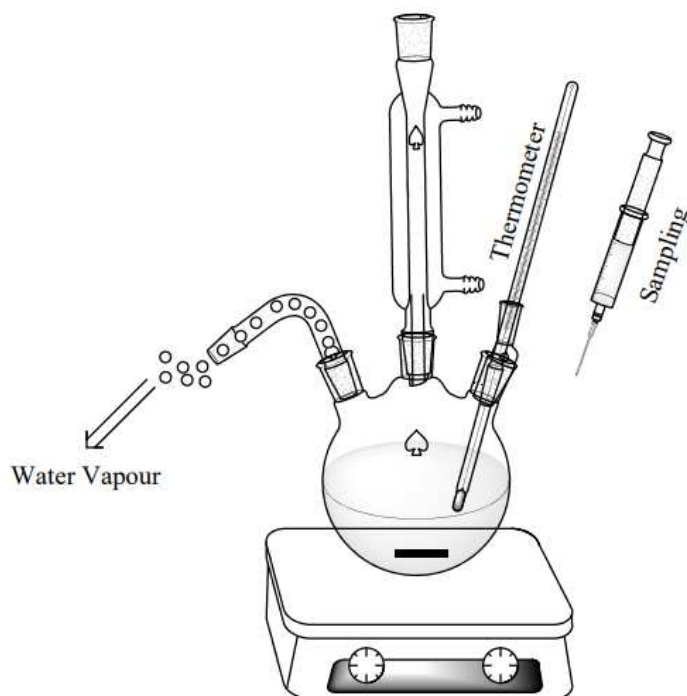


Figure 1 The Schematic presentation of the Synthesis Setup of SOA2 and SOA3.

## 2.4 Experimental Methods

### *Acid number analysis*

The acid numbers of SOA2 and SOA3 were measured by KOH titration using phenolphthalein as the indicator. This method originally adopted from [36], and modified for the present work. A  $0.02 \text{ mol L}^{-1}$  KOH solution prepared in an ethanol: water mixture (90:10, v/v) was used as the titrant. A 0.10 g sample of the synthesized extractant was dissolved in 50 mL of n-heptane, followed by the addition of 3-4 drops of phenolphthalein solution to prepare the titration mixture. The solution was then titrated with the KOH solution until a persistent pale pink color appeared, at which point the consumed titrant volume was recorded. The acid number was calculated using Eq. (1).

$$AN = (V_{eq} - V_{Beq}) \times N \times \frac{56.1 \text{ g}\cdot\text{mol}^{-1}}{M_{SOA2/SOA3}} \quad (1)$$

In Eq. (1),  $V_{eq}$  and  $V_{Beq}$  represent the volumes of KOH solution consumed to neutralize the sample containing medium and the blank medium, respectively.  $N$  denotes the normality of the KOH titrant, and  $56.1 \text{ g}\cdot\text{mol}^{-1}$  is the molar mass of KOH.  $M_{SOA2/SOA3}$  corresponds to the mass (g) of the SOA2 or SOA3 sample present in the titrated medium.

#### *Determination of the densities of SOA2 and SOA3*

A 25 mL pycnometer was used to determine the densities of SOA2 and SOA3. The pycnometer was filled with deionized water at 25 °C and weighed. The actual volume of the pycnometer was calculated by dividing the mass of deionized water by its known density at 25 °C. The pycnometer was then filled with SOA2 and SOA3 and weighed, and the net mass of SOA2 and SOA3 was divided by the calibrated pycnometer volume to calculate their densities. The equation used to calculate the pycnometer volume is presented in Eq. (2), while the density calculations for SOA2 and SOA3 are given in Eq. (3).

$$\text{Pycnometer Volume (PV): } \frac{b-a}{d_{aq}} \quad (2)$$

$$\text{SOA2 and SOA3 Density: } \frac{c-a}{PV} \quad (3)$$

In the density calculation,  $a$  represents the mass of the empty pycnometer (g),  $b$  denotes the mass of the pycnometer filled with deionized water (g), and  $c$  corresponds to the mass of the pycnometer filled with SOA2 or SOA3 (g) and  $d_{aq}$  is the density of deionized water ( $\text{g mL}^{-1}$ ).

#### *Solvent Extraction Studies*

SOA2 and SOA3 were employed as the organic phases in the solvent extraction experiments. The aqueous phase was prepared to contain  $\text{Th}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Eu}^{3+}$ , each at a concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$ . The effects of initial aqueous phase pH and contact time on the  $K_D$  and SF were investigated. The organic to aqueous phase ratio was predetermined through preliminary experiments and fixed at 1:4 throughout the study and all experiments were carried out at 25°C.

## 2.5 Instrumental analysis

### *FTIR*

The FTIR spectra of SOA2 and SOA3 was taken in comparison with sorbitol and oleic acid to evaluate the structural changes occurring after the esterification reaction and the specific characteristic peaks of SOA2 and SOA3.

### *XPS*

SOA2 and SOA3 are liquid materials therefore, direct XPS analysis is challenging due to the high vacuum requirements of the turbomolecular pump when handling liquid samples. In order to address this limitation, SOA2 and SOA3 were impregnated onto nano-sized Zr oxide powder synthesized in the previous study [11]. SOA2 and SOA3 were dissolved in isopropanol to obtain a 75 wt% solution, and 50 mL of this solution was poured onto 1 g of Zr oxide powder. The mixture was then placed in a thermostatic shaker and contacted for 24 h at 20 °C and 150 rpm. The impregnated powders were then filtered, dried, and analyzed by XPS, in comparison with pristine Zr oxide powder.

## **3 Results and Discussion**

### 3.1 Chemical and Structural Analyses

#### *Acid Number and Density Determination*

Acid numbers (AN) of both SOA2 and SOA3 have shown a decreasing trend as a function of reaction time, due to the esterification of fatty acids. The acidic (-COOH) part of the fatty acids react with -OH of sorbitol molecules to form ester (-COOR). As a result, AN decreased dramatically within 2h, and the decrease rate slowed down due to the decreasing fatty acid in the reaction media. The results of AN analysis is graphically presented in Figure 2.

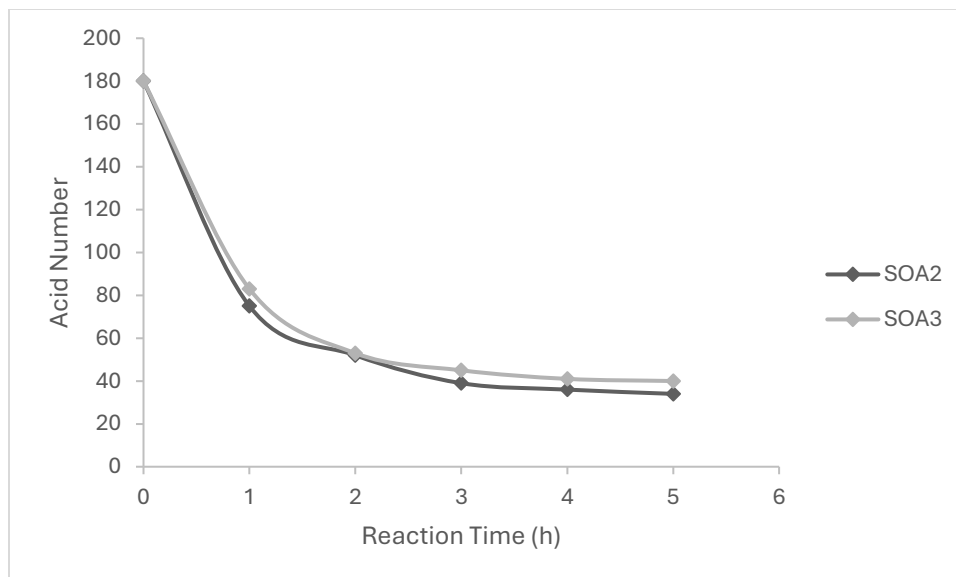


Figure 2 Acid numbers of SOA2 and SOA3 as a function of reaction time.

After 5h AN number did not change significantly, to preserve energy, the reaction stopped at this point. Initially, the acid number (AN) was 180 for both systems. At the end of the reaction, the AN decreased to 40 for SOA3 and 34 for SOA2. Although both reactions started from the same initial AN, the final AN of SOA2 was slightly lower than that of SOA3, which can be attributed to its lower free oleic acid content in the reaction medium. Based on the AN reduction, 77.7% and 81.1% of oleic acid were esterified for SOA3 and SOA2 respectively.

Densities of SOA2 and SOA3 was measured with 25mL pycnometer, and the densities of the two solvents were found to be  $0.963 \text{ g.mL}^{-1}$  and  $0.945 \text{ g. mL}^{-1}$  respectively.

#### *FTIR analysis of SOA2 and SOA3*

The FTIR spectrum of SOA2 and SOA3 is presented in comparison with oleic acid and sorbitol in Figure 3. The peaks at  $1742 \text{ cm}^{-1}$  and  $1168 \text{ cm}^{-1}$  correspond to ester bonds and are attributed to C=O stretching and C-O stretching, respectively [37]. These peaks are specific to SOA2 and SOA3 and are not observed in either oleic acid or sorbitol, suggesting successful synthesis of the bio-based solvents with an ester structure.

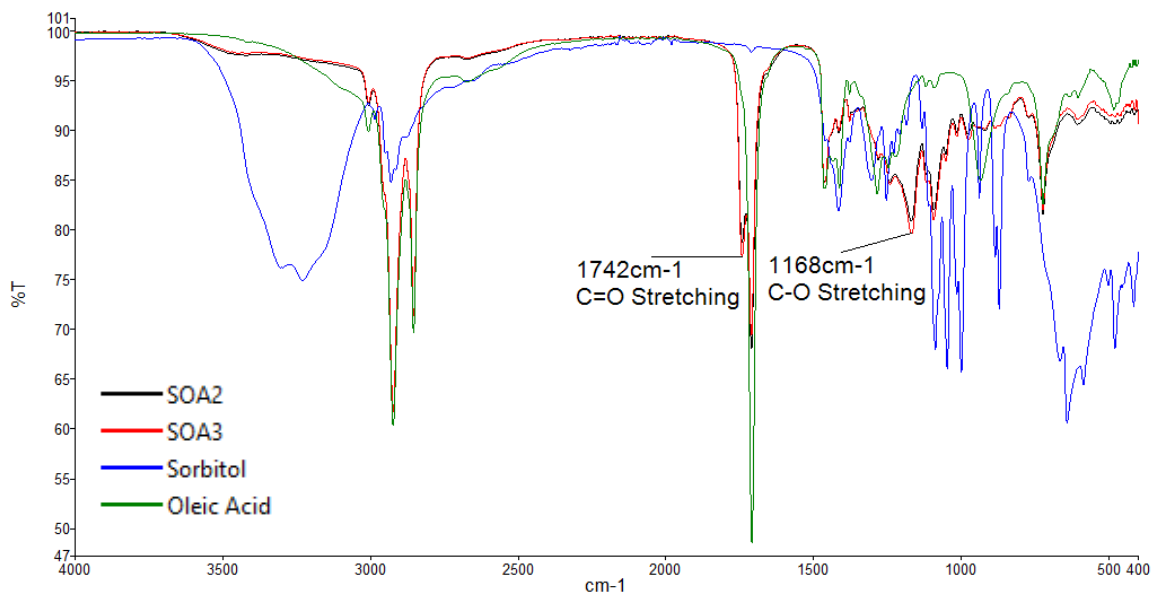
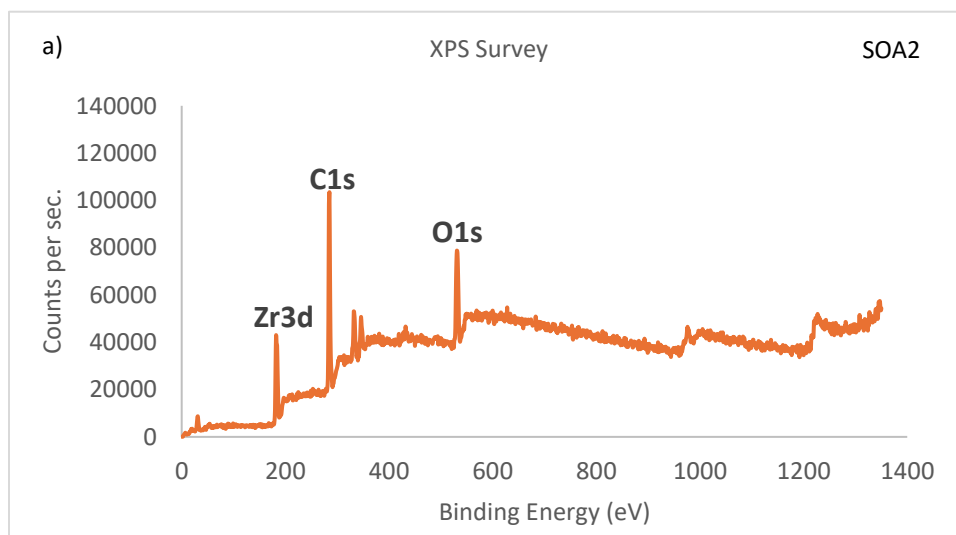
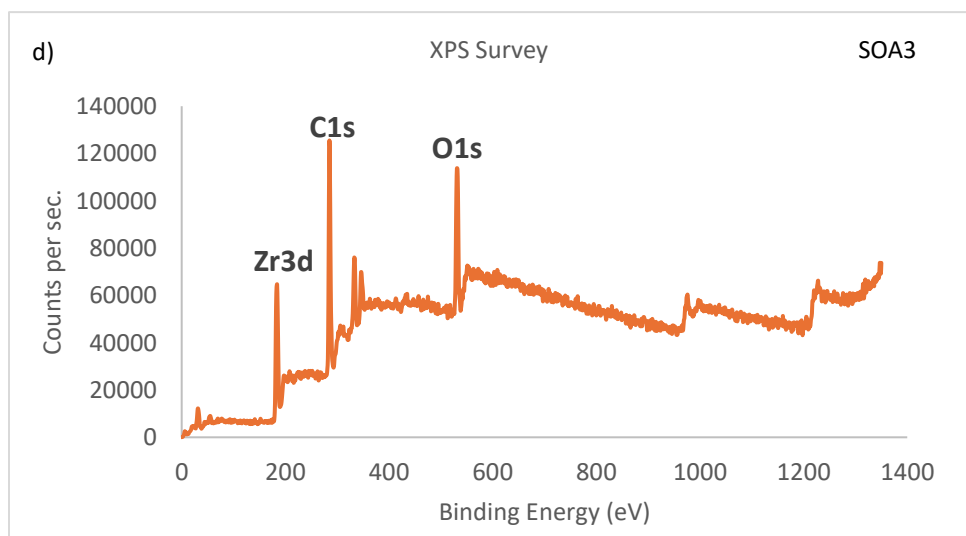
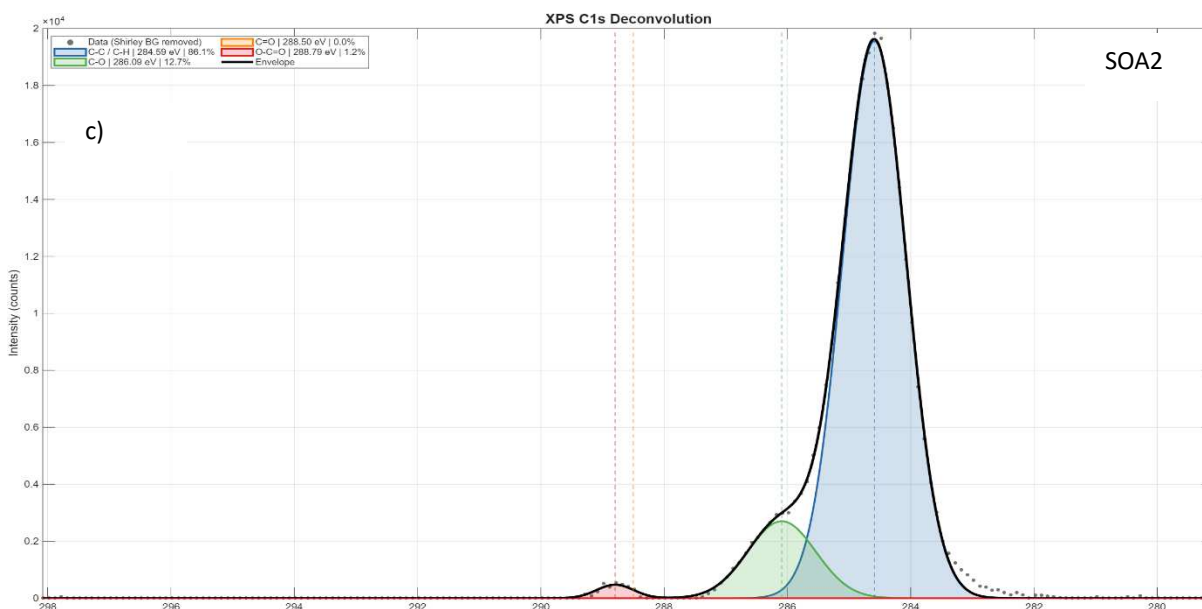
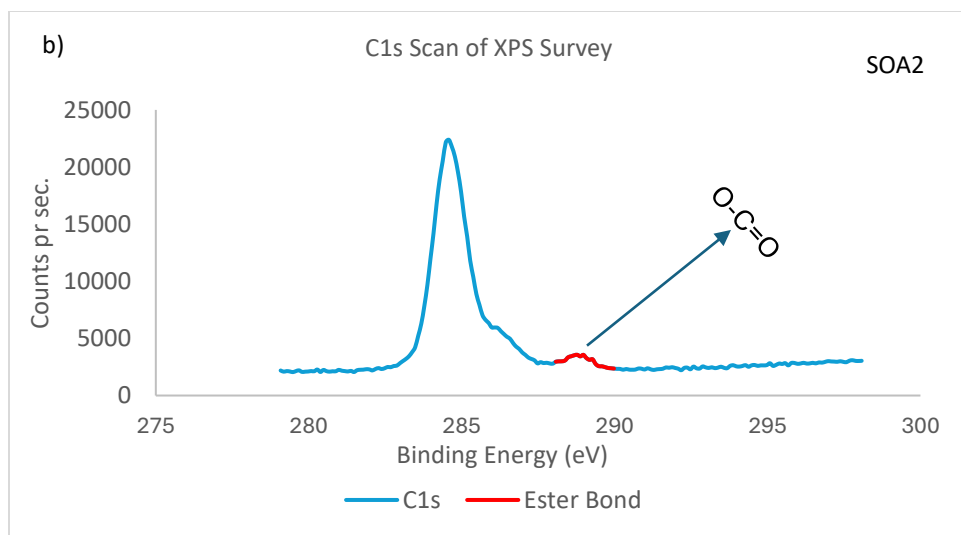


Figure 3 FTIR diagrams of SOA2 and SOA3 in comparison with Oleic Acid and Sorbitol.

### *XPS analysis of SOA2 and SOA3*

In the survey spectrum, O1s, C1s, and Zr3d peaks were clearly observed at binding energies of approximately 532.08, 285.08 and 184.08 eV, respectively. To further investigate ester bond formation, peak deconvolution of the XPS spectra was conducted using MATLAB via nonlinear least-squares fitting with Gaussian–Lorentzian line shapes to resolve individual chemical structures, the fitted components are presented alongside the full XPS survey in Figure 4(a-f).





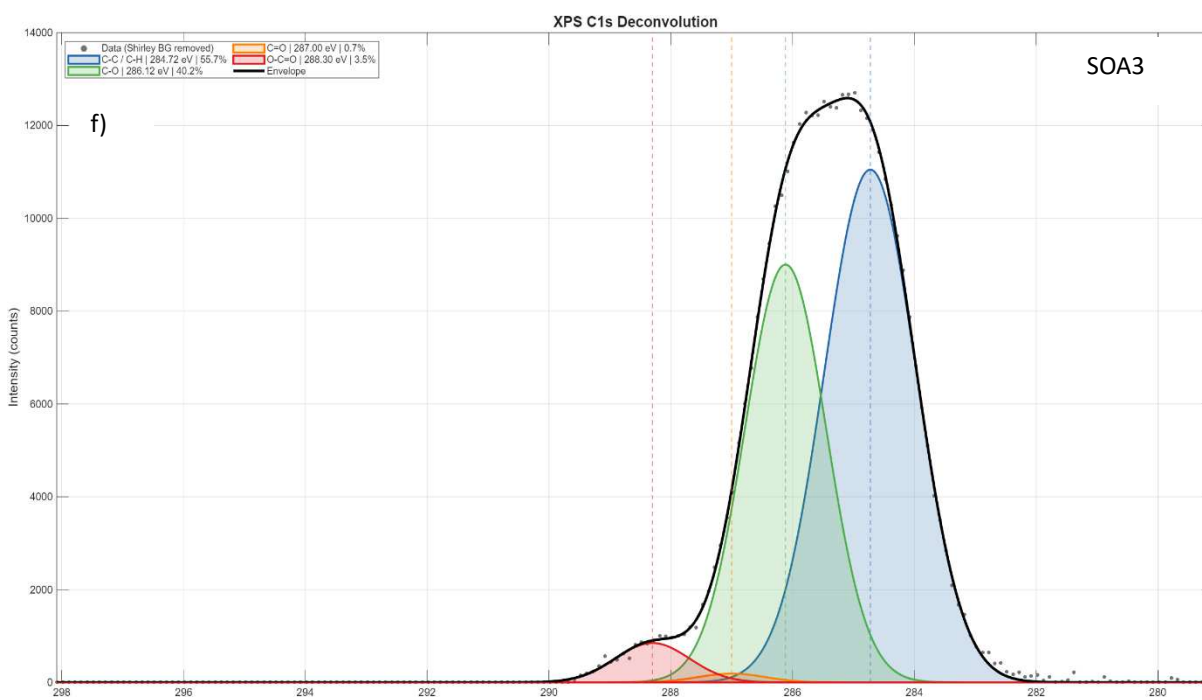
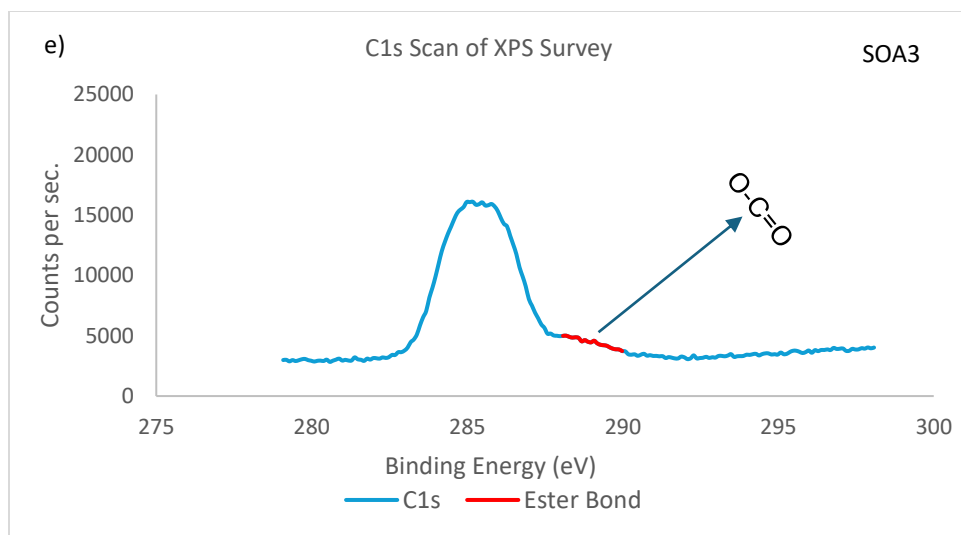


Figure 4 XPS surveys of SOA2 and SOA3 including C1s Scans, a) SOA2 XPS survey, b) SOA2 C1s Scan, c) SOA2 C1s Scan Convolution d) SOA3 XPS survey, e) SOA3 C1s Scan, f) SOA3 C1s Scan Convolution.

The dominant peak centered approximately around 285 eV is predominantly consist of C-C/C-H and C-O bonds. High binding energy side of the peak which is in between 286-287 eV region corresponds to C=O bonds originating from the unesterified hydroxyl groups of sorbitol in SOA2 and SOA3.

In conclusion, the substantial decrease in acid number, together with the appearance of characteristic ester bands at 1742 and 1168  $\text{cm}^{-1}$  in the FT-IR spectra which were absent in the spectra of both sorbitol and oleic acid. The corresponding O-C=O contribution in the XPS spectra collectively confirms the successful synthesis of an ester structured bio-based solvent via single step Fischer esterification.

In the solvent extraction experiments, the effect of contact time and initial aqueous phase pH on  $K_D$  values were investigated. The variation in  $K_D$  as a function of contact time for each initial pH value for all solvents are presented in Figures 5-8.

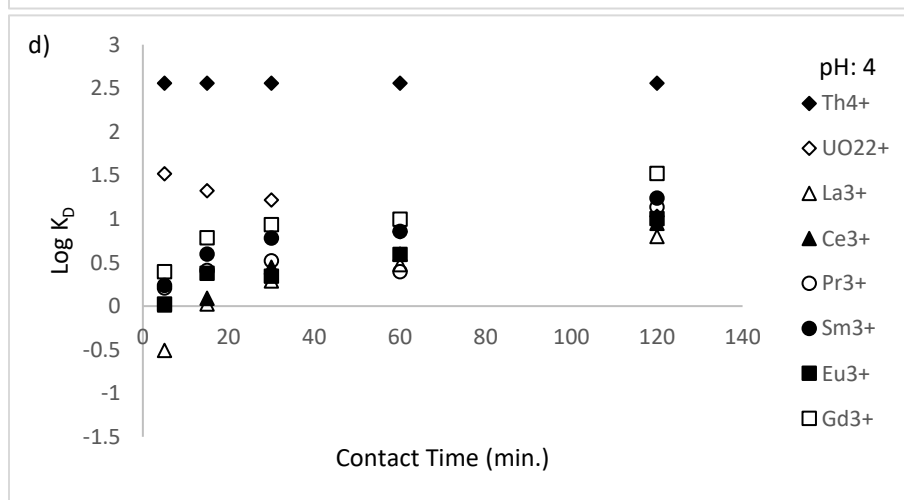
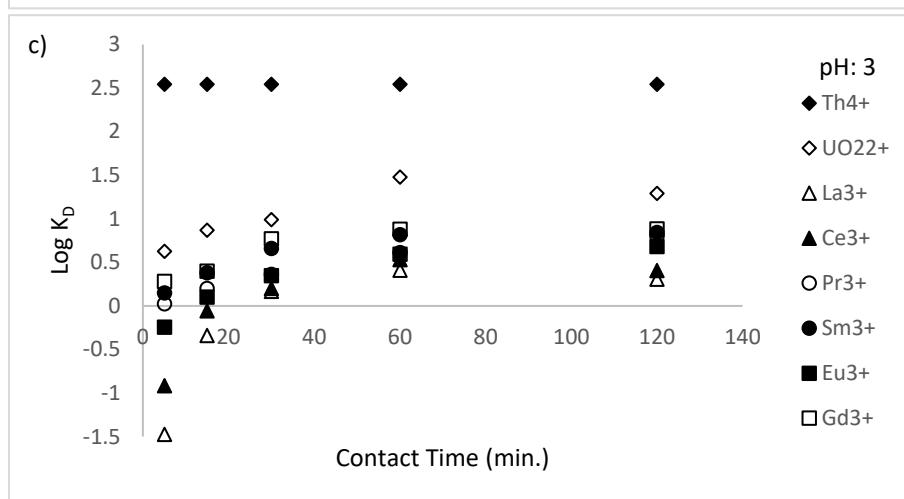
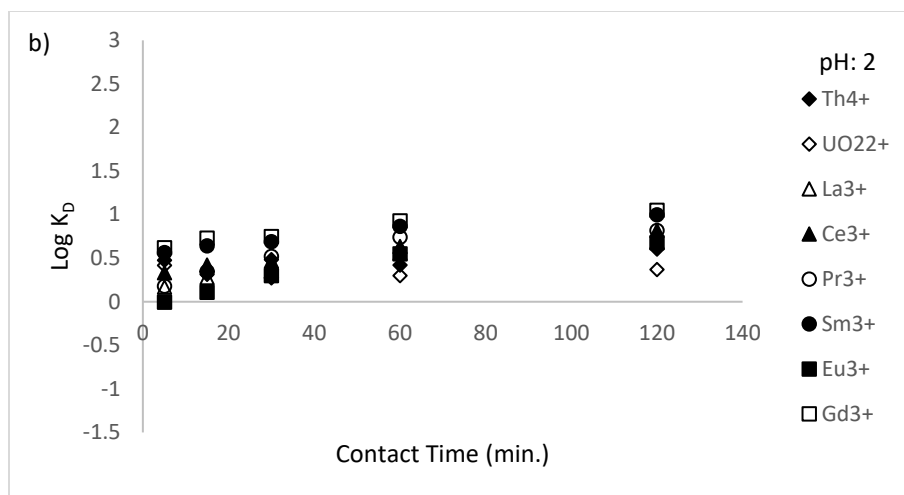
a)

Y-axis:  $\text{Log } K_D$

X-axis: Contact Time (min.)

pH: 1

- Th4+
- UO<sub>2</sub>2+
- La3+
- Ce3+
- Pr3+
- Sm3+
- Eu3+
- Gd3+



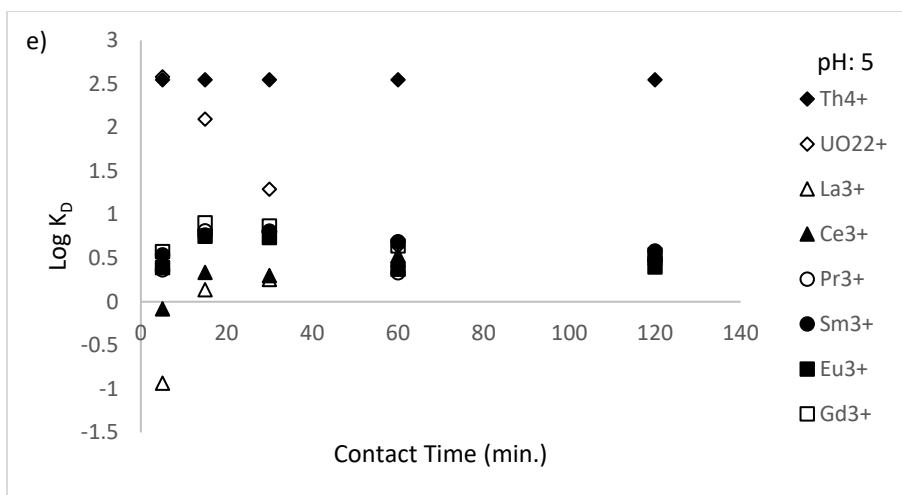
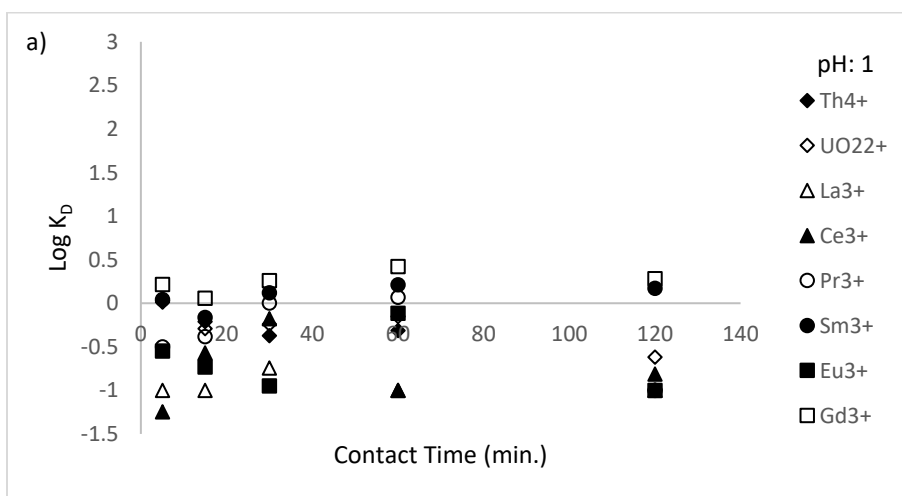
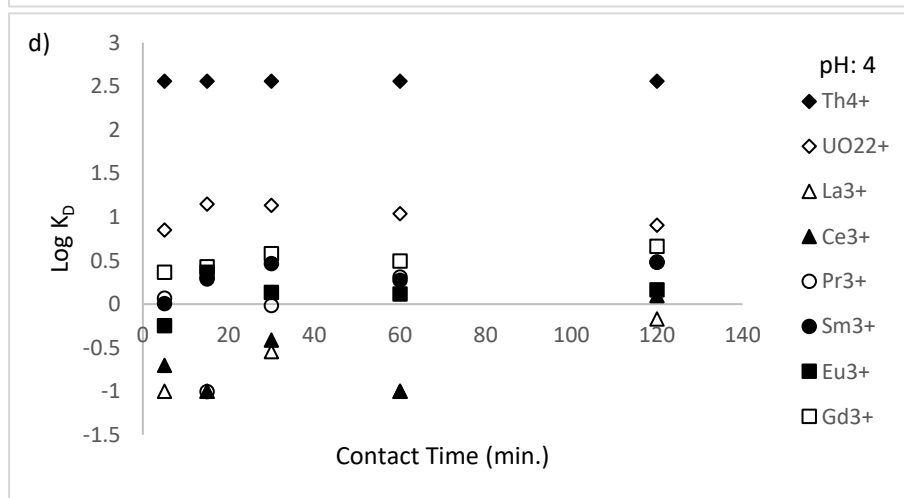
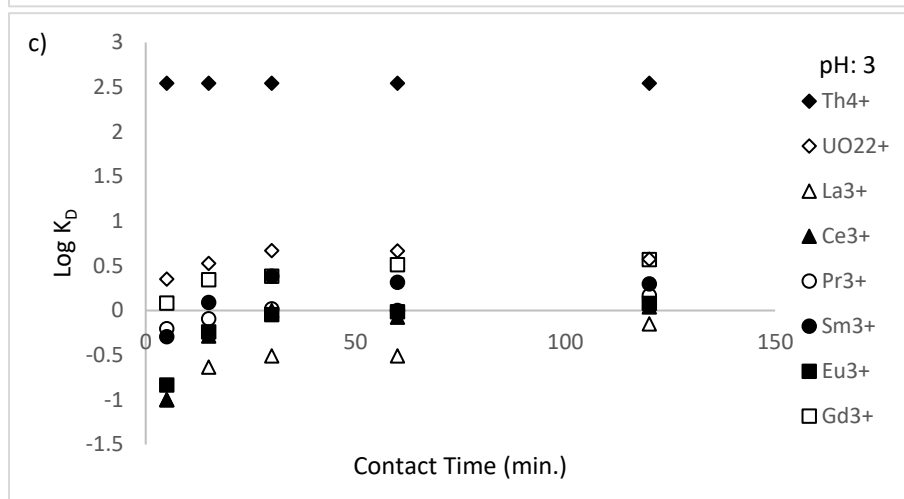
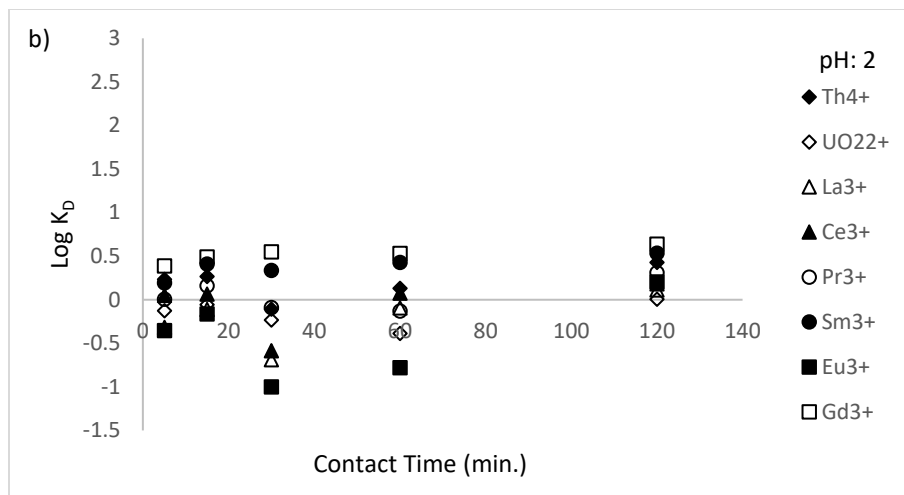


Figure 5 The Log  $K_D$  values of metal ions extracted by SOA2 as a function of contact time a)pH: 1 b)pH: 2 c)pH: 3 d)pH: 4 e)pH: 5

SOA2 demonstrated strong separation performance for Th<sup>4+</sup> ions, achieving effective extraction from the mixed solution at pH values above 3 with log  $K_D$  values around 2.5. Under more acidic conditions, extraction was limited due to competition between Th<sup>4+</sup> and H<sup>+</sup> ions. Increasing the initial pH of the aqueous phase enhanced the uptake of REE<sup>3+</sup> ions; however, their log  $K_D$  values were in between 0.5 and 1.5, notably lower than those of Th<sup>4+</sup>. UO<sub>2</sub><sup>2+</sup> ions were primarily extracted at higher pH values, but this extraction was not stable, as REE<sup>3+</sup> ions gradually transfer to the organic phase with extended contact time. Overall, the extraction performance of SOA2 followed the order Th<sup>4+</sup> > UO<sub>2</sub><sup>2+</sup> > REE<sup>3+</sup>.

### SOA3





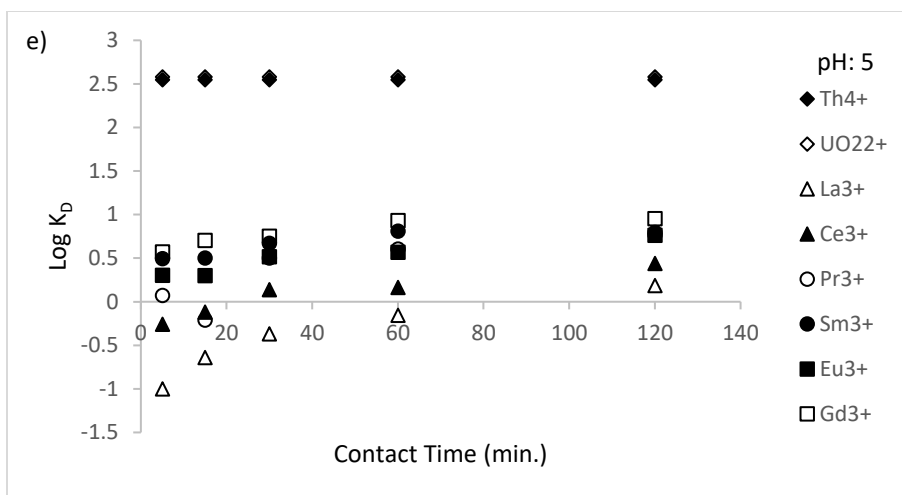
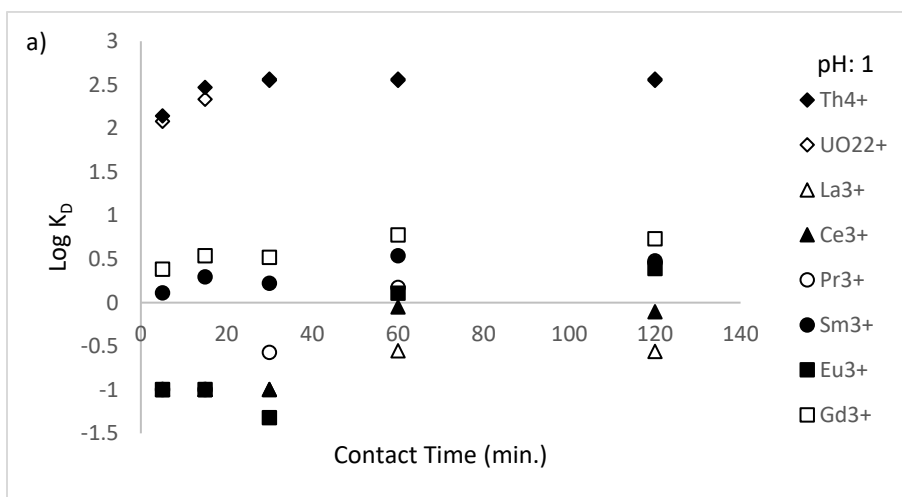
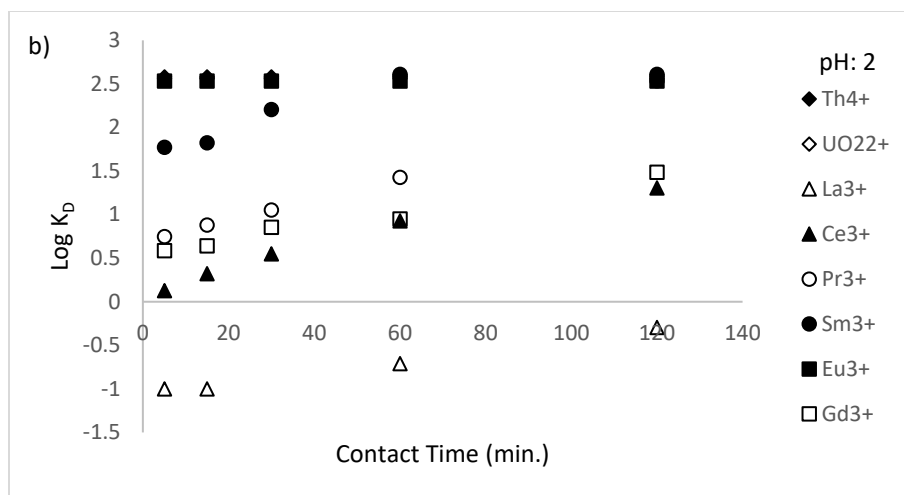


Figure 6 The Log  $K_D$  values of metal ions extracted by SOA3 as a function of contact time a)pH: 1 b)pH: 2 c)pH: 3 d)pH: 4 e)pH: 5

SOA3 did not effectively extract any metal ions under strongly acidic pH conditions; however, at pH 3 and above, it was able to separate  $\text{Th}^{4+}$  from the aqueous phase with log  $K_D$  values above 2.5. With increasing aqueous phase pH,  $\text{UO}_2^{2+}$  ions were progressively extracted, increasing its log  $K_D$  value from -0.1 to 2.58, at pH 5  $\text{UO}_2^{2+}$  ions almost completely transferred to the organic phase together with  $\text{Th}^{4+}$ . Compared to SOA2, SOA3 demonstrated similar affinity toward  $\text{Th}^{4+}$ , higher affinity toward  $\text{UO}_2^{2+}$ , and lower affinity toward  $\text{REE}^{3+}$  ions. In a general perspective, its selectivity order can be ranked as  $\text{Th}^{4+} \geq \text{UO}_2^{2+} > \text{REE}^{3+}$ .

#### Cyanex 272





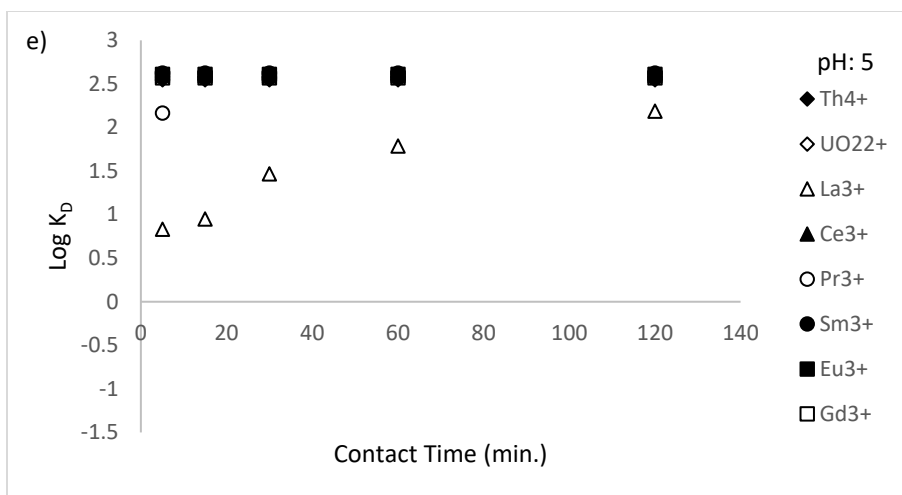
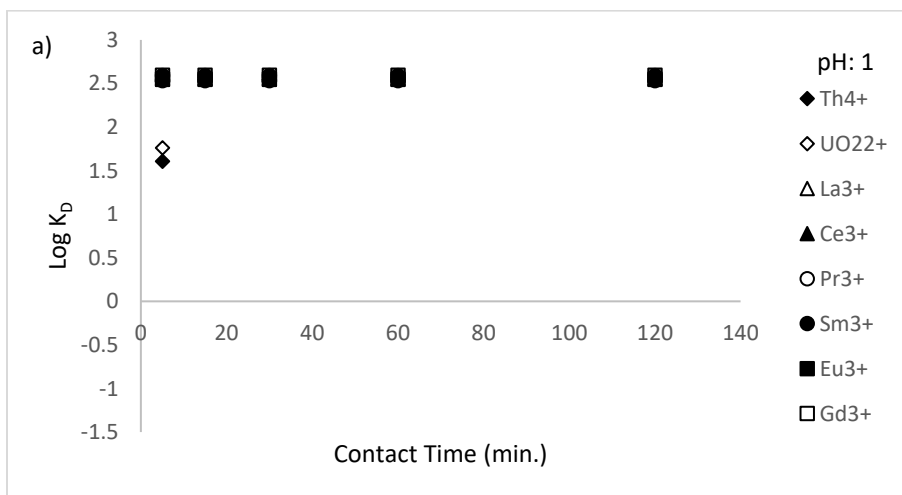
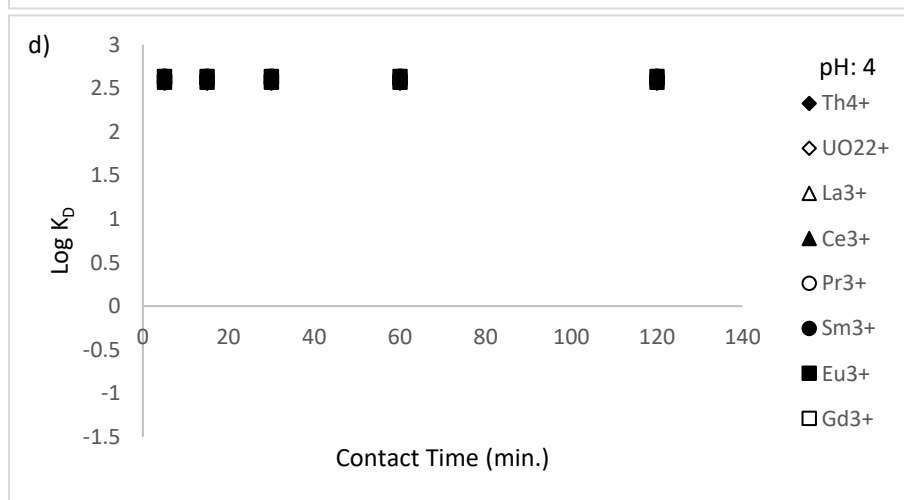
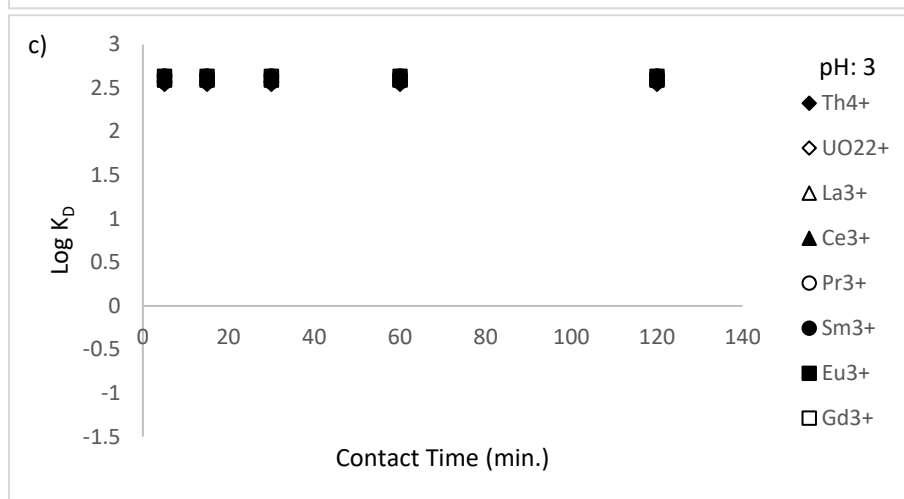
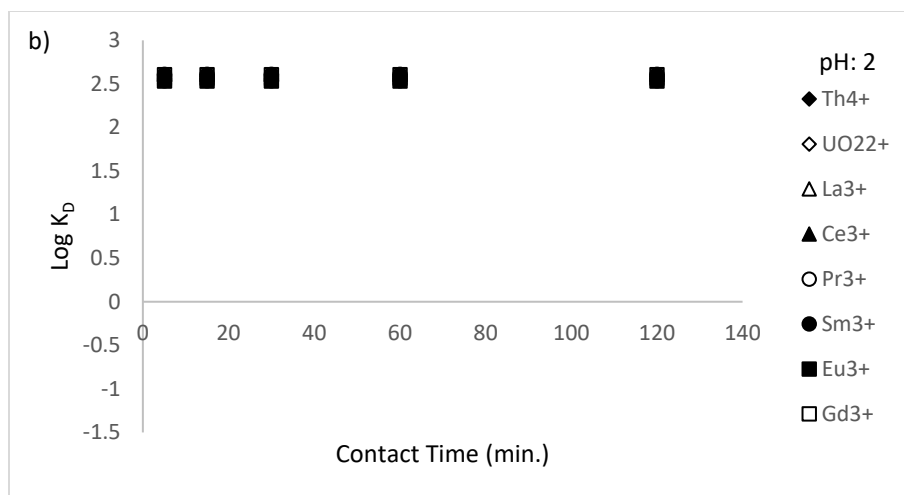


Figure 7 The Log KD values of metal ions extracted by Cyanex 272 as a function of contact time a)pH: 1 b)pH: 2 c)pH:3 d) pH:4 e)pH: 5

Cyanex 272 was able to extract  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  under acidic conditions; however, selective separation of  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  from the mixed solution was only achieved at pH 1. at pH 1 as the log  $K_D$  values of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  were 2.56 and 2.54 respectively where the log  $K_D$  values of  $\text{REE}^{3+}$  ions in between -0.56 and 0.73. As the pH increased, Cyanex 272 was no longer able to effectively separate the metal ions from each other and gradually lost its selectivity. Above pH 3, after 60 minutes of contact time only  $\text{La}^{3+}$  remained in the aqueous phase.

#### D2EHPA





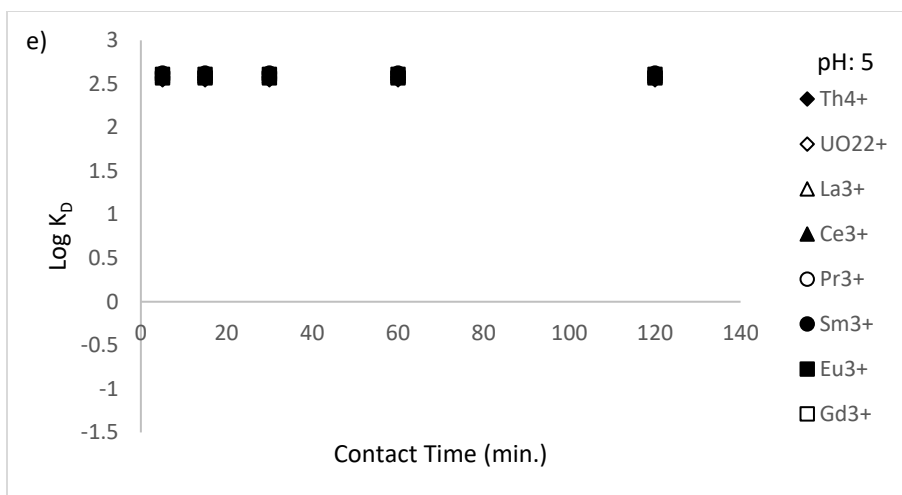


Figure 8 The Log  $K_D$  values of metal ions extracted by D2EHPA as a function of contact time a) pH: 1 b) pH: 2 c) pH: 3 d) pH: 4 e) pH: 5

D2EHPA proved to be the most aggressive extractant in this study, as it extracted all metal ions from the aqueous phase rapidly. This behavior can be attributed to its high acidity and strong ion-exchange capability, enabling the formation of strong metal ion - phosphoryl interactions through its phosphoric acid functional group. Although Cyanex 272 has a similar chemical structure, the presence of P-O-C linkages in D2EHPA makes it a significantly stronger acid. As a result, D2EHPA exhibits high extraction capacity but comparatively lower selectivity among metal ions, suggesting that it may be more suitable for recovery applications than for selective separation within investigated conditions.

### 3.5 Comparison of Optimal Separation Factors

Within this study, the highest separation factors obtained for  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  with each solvent are reported in Table 1 for comparison. For Cyanex 272 and D2EHPA, the maximum separation factors for both  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  were observed at pH 1. For SOA2 and SOA3, the highest separation factors were obtained at pH 3 for  $\text{Th}^{4+}$  and at pH 5 for  $\text{UO}_2^{2+}$ . These values were selected because they represent the optimum selectivity window of each extractant and enable a comparison of their maximum separation capability.

Table 1 Optimal SF values for  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  separation for each studied solvent.

|                  | Cyanex 272       |                    | D2EHPA           |                    | SOA2             |                    | SOA3             |                    |
|------------------|------------------|--------------------|------------------|--------------------|------------------|--------------------|------------------|--------------------|
|                  | $\text{Th}^{4+}$ | $\text{UO}_2^{2+}$ | $\text{Th}^{4+}$ | $\text{UO}_2^{2+}$ | $\text{Th}^{4+}$ | $\text{UO}_2^{2+}$ | $\text{Th}^{4+}$ | $\text{UO}_2^{2+}$ |
| $\text{Th}^{4+}$ | -                | 1.04               | -                | 1.04               | -                | 1.08               | -                | 1.08               |

|                               |      |      |      |      |       |      |      |      |
|-------------------------------|------|------|------|------|-------|------|------|------|
| UO <sub>2</sub> <sup>2+</sup> | 0.96 | -    | 0.96 | -    | 84    | -    | 156  | -    |
| La <sup>3+</sup>              | 3527 | 3669 | 1.00 | 1.04 | 10530 | 3269 | 3501 | 3804 |
| Ce <sup>3+</sup>              | 3527 | 3669 | 0.96 | 1.00 | 2911  | 460  | 3501 | 689  |
| Pr <sup>3+</sup>              | 1317 | 1370 | 1.03 | 1.07 | 335   | 163  | 562  | 321  |
| Sm <sup>3+</sup>              | 212  | 220  | 1.03 | 0.94 | 250   | 110  | 686  | 122  |
| Eu <sup>3+</sup>              | 7405 | 7703 | 0.91 | 1.03 | 620   | 155  | 2394 | 190  |
| Gd <sup>3+</sup>              | 107  | 112  | 0.89 | 0.93 | 184   | 101  | 291  | 102  |

Log K<sub>D</sub> values represent the affinity of a solvent toward individual metal ions, whereas SF provides a more direct measure of separation performance between metals. Although Cyanex 272 did not exhibit the highest log K<sub>D</sub> values for Th<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup>, its very low extraction of REE<sup>3+</sup> ions at pH 1 caused the SF values to increase sharply compared with SOA2 and SOA3. Only in two cases; in the Th<sup>4+</sup>/La<sup>3+</sup> and Th<sup>4+</sup>/UO<sub>2</sub><sup>2+</sup> separation pairs Cyanex 272 did noticeably fall behind the SF values of SOA2 and SOA3. Overall, the results indicate that, under optimized conditions, Cyanex 272 provides the strongest separation capability, even though this performance is limited to pH 1. SOA2 and SOA3 showed comparable separation behavior, with SOA3 performing slightly better overall; additionally, SOA3 was able to separate UO<sub>2</sub><sup>2+</sup> from REE<sup>3+</sup> at pH 5 across all tested contact times. In contrast, D2EHPA did not demonstrate selective separation among Th<sup>4+</sup>, UO<sub>2</sub><sup>2+</sup>, and REE<sup>3+</sup> ions, as it extracted nearly all metal ions across the tested conditions.

### 3.6 Hypothesized Extraction mechanism

In this study, the extraction mechanism was hypothesized based on the chemical structures of the extractants. SOA2 and SOA3 are neutral solvents and therefore do not interact with metal ions through ligand-metal ion complexation mechanisms. Instead, they operate through a solvation driven mechanism in which extractant molecules coordinate the metal ions via oxygen-containing functional groups and partially replace water molecules in the hydration sphere. This interaction is primarily between ion-dipole and is weaker than the ionic interactions observed with acidic extractants. Because neutral extractants provide lower interaction intensity, they may preferentially extract metal ions whose hydration shells can be more readily destabilized, which can support selective separation under controlled conditions. The disadvantage is lower extraction capacity and lower stability of metal ions in organic phase.

In contrast, acidic organophosphorus extractants such as Cyanex 272 and D2EHPA extract metal ions through strong ligand-metal ion complexation mechanisms involving their phosphoryl functional groups [32, 33, 39]. These stronger interactions enable higher loading capacity and more stable metal ion-extractant complexes but could reduce selectivity because multiple metal ions can be transferred efficiently under the same conditions particularly in diluted metal ion bearing solutions. Consistent with this behavior, SOA2 and SOA3 showed selective separation of  $\text{Th}^{4+}$  from  $\text{UO}_2^{2+}$  and  $\text{REE}^{3+}$  ions, and SOA2 additionally separated  $\text{UO}_2^{2+}$  from  $\text{REE}^{3+}$  at pH 5. Cyanex 272 provided selective separation only within a narrow pH window, whereas D2EHPA extracted nearly all metal ions and therefore showed the highest capacity but the lowest selectivity among the tested extractants. The comparatively lower extraction capacity and higher selectivity of Cyanex 272 relative to D2EHPA can be attributed to its weaker acidic character. Accordingly, Cyanex 272 may operate through a partially mixed mechanism that includes both ion-exchange and solvating contributions rather than purely strong ionic complexation. The SF values of  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  using D2EHPA may further increase at concentrated metal ion containing aqueous phase, since acidic extractants with strong ion uptake capacity sustain higher loading, while neutral solvating solvents are more prone to saturation and capacity limitations at concentrated solutions. A straightforward version of the proposed extraction mechanism is schematically presented in Figure 8.

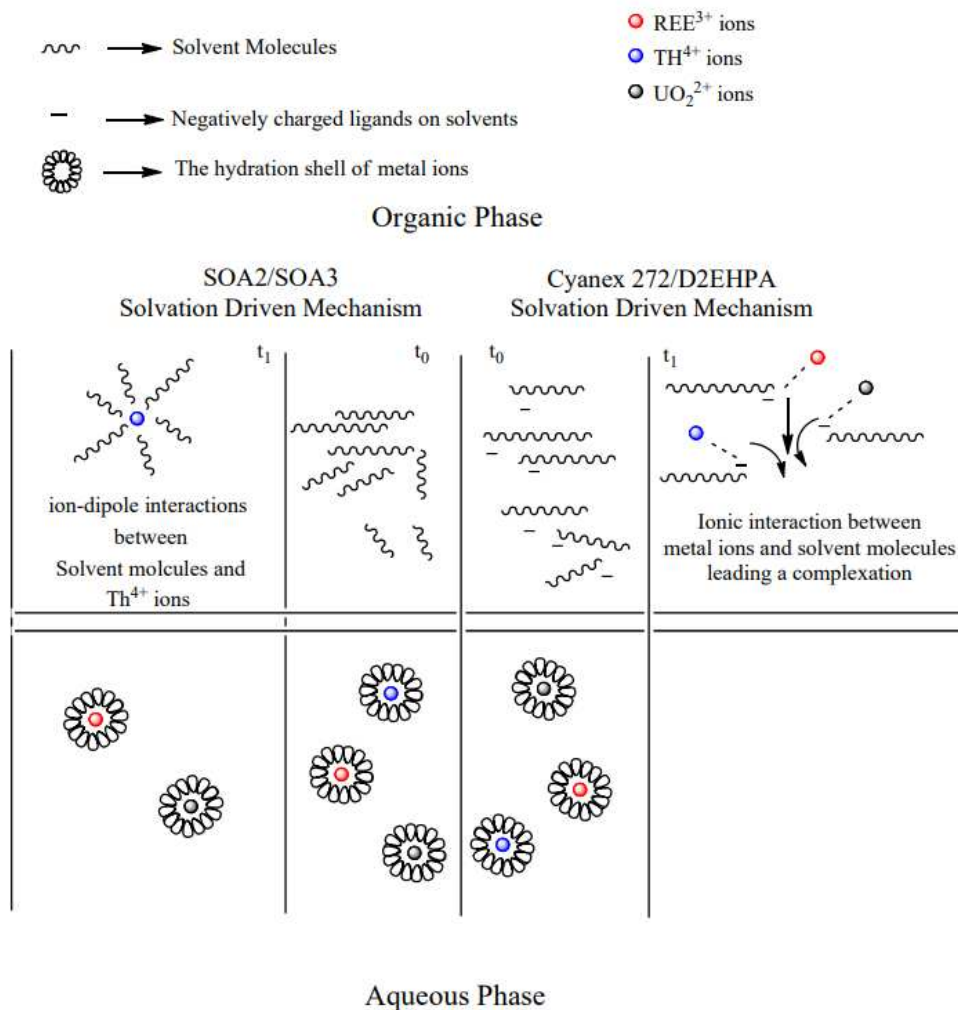


Figure 8 Proposed extraction mechanism for neutral (SOA2/SOA3) and acidic/ionic (Cyanex 272 and D2EHPA) type solvents.

### 3.7 Literature comparison

Table 2 presents a comparison of SFs for  $\text{Th}^{4+}/\text{REE}^{3+}$  and  $\text{UO}_2^{2+}/\text{REE}^{3+}$  including SOA3 from this study and solvents reported in the literature. The corresponding aqueous solvent type and chemical structure/composition are also included. The values presented in Table 2 were either directly reported in the papers or calculated according to the presented data.

Table 2 Literature comparison of  $SF_{\text{Th}^{4+}/\text{REE}^{3+}}$  and  $SF_{\text{UO}_2^{2+}/\text{REE}^{3+}}$  obtained using SOA3

| Solvent Name | $SF_{\text{Th}^{4+}/\text{REE}^{3+}}$ | $SF_{\text{UO}_2^{2+}/\text{REE}^{3+}}$ | Solvent Type | Chemical Structure/Composition | Ref.          |
|--------------|---------------------------------------|-----------------------------------------|--------------|--------------------------------|---------------|
| SOA3         | 1822                                  | 871                                     | Neutral      | Sorbitol-Fatty Acid Ester      | Present Study |
| CMPO*        | 167                                   | -                                       | Neutral      | Phosphine Oxide                | [21]          |
| DMDBTDMA**   | 480                                   | 980                                     | Neutral      | Malonamide                     | [22]          |
| THMA***      | 3500                                  | 1250                                    | Neutral      | Malonamide                     | [22]          |

|                            |       |     |              |                                    |      |
|----------------------------|-------|-----|--------------|------------------------------------|------|
| Primene JM-T / Alamine 336 | 145   | 292 | Neutral      | Primary and Tertiary Amine Mixture | [40] |
| SCA****                    | 1318  | -   | Acidic/Ionic | Amide-Carboxylic Acid              | [41] |
| Cyanex 572                 | 43800 | -   | Acidic/Ionic | Phosphonic/Phosphinic Acid Mixture | [42] |

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\*Carbamoyl methyl phosphine Oxide  
\*\*N,N'-dimethyl,N,N'-dibutylteradecylmalonamide  
\*\*\*N,N,N',N'-tetrahexylmalonamide  
\*\*\*\*N,Ndialkyl-succinamide acid

The literature comparison in Table 2 shows that separation factors reported for  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  span a wide range across different extractant types. There is no specific trend observed because separation performance depends strongly on extractant functional groups, aqueous phase composition and extraction mechanism. When comparing the SF values in accordance with solvent type, neutral solvating extractants such as malonamides, CMPO, amines, and the SOA3 exhibit comparable SF values, showcasing similar selectivity behavior driven by solvation-type interactions. Acidic organophosphorus solvents, such as Cyanex 572, can reach very high SF values in *concentrated* metal ion bearing solutions, as mentioned under extraction mechanism. Overall, the performance potential of SOA3 within the neutral type extractant SF range supports the potential of bio-based solvents as viable candidates for selective  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$  separation in diluted metal ion bearing solutions.

#### 4. Conclusion

The bio-based extractants were successfully synthesized via single-step Fischer esterification of sorbitol and oleic acid at molar ratios of 1:2 and 1:3, yielding SOA2 and SOA3, respectively. The significant decrease in acid number from 180 to 34 (SOA2) and 40 (SOA3), the appearance of characteristic ester peaks at 1742 and 1168  $\text{cm}^{-1}$  in FT-IR spectra, and the presence of O-C=O contributions in the 288-289 eV region of the XPS C1s spectra collectively confirm the successful formation of ester-structured bio-based solvents.

At low pH range, SOA2 and SOA3 did not extract  $\text{Th}^{4+}$  ions effectively due to strong competition with  $\text{H}^+$  ions. At and above pH 3,  $\text{Th}^{4+}$  was selectively extracted by both SOA2 and SOA3 with log  $K_D$  values above 2.55, whereas their affinity toward  $\text{REE}^{3+}$  ions remained limited, in contrast, Cyanex 272 and especially D2EHPA extracted most metal ions across the investigated conditions, indicating substantially higher overall extraction capacity. Extraction mechanism proposal and

literature comparison strongly indicate that acidic/ionic type extractants tend to exhibit superior capacity towards neutral extractants, additionally their separation potentials only excel when used with concentrated metal ion bearing aqueous phases. Which clearly presents the drawbacks of neutral bio-based solvents such as SOA2 and SOA3, their extraction capacity.

Future studies should aim to increase the extraction capacity of bio-based solvents without losing their selectivity, which is a difficult balance to achieve. A practical approach could be to design polymeric bio based extractants that contain a limited number of ionic ligand groups. Such materials may combine selective ligand-metal ion binding with solvation-based extraction, leading to higher loading capacity and better complex stability while still maintaining selective separation. This direction could support the development of efficient and sustainable separation and purification processes for Th, U, and REEs.

#### **Credit authorship contribution statement**

**Bekir Özkan:** Conceptualizing, conducting experiments, data evaluation, writing original draft.

**Süleyman İnan:** Conceptualizing, experimental planning, data evaluation, reviewing and editing.

**Bariş Oğuz Gürses:** Data Processing, data evaluation.

#### **Ethics declarations**

##### **Competing Interest**

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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##### **Data availability**

All of the data presented in this paper will be made available upon request.

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