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Basis for a new process for producing REE oxides from *Dicranopteris linearis*

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Abstract

Dicranopteris linearis (also known as *Dicranopteris dichotoma*) is a fern that grows naturally on the tailings of former rare earth element (REE) mines in southern China. It accumulates these elements in its aerial parts at concentrations that classify this plant as hyperaccumulator. The main objective of this research is to design a process to recover REEs directly from the dry biomass, without burning it. This process involves three steps: (i) extraction of REEs from the dry plant by leaching with a solution containing acid and/or complexing agents, (ii) precipitation of REEs with oxalate and (iii) calcination to prepare REE oxide. A methodology based on speciation calculation made it possible to determine operating conditions for precipitation by taking into account the influence of the species present according to the extraction method. Simulations were carried out using Chess software, allowing the calculation of the composition of a multicomponent solution at thermodynamic equilibrium. These operating conditions were then validated experimentally. REE extraction from the dry plant was significantly improved under acid conditions (with H_2SO_4) or with a strong complexing agent such as ethylenediaminetetraacetic acid (H_4EDTA). After optimization of the precipitation

conditions, REE precipitation yields were above 90%. After calcination, the final solid (REE oxide) contained ca 69% of the REEs present in the initial biomass. The use of sulphuric acid as an extracting agent resulted in the recovery of a solid composed of 52 wt % of REEs (based on metal content). Thus, this study proposes a new recovery route for these strategic elements with a REE concentration factor from soil to final solid of 2500.

Keywords

Agromining; hyperaccumulator plant; hydrometallurgy; leaching; EDTA; REE speciation

1. Introduction

Rare earth elements (REEs), including the 15 lanthanides as well as yttrium and scandium, share similar chemical properties. In recent years, they have been widely used in functional materials (especially in green and electronic technologies), as catalysts or as diagnostic reagents for magnetic resonance imaging, *etc.* [1]. The disparity of their resource around the world requires increasing extraction yields from primary ores, but also increasing their recovery from secondary materials (*e.g.* phosphogypsum from phosphoric acid production or red mud from bauxite) [2, 3]. Among these secondary resources, low grade soils and tailings from old mines could be suitable for REE recovery. However, new concentration processes have to be developed to be economically and environmentally competitive. Agromining represents a promising means of achieving this goal.

Agromining is an emerging phytotechnology, which uses natural and local hyperaccumulating plants to “harvest” metals [4]. The plants, which accumulate metals in their aerial parts at very high levels, are already being used to produce nickel from ultramafic soils, which are not concentrated enough for conventional mining industry [5, 6]. The extraction yield is over 100 kg of nickel per hectare in Mediterranean climate (with *Alyssum murale* [7] and is very promising in tropical areas (with *Phyllanthus rufuschaneyi*) [8]. The metal is then generally recovered by hydrometallurgical

processes from biomass ashes after burning [6]. The combustion stage removes organic matter and concentrates the metal. It also generates energy, which can be wittingly used. The direct extraction of the metal from the plants, without burning, has also been reported [9, 10]. The main advantages of this route are to limit the issue of gas treatment after metal contamination, and to use biomass after metal extraction for other applications (*e.g.* composting, anaerobic digestion, *etc*.). However, part of the soluble organic matter is co-extracted, which implies the development of specific processes to recover the metal [10].

The general objective of this work is to develop the agromining of REEs. Several hyperaccumulating plants have been identified worldwide [11], the concentration threshold being set at 0.1wt% of the dry biomass. One of them, *Dicranopteris linearis* (also known as *Dicranopteris dichotoma*) is a fern growing in southeastern China (subtropical climate). It is found naturally on the tailings of former mines (ionic adsorption clay deposits), at a plant density that makes large-scale cultivation possible.

While the interactions soil nutrients/*D. linearis* and metal translocation in the fern are fairly well documented [12-14], only one process for the extraction and purification of REEs has been reported. Recently, it has been demonstrated that the recovery of REE mixtures is possible by direct extraction, without burning the plant [15]. The recovery step consists of nitric acid extraction followed by adsorption of the elements on an ion exchange resin. Selective elution with nitric acid solutions of several concentrations allows recovery of aqueous REEs with a yield of *ca* 75% and a purity close to 80%. The main impurity is aluminium (Al), which the fern contains in large quantities; actually, this fern is also an hyperaccumulator of Al. Other strategies should therefore be applied to avoid this contamination, and among them, the precipitation of REE-oxalate ($C_2O_4^{2-}$) seems to be relevant. These intermediates are often studied to produce concentrated solids (REE-oxides) after calcination [16]. One of the main advantages of this strategy is the high efficiency of selective REE precipitation. In addition, solids after combustion are relatively pure, due to the transformation of oxalate with few residues (a molecule composed only of carbon and oxygen).

The aim of this research is therefore to synthetize REE-oxides after direct extraction of REE from the hyperaccumulator *D. linearis* and precipitation as oxalate. It consists of three steps: (i) a leaching step using extracting agents (organic or inorganic) followed by (ii) a selective precipitation step with oxalate, and (iii) calcination of the intermediate (Fig. 1). Considering that REEs are complexed by carboxylic acids in the plant tissues, the strategy is either to break these complexes using an acid solution or to shift the complexing equilibrium using a more powerful complexing agent than the one present in the plant. Sulphuric and citric acids have been selected for their acidic properties, and H_4EDTA and citrate for their complexing properties. H_4EDTA is a well-known complexing agent for REEs [17,18], as is citrate, which naturally transports REEs in plants through the xylem [13]. During precipitation with oxalate, competitive reactions must be taken into account. They are due to the presence of extracting agents introduced in the previous step, and to soluble organic matter (SOM) of the plant, which may interfere. No data are available on the precipitation of REEs by oxalic acid $C_2H_2O_4$ in the presence of high concentrations of sulphate, H_4EDTA and citrate. The proposed methodology relies on post-extraction stage speciation studies to investigate the feasibility of downstream unit operations. Hence to determine the optimal precipitation conditions (pH and molar ratio), simulations of REE speciation were first performed. In order to validate the model, an experiment was prepared with a synthetic solution of lanthanum (La) (chosen as representative REEs). The simulations were performed under the assumption that SOM plays no role during precipitation. Tests with a real extract allow us to evaluate its role during REEs recovery. The whole process is finally evaluated according to the composition of the REE oxide obtained after calcination.

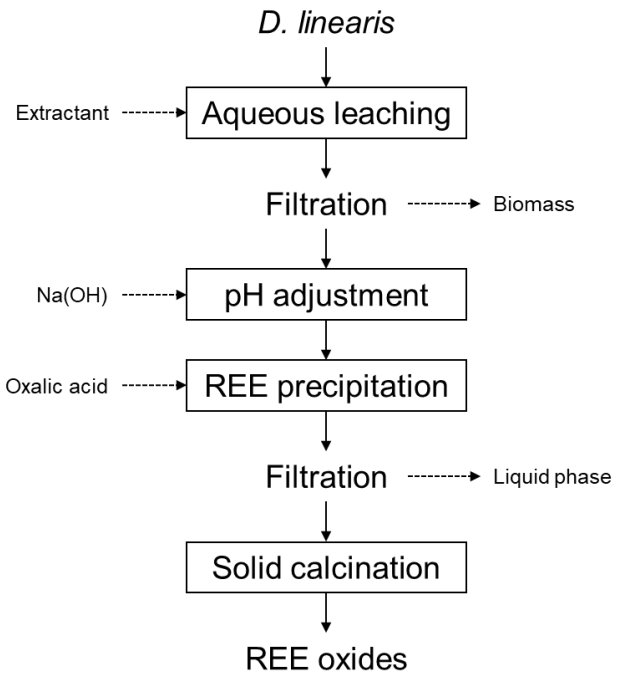


Fig. 1: Flowsheet of the proposed process to recover REEs from *D. linearis*

2. Materials and methods

2.1 Plant material

Samples of *Dicranopteris linearis* were collected in a former REE mine in Jiangxi Province (China), and dried for 24 h, at 70 °C. The concentration of REEs in the soil was in the range 300 to 700 mg per kg of dry soil [19]. The entire biomass (leaves and stem) was crushed with a blade grinder (SEB type 8100) before use. The median particle size, determined by laser diffraction (Malvern Mastersizer hydro 2000SM), was 369 µm.

2.2 Chemicals

Nitric acid (67-69%, Sigma Aldrich) was used for digestion prior to elemental analysis. Dehydrated disodium salt of ethylenediaminetetraacetic acid (99%), ACS reagent citric acid monohydrate (≥ 99.0%) and L(+)-glutamic acid monosodium salt monohydrate (99%) (supplied by Fisher Chemicals) and sulfuric acid (95-98%, Sigma Aldrich) were tested in the leaching step. Oxalic acid dihydrate ACS (≥ 99.5%, Sigma Aldrich) was used for the precipitation step, and synthetic solutions were prepared with lanthanum

nitrate hexahydrate (> 98%, ACROS Organics). Deionized (DI) water (Elga - Purelab Option) was used for all experiments.

2.3 **Elemental and structural analysis**

Prior to elemental analysis, the solid and liquid samples were digested in a microwave oven (UltraWave, Milestone) for 40 min with a set-point of 200 °C. Biomass samples or precipitates (*ca* 0.1 g) were randomly collected and digested by adding 5 mL of concentrated nitric acid (5 repetitions each time). For liquids, 2 mL of nitric acid was added to 2 mL of sample. After digestion, the leachate was introduced into a 50 mL flask with deionized water, then filtered by syringes equipped with filters (Phenomenex, pore size: 0.45 µm) and analysed by ICP-AES (Thermo ICAP6000). Calibration was performed with the custom standard PlasmaCAL (SCP Science) in a 5% vol. HNO_3 matrix. Two ranges of standard solutions were used, one for the REEs and one for the other elements. The major elements were analysed by radial measurement while the minor elements were analysed by axial measurement. Three replicates were made for each sample and a quality test was performed every 10 measurements with a control solution (PlasmaCAL, SCP Science).

X-ray diffraction analyses (XRD) were performed with a D8-Discover diffractometer (Brucker) (cobalt probe). The crystals were identified with PDF-02 databank of ICDD (International Centre for Diffraction Data). EDX (Energy dispersive X-ray spectrometry) analyses were performed with a JSM-6490LV microscope (Jeol).

2.4 **REE extraction and recovery from biomass**

To study the effect of each agent on the efficiency of REE extraction, the fern biomass was leached with six aqueous solutions (solid/liquid ratios S/L = 3 g/100 mL, 2 h, magnetic stirring): deionized water, H_2SO_4 (0.25 M), citric acid (1 M) (pH = 1.6 and 4.0, adjusted with NaOH), citrate (1M) (pH = 8.0, adjusted with NaOH) and *EDTA* (0.05 M) (in the following text, EDTA written in italic refer to the generic ethylenediaminetetraacetic acid, whatever its chemical form). The latter complexing agent was added in the disodic form Na_2H_2EDTA (to obtain an extraction at pH 4.5 (predominance area of H_2EDTA^{2-}). This agent can create a complex with REE, without

generating insoluble REE hydroxides (at pH higher than 7-8). Solid particles were separated from solutions using 0.45 µm porosity cellulose filter papers (Whatman).

REE speciation was investigated and simulated at 25 °C using CHESS (Chemical Equilibrium with Species and Surfaces, version 5.0.8) software [20]. The stability constants of La with *EDTA* and oxalate were implemented in the default database EQ3/6 (already containing data on La and sulphate interactions) [21].

A synthetic solution (*ca* 300 mL) was prepared, containing lanthanum ($La(NO_3)_3$, $2.3\ 10^{-3}$ mol) and Na_2H_2EDTA ($4\ 10^{-3}$ mol). The pH adjustment (between 2 and 8.5) was carried out with 1 M HNO_3 solution and oxalic acid was added in a molar ratio of 1 with Na_2H_2EDTA ($4\ 10^{-3}$ mol). The final pH was measured. After one hour of mixing, precipitates were filtered and dried. The liquid phases were analysed by ICP.

After simulation and determination of optimal precipitation conditions, pH was adjusted to 2.6 (with 1 M NaOH solution) and to 2.3 (with 1 M HNO_3 solution) for H_2SO_4 and Na_2H_2EDTA extracts respectively. In the latter case, this caused the formation of a solid S1, which was separated and analysed (ICP and XRD). Oxalic acid was then added (molar ratio of 0.16 and 1.56, respectively) and the solutions were stirred during 1 h at 20 °C. Precipitates (S2 and S3 respectively) were filtered, washed with deionized water and dried at 100 °C. They were calcined at 700 °C for 2 h to obtain S4 and S5.

3. Theory

The addition of oxalic acid to a solution containing REEs and *EDTA* will affect the speciation

. The distribution of the chemical forms of the three species as a function of pH is exhibited in Fig. 2. In this environment, many competitive reactions can take place, including those represented by Equations 1-3.

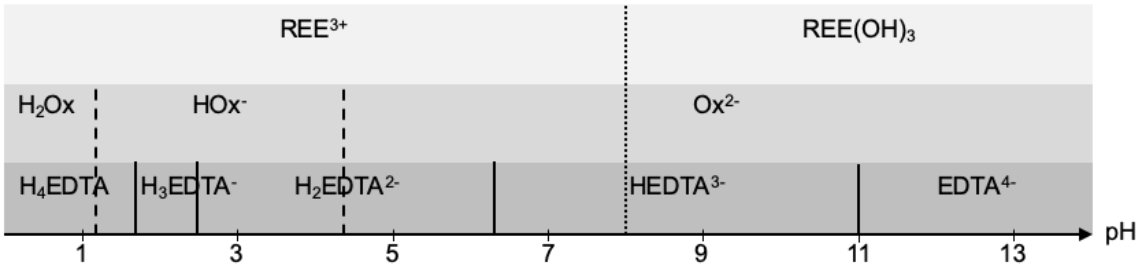


Fig. 2: Species prevalence as function of pH for REE, oxalic acid and *EDTA*

Precipitation of REE-oxalates:	$3\ Ox^{2-} + 2\ REE^{3+}$	$\overset{1}{\underset{2}{\rightleftharpoons}}$	$REE_2Ox_{3(s)}$	Eq. 1
Complexation of REE-*EDTA*:	$EDTA^{4-} + REE^{3+}$	$\overset{1}{\underset{2}{\rightleftharpoons}}$	$REEEDTA^-$	Eq. 2
Deprotonation of oxalate:	HOx^-	$\overset{1}{\underset{2}{\rightleftharpoons}}$	$Ox^{2-} + H^+$	Eq. 3

Ideally, to promote precipitation, the REE^{3+} and Ox^{2-} ($C_2O_4^{2-}$) forms should be preferred to obtain the insoluble complex REE_2Ox_3. However, in the presence of *EDTA*, the REEs are theoretically complexed at pH higher than 1.9 (Fig. 2). Two other aspects must also be taken into account:

(i) the very low solubility of the precipitate REE_2Ox_3 (Ks between $5\ 10^{-30}$ and $4.5\ 10^{-32}$ [22]). This implies that the presence of a very small quantity of deprotonated oxalic acid can lead to the formation of the precipitate. The latter inevitably leads to the displacement of reaction 3 in the forward direction;

(ii) only stability constants between $EDTA^{4-}$ and $HEDTA^{3-}$ are available. However, due to the *EDTA* excess introduced during extractions, REEs are complexed in totality with these two forms below pH 2.

Only modelling that takes all these data into account can enable optimum precipitation conditions to be found. Due to the large number of species involved, the Chess software was used [20], after having completed its database with the stability constants given in Table 1. Conventionally, the stability constant of the formation reaction of a species

(Eq. 4) is given by Eq. 5. The species present on the left side of the equilibrium, called "basis species", are usually written in their deprotonated form.

$$xA^{a+} + yB^{b-} \rightleftharpoons A_xB_y{}^{(ax-by)} \quad \text{Eq. 4}$$

$$K = \frac{\left[A_xB_y{}^{(ax-by)}\right]}{[A^{a+}]^x.[\,B^{b-}]^y} \quad \text{Eq. 5}$$

Table 1: Stability constants used for speciation determination

Basis species		Species formed	Log K (25 °C)*
$Ox^{2-} + H^+$	⇌	HOx^-	4.27
$Ox^{2-} + 2\ H^+$	⇌	H_2Ox	5.52
$Ox^{2-} + La^{3+}$	⇌	LaOx+	6.00
$2\ Ox^{2-} + La^{3+}$	⇌	$LaOx_2^-$	9.55
$3\ Ox^{2-} + La^{3+}$	⇌	$LaOx_3^{3-}$	11.59
$3\ Ox^{2-} + 2\ La^{3+}$	⇌	La_2Ox_3	28.23
$EDTA^{4-} + H^+$	⇌	$HEDTA^{3-}$	10.95
$EDTA^{4-} + 2\ H^+$	⇌	H_2EDTA^{2-}	17.22
$EDTA^{4-} + 3\ H^+$	⇌	H_3EDTA^-	20.34
$EDTA^{4-} + 4\ H^+$	⇌	H_4EDTA	22.56
$EDTA^{4-} + 5\ H^+$	⇌	H_5EDTA^+	24.06
$EDTA^{4-} + La^{3+}$	⇌	$LaEDTA^-$	17.94
$EDTA^{4-} + H^+ + La^{3+}$	⇌	LaHEDTA	20.40

*The data is corrected to zero ionic strength using Davies equation.

4. Results and discussion

4.1 Elemental composition of *Dicranopteris linearis*

The results of the *D. linearis* elemental analysis are presented in Table 2. Like all plants, the fern is rich in K, Ca, Mg. However, it contains high levels of Si and Al, which is a common characteristic of this plant [23]. The threshold for Al hyperaccumulation is set at

0.1%, indicating that this plant can be considered as Al - hyperaccumulator. Concerning REEs, La, Nd and Ce were the main elements identified. Pr, Sm, Y and Gd were also present but at lower concentrations. The analysis shows that *D. linearis* can accumulate more than 3 g of REEs per kg of dry biomass (0.30%). This means that this plant batch can be considered as a REE hyperaccumulator (threshold fixed at 1 g kg^{-1}).

In the literature, concentration in plant tissues are generally measured between 0.023 and 0.26% [15]. The plant studied is therefore very rich. It mainly accumulates light REEs.

Table 2: Composition in major cations and rare earths in *Dicranopteris linearis* (wt%) (confidence ranges are determined with 3 replicates)

Element		Dry biomass
REEs	La	0.128 ± 0.010
	Ce	0.113 ± 0.013
	Nd	0.088 ± 0.014
	Pr	0.027 ± 0.007
	Sm	0.014 ± 0.002
	Y	0.012 ± 0.002
	Gd	0.007 ± 0.001
	Total	0.389 ± 0.045
Other elements	Si	1.65 ± 0.05
	K	0.254 ± 0.031
	Al	0.205 ± 0.043
	Ca	0.174 ± 0.036
	Mn	0.051 ± 0.012
	Mg	0.048 ± 0.007

4.2 **Extraction of REEs from *D. linearis***

The extraction yield of REEs is defined by Eq. 6:

$$Extraction\ yield\ of\ REEs = \frac{mass\ of\ REEs\ in\ the\ extract}{intial\ mass\ of\ REEs\ in\ the\ plant}\ x\ 100 \qquad \text{Eq. 6}$$

Fig. 3 compares the extraction yield of REEs (Eq. 6) from biomass with the six extracting solutions: deionized water (blank sample), H_2SO_4 (0.25 M) (strong mineral acid, pH < 0.5), citric acid (1 M) (weak carboxylic acid) at two pHs (1.6 and 4), citrate (1 M) (complexing agent) at pH 8, and *EDTA* (0.05 M) (strong chelating agent) at pH 4.5. Experiments were carried out under optimal conditions because the biomass had been

finely ground (therefore the diffusion limitations were low), and the solid/liquid ratio was low.

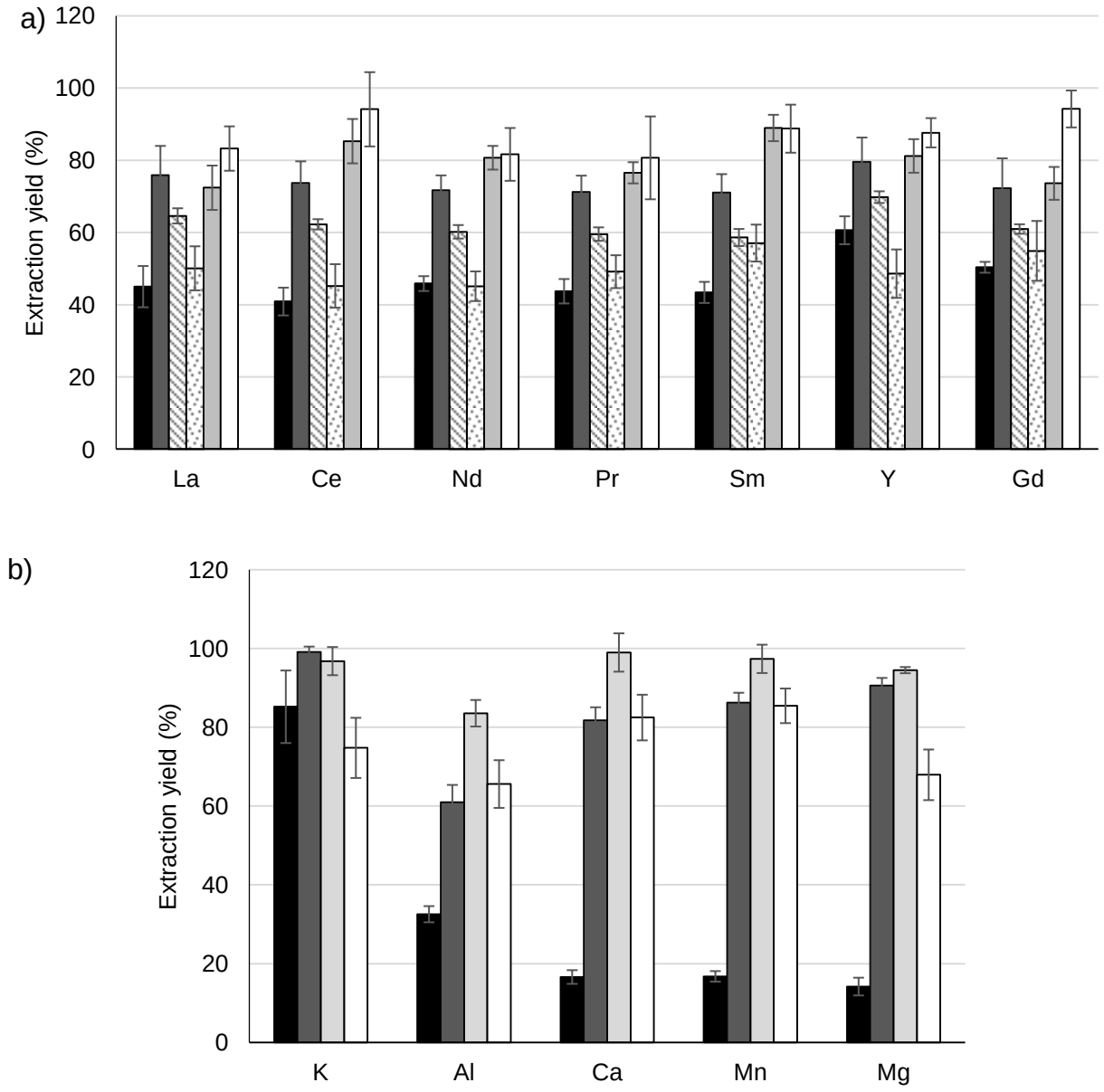


Fig. 3: Extraction efficiency of REEs (a) and other elements (b) using, H_2O ■, citric acid (1 M, pH 1.6) ■, citric acid (1 M, pH 4) ▨, citrate (1 M, pH 8) ⊡, H_2SO_4 (0.25 M) □, and Na_2EDTA (0.05 M) □

The results show, as a first observation, that the major REEs contained by the plant behaved in a very similar way during their extraction. With water, an extraction yield between 40 and 60% was obtained. Na_2EDTA and H_2SO_4 were the most efficient extracting agents with an almost similar yield > 80%. Citric acid had less effect, but its efficiency increased as the pH decreased. At pH 8, no difference with water was recorded. The results indicate that REEs can be extracted with very good yields under acidic conditions, or with a strong complexing agent. Indeed, the only acidity of the *ETDA* solution cannot explain the results obtained with this molecule (better extraction yields at high pH compared to citric acid).

The stability constants of REEs with the *EDTA* ligand are relatively high, with a log K between 15 and 20 [17, 18]. They are certainly higher than those of the various REE related compounds in biomass. The formation of REE-EDTA complexes can thus make it possible to displace the reactions that are at the origin of the interactions between REE and organic matter. Insofar as these interactions help to maintain the REEs within the biomass, this leads to better extraction. In the case of citrates, the stability constants of the REE-citrate complexes are lower. The fact that the equilibria involved do not allow sufficient displacement of the reactions at the origin of these interactions could explain a low extraction. For the other elements, yields in water were low (< 20%), except for K which had a very high extraction yield (> 80%). This was also the case for all the other solutions used. K is known as a very extractable element from hyperaccumulators [10]. The extraction of divalent and trivalent elements was improved by the addition of an acid or a complexing molecule. However, lowering the pH is to be preferred to increase their extraction yields.

In conclusion, even if REEs are directly extractable from biomass with water, higher yields (> 80%) are obtained either with strong complexing agents (*EDTA*) or with strong acid. These two options were selected for the following.

4.3 **Precipitation of REEs in *EDTA* medium with oxalate**

4.3.1 **REE speciation in presence of *EDTA* and oxalic acid**

To precipitate REEs, oxalic acid was added to the *EDTA* extract. The co-existence of *EDTA* and oxalic acid leads to the formation of a large number of chemical species. As the former is a tetraacid and the latter a diacid, the concentrations of the different chemical forms depend on the pH. These different forms react with the REEs to form soluble species such as $REEEDTA^-$ or insoluble species such as REE_2Ox_3, this last compound being the desired one. The concentrations of $EDTA^{4-}$ and Ox^{2-} increase with increasing pH, but the precipitation of insoluble REE hydroxides increases at the same time. Therefore, the search for a pH high enough to obtain the Ox^{2-} form that allows the precipitation of REEs (Eq. 1) under the oxalate form is a compromise to avoid high solubilization of REEs due to the complex formed with $EDTA^{4-}$ (Eq. 2).

Lanthanum was chosen as a representative REE, and the composition of a solution containing La, oxalate and *EDTA* was simulated as a function of pH, using Chess software. Results are represented by lines in Fig. 4. The concentration term on the y-axis does not correspond to the conventional definition of concentration. In the Chess nomenclature, for a solid, it is the number of moles of precipitates per litre of solution. Only the main species are shown in this figure. Under very acid conditions (pH < 1), La is a trivalent cation (La^{3+}). As the pH increases, it reacts with oxalate to form insoluble La oxalate ($La_2(C_2O_4)_3$), then it is complexed with *EDTA* (to give soluble $LaEDTA^-$). Finally, at very high pH (> 12), La hydroxide precipitates. At pH between 1 and 2, La is totally precipitated as oxalate. Above this pH range, $LaEDTA^-$ appears to become predominant at pH 4.5, and the only species at pH > 5.3.

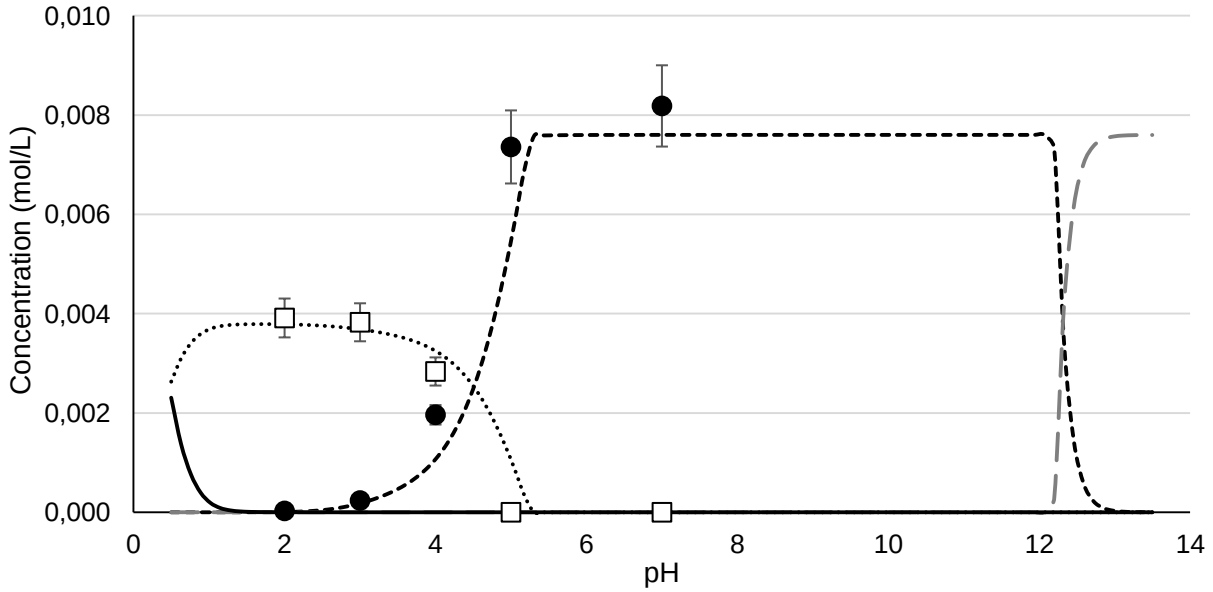


Fig. 4: Speciation of lanthanum in oxalic acid and EDTA solutions (simulations represented with lines and experimental points with dots): La^{3+} ▬, La_2Ox_3 ..... and □, $LaEDTA^-$ ▬ ▬ and ●, $La(OH)_3$ – –

4.3.2 Validation of speciation simulations and determination of optimal conditions

In order to validate the results obtained in the previous part, a synthetic solution containing La, *EDTA* and oxalic acid was prepared at different pH values (2 to 7). Precipitate masses and concentrations of La were measured after reaction (confidence intervals were estimated at 10%). The experimental results are plotted in Fig. 4. Overall, a very good agreement was found between the experimental results and the simulations.

Based on these results, it can be concluded that at a pH between 1.2 and 2.3, REEs precipitate as oxalate, even in the presence of a high concentration of *EDTA* in solution. The simulations also indicate that as *EDTA*/$C_2H_2O_4$ molar ratio increases, the pH corresponding to the total complexation of La with *EDTA* decreases (from 5.2 to 4.6, when the *EDTA* concentration is multiplied by 5). Conversely, when the amount of oxalic

acid is multiplied by 5, this pH increases to 6. In addition, for a given concentration of La, increasing the addition of oxalic acid limits the formation of La^{3+} and increases the pH range (especially at low pH) at which lanthanum can be precipitated.

4.3.3 **Precipitation of REEs in biomass extract**

a) pH adjustment

Firstly, the extract at pH 4.1 was acidified in order to reach the previously defined pH (*ca* 2.3), resulting in the formation of a first precipitate S_1 (6.5 g L^{-1}) from the protonation of *EDTA* in the H_4EDTA form, which has a low aqueous solubility. This precipitation was confirmed by XRD analysis (Fig. 5). All identified peaks corresponded to *EDTA*. No other molecules have been identified. During extraction, the molar ratio *EDTA*/REEs was approximately 21 so that competitive reactions between REEs and the other elements present in solution did not influence their extraction. This molar ratio could be optimized, however, even in the present conditions, half of the *EDTA* (45%) can be recovered and reused after filtration.

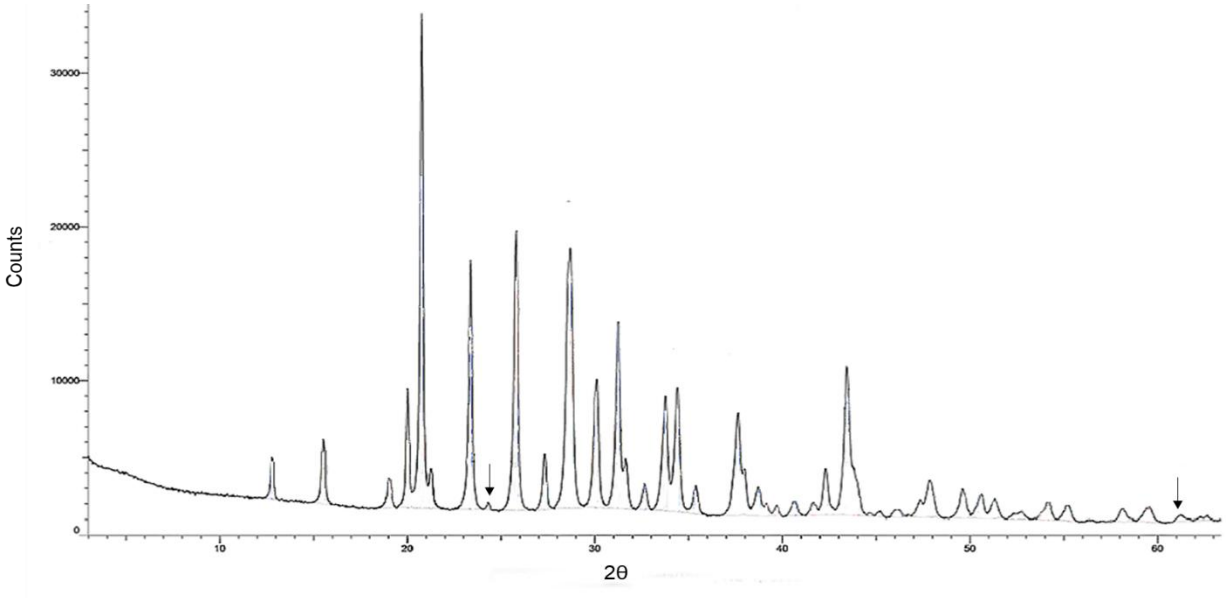


Fig. 5: Diffractogram of the solid S_1 obtain after pH adjustment for extraction with *EDTA.*

All the peaks correspond to *EDTA* (except the two marked with an arrow)

Analysis of this solid showed that less than 2% of the REEs were lost at this stage. This percentage was calculated from the amount of initial biomass. Other elements are also identified: 6.5% and 1.5% for P and Ca respectively. For the other elements, only 0.4 to 0.6% of the initial biomass content is found in S_1. This step could be a way to recycle.

b) REE precipitation using oxalic acid

The addition of oxalic acid caused a decrease in pH. To ensure that the pH is far from the lower limit of precipitation, a large excess was introduced (molar ratio oxalate/REE = 70), giving a final pH of 1.3. The large amount of reagent was also chosen to reduce competition from other cations and SOM (organic carbon concentration: 7.0 ± 0.2 g L^{-1}).

The formation of the oxalate precipitate (S_2) was instantaneous. After filtration, analysis of the extract showed that REE precipitation was almost complete. Concentrations of Ce, Gd, Pr and Sm were below the detection limit (10 µg L^{-1}) and less than 1% remained in solution for the other three main REEs (La, Nd, Y). Thus, this process can recover 65.9 to 72.2% of the REEs present in the initial biomass. The organic matter had no influence on the operations implemented.

The recovered solid (2.56 g L^{-1} of extract, 42.6 mg g^{-1} of raw biomass) was washed with deionized water, which removed most of the sodium, coming from the addition of *EDTA* during extraction. Finally, the precipitate contained 4.62% (27.3 mg) of REEs, which was 13 times more concentrated than the starting plant (Table 3). Calcium was the major impurity in the solid.

Table 3: Elemental composition of the precipitate S_2 (%), obtained after oxalic acid addition in the extract with *EDTA* (confidence ranges are determined with 3 replicates)

Element		**wt%**
REEs	**Total**	4.621 ± 0.489
Other elements	Ca	0.456 ± 0.012
	P	0.117 ± 0.003
	K	0.043 ± 0.001
	Al	0.029 ± 0.001
	Pb	0.028 ± 0.001
	Na	0.020 ± 0.001
	S	0.015 ± 0.001

Stricter pH control and optimization of the amounts of *EDTA* and oxalic acid used during the extraction would certainly improve the REE content of the S_2 precipitate. Due to the low content (REEs and impurities), it appears that an excessive amount of *EDTA* has still precipitated. This was confirmed by an XRD analysis of the precipitate, where only *EDTA* was identified.

Even in choosing better conditions, it seems difficult to avoid completely this co-precipitation of EDTA, which will be lost during the calcination step. As it is an expensive reactant, precipitation in H_2SO_4 medium was also tested.

4.4 Precipitation of REEs in H_2SO_4 with oxalate

4.4.1 REE speciation in the presence of H_2SO_4 and oxalic acid

As with the previous approach, the objective is to precipitate REEs as oxalate. The insoluble form referred to is $La_2(C_2O_4)_3$. However, in the presence of sulphuric acid, REE sulphate complexes are formed, with $REE(SO_4)^+$ being the predominant species ($REE(SO_4)_2^-$ is negligible all the time). A typical simulation of the equilibria is exhibited in Fig. 6. The precipitation of REEs as oxalate depends on pH. At low pH, sulphate forms solubilize REEs (pH is below the pKa of oxalic acid (1.2), $C_2H_2O_4$ is predominant), while hydroxides are formed under alkaline conditions. When the sulphate concentration is divided by 2, the pH corresponding to the formation of $REE(SO_4)^+$ decreases from 2.5 to 2. Around pH 3.5 - 4 and above, two species of oxalate coexist, $La_2(C_2O_4)_3$ and $La(C_2O_4)_3^{3-}$. Of course, the higher the oxalate/REEs ratio, the higher the concentration of $La(C_2O_4)_3^{3-}$ (this species is very low when the oxalate/REE molar ratio is less than about 30). Therefore, there are two advantages to not raising the pH of the solution too much: less reagent used and no risk of formation of an ionic REE oxalate compound. Based on these results, the pH of the solution should be set between 2.5 and 3.0 to optimize REE oxalate precipitation.

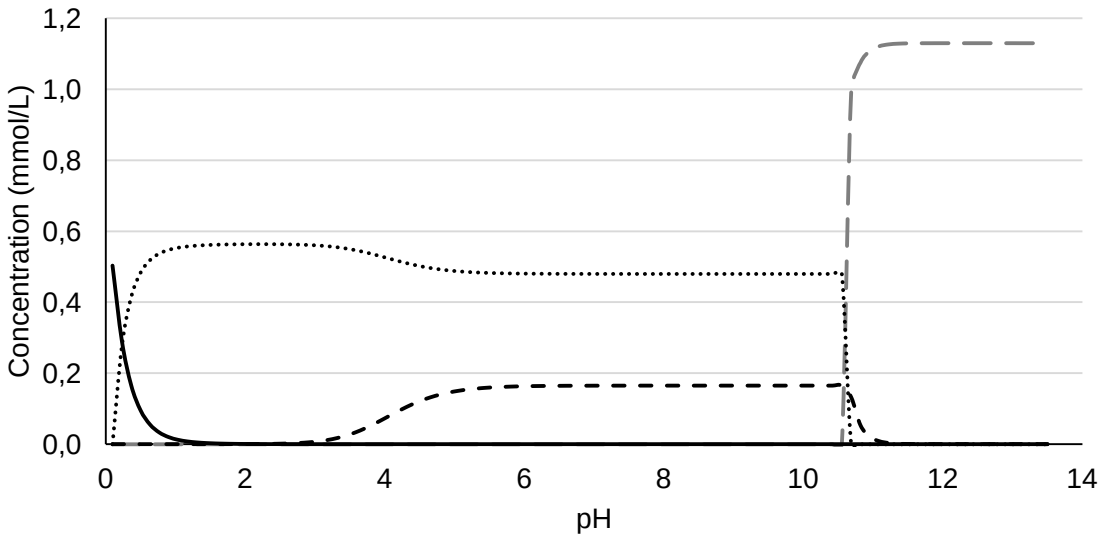


Fig. 6: Simulations of lanthanum (1.13 mM) speciation in oxalic acid (80 mM) and sulphate (250 mM) solutions:

$LaSO_4^+$ ▬, La_2Ox_3 ....., $LaOx_3^{3-}$ ▬ ▬, $La(OH)_3$ ▬ ▬

4.4.2 **Precipitation of REEs in biomass extract**

Following the recommendations determined by simulation, the pH of the extract obtained with *D. linearis* was first adjusted to 2.6 by NaOH addition (the initial pH was 0.8). After addition of oxalic acid (8 mmol for 0.37 mmol of REE), a precipitate S_3 appeared directly. After filtration, analysis of the aqueous solutions showed that 90% of REEs precipitated. The 10% remaining in solution were mainly La and Y. Fig. 7 shows the percentage of REE oxalate precipitation in relation to the initial content of the plant, as well as what remained in solution. The addition of oxalic acid resulted in the precipitation of 68.6% of the initial REEs (present in the initial biomass).

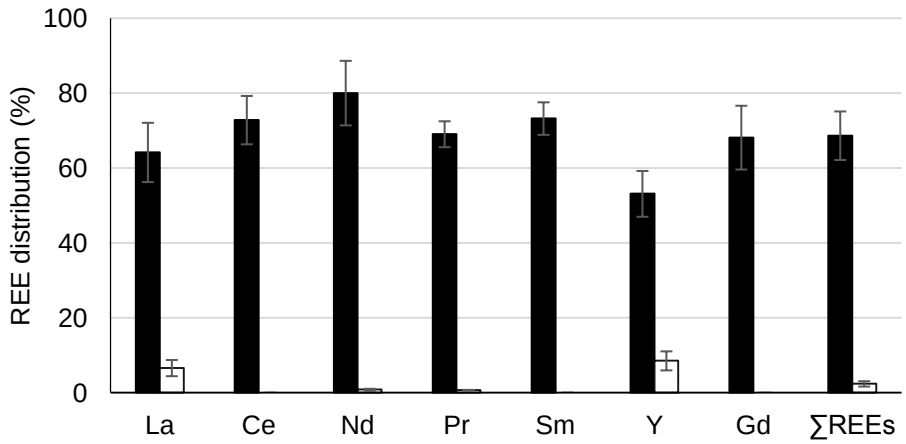


Fig. 7: Distribution (relative to the initial plant content) of REEs after precipitation with oxalic acid in H_2SO_4 extracts: oxalate precipitates ■, final solutions □

The other elements were also analysed to assess the purity of the REE-oxalate precipitate (Table 4). The mass ratio of REEs in this solid was 52.35%. Identified impurities represent 3.13% by mass. Considering that REEs are precipitated as Ox_3REE_2 the remainder of this mass corresponded to the oxalate. The main impurity was Na, from the sodium hydroxide solution used to neutralize the extract. A better washing of the solid could certainly reduce this impurity.

These results prove that SOM did not inhibit precipitation under these conditions. The REE content is more than 10 times higher in S_3 (H_2SO_4) than in S_2 (*EDTA*) (52.4 and 4.62% respectively), while the recovery yields are similar (68.6 and 69.3% respectively). This is due to the presence of *EDTA* in S_2.

Table 4: Elemental composition of the precipitate S_3 (wt%), obtained after oxalic acid addition in the extract with H_2SO_4 (confidence ranges are determined with 3 replicates)

Element	S_3 (wt%)

REEs	La	21.00 ± 4.86
	Ce	7.42 ± 2.29
	Nd	14.66 ± 2.70
	Pr	4.08 ± 1.88
	Sm	2.31 ± 0.89
	Y	1.84 ± 0.45
	Gd	0.99 ± 0.37
Other elements	Na	2.00± 0.69
	K	0.22 ± 0.10
	Al	0.31 ± 0.17
	Ca	0.39 ± 0.13
	S	0.11 ± 0.05

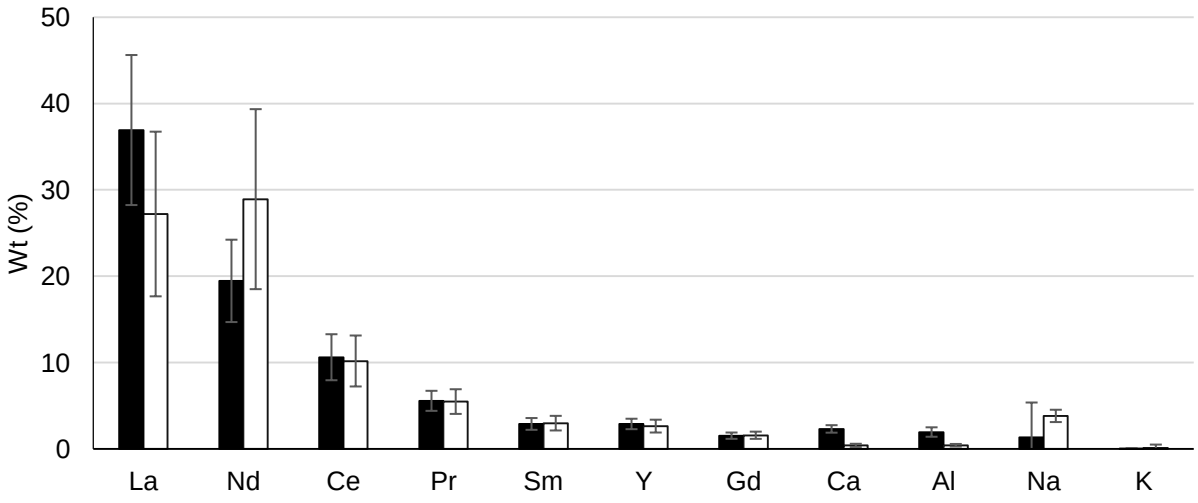
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428 4.5 **Calcination of the oxalate precipitate**

429 To obtain REE-oxides, S_2 and S_3, obtained from *EDTA* and sulphuric acid extractions
430 respectively, were burnt. Many parameters can influence the final composition of the
431 solids; to compare the two processes, a calcination step at 700 °C for 2 h was chosen in
432 a first approach. Fig. 8 shows the mass ratios of the various elements identified in the
433 two precipitates after calcination (determined by ICP analyses using the method
434 described in paragraph 2.3.).

435



436

437 Fig. 8: Elemental composition of the calcinated precipitates:

438 from *EDTA* extract ■, from H_2SO_4 extract □

439

In the case of *EDTA* leaching, REEs represented 79.8% of the mass of the calcination residue. The identified impurities were Ca (2.30%) and Al (1.94%) coming from the plant and Na (1.34%) mainly from *EDTA*. Given that the elements were in the form of oxides (REE_2O_3, CaO, etc.) the remainder of this mass mainly corresponded to oxygen.

In the case of H_2SO_4 leaching, REEs represented 78.9% of the calcination residue mass while the mass ratio of impurities was 5.2% of which 3.8% is Na. It can be noted that the calculated uncertainties are high. They take into account the different stages from the acid leaching to calcination. It is important to note that experiments are carried out with very low masses and that the mass of the final product obtained is 300 times smaller than the initial mass of plant.

The two leaching methods led to close purities with a slightly different impurity profile. For example, Ca content was slightly higher when *EDTA* leaching was used (2.3% against 0.4%). This can be explained by the stability of the Ca-EDTA complex.

XRD and EDX analyses showed a better crystallized solid when extraction was performed with sulphuric acid. For example, cerium oxide (Ce_7O_{12}) was well identified. In the case of an extraction with EDTA, the final solid contains carbon, coming from EDTA calcination.

5. Conclusion and perspectives

A three-step process involving extraction, oxalate precipitation and calcination has been developed to produce REE oxides from hyperaccumulator *D. linearis* fern. Proof of concept has been established. Experimental study of the extraction showed that REEs can be extracted from the plant using either EDTA or sulphuric acid. A methodology based on speciation studies was successful in determining the operating conditions for precipitating REEs in oxalate form. The pH range to be maintained, close to pH 2 for both extraction methods, was found to be critical. The experimental study showed that the soluble organic matter was also extracted from the plant but did not inhibit the precipitation of REE oxalate.

Overall, REE purity was similar in solids after calcination (impurity content close to 5 wt%). However, even if extraction yields were higher with *EDTA* (87.5% against 79. %),

the yield for the whole process was higher with H_2SO_4 (72. % against 60.5%). The final solid contained 0.7 g of REES per g.

The proposed process has a major advantage not to precipitate Al with oxalate (even if more than 50% is extracted). Here, and especially after H_2SO_4 extraction, the final solid contained only 0.4% Al.

Experiments have shown that the choice of H_2SO_4 as the extraction agent was relevant to EDTA. Yields are better, it is cheaper, and a part of *EDTA* is burnt (lost) during calcination. Further studies are required to optimize this process (amount of H_2SO_4 and oxalic acid, combustion temperature *etc.*). Reducing the quantity of reactants and studying the possibility of recycling certain solutions is necessary to design and scale up a process, which will allow the development of agromining development to recover REEs from secondary resources with more environmentally friendly techniques.

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