

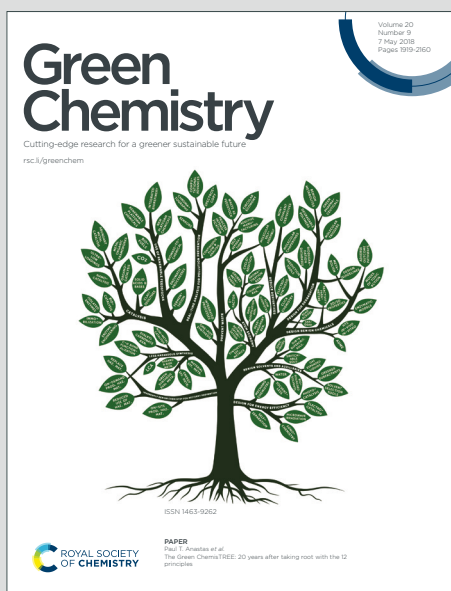
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1. This work investigates the recovery of rare earth elements by solvent extraction from waste permanent magnets leachates using a hydrophobic eutectic solvent (HES) composed of *N,N,N',N'*-Tetraoctyldiglycolamide (TODGA) and decanoic acid.
2. Compared to conventional diluent-based solvent extraction, the HES system exhibited a similar extraction mechanism but an enhanced extraction performance, with an excellent selectivity against iron and boron without the need of diluents or phase modifiers.
3. A comparative life cycle analysis of the separation indicates a lower environmental impact of the HES to purify 1 kg of neodymium relative to a traditional solvent extraction phase due to its lower volatility and greater metal loading capacity.



Improved rare earth elements recycling using a sustainable diglycolamide-based hydrophobic eutectic solvent

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Abstract

The sustainable recycling of rare earth elements (REEs) is essential for environmental preservation due to their significant role in facilitating green technologies. These elements are crucial for the ecological transition, especially in renewable energy systems. Hydrometallurgical techniques, such as liquid-liquid extraction, are commonly used but often rely on large volume of environmentally harmful volatile solvents. Growing environmental concerns are encouraging industries to reduce their reliance on these compounds, challenging the traditional extraction methods. Neoteric systems, such as deep eutectic solvents (DES), offer promising alternatives with advantageous physical properties, and in some cases, better extraction performance. Despite their potential, they remain underutilized because they require further optimization and understanding. This study focuses on the hydrophobic eutectic solvent (HES) *N,N,N',N'*-Tetraoctyldiglycolamide (TODGA) and decanoic acid for the extraction of REEs from a nitric acid leachate. The results are complemented by a systematic comparative study between the hydrophobic eutectic solvent and traditional solvent equivalent for REE extraction. The HES exhibits enhanced extraction performance and achieves extraction efficiencies for the lanthanides with distribution coefficients ranging from 30 to 20,000. Under the condition considered, the extraction efficiencies are greater than 96%, and demonstrating selectivity against iron, with a $SF_{Dy/Fe} > 10,000$. UV-vis-near infrared measurements support the hypothesis of a similar extraction mechanism to that in the conventional reference solvent, attributing the higher obtained extraction efficiency to the greater concentration of TODGA in the HES, without the need of a phase modifier to prevent phase separation. The eutectic mixture also exhibits lower volatility (16 times less than the conventional system studied) as measured by thermal gravimetric analysis (TGA), improving the operational safety and environmental sustainability of the extraction process. A life cycle assessment further demonstrates this improvement, showing more favourable results for the HES system to purify 1 kg of neodymium (Nd).

1-Introduction

The production of minerals and metals currently accounts for approximately 10% of global energy-related greenhouse gas emissions, due to its high energy demand¹. In 2022, 96 million tons of electronic goods were placed on the market, generating 62 million tons of e-waste, an issue which is expected to increase to 82 million tons by 2030. Recycling rates for metals, such as rare earth elements (REEs), remain below 1%, highlighting the need for significant progress to achieve a truly circular economy². The specific case of REEs is crucial for environmental sustainability due to their role in enabling green technologies and sustainable solutions. Sustainable extraction and recycling of REEs is therefore necessary to close the resource cycle, both by targeting extraction processes with low environmental impact and by recovering metals from end-of-life devices.

Among the various metallurgical processes, hydrometallurgy is recognized as an environmentally friendly alternative due to its ability to recover metals from low-grade matrices, milder process conditions, greater flexibility, solvent regeneration, and limited gaseous emissions^{3,4}. Solid-liquid extraction with ion-exchangers or sorbents is often considered as it is an efficient method that uses small



amounts of sorbents and exhibits proper regeneration and good stability. However, it provides reduced loading capacity and selectivity compared to the liquid-liquid extraction process^{5,6}. Ion foam flotation techniques^{7,8} are also increasingly being investigated as they allow effective regeneration of the extracted material and minimal waste generation, but they still have limited applicability. As such, the current industrial hydrometallurgical process primarily relies on solvent extraction to transfer metal ions, such as lanthanides⁹ or actinides^{10–12} from leachates to an immiscible organic phase¹³. However, solvent extraction has important drawbacks such as the use of significant volumes of effluents, which are often environmentally toxic and volatile. Traditional solvents commonly used in solvent extraction such as kerosene, tetrahydrogenated propylene, *n*-dodecane, *n*-hexane, chloroform and toluene are widely known to pose environmental and health risks: volatility and flammability, toxicity¹⁴. These effluents are associated with air pollution issues such as smog and ozone depletion, and groundwater contamination^{15,16}. In this context, the development of new types of solvents with higher efficiency and a lower environmental impact is crucial.

The quest to reduce the impact of organic compounds in metal recovery has led to the exploration of various alternatives. Solvents presenting lower volatilities, including ionic liquids, have emerged as advanced options¹⁵. Despite their widespread application in metal recovery^{17,18,19}, these solvents face limitations in large-scale implementation owing to their resource-intensive synthesis, high cost, and increased viscosity compared to conventional solvents. Recently, hydrophobic eutectic solvents (HES) gained attention as a promising substitute for traditional organic phases in solvent extraction following its introduction by van Osch et al.²⁰. HES are characterized as low-melting binary mixtures²¹ consisting of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), with hydrogen bonding between these components resulting in potential deviations to ideality²². The unique liquefaction property of HES enables it to incorporate substantial amounts of extractant molecules as either HBA or HBD. Initial research focused on HES incorporating ionic quaternary ammonium and carboxylic acids for the extraction of various metals, including chromium, iron, platinum group elements, and others metals^{23,24}. However, HES encountered challenges similar to ionic liquids, such as high viscosity and substantial cost. The concept of deep eutectic solvents has since evolved to include type V systems^{25–27}, which are mixtures of two non-ionic compounds that exhibit significant deviations from ideal behavior due to enhanced intermolecular hydrogen bonding. This non-ionic nature addresses traditional issues associated with ionic HES and expands potential applications. For instance, researchers have employed HES composed of trioctylphosphine oxide (TOPO) as the acceptor and bio-derived donors such as fatty alcohols or acids to extract transition and platinum group metals²⁵, as well as the uranyl cation²⁸ or lanthanides^{29,30}. These studies have yielded promising results in terms of loading capacity and selectivity although the efficacy of HES is strongly influenced by the specific compounds used in their formulation. In addition to their performance, several advantages are commonly cited to justify the use of HES, including low volatility, absence of third-phase formation, potential biosourcing of HES components, reduced toxicity, and lower viscosity compared to ionic systems²⁹. However, comprehensive studies evaluating these claims are still lacking.

With this in mind, our study aims to investigate new HES systems for lanthanide recovery. We selected the *N,N,N',N'*-Tetraoctyldiglycolamide (TODGA) and decanoic acid (DA) HES system, which was previously described to form an eutectic mixture³¹ but has never been engaged as an extracting phase for lanthanide extraction (component structure presented in Figure 1). TODGA was chosen for its well-known efficacy as an extractant for lanthanide and actinide (III) recovery^{32–34} and its excellent HBA capability. DA is a biosourced compound that was applied as an HBD in HES mixtures as it is more resistant to chemical degradation under acidic and/or oxidizing conditions compared to alcohol or phenolic HBDs³⁰. The HES mixtures of TODGA and DA were evaluated under various conditions to assess their potential as replacement for conventional systems for the recovery of REEs from real permanent magnet leachates. The extraction of REE elements and competitive metals was measured for the TODGA/DA mixtures after their contact with different aqueous REE leachates. Key parameters such as loading capacity, metal stripping efficiency, solvent reuse, viscosity, volatility and phase separation



were investigated. The results were systematically compared with those obtained using a reference organic phase simulating a conventional process (TODGA in dodecane with a phase modifier). The key point of this study is to compare the feasibility of a lanthanide recycling process using eutectic solvents with a conventional process using a diluent and an extractant. A preliminary mechanistic study was performed to explain the superior performance of the HES. Finally, since the HES systems are often claimed to be more sustainable, a life cycle assessment (LCA) was conducted to objectively compare the environmental sustainability of the HES system with that of the conventional extractant system.

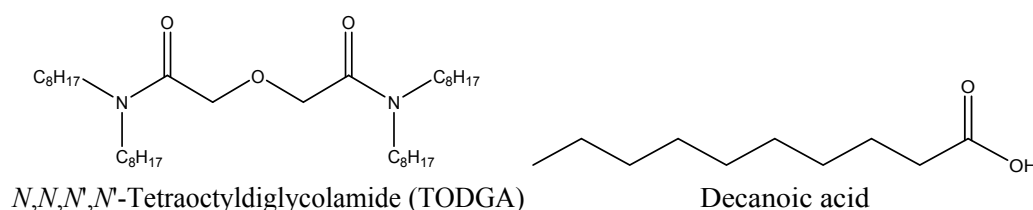


Figure 1: Compounds of the HES

2-Methodology

2.1-Materials

Aqueous phase: Lanthanide nitrate salts with a purity of >99% ($\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$): La, Nd, Eu, Dy, Gd, Y, and Yb) and $\text{Fe}(\text{NO}_3)_3$ were purchased from Sigma-Aldrich and used without further purification.

Leaching agents: Nitric acid (69.5%), acetic acid (99%), sulfuric acid (96%), hydrochloric acid (37%) were purchased from Carlo Erba and used without any further purification.

Organic phase: Decanoic acid (DA), 1-octanol, *n*-dodecane purchased from Sigma Aldrich and used without any further purification, N,N,N',N' -tetraoctyl-3-oxapentanediamide (TODGA) was synthesized (purity >95%) according to a procedure adapted from the literature^{35–37} with ^1H and ^{13}C NMR characterizations in agreement with those reported in the literature. Synthesis details are provided in the supporting information.

Stripping agent: Ethylenediaminetetraacetic acid (EDTA) purchased from sigma Aldrich and used without and N,N,N',N' -tetraethyl-3-oxapentanediamide (TEDGA) was synthesized (purity > 95%) according to a procedure adapted from the literature^{35–37}

NdFeB magnet powder was used as the NdFeB waste stream in its original form (as received from Terra Nova Development TND, particle size < 1 mm).

2.2-Analytical methods

Concentrations of metals in the aqueous phase were measured by inductively coupled plasma/optical emission spectroscopy (ICP-OES Spectro Arcos - AMETEK Materials Analysis). The ICP calibration samples were prepared from 1000 ± 4 mg/L iron, lanthanum, neodymium, europium, dysprosium, gadolinium, ytterbium and yttrium standard solutions (SCP Science Plasma Cal). Uncertainties in metal concentrations were statistically determined by repeated measurements. As commonly defined in liquid-liquid extraction, the distribution ratio D_M of an element M corresponds to the ratio between the concentrations of this element in the organic and aqueous phases at equilibrium. The metal concentration in the organic phase at equilibrium, $[M]_{\text{org,eq}}$ was estimated by the difference between the initial concentration in the aqueous phase, $[M]_{\text{aq,ini}}$ and the concentration at equilibrium, $[M]_{\text{aq,eq}}$ (equation (1)).

$$D_M = \frac{[M]_{\text{org,eq}}}{[M]_{\text{aq,eq}}} = \frac{[M]_{\text{aq,i}} - [M]_{\text{aq,eq}}}{[M]_{\text{aq,eq}}} \times \frac{V_{\text{aq}}}{V_{\text{org}}} \quad (1)$$



D_M : distribution coefficient of metal M, $[M]_{org}$ and $[M]_{aq}$: concentration of metal M in organic phase and in aqueous phase, i and f are initial and final concentrations, $[M]_{aq,i}$ and $[M]_{aq,f}$ are determined by ICP-OES. A previous study on the HES system shows that the two phases are not significantly miscible,³¹ and the absence of a third phase allows reliable mass balance to determine the distribution coefficient.

Furthermore, the separation factor for a specific metal concerning another metal is defined by the ratio of their respective distribution coefficients (2):

$$SF_{M1/M2} = \frac{D_{M1}}{D_{M2}} \quad (2)$$

The viscosity measurement was performed with a Microvisc from Rheosense at a temperature between 25°C and 50°C with a shear rate of 200 s⁻¹, two microchips were used one for a viscosity range from 0 to 100 mPa.s and the other one with a range from 60 to 5000 mPa.s when the samples show higher viscosity than 100 mPa.s. Measurements were made 5 times with an error of less than 5%. 100 µL of samples from the organic phase after contact with metallic solutions at different concentrations were used for the different experiments.

UV-vis-near infrared spectra (NIR) were recorded between 350 nm and 850 nm with a Shimadzu UV-3600 spectrometer and a deuterium source for UV measurements and a tungsten source for vis-NIR region, in quartz cells with a 2 mm optical path. The absorbance of contacted, pre-contacted, and non-contacted samples was measured using an empty cell in the second beam as a reference. Subtractions were calculated post-processing.

2.3-Leaching of permanent magnets

The extraction experiments focused on extraction in a real NdFeB permanent magnet leachate in different inorganic acid media, namely HCl, HNO₃, and H₂SO₄, for a fixed acid concentration of 1.0 mol/L. The magnet powder is placed in the acid medium and then stirred at 200 rpm for 16h at 25°C with a solid to liquid ratio of 0.07 (S/L= 1/14 g.mL⁻¹). After centrifugation at 4000 rpm for 20 min, the supernatant was collected and filtered (Vivaspin 20 PES 30 kDa MWCO) before being placed in contact with the eutectic mixture for extraction. A modified protocol was applied for acetic acid leaching, where the magnetic powder was contacted with 1.6 mol/L acetic acid heated to 60°C for 24 hours with a solid to liquid ratio of 0.02 (S/L= 1/50 g.mL⁻¹). After stirring, the solution obtained is centrifuged at 11,000 rpm for 5 minutes and the supernatant is filtered through cellulose (0.45 µm). This solution was then used to perform the solvent extraction step with the eutectic system.

2.4-Solvent extraction procedure

a) Eutectic preparation

The mixtures of TODGA (HBA) with DA by varying the HBA molar fraction (x_{HBA}), were prepared gravimetrically in glass vials (10 g). They were mixed by magnetic stirring (300 rpm) and heated at 60°C until they liquefied and then allowed to cool at room temperature for 8 hours. If no demixing or recrystallization was observed, the mixture is then used for the liquid-liquid extraction step.

For extractions using synthetic leachates, the aqueous phases were prepared by dissolving the salts of lanthanide nitrates and iron (III) nitrates in water at the desired concentration. The lanthanides selected are: La, Nd (light rare earths), Eu, Gd, Dy, Y, and Yb. Concentrated nitric acid (69%) was then added to obtain a solution of REEs at the desired nitric acid concentration. The solutions were then titrated to determine the actual concentration of nitric acid in the solution.

b) Equilibration



Before contacting the aqueous metal solution, we first carried out a pre-contact step between the HES and an aqueous phase containing the same acid concentration as the metal solution. This step allows the HES to be balanced in terms of water and acid. Contact and pre-contact are carried out with an organic to aqueous (O/A) ratio of =1/2. The pre-contact stage is carried out with stirring at 250 rpm for 1 hour at 25°C. This was followed by centrifugation at 8000 rpm for 10 min. Solvent extraction experiments were carried out in 5 mL Eppendorf vials. The acid-equilibrated organic phase was then separated from the aqueous pre-contact phase and contacted with the metal solution. Each extraction was carried out by contacting an aqueous phase with an organic phase pre-equilibrated in a 5 mL flask stirred at 250 rpm in a thermostatically controlled cell (Infor-ht® ecotron) at 25 °C for 1 hour aqueous and organic phases were separated by centrifugation at 8000 rpm for 10 min (Rotina 380R).

c) Optimization

A kinetic study of lanthanide and Fe extraction was conducted to ensure equilibrium is reached in all extraction experiments. Different HES mixtures with $x_{\text{TODGA}}=0.3$ were contacted with an aqueous phase (HNO_3 1 mol/L) containing 0.005 mol/L of Fe, La, Nd, Eu, Gd, Dy, Y and Yb, for durations ranging from 1 minute to 2 hours at 250 rpm. Subsequently the samples were centrifuged at 8000 rpm for 1 minute prior to phase separation. Figure S1 demonstrates that thermodynamic equilibrium is reached in less than 1 minute for the various REEs, except for lanthanum which requires 5 to 10 minutes to reach equilibrium after contact.

The aqueous phases obtained from the extractions were diluted in 1 % of nitric acid and analyzed by ICP-OES.

d) Stripping and reuse

Each stripping was carried out by contacting an aqueous stripping phase with the organic loaded phase in a 5 mL flask stirred at 250 rpm in a thermostatically controlled cell (Infor-ht® ecotron) at 25 °C. At the end of the shaking period, the mixture was centrifuged (8000 rpm–10 min) and the aqueous and organic phases were separated from each other.

The aqueous phases obtained from the extractions were diluted in 1 % of nitric acid and analyzed by ICP-OES.

The stripping yield corresponds to the ratio between the concentrations of this element in the aqueous phase after stripping and in the loaded organic phase before stripping at equilibrium expressed in % and equal to (3):

$$\% \text{ Stripping} = \frac{[M]_{\text{aq,sp}}}{[M]_{\text{org,load}}} \times \frac{V_{\text{aq}}}{V_{\text{org}}} \times 100 \quad (3)$$

where $[M]_{\text{aq,pt}}$ and $[M]_{\text{org,load}}$ are the concentrations of the metal ions in the stripping aqueous phase after stripping and in the loaded organic phase before stripping, respectively.

The recyclability of the organic phase was evaluated through 5 cycles of extraction and stripping with the same protocol as above, after each step the metal concentration was determined by ICP-OES with the aqueous phase obtained from the extraction and diluted after with 1% of nitric acid.

2.5- Determination of extraction systems stability over time

To evaluate the environmental impact of the HES systems compared to a reference one containing the same TODGA extractant (0.25 mol/L) in dodecane with 5% octanol as phase modifier, two experiments were carried out to evaluate the thermal stability and volatility. Analysis was performed on prepared solvents in the absence of metal ions. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo (Greifensee, Switzerland) TG device using STARE V 13.00 software. Measurements were



conducted in 150 μL alumina crucibles. The mass loss was measured between 25 and 700 $^{\circ}\text{C}$ with a ramp of 10 $^{\circ}\text{C}$ per minute. After the experiment, the crucible was cooled down under air flow. To determine the sample volatility closer to industrial application, 1 gram of HES sample for $x_{\text{TODGA}}=0.3$ and 0.45 as well as the reference systems were kept in an oven (Venticell® from MMM Medcenter, Germany) at a fixed temperature of 50 $^{\circ}\text{C}$ for 2 months and weighted daily with a Mettler Toledo XS205 analytical balance with an accuracy of ± 0.00001 g.

2.6- Environmental impact

The environmental impact was evaluated at the laboratory scale by applying LCA methodology according to ISO 14040³⁸ and ISO 14044³⁹ standards. LCA consists in quantifying the environmental impacts of products, processes or systems throughout their life cycle. A cradle-to-gate approach was adopted including the stages of raw material production and solvent extraction stage. Data on the amounts of chemicals and electricity consumed, as well as volatile organic compounds (VOCs) emitted during solvent extraction stage, were measured during the experiments (Tables S1 and S2). Data on the environmental impacts of the production of the reagents and electricity consumed were sourced from the ecoinvent v.3.9.1 database⁴⁰ (Table S3). The impact assessment method selected to convert the consumption of resources and emissions into environmental impacts was the Environmental Footprint 3.1⁴¹.

3-Results and Discussion

3.1-Extraction and separation

An important aspect of extraction with HES is the effect of the ratio of HBD to HBA components. In this section, the ability of HES to extract REEs and iron (Fe) was evaluated as a function of the nitric acid concentration using three different molar ratios for the TODGA/DA system ($x_{\text{TODGA}} = 0.3, 0.45$ or 0.7). The results are compared with a reference system consisting of 0.25 mol/L TODGA in dodecane with 5% octanol, which is commonly used as a phase modifier to prevent third phase formation (Figure 2 and Figures S2 and S3). The experiments were conducted with different acidities in the aqueous phase (0.1, 1.0 and 3.0 mol/L of HNO_3) and with a constant concentration of 0.005 mol/L for all cations (Fe, La, Nd, Eu, Dy, Y) in the multi-element solution. The purpose of extending the study to other REEs beyond those found in permanent magnets is to evaluate the potential of the HES for intra-lanthanide separation as well as their separation from other trivalent cation contaminants, represented by Fe.



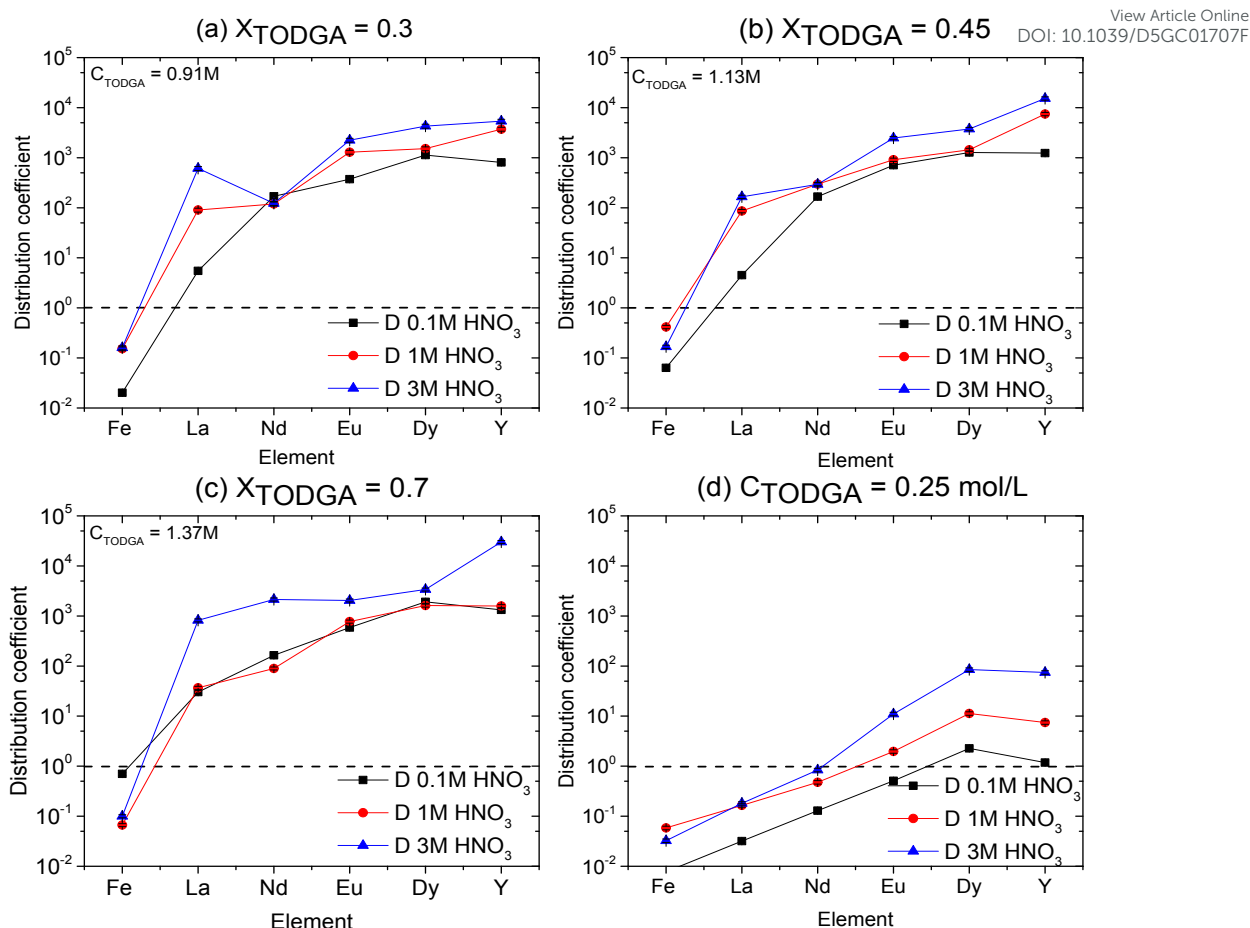


Figure 2: Distribution coefficient of lanthanides and iron for TODGA/DA systems at 0.1, 1.0, and 3.0 mol/L of HNO_3 : (a) $x_{\text{TODGA}} = 0.3$ ($[\text{TODGA}] = 0.91$ mol/L), (b) $x_{\text{TODGA}} = 0.45$ ($[\text{TODGA}] = 1.13$ mol/L), (c) $x_{\text{TODGA}} = 0.7$ ($[\text{TODGA}] = 1.37$ mol/L) and (d) reference system TODGA at 0.25 mol/L in dodecane with 5% volume of octanol.

Figure 2 shows that the extraction of Fe remains consistently low ($D < 1$) across all ratios and acidity conditions tested. In contrast, the extraction of REEs is remarkably efficient for the HES mixtures, with distribution coefficients ranging from 30 to an impressive value of 20,000, corresponding respectively to extraction efficiencies of 96.77% and 99.99%, respectively (Figure S2). In addition, nitrates are conventionally known to play a crucial role in the REEs extraction mechanism with TODGA. Consequently, the extraction efficiency increases with higher concentrations of nitric acid in the initial aqueous phase and is supported by the literature^{42,43}.

In comparison, the reference system extracts significantly fewer REEs, with a greater variation between light and heavy REEs. In contrast to the HES systems, significant extraction of heavy lanthanides occurs when HNO_3 concentration in the aqueous phase exceeds 1 mol/L, while light REEs are extracted to a lesser extent (with extraction percentages less than 50%). These results are consistent with data from the literature, which reports that TODGA selectively extracts REEs with a preference for heavy REEs over light ones^{44,45,46}. Comparing the TODGA/DA mixtures with the reference system (0.25 mol/L of TODGA), it can also be observed that the efficiency of REEs extraction improves with increasing TODGA content. The TODGA concentrations are of 0.9, 1.13 and 1.37 mol/L for the TODGA/DA mixtures ($x_{\text{TODGA}} = 0.3$; 0.45; 0.7), respectively. This observation supports the expectation that TODGA acts as a primary promoter in the metal extraction process. The HES systems also demonstrate greater values of separation factors (Figure S3) between lanthanides and Fe, and lower values for intra-lanthanides separation. This is consistent with the higher TODGA concentration in the HES systems, which enhances lanthanide extraction without significantly discriminating between individual



lanthanides. Conversely, the reference system achieves greater lanthanide separation at low acidity (Figure S3a), with a separation factor of 7 at 0.1 mol/L of HNO_3 , between Eu and Dy that are two of the more closely related lanthanides. This is notably higher than the separation factors below 2 observed for the HES. This effect is even more pronounced with the separation factor between Dy and La, which is about 1000 in the reference system compared to just 10 in the HES system. An HES system could therefore be advantageously applied to accumulate large amounts of lanthanides and no Fe, while the reference system at low acidity could be used as a secondary step to separate heavy and light lanthanides.

3.2-Loading capacity:

To evaluate the interest of the HES TODGA/DA system, it is essential to quantify the maximum extraction of metal. The loading capacity of Dy was measured by contacting the organic phases with aqueous phases of increasing Dy concentration. Different TODGA/DA mixtures (of $x_{\text{TODGA}} = 0.3, 0.45$, and 0.7) were contacted for 1 hour at 250 rpm with an aqueous phase (HNO_3 1 mol/L) containing Dy concentrations ranging from 0.1 g/L to 50 g/L. These results were compared with two reference systems using TODGA at 0.25 mol/L or 0.91 mol/L in dodecane containing 5% of octanol.

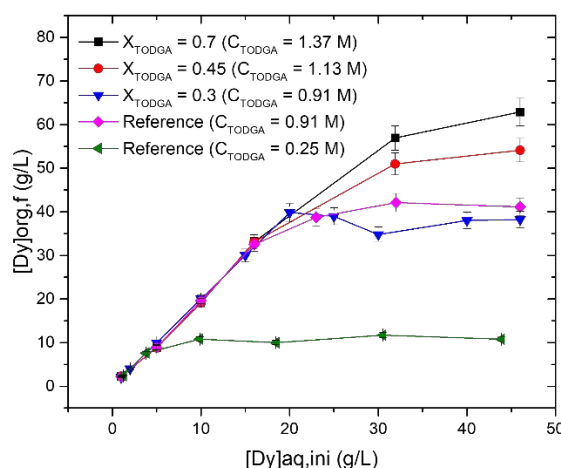


Figure 3: Loading capacity of the Dy of TODGA in the HES and the conventional system.

Figure 3 illustrates that the TODGA/DA ($x_{\text{TODGA}} = 0.3$) system can achieve a remarkable Dy recovery of up to 38 g/L at saturation. This performance is further enhanced in the TODGA/DA ($x_{\text{TODGA}} = 0.45$) and TODGA/DA ($x_{\text{TODGA}} = 0.7$) systems, which can reach Dy recoveries of up to 54 g/L and 62 g/L, respectively. These extraction capacities significantly exceed those of the conventional TODGA system (0.25 mol/L) in dodecane with 5% octanol, which reaches 13 g/L. In particular, the DES system with 30% of TODGA increases the extraction capacity by a factor of 3 compared to the conventional system. When comparing the performance at an equivalent TODGA concentration (0.91 mol/L) corresponding to $x_{\text{TODGA}} = 0.3$, the HES system and the conventional aliphatic solvent, exhibit comparable extraction efficiencies, with a ratio $\frac{[\text{Dy}]}{[\text{TODGA}]}$ of 3 to 4 for both systems as observed in previous studies^{47–49}. Although TODGA in the HES system does not provide a superior extraction efficiency when using an equivalent amount of TODGA in dodecane, the use of the HES system offers distinct advantages over the conventional system: it eliminates the need for a phase modifier to prevent third-phase formation, allows the use of significantly higher extractant concentrations, increases the metal loading capacity without any issue related to phase demixing^{50–52}.



As it can influence the mass transfer rates and the overall efficiency of the extraction process, viscosity can be considered as one of the main drawbacks of HES compared to the usual organic solvent/diluent used in liquid-liquid extraction^{28,29,53}. Therefore, it is crucial to thoroughly evaluate rheological behavior of HES to assess its suitability and reliability for industrial processes. A comprehensive study of HES viscosity, including temperature and concentration dependencies was therefore conducted. Using the same organic phase that was used in the loading capacity experiments at 25°C, the viscosity was measured as a function of temperature (Figure S4) and of the Dy loading in the organic phase (Figure 4).

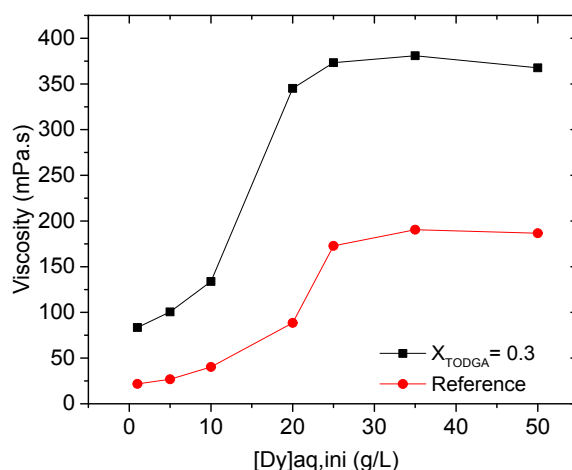


Figure 4: Evolution of the viscosity of the organic phase after contact with an aqueous phase containing different concentrations of Dy for the HES system (TODGA/DA ($x_{\text{TODGA}} = 0.3$; $[\text{TODGA}] = 0.91 \text{ mol/L}$) and the conventional system (TODGA 0.91 mol/L in dodecane + 5% octanol)

Figures S4 and 4 show that the viscosity is consistently higher for the HES than for the reference system, with values increased by a factor of 2 to 3. However, this behavior, which could pose challenges for the application, can be mitigated by increasing the temperature. As illustrated in Figure S4, the viscosity decreases significantly, from 400 to 100 mPa.s, when the temperature is raised from 25 to 50 °C for a HES loaded with 50g/L of Dy. Both figures also show that the viscosity is highly dependent on the metal extraction. In Figure 4, a significant increase in viscosity is observed after metal saturation, which occurs around $[\text{Dy}]_{\text{aq, ini}} = 20 \text{ g/L}$. The viscosity increases by a factor of 4 compared to its initial value before contact, rising from 71 mPa.s to over 375 mPa.s. This significant increase is attributed to the transition from a system dominated by hydrogen-bonding interactions prior to extraction, to one presenting ionic interactions between TODGA-Dy clusters after extraction.^{54,55} The emergence of these ionic interactions significantly alters the rheological properties of the solution, highlighting the importance of understanding the molecular interactions within the system to optimize the extraction process and ensure an efficient phase separation. It is important to note that the viscosity of organic phases can be significantly affected by their interaction with aqueous phases, especially after metal extraction.

In an industrial application, such increased viscosity could hinder the efficiency of the extraction process. However, traditional mixer-settler systems could be replaced by centrifugation to achieve clear phase separation. Furthermore, kinetic experiments presented in Figure S1, show that diffusion rates and kinetics are not affected in this viscosity range.

3.3-Determination of metals speciation by UV-vis spectroscopy



UV-vis spectroscopy experiments were performed to compare the extraction mechanism of Nd in the HES system and in the reference organic phase as it provides a unique signature of the complex formed with the extracted metal. The UV-vis spectrum of Nd complexes was also measured in the initial aqueous phase for comparison (Figure 5). Nd was chosen as a representative element for REEs and exhibits hypersensitive transitions in the visible wavelength region that are affected by complexation and notably by diglycolamide extractants^{56,57}.

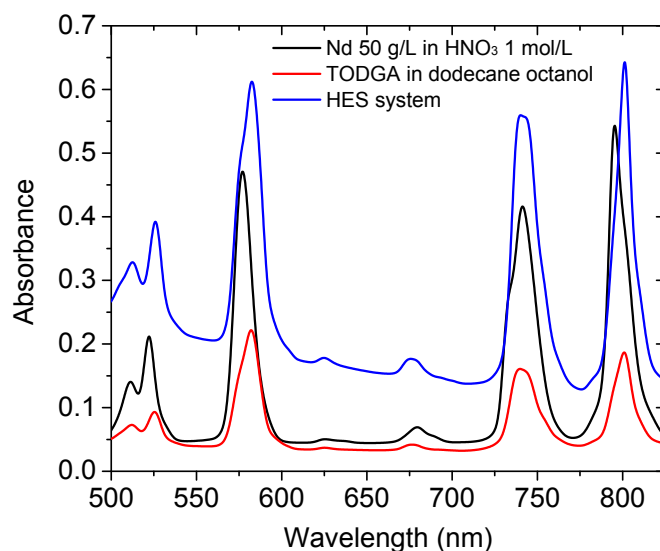
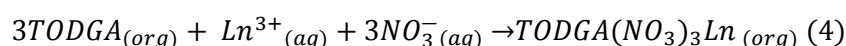


Figure 5: UV-vis-NIR spectra of Nd in HES (blue, [Nd] = 40 g/L in HES phase), reference 0.25 mol/L TODGA in dodecane with 5 vol% octanol (red, [Nd] = 12 g/L in organic phase), and in an aqueous phase (black, [Nd] = 50 g/L in 1 mol/L HNO₃)

The UV-vis spectra indicate that the signals are different between the aqueous and the organic phases, as evidenced by the shift to higher wavelengths of the peaks at 575 nm and 800 nm. This observation is consistent with a distinct Nd environment in the aqueous phase and its dehydration when it is chelated by the TODGA extractant in the organic phase, as observed in previous studies⁵⁷.

When comparing the spectra obtained from the HES and the reference organic phase, it is evident that the spectral fingerprints are identical, with no shift of the different peaks. This indicates that the Nd environment remains unchanged, and that the DA is not directly involved in the metal extraction process. Based on the results obtained for the loading capacity, and on the TODGA/REEs spectroscopic studies from the literature,^{56,58,59} it can be hypothesized that Nd is extracted by three TODGA molecules in the same metal environment in the eutectic mixture and in the conventional organic phase. Since the DA is not involved in the extraction mechanism, the extraction is only due to the TODGA component in the HES system, which operates by solvation in the same way as in a conventional solvent according to the following equation (4):



In order to evaluate the potential of the HES TODGA/DA system as an alternative to a conventional organic phase, additional key parameters essential for an efficient extraction process are investigated in the following sections.

3.4-REE stripping and HES recycling:

An important aspect to verify before asserting the reliability of the process is the feasibility of back extraction, also known as the stripping step. In industry, various reagents such as nitrates, chlorides,



sulfates, and also extractants are used as stripping solutions^{60–63}. Therefore, a preliminary screening of various stripping agents was first carried-out. After prior contact with an aqueous metal solution of 1 mol/L HNO₃ containing 1000 mg/L of Nd, the TODGA/DA HES phase ($x_{\text{TODGA}} = 0.3$) loaded with metallic elements was back-extracted by one contact with different aqueous phases, namely pure water, 1 mol/L HNO₃, 0.05 mol/L ethylenediaminetetraacetic acid (EDTA), and 0.1 to 1.0 mol/L *N,N,N',N'*-Tetraethyl Diglycolamide (TEDGA) in 1 mol/L HNO₃. EDTA is commonly used as a metal complexing agent, particularly for transition metals^{18,64}, while TEDGA⁶⁰ is a water soluble analog of TODGA. Their structures are available in Figure S5 of the ESI. As shown in Figure S6, this screening test demonstrates that the best results were obtained with a solution of 1 mol/L TEDGA diluted in 1 mol/L of nitric acid, which allowed the recovery of 95% of the extracted Nd after one cycle. This solution was therefore applied to successive extraction and stripping (back-extraction) cycles to evaluate recyclability of the HES.

Figure 6 shows the extraction efficiencies of 1000 mg/L each of Fe, La, Nd, Eu, Gd, Dy, Y and Yb from 1 mol/L HNO₃ solutions after 5 cycles of extraction and stripping. With the exception of Fe, which is not extracted, each extraction cycle recovers 95–100% of the REEs examined. Notably, the extraction efficiency for lanthanum decreases to 70% after the second cycle. This decrease is consistent with the preference of the TODGA system and the TODGA/DA system for heavy REEs.⁶⁵ Regarding the stripping cycles, the back-extraction process is very efficient for light REEs and less quantitative for some heavy REEs, such as Yb and Dy. This incomplete stripping slightly reduces the available extractants for the subsequent cycles, an issue that could be overcome in a real process by employing multiple stripping stages. Overall, this experiment demonstrates that the HES TODGA/DA mixture is reusable and remains highly effective after five cycles. This solvent recycling is a critical factor in the overall sustainability and cost-effectiveness of the extraction process. The ability to maintain high extraction efficiencies over multiple cycles reduces the need for frequent replacement of the extracting system, thereby reducing operating costs and waste generation.

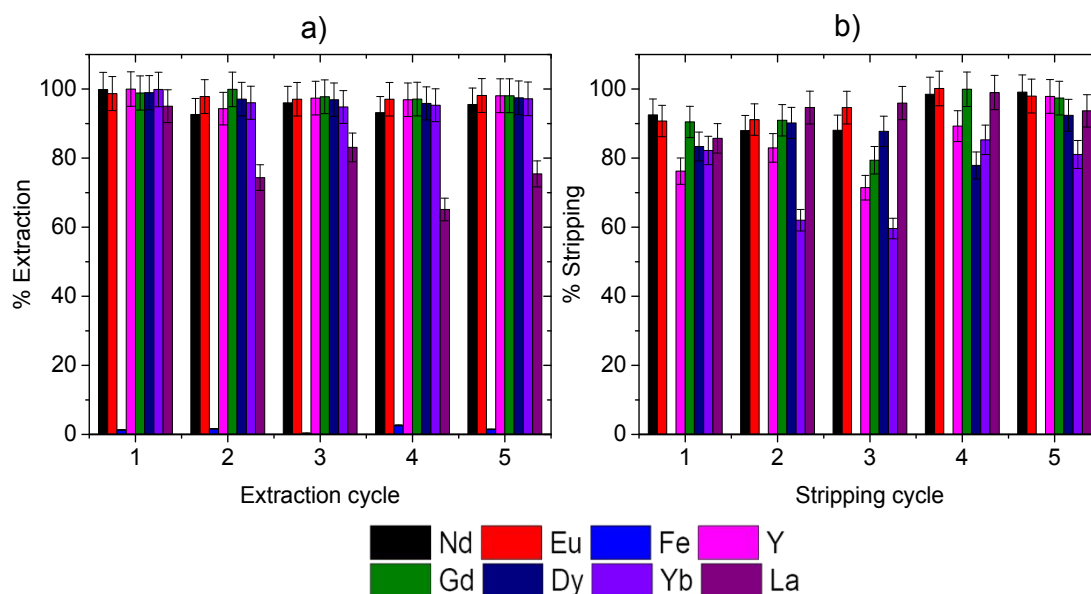


Figure 6: (a) Extraction cycle of Fe and REEs with the TODGA/DA system ($x_{\text{TODGA}} = 0.3$) (b) Stripping cycle of extracted REEs with TEDGA 1 mol/L after contact with TODGA/DA ($x_{\text{TODGA}} = 0.3$)

3.5-Validation on real leachate

To validate the capacity of HES for the recycling of REEs from permanent magnets, an extraction experiment was performed with HES systems composed of TODGA and DA ($x_{\text{TODGA}} = 0.3$) contacted





with different leachates derived from permanent magnets. These leachates were obtained from dissolution experiments conducted on NdFeB magnet powders using classical mineral acids, such as hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄) at a concentration of 1 mol/L, and acetic acid (AcOH) at a concentration of 1.6 mol/L. The resulting leachates contained neodymium (Nd), iron (Fe), boron (B), praseodymium (Pr), and dysprosium (Dy) at the concentrations listed in Table 1. It is worth emphasizing that the optimization of leaching conditions is not considered, with the purpose of this study to understand the metal partition in these various leachate compositions. After contact with the HES system (TODGA/DA, $x_{TODGA} = 0.3$), the extraction efficiencies for Nd, Dy, Pr, Fe and B were determined by ICP-OES measurements and plotted as distribution coefficients in Figure 7 and also plotted as extraction percentages in figure S7.

Table 1: Compositions of the leachates in the various tested leach solutions in mg of element leached for 1 g of magnets

Element	HCl (1 mol/L)	H ₂ SO ₄ (1 mol/L)	HNO ₃ (1 mol/L)	Acetic Acid (1.6 mol/L)
B	7.93	8.02	2.95	26.02
Fe	244.95	559.32	203.04	600.03
Dy	5.48	8.07	3.22	23.16
Nd	227.37	241.68	115.72	868.75
Pr	38.02	41.82	19.36	146.18

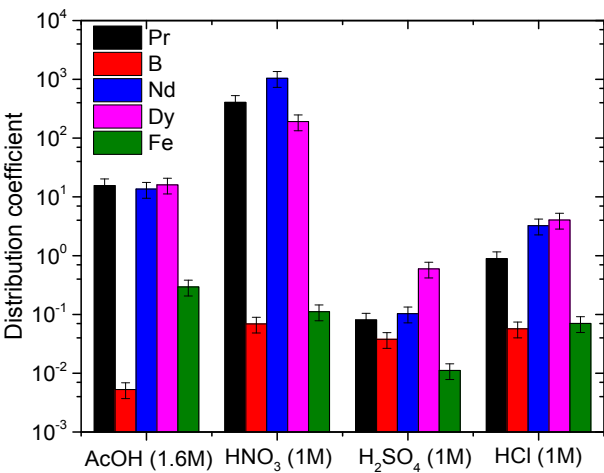


Figure 7: Extraction of cations (Pr, B, Nd, Dy, Fe) from various leaching solutions by the HES system with TODGA/DA ($x_{TODGA} = 0.3$).

These extraction results from real leachates show significant extraction of Pr, Dy, and Nd (with distribution coefficients, $D > 10$) when the extraction is performed with acetic acid or nitric acid solutions. A better selectivity towards Fe is obtained with the nitric acid leachate compared to the acetic acid. In contrast, the extraction of Pr, Nd, and Dy is significantly lower ($D < 1$) with leached solutions of HCl or H₂SO₄. Overall, the extraction efficiency of REEs follows the order HNO₃ > AcOH > HCl > H₂SO₄. This trend suggests that in a nitrate-rich medium both extraction efficiency and selectivity towards iron are enhanced, which is consistent with previous studies demonstrating the high efficacy of TODGA in extracting REEs from nitrate-containing media compared to the sulfuric or hydrochloric

media^{66,67}. The different extraction experiments confirm therefore that HES mixture can be applied as suitable media for lanthanide recovery. The distribution coefficient measured at 1 mol/L HNO₃ for the model solution is comparable in magnitude to that obtained from the real leachates. This further supports the suitability of the HES mixture for lanthanide recovery.

3.6-Comparison of the volatility between HES and reference system

Hydrophobic eutectic solvents are often praised for their low volatility. If this is true, low volatility in solvent extractions is particularly advantageous in applications aiming at reducing VOCs emissions, contributing to safer and more environmentally friendly processes. However, it was shown that the volatility of the non-ionic HES is determined by the volatility of the component with the highest vapor pressure⁶⁸. To compare the volatility of the HES and conventional extraction processes, thermogravimetric analyses were performed on the TODGA/DA system, in two compositions, as well as on the reference systems TODGA in dodecane without and with octanol (5% v/v) phase modifier (Figure 8a).

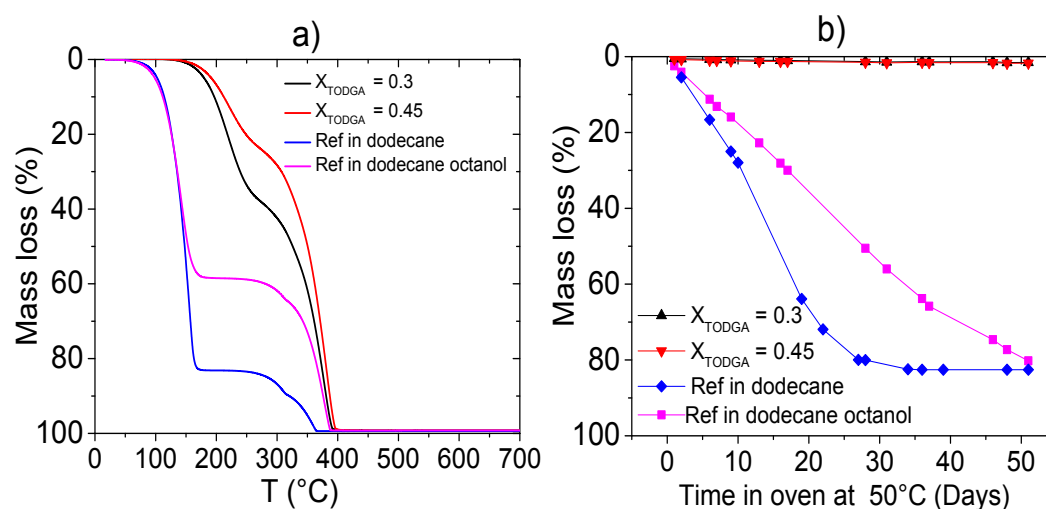


Figure 8: (a) Thermogravimetric analysis of TODGA/DA mixtures at various TODGA molar percentages and of the reference system TODGA in dodecane. (b) Mass loss due to evaporation in an oven at 50°C for each system

The results demonstrate that the reference system TODGA in dodecane (depicted in blue) undergoes significant evaporation and degradation, with over 80% of the substance lost at 163 °C. In contrast, the HES mixtures exhibit significantly higher thermal stability, with evaporation and degradation occurring at 150 °C with almost 60% of the substance lost at 350°C for $x_{\text{TODGA}} = 0.3$ and 50% for $x_{\text{TODGA}} = 0.45$ °C. This observation is further supported by the onset decomposition temperature, which corresponds to the temperature at which 5% mass loss occurs. The onset decomposition temperature is 100°C for the reference system and 180°C and 190°C for the two tested HES systems, which further demonstrates the higher thermal stability of the eutectic mixtures. To more accurately represent industrial conditions, an additional experiment was performed by maintaining the sample at a constant temperature of 50 °C for several days, with periodic weight measurements (Figure 8b). Under these conditions, TODGA in dodecane exhibited significant mass loss, with 80 % of its mass evaporating within 30 days corresponding to the total loss of dodecane. In stark contrast, the HES mixtures demonstrated remarkable stability, with a mass loss of only 5 % after 50 days. Considering the mass loss after 30 days at 50 °C, it can be estimated that the volatility of this HES has been reduced by a factor of 16, suggesting that the HES system could significantly reduce the evaporation of organic compounds if the HES precursors are carefully selected.



3.7-Environmental impact comparison of HES and reference systems using LCA methodology

The lower volatility of the HES system provides a significant operational advantage. It improves safety by minimizing the risk of vapor-related incidents and increases the process efficiency by reducing solvent losses through evaporation. To determine whether the lower volatility of the HES makes it a more sustainable solution, it is also important to evaluate the upstream impact of the solvent and chemical reagents required for its synthesis. This evaluation should include an analysis of the environmental footprint of the raw materials and the energy consumed in their production. Additionally, the extra energy requirements associated with centrifugation must be taken into account, as these factors could offset some of the environmental benefits gained from the lower volatility of the HES.

To validate the environmental benefits of replacing a conventional solvent with the proposed HES, a comparative LCA was conducted. LCA is inherently a multi-criteria approach, requiring to make several methodological choices. The proposed LCA does not represent a full-scale analysis capable of capturing the environmental impact of an industrial process. Rather, two laboratory-scale processes that use either a conventional solvent or the proposed HES systems to extract 1 kg of Dy are compared. Since these solvents are not currently applied at an industrial scale (for example, in Dy recycling from magnet leaching or Dy extraction from ores), it is currently impossible to accurately account for the parameters of a full-scale industrial process. Critical parameters such as solvent flows and volumes under industrial conditions are highly context-dependent and would be extremely difficult to estimate reliably.

Therefore, the LCA addresses a smaller scale, which still offers a meaningful representation of the environmental impact of replacing a conventional solvent with the proposed eutectic mixtures. The primary parameters to be assessed are those expected to differ the most between systems: the extraction efficiency, the chemical nature of the solvents, their viscosity, and their volatility. Indeed, the HES system exhibits extraction capacities that increase by a factor of 4, and due to the presence of dodecane, the volatility is 16 times higher for the reference system. This will have an effect on the comparative environmental impact study. In this comparative study, it is assumed that all other process parameters would remain constant in a hypothetical application. The LCA included the chemical production required to provide one ton of each solvent, as well as subsequent VOC emissions. These emissions were calculated based on the evaporation losses shown in Figure 9. The LCA also considered the increased energy demand of the centrifuge system required to separate the HES from the aqueous phases due to its viscosity, which is two to three times higher than that of the reference system. LCA inventory parameters are reported in Tables S1 and S2 for the conventional solvent extraction system (based on TODGA in dodecane with 5 vol% of octanol) and for the HES system at three ratios of TODGA ($x_{\text{TODGA}} = 0.3; 0.45; 0.7$).

The input and output flows were initially estimated per ton of solvent for the four systems, as shown in Figure S8 and S9. To reflect a functional unit representative of the extraction process efficiency, these flows were subsequently recalculated per kilogram of Dy extracted by each system, based on their respective extraction efficiencies at 1 mol/L HNO_3 (extracted from Figure 2). Seven impact categories were assessed based on the functional unit of 1 kg of Dy extracted under conditions of 1 mol/L HNO_3 . The impact factors representing significant environmental concerns related to chemical production and solvent use are illustrated in Figure 9. The other impact categories, such as the resource use in terms of fossil fuels, minerals and metals, and marine eutrophication, are presented in supplementary information (Figure S10).



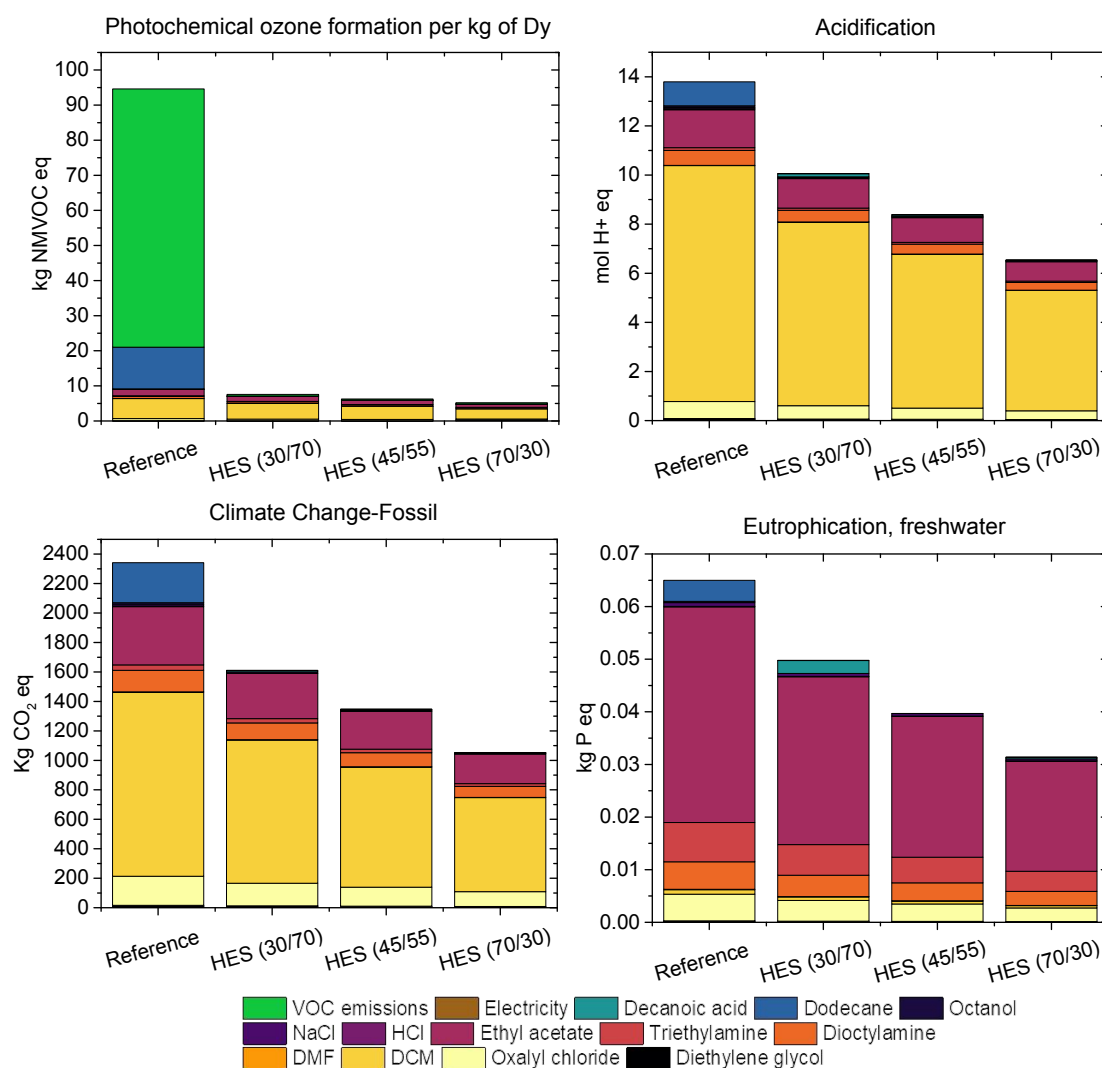


Figure 9: LCA assessment comparison between reference and HES systems to extract 1 kg of Dy

The results indicate that the primary impact is attributable to the TODGA synthesis (synthesis details are provided in the supporting information), as it relies on the use of solvents such as dichloromethane or ethyl acetate. These substances not only involve substantial upstream emissions but are also associated with high volatility, leading to the release of VOCs during the synthesis. Conversely, for photochemical ozone formation, the impact is mainly due to the volatility of the solvent, which results in the emission of VOCs. The reference system exhibits the highest environmental impact across all categories studied. In the climate change category, the reference system shows the largest carbon footprint, primarily driven by VOC emissions and energy-intensive synthesis steps related to the amount of TODGA needed to extract 1 kg of Nd. This is further exacerbated by the use of dodecane as a diluent.

Overall, the analysis shows that the use of HES systems reduces the global impact indicators studied. Specifically, the photochemical ozone formation is reduced by a factor of 9. Acidification is also reduced, with the impact decreasing from 13.5 mol H⁺ eq to 10 mol H⁺ eq and goes to 6 mol H⁺ eq for the system at 70% molar of TODGA. The reduction in acidification potential is crucial for minimizing soil and water acidification, which can have detrimental effects on ecosystems. Eutrophication of freshwater is another impact category that shows improvement with the use of HES systems. It is reduced from 0.065 kg P eq to 0.050 kg P eq., highlighting a reduction in nutrient pollution that can lead to ecological imbalances in aquatic environments. The climate change impact, the most commonly cited



indicator, is also significantly reduced when using HES systems. It decreases from 2300 kg CO₂ eq to 1600 kg CO₂ eq for the HES ($x_{\text{TODGA}} = 0.3$) system and further to 1000 kg CO₂ eq for the HES ($x_{\text{TODGA}} = 0.7$) system. View Article Online
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When comparing the impacts of producing one ton of solvent (as presented in Figures S8 and S9), it is interesting to note that the HES system only demonstrates an advantage in terms of photochemical ozone formation. This impact is reduced by a factor of three for the HES system due to its lower volatility. For the other impact categories, the HES system performs worse in all cases due to the larger amount of TODGA required by the HES system compared to the reference system. As previously described by Guerinoni et al.⁶⁹, reducing the evaporation of the organic phase is not sufficient for developing a more environmentally sustainable solvent extraction system. The less volatile system should also extract metals more efficiently.

Since the main impact comes from the extractant synthesis, even better results could be achieved by using bio-sourced products or with products that do not require environmentally toxic solvents for their synthesis. For the HES proposed in this study, the sole bio-sourced component is DA, which can be derived from coconut oil or palm kernel oil⁶⁴. To improve the sustainability of our system, the primary challenge would be the TODGA synthesis, which requires significant amounts of dichloromethane or ethyl acetate for synthesis or purification.

As mentioned above, this comparative study considers only lab scale parameters and assumes that all other process parameters would remain constant in a hypothetical application. To refine this analysis, it would be necessary to apply data obtained at the industrial scale in order to more accurately assess the impact of substituting traditional solvent mixtures with eutectic mixtures. This approach was not feasible in the preliminary analysis due to the necessity of estimating solvent flows and volumes under industrial conditions, which can vary significantly based on specific operational parameters and process scale. Applying such a lab scale approach is a significant approximation, but we believe the results of this LCA study still provide valuable insights into the potential environmental benefits of using eutectic mixtures over conventional solvents. Additionally, using the same solvent volume for both systems is an approximation, as in a real process, a lower volume would be used for the more efficient HES system. This effect could be taken into account in a sensitivity analysis, but it would not change the conclusion of this LCA study.

4-Conclusion

This study highlights the potential of a hydrophobic eutectic solvent (HES) composed of DA and TODGA, as a sustainable and efficient alternative for lanthanide extraction from nitric acid leachates. The investigated HES demonstrate highly efficient extraction of REEs, even at low acid concentrations, allowing a significant reduction of acid consumption and associated environmental impact.

This innovation offers distinct advantages over conventional organic phases by eliminating the need for volatile diluents and phase modifiers, thus simplifying the process and reducing the environmental and health risks. Key findings confirm that HES provides higher extraction due to the ability to increase the extractant concentration without causing third phase issue. As verified by UV-Vis analysis, HES systems containing a comparable extractant concentration achieve similar extraction performance to conventional TODGA-based systems due to the same metal-complex formation mechanisms. Importantly, it was pointed out that the hydrogen bond donor, DA, is not directly involved in the metal extraction process, but contributes to the overall solvent behavior.

This study further shows that the HES extracted lanthanides can be effectively stripped using an aqueous TEDGA solution, and that the HES can be reused at least five times with negligible loss of extraction performance. While the HES viscosity was found to be 2-3 times higher than that of conventional



systems, this did not affect the extraction kinetics nor efficient metal transfer. In the case of an industrial scale issue for easy phase separation, it could be mitigated by increasing the temperature or using centrifugation.

TODGA-based HES systems are therefore demonstrated to be a very efficient alternative to replace the conventional organic phases, which often relies on volatile diluents. Indeed, it has been quantified that the HES reduces the volatility of a classical organic phase by a factor of 16 thanks to a total mass loss reduced from 80% to 5%. Additionally, an LCA was conducted to objectively compare the environmental impact of the HES system with that of the extractant system conventionally used for REEs extraction. Considering the input and output flows in kilograms for the production of 1 kg of Nd by three HES mixtures and by a reference system TODGA in dodecane, a series of seven environmental indicators demonstrated that the HES system significantly improves the sustainability of the process.

Despite the high impact of extractant synthesis, which is used in higher amount in the HES, the new systems are less harmful to both the environment and human health, thanks to a higher Nd extraction capacity and highly reduced emissions of organic volatile compounds. Notably, the impact of additional centrifugation associated with the higher viscosity of the HES system, a common step in the extraction process, was found to be negligible.

Overall, the findings of this study show that the HES system composed of DA and TODGA offers a promising alternative for the extraction of lanthanides from nitric acid leachates. Its ability to maintain high extraction capacity, selectivity, reusability, and effective stripping capabilities without the need for volatile diluents and phase modifiers, coupled with its stability at elevated temperatures, makes it an attractive option for sustainable industrial processes. This innovative approach improves not only the efficiency but also the sustainability of lanthanide extraction.

Continued research into the fundamental interactions within HES will pave the way for even greater efficiencies and broader applications. Investigating the interactions between solvent components, particularly after metal and acid extraction, will optimize both structural stability and efficiency. The development of bio-sourced extractants could further increase the sustainability of HES systems. Addressing the impact of metal extraction on viscosity will also be critical to maintaining scalability and operational efficiency. This dual focus on mechanistic understanding and materials innovation ensures that HES will play a key role in the future of solvent extraction technologies.

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6-Conflict of interest

There are no conflicts of interest to declare.



7-Bibliography

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Data Availability Statement

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Data for this article, including metal partition results, solvent viscosity, UV-vis spectra, and LCA data, are available in the ESI and/or at Zenodo at URL – <https://zenodo.org/communities/designsx/>.

