

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

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13

14 **Abstract**

15

16 *Dicranopteris linearis* (also known as *Dicranopteris dichotoma*) is a fern that grows  
17 naturally on the tailings of former rare earth element (REE) mines in southern China. It  
18 accumulates these elements in its aerial parts at concentrations that classify this plant  
19 as hyperaccumulator. The main objective of this research is to design a process to  
20 recover REEs directly from the dry biomass, without burning it. This process involves  
21 three steps: (i) extraction of REEs from the dry plant by leaching with a solution  
22 containing acid and/or complexing agents, (ii) precipitation of REEs with oxalate and (iii)  
23 calcination to prepare REE oxide. A methodology based on speciation calculation made  
24 it possible to determine operating conditions for precipitation by taking into account the  
25 influence of the species present according to the extraction method. Simulations were  
26 carried out using Chess software, allowing the calculation of the composition of a  
27 multicomponent solution at thermodynamic equilibrium. These operating conditions were  
28 then validated experimentally. REE extraction from the dry plant was significantly  
29 improved under acid conditions (with H<sub>2</sub>SO<sub>4</sub>) or with a strong complexing agent such as  
30 ethylenediaminetetraacetic acid (H<sub>4</sub>EDTA). After optimization of the precipitation

31 conditions, REE precipitation yields were above 90%. After calcination, the final solid  
32 (REE oxide) contained ca 69% of the REEs present in the initial biomass. The use of  
33 sulphuric acid as an extracting agent resulted in the recovery of a solid composed of 52  
34 wt % of REEs (based on metal content). Thus, this study proposes a new recovery route  
35 for these strategic elements with a REE concentration factor from soil to final solid of  
36 2500.

37

### 38 **Keywords**

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

40

### 41 **1. Introduction**

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

53 Agromining is an emerging phytotechnology, which uses natural and local  
54 hyperaccumulating plants to “harvest” metals [4]. The plants, which accumulate metals  
55 in their aerial parts at very high levels, are already being used to produce nickel from  
56 ultramafic soils, which are not concentrated enough for conventional mining industry [5,  
57 6]. The extraction yield is over 100 kg of nickel per hectare in Mediterranean climate  
58 (with *Alyssum murale* [7] and is very promising in tropical areas (with *Phyllanthus*  
59 *rufuschaneyi*) [8]. The metal is then generally recovered by hydrometallurgical

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

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

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

89 The aim of this research is therefore to synthesize REE-oxides after direct extraction of  
90 REE from the hyperaccumulator *D. linearis* and precipitation as oxalate. It consists of  
91 three steps: (i) a leaching step using extracting agents (organic or inorganic) followed by  
92 (ii) a selective precipitation step with oxalate, and (iii) calcination of the intermediate (Fig.  
93 1). Considering that REEs are complexed by carboxylic acids in the plant tissues, the  
94 strategy is either to break these complexes using an acid solution or to shift the  
95 complexing equilibrium using a more powerful complexing agent than the one present in  
96 the plant. Sulphuric and citric acids have been selected for their acidic properties, and  
97 H<sub>4</sub>EDTA and citrate for their complexing properties. H<sub>4</sub>EDTA is a well-known complexing  
98 agent for REEs [17,18], as is citrate, which naturally transports REEs in plants through  
99 the xylem [13]. During precipitation with oxalate, competitive reactions must be taken  
100 into account. They are due to the presence of extracting agents introduced in the  
101 previous step, and to soluble organic matter (SOM) of the plant, which may interfere. No  
102 data are available on the precipitation of REEs by oxalic acid C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> in the presence of  
103 high concentrations of sulphate, H<sub>4</sub>EDTA and citrate. The proposed methodology relies  
104 on post-extraction stage speciation studies to investigate the feasibility of downstream  
105 unit operations. Hence to determine the optimal precipitation conditions (pH and molar  
106 ratio), simulations of REE speciation were first performed. In order to validate the model,  
107 an experiment was prepared with a synthetic solution of lanthanum (La) (chosen as  
108 representative REEs). The simulations were performed under the assumption that SOM  
109 plays no role during precipitation. Tests with a real extract allow us to evaluate its role  
110 during REEs recovery. The whole process is finally evaluated according to the  
111 composition of the REE oxide obtained after calcination.

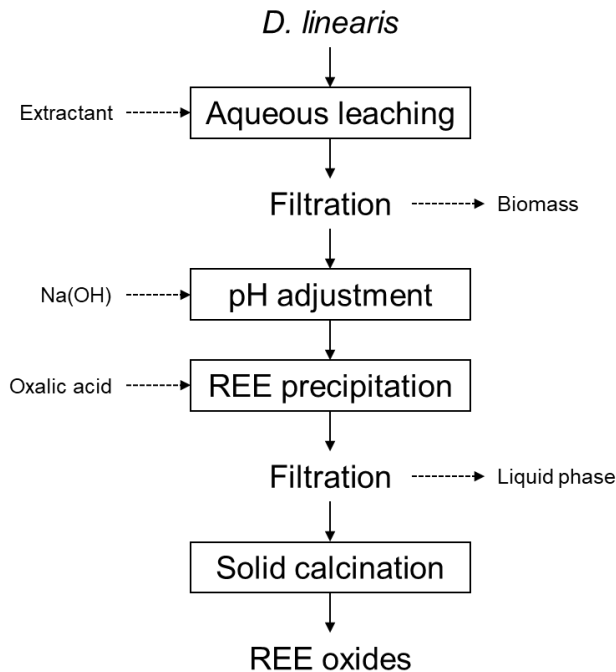


Fig. 1: Flowsheet of the proposed process to recover REEs from *D. linearis*

## 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

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

### 131 2.3 **Elemental and structural analysis**

132 Prior to elemental analysis, the solid and liquid samples were digested in a microwave  
133 oven (UltraWave, Milestone) for 40 min with a set-point of 200 °C. Biomass samples or  
134 precipitates (ca 0.1 g) were randomly collected and digested by adding 5 mL of  
135 concentrated nitric acid (5 repetitions each time). For liquids, 2 mL of nitric acid was  
136 added to 2 mL of sample. After digestion, the leachate was introduced into a 50 mL flask  
137 with deionized water, then filtered by syringes equipped with filters (Phenomenex, pore  
138 size: 0.45 µm) and analysed by ICP-AES (Thermo ICAP6000). Calibration was  
139 performed with the custom standard PlasmaCAL (SCP Science) in a 5% vol. HNO<sub>3</sub>  
140 matrix. Two ranges of standard solutions were used, one for the REEs and one for the  
141 other elements. The major elements were analysed by radial measurement while the  
142 minor elements were analysed by axial measurement. Three replicates were made for  
143 each sample and a quality test was performed every 10 measurements with a control  
144 solution (PlasmaCAL, SCP Science).

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

149

### 150 2.4 **REE extraction and recovery from biomass**

151 To study the effect of each agent on the efficiency of REE extraction, the fern biomass  
152 was leached with six aqueous solutions (solid/liquid ratios S/L = 3 g/100 mL, 2 h,  
153 magnetic stirring): deionized water, H<sub>2</sub>SO<sub>4</sub> (0.25 M), citric acid (1 M) (pH = 1.6 and 4.0,  
154 adjusted with NaOH), citrate (1M) (pH = 8.0, adjusted with NaOH) and *EDTA* (0.05 M)  
155 (in the following text, *EDTA* written in italic refer to the generic  
156 ethylenediaminetetraacetic acid, whatever its chemical form). The latter complexing  
157 agent was added in the disodic form Na<sub>2</sub>H<sub>2</sub>EDTA (to obtain an extraction at pH 4.5  
158 (predominance area of H<sub>2</sub>EDTA<sup>2-</sup>). This agent can create a complex with REE, without

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

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

165 A synthetic solution (ca 300 mL) was prepared, containing lanthanum ( $\text{La}(\text{NO}_3)_3$ ,  $2.3 \cdot 10^{-3}$   
166 mol) and  $\text{Na}_2\text{H}_2\text{EDTA}$  ( $4 \cdot 10^{-3}$  mol). The pH adjustment (between 2 and 8.5) was carried  
167 out with 1 M  $\text{HNO}_3$  solution and oxalic acid was added in a molar ratio of 1 with  
168  $\text{Na}_2\text{H}_2\text{EDTA}$  ( $4 \cdot 10^{-3}$  mol). The final pH was measured. After one hour of mixing,  
169 precipitates were filtered and dried. The liquid phases were analysed by ICP.

170 After simulation and determination of optimal precipitation conditions, pH was adjusted  
171 to 2.6 (with 1 M NaOH solution) and to 2.3 (with 1 M  $\text{HNO}_3$  solution) for  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2$   
172  $\text{H}_2\text{EDTA}$  extracts respectively. In the latter case, this caused the formation of a solid S1,  
173 which was separated and analysed (ICP and XRD). Oxalic acid was then added (molar  
174 ratio of 0.16 and 1.56, respectively) and the solutions were stirred during 1 h at 20 °C.  
175 Precipitates (S2 and S3 respectively) were filtered, washed with deionized water and  
176 dried at 100 °C. They were calcined at 700 °C for 2 h to obtain S4 and S5.

177

### 178 3. Theory

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

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

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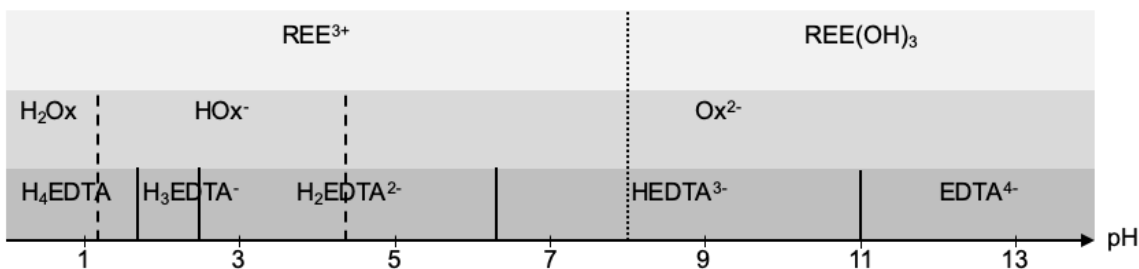
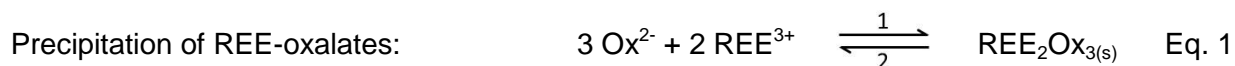


Fig. 2: Species prevalence as function of pH for REE, oxalic acid and *EDTA*



Ideally, to promote precipitation, the  $\text{REE}^{3+}$  and  $\text{Ox}^{2-}$  ( $\text{C}_2\text{O}_4^{2-}$ ) forms should be preferred to obtain the insoluble complex  $\text{REE}_2\text{Ox}_3$ . 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  $\text{REE}_2\text{Ox}_3$  ( $K_s$  between  $5 \cdot 10^{-30}$  and  $4.5 \cdot 10^{-32}$  [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  $\text{EDTA}^{4-}$  and  $\text{HEDTA}^{3-}$  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



206 (Eq. 4) is given by Eq. 5. The species present on the left side of the equilibrium, called  
 207 "basis species", are usually written in their deprotonated form.  
 208



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

209  
 210  
 211

Table 1: Stability constants used for speciation determination

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

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

212  
 213  
 214

## 215 4. Results and discussion

### 216 4.1 Elemental composition of *Dicranopteris linearis*

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

220 0.1%, indicating that this plant can be considered as Al - hyperaccumulator. Concerning  
 221 REEs, La, Nd and Ce were the main elements identified. Pr, Sm, Y and Gd were also  
 222 present but at lower concentrations. The analysis shows that *D. linearis* can accumulate  
 223 more than 3 g of REEs per kg of dry biomass (0.30%). This means that this plant batch  
 224 can be considered as a REE hyperaccumulator (threshold fixed at 1 g kg<sup>-1</sup>).  
 225 In the literature, concentration in plant tissues are generally measured between 0.023  
 226 and 0.26% [15]. The plant studied is therefore very rich. It mainly accumulates light  
 227 REEs.

228

229 Table 2: Composition in major cations and rare earths in *Dicranopteris linearis* (wt%)  
 230 (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
<b>Total</b>		<b>0.389 ± 0.045</b>
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

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#### 233 4.2 Extraction of REEs from *D. linearis*

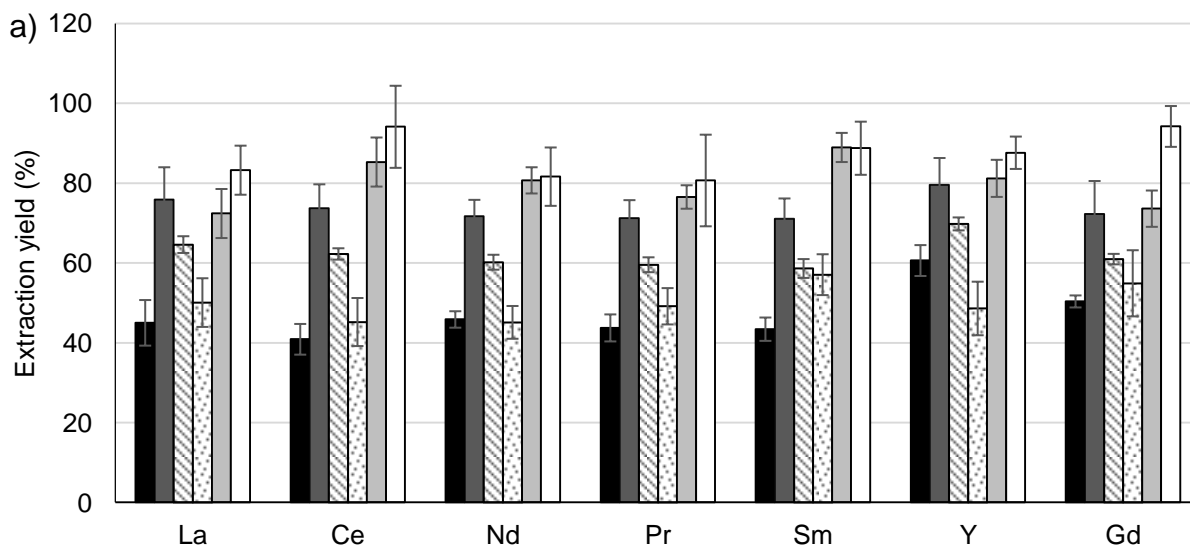
234 The extraction yield of REEs is defined by Eq. 6:

$$235 \quad \text{Extraction yield of REEs} = \frac{\text{mass of REEs in the extract}}{\text{initial mass of REEs in the plant}} \times 100 \quad \text{Eq. 6}$$

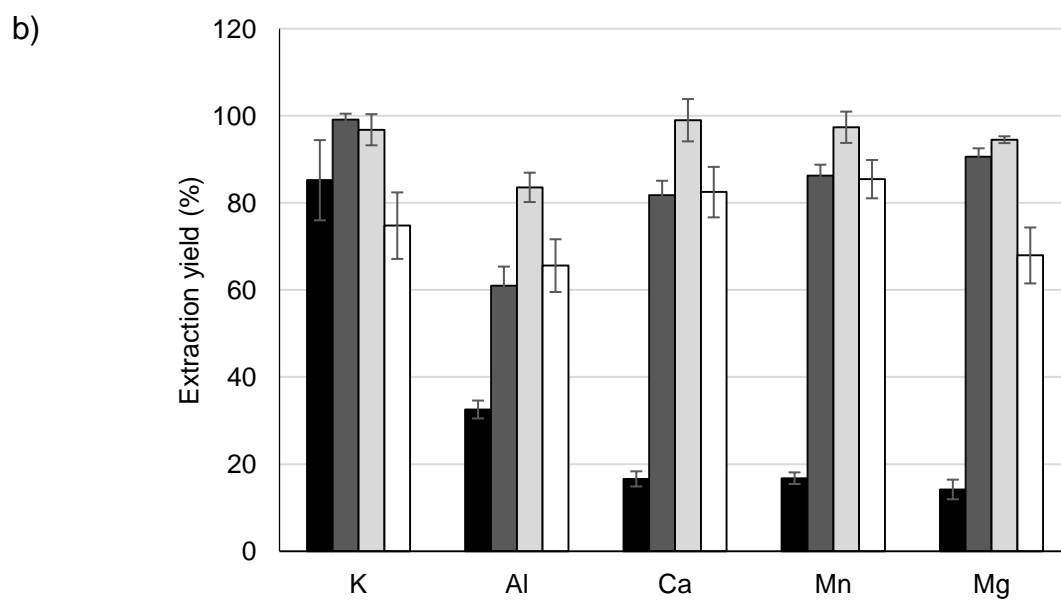
236 Fig. 3 compares the extraction yield of REEs (Eq. 6) from biomass with the six extracting  
 237 solutions: deionized water (blank sample), H<sub>2</sub>SO<sub>4</sub> (0.25 M) (strong mineral acid, pH <  
 238 0.5), citric acid (1 M) (weak carboxylic acid) at two pHs (1.6 and 4), citrate (1 M)  
 239 (complexing agent) at pH 8, and EDTA (0.05 M) (strong chelating agent) at pH 4.5.  
 240 Experiments were carried out under optimal conditions because the biomass had been

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

243



244



245

246 Fig. 3: Extraction efficiency of REEs (a) and other elements (b) using, H<sub>2</sub>O ■,  
247 citric acid (1 M, pH 1.6) ■, citric acid (1 M, pH 4) ▨, citrate (1 M, pH 8) ▩, H<sub>2</sub>SO<sub>4</sub> (0.25 M) □,  
248 and Na<sub>2</sub>EDTA (0.05 M) □

249

250 The results show, as a first observation, that the major REEs contained by the plant  
251 behaved in a very similar way during their extraction. With water, an extraction yield  
252 between 40 and 60% was obtained. Na<sub>2</sub>EDTA and H<sub>2</sub>SO<sub>4</sub> were the most efficient  
253 extracting agents with an almost similar yield > 80%. Citric acid had less effect, but its  
254 efficiency increased as the pH decreased. At pH 8, no difference with water was  
255 recorded. The results indicate that REEs can be extracted with very good yields under  
256 acidic conditions, or with a strong complexing agent. Indeed, the only acidity of the  
257 *EDTA* solution cannot explain the results obtained with this molecule (better extraction  
258 yields at high pH compared to citric acid).

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

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

276

## 277 4.3 Precipitation of REEs in *EDTA* medium with oxalate

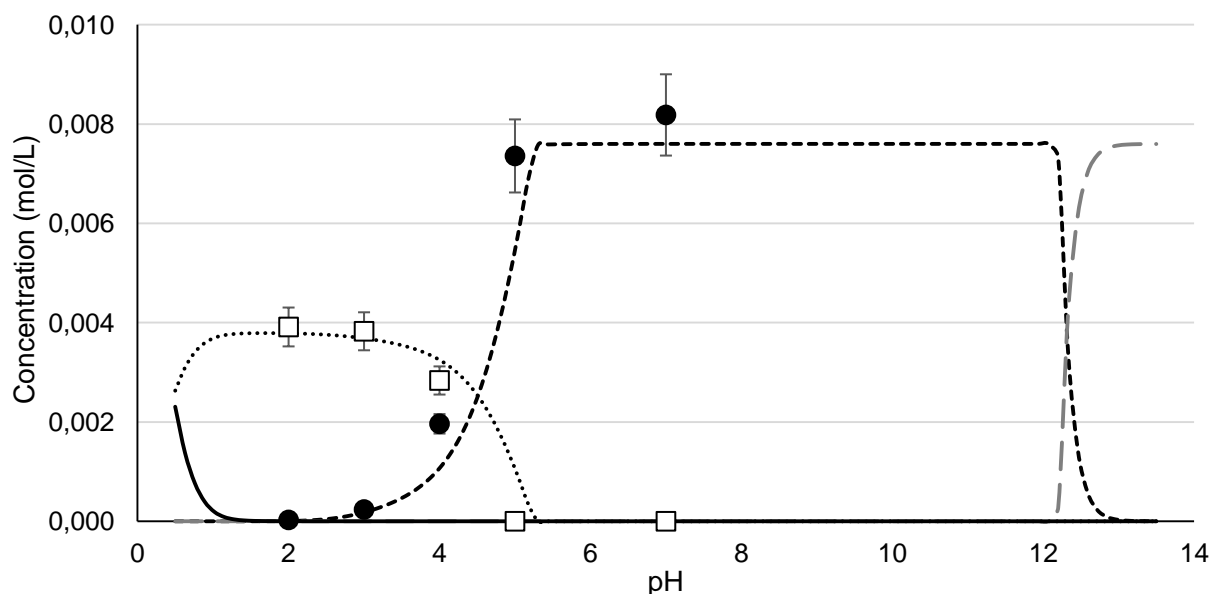
### 278 4.3.1 REE speciation in presence of *EDTA* and oxalic acid

279 To precipitate REEs, oxalic acid was added to the *EDTA* extract. The co-existence of  
280 *EDTA* and oxalic acid leads to the formation of a large number of chemical species. As  
281 the former is a tetraacid and the latter a diacid, the concentrations of the different  
282 chemical forms depend on the pH. These different forms react with the REEs to form  
283 soluble species such as REEEDTA<sup>-</sup> or insoluble species such as REE<sub>2</sub>Ox<sub>3</sub>, this last  
284 compound being the desired one. The concentrations of EDTA<sup>4-</sup> and Ox<sup>2-</sup> increase with  
285 increasing pH, but the precipitation of insoluble REE hydroxides increases at the same  
286 time. Therefore, the search for a pH high enough to obtain the Ox<sup>2-</sup> form that allows the  
287 precipitation of REEs (Eq. 1) under the oxalate form is a compromise to avoid high  
288 solubilization of REEs due to the complex formed with EDTA<sup>4-</sup> (Eq. 2).

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

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301



302

303 Fig. 4: Speciation of lanthanum in oxalic acid and EDTA solutions (simulations represented with  
304 lines and experimental points with dots):  $\text{La}^{3+}$  —,  $\text{La}_2\text{Ox}_3$  ..... and  $\square$ ,  
305  $\text{LaEDTA}^-$  --- and  $\bullet$ ,  $\text{La}(\text{OH})_3$  - -

306

307

#### 308 4.3.2 Validation of speciation simulations and determination of optimal 309 conditions

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

316 Based on these results, it can be concluded that at a pH between 1.2 and 2.3, REEs  
317 precipitate as oxalate, even in the presence of a high concentration of *EDTA* in solution.  
318 The simulations also indicate that as *EDTA*/ $\text{C}_2\text{H}_2\text{O}_4$  molar ratio increases, the pH  
319 corresponding to the total complexation of La with *EDTA* decreases (from 5.2 to 4.6,  
320 when the *EDTA* concentration is multiplied by 5). Conversely, when the amount of oxalic

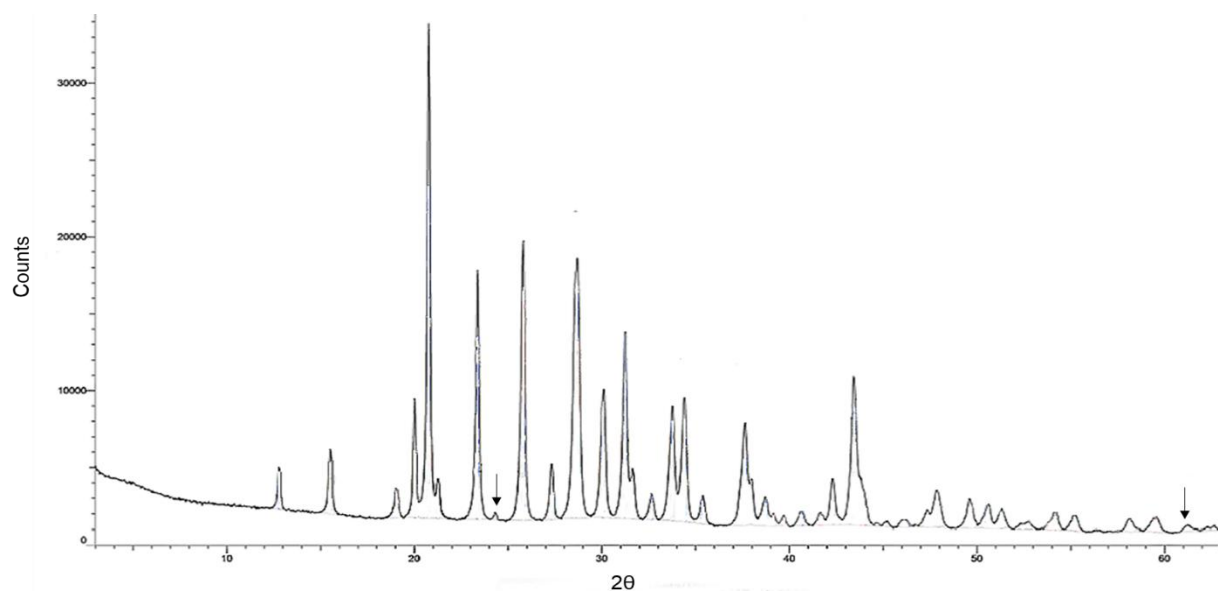
321 acid is multiplied by 5, this pH increases to 6. In addition, for a given concentration of La,  
322 increasing the addition of oxalic acid limits the formation of  $\text{La}^{3+}$  and increases the pH  
323 range (especially at low pH) at which lanthanum can be precipitated.

324

### 325 4.3.3 Precipitation of REEs in biomass extract

#### 326 a) pH adjustment

327 Firstly, the extract at pH 4.1 was acidified in order to reach the previously defined pH (ca  
328 2.3), resulting in the formation of a first precipitate  $S_1$  ( $6.5 \text{ g L}^{-1}$ ) from the protonation of  
329 *EDTA* in the  $\text{H}_4\text{EDTA}$  form, which has a low aqueous solubility. This precipitation was  
330 confirmed by XRD analysis (Fig. 5). All identified peaks corresponded to *EDTA*. No other  
331 molecules have been identified. During extraction, the molar ratio *EDTA*/REEs was  
332 approximately 21 so that competitive reactions between REEs and the other elements  
333 present in solution did not influence their extraction. This molar ratio could be optimized,  
334 however, even in the present conditions, half of the *EDTA* (45%) can be recovered and  
335 reused after filtration.



336

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

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

339

340 Analysis of this solid showed that less than 2% of the REEs were lost at this stage. This  
 341 percentage was calculated from the amount of initial biomass. Other elements are also  
 342 identified: 6.5% and 1.5% for P and Ca respectively. For the other elements, only 0.4 to  
 343 0.6% of the initial biomass content is found in S<sub>1</sub>. This step could be a way to recycle.

#### 344 **b) REE precipitation using oxalic acid**

345 The addition of oxalic acid caused a decrease in pH. To ensure that the pH is far from  
 346 the lower limit of precipitation, a large excess was introduced (molar ratio oxalate/REE =  
 347 70), giving a final pH of 1.3. The large amount of reagent was also chosen to reduce  
 348 competition from other cations and SOM (organic carbon concentration: 7.0 ± 0.2 g L<sup>-1</sup>).  
 349 The formation of the oxalate precipitate (S<sub>2</sub>) was instantaneous. After filtration, analysis  
 350 of the extract showed that REE precipitation was almost complete. Concentrations of  
 351 Ce, Gd, Pr and Sm were below the detection limit (10 µg L<sup>-1</sup>) and less than 1% remained  
 352 in solution for the other three main REEs (La, Nd, Y). Thus, this process can recover  
 353 65.9 to 72.2% of the REEs present in the initial biomass. The organic matter had no  
 354 influence on the operations implemented.

355 The recovered solid (2.56 g L<sup>-1</sup> of extract, 42.6 mg g<sup>-1</sup> of raw biomass) was washed with  
 356 deionized water, which removed most of the sodium, coming from the addition of *EDTA*  
 357 during extraction. Finally, the precipitate contained 4.62% (27.3 mg) of REEs, which was  
 358 13 times more concentrated than the starting plant (Table 3). Calcium was the major  
 359 impurity in the solid.

360

361 Table 3: Elemental composition of the precipitate S<sub>2</sub> (%), obtained after oxalic acid  
 362 addition in the extract with *EDTA* (confidence ranges are determined with 3 replicates)

Element		wt%
REEs	<b>Total</b>	4.621 ± 0.489
	Ca	0.456 ± 0.012
	P	0.117 ± 0.003
Other elements	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

363



364 Stricter pH control and optimization of the amounts of *EDTA* and oxalic acid used during  
365 the extraction would certainly improve the REE content of the S<sub>2</sub> precipitate. Due to the  
366 low content (REEs and impurities), it appears that an excessive amount of *EDTA* has  
367 still precipitated. This was confirmed by an XRD analysis of the precipitate, where only  
368 *EDTA* was identified.

369 Even in choosing better conditions, it seems difficult to avoid completely this co-  
370 precipitation of *EDTA*, which will be lost during the calcination step. As it is an expensive  
371 reactant, precipitation in H<sub>2</sub>SO<sub>4</sub> medium was also tested.

372

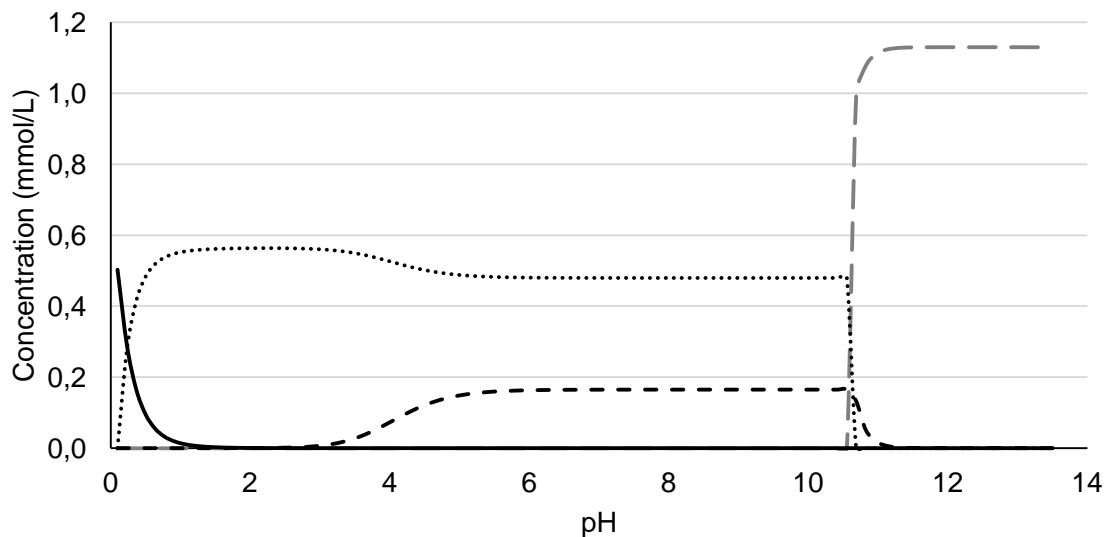
#### 373 4.4 Precipitation of REEs in H<sub>2</sub>SO<sub>4</sub> with oxalate

##### 374 4.4.1 REE speciation in the presence of H<sub>2</sub>SO<sub>4</sub> and oxalic acid

375 As with the previous approach, the objective is to precipitate REEs as oxalate. The  
376 insoluble form referred to is La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>. However, in the presence of sulphuric acid, REE  
377 sulphate complexes are formed, with REE(SO<sub>4</sub>)<sup>+</sup> being the predominant species  
378 (REE(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> is negligible all the time). A typical simulation of the equilibria is exhibited in  
379 Fig. 6. The precipitation of REEs as oxalate depends on pH. At low pH, sulphate forms  
380 solubilize REEs (pH is below the pKa of oxalic acid (1.2), C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> is predominant), while  
381 hydroxides are formed under alkaline conditions. When the sulphate concentration is  
382 divided by 2, the pH corresponding to the formation of REE(SO<sub>4</sub>)<sup>+</sup> decreases from 2.5 to  
383 2. Around pH 3.5 - 4 and above, two species of oxalate coexist, La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and  
384 La(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>. Of course, the higher the oxalate/REEs ratio, the higher the concentration of  
385 La(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup> (this species is very low when the oxalate/REE molar ratio is less than about  
386 30). Therefore, there are two advantages to not raising the pH of the solution too much:  
387 less reagent used and no risk of formation of an ionic REE oxalate compound. Based on  
388 these results, the pH of the solution should be set between 2.5 and 3.0 to optimize REE  
389 oxalate precipitation.

390

391



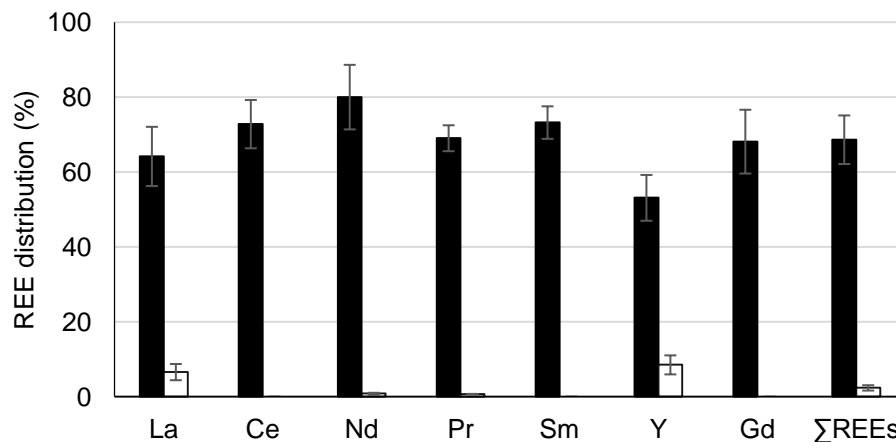
392  
 393 Fig. 6: Simulations of lanthanum (1.13 mM) speciation in oxalic acid (80 mM) and sulphate (250  
 394 mM) solutions:  
 395 LaSO<sub>4</sub><sup>+</sup> —, La<sub>2</sub>Ox<sub>3</sub> ....., LaOx<sub>3</sub><sup>3-</sup> ----, La(OH)<sub>3</sub> - -

396  
 397

#### 398 4.4.2 Precipitation of REEs in biomass extract

399 Following the recommendations determined by simulation, the pH of the extract obtained  
 400 with *D. linearis* was first adjusted to 2.6 by NaOH addition (the initial pH was 0.8). After  
 401 addition of oxalic acid (8 mmol for 0.37 mmol of REE), a precipitate S<sub>3</sub> appeared directly.  
 402 After filtration, analysis of the aqueous solutions showed that 90% of REEs precipitated.  
 403 The 10% remaining in solution were mainly La and Y. Fig. 7 shows the percentage of  
 404 REE oxalate precipitation in relation to the initial content of the plant, as well as what  
 405 remained in solution. The addition of oxalic acid resulted in the precipitation of 68.6% of  
 406 the initial REEs (present in the initial biomass).

407



408  
 409 Fig. 7: Distribution (relative to the initial plant content) of REEs after precipitation with oxalic acid  
 410 in  $H_2SO_4$  extracts: oxalate precipitates ■, final solutions □

411  
 412 The other elements were also analysed to assess the purity of the REE-oxalate  
 413 precipitate (Table 4). The mass ratio of REEs in this solid was 52.35%. Identified  
 414 impurities represent 3.13% by mass. Considering that REEs are precipitated as  
 415  $Ox_3REE_2$  the remainder of this mass corresponded to the oxalate. The main impurity  
 416 was Na, from the sodium hydroxide solution used to neutralize the extract. A better  
 417 washing of the solid could certainly reduce this impurity.

418 These results prove that SOM did not inhibit precipitation under these conditions. The  
 419 REE content is more than 10 times higher in  $S_3$  ( $H_2SO_4$ ) than in  $S_2$  (*EDTA*) (52.4 and  
 420 4.62% respectively), while the recovery yields are similar (68.6 and 69.3% respectively).  
 421 This is due to the presence of *EDTA* in  $S_2$ .

422  
 423  
 424 Table 4: Elemental composition of the precipitate  $S_3$  (wt%), obtained after oxalic acid  
 425 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

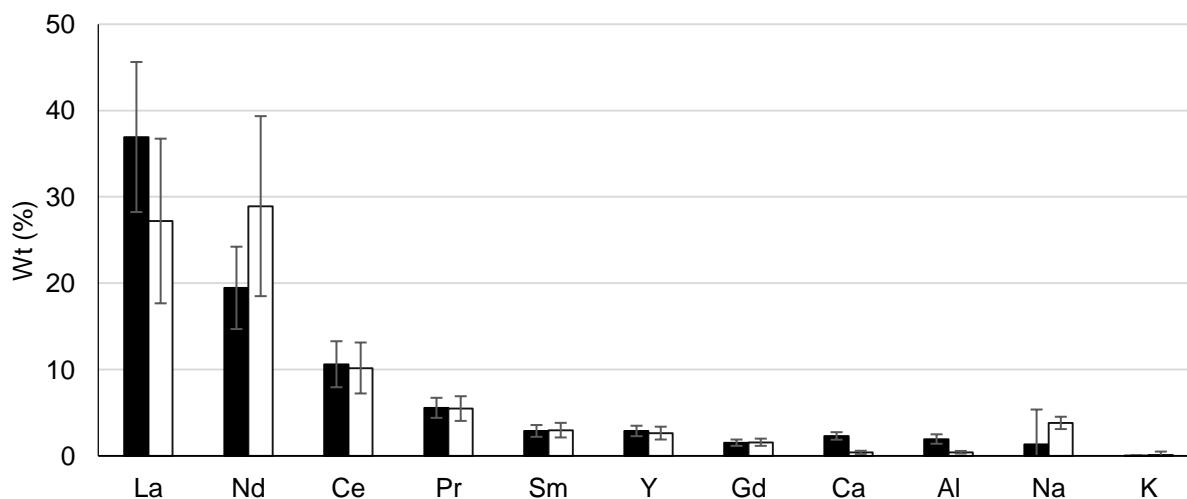
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427

#### 428 4.5 Calcination of the oxalate precipitate

429 To obtain REE-oxides, S<sub>2</sub> and S<sub>3</sub>, 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

438

Fig. 8: Elemental composition of the calcinated precipitates:  
 from *EDTA* extract ■, from H<sub>2</sub>SO<sub>4</sub> extract □

439

440 In the case of *EDTA* leaching, REEs represented 79.8% of the mass of the calcination  
441 residue. The identified impurities were Ca (2.30%) and Al (1.94%) coming from the plant  
442 and Na (1.34%) mainly from *EDTA*. Given that the elements were in the form of oxides  
443 ( $\text{REE}_2\text{O}_3$ , CaO, etc.) the remainder of this mass mainly corresponded to oxygen.

444 In the case of  $\text{H}_2\text{SO}_4$  leaching, REEs represented 78.9% of the calcination residue mass  
445 while the mass ratio of impurities was 5.2% of which 3.8% is Na. It can be noted that the  
446 calculated uncertainties are high. They take into account the different stages from the  
447 acid leaching to calcination. It is important to note that experiments are carried out with  
448 very low masses and that the mass of the final product obtained is 300 times smaller  
449 than the initial mass of plant.

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

453 XRD and EDX analyses showed a better crystallized solid when extraction was  
454 performed with sulphuric acid. For example, cerium oxide ( $\text{Ce}_2\text{O}_3$ ) was well identified. In  
455 the case of an extraction with *EDTA*, the final solid contains carbon, coming from *EDTA*  
456 calcination.

## 457 **5. Conclusion and perspectives**

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

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

469 the yield for the whole process was higher with H<sub>2</sub>SO<sub>4</sub> (72. % against 60.5%). The final  
470 solid contained 0.7 g of REES per g.

471 The proposed process has a major advantage not to precipitate Al with oxalate (even if  
472 more than 50% is extracted). Here, and especially after H<sub>2</sub>SO<sub>4</sub> extraction, the final solid  
473 contained only 0.4% Al.

474 Experiments have shown that the choice of H<sub>2</sub>SO<sub>4</sub> as the extraction agent was relevant  
475 to EDTA. Yields are better, it is cheaper, and a part of *EDTA* is burnt (lost) during  
476 calcination. Further studies are required to optimize this process (amount of H<sub>2</sub>SO<sub>4</sub> and  
477 oxalic acid, combustion temperature *etc.*). Reducing the quantity of reactants and  
478 studying the possibility of recycling certain solutions is necessary to design and scale up  
479 a process, which will allow the development of agromining development to recover  
480 REEs from secondary resources with more environmentally friendly techniques.

481

## 482 **Acknowledgment**

483  
484 The authors would like to thank Bro-Penny (Lebanon) for financial support. They thank  
485 LabEx Ressources 21 (ANR-10-LABX-21), Institut Carnot ICEEL (REEcovery Project)  
486 and are grateful to Mr. S. Pontvianne for his assistance in the analytical work.

487

488

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