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Research article

A green method based on living macroalgae for the removal of rare-earth elements from contaminated waters

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ABSTRACT

Low recycling rates of rare earth elements (REEs) are a consequence of inefficient, expensive and/or contaminating methods currently available for their extraction from solid wastes or from liquid wastes such as acid mine drainage or industrial wastewaters. The search for sustainable recovery alternatives was the motivation for this study. For the first time, the capabilities of 6 living macroalgae (*Ulva lactuca, Ulva intestinalis, Fucus spiralis, Fucus vesiculosus, Osmundea pinnatifida and Gracilaria* sp.) to remove REEs (Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy) from laboratory-prepared seawater spiked with REE solutions were evaluated. The assays lasted 72 h with REEs concentrations ranging from 10 to 500 μg L^{-1}. The link between REEs uptake and algal metabolism, surface morphology and chemistry were addressed. Kinetics varied among the species, although most of the removal occurred in the first 24 h, with no equilibrium being reached. Lack of mortality reveal that the algae maintained their metabolism in the presence of the REEs. Green alga *U. lactuca* stood out as the only capable of efficiently removing at least 60% of all elements, reaching removals up to 90% in some cases. The high bioconcentration factors, derived from mass balance analysis (c.a. 2500) support that the REEs enriched algal biomass (up to 1295 μg g^{-1}) may constitute an effective and environmentally friendly alternative source of REEs to conventional extraction from ores.

1. Introduction

Taking into consideration the supply risk and the relevance in developing new technologies, the European Commission has classified certain chemical elements as "Critical Raw Materials" (Massari and Ruberti, 2013). Among them, Rare Earth Elements (REEs) present an elevated risk as result of the European Union's high dependence on their importation, as well as their low recycling rates (Bradshaw and Hamacher, 2012; Chen, 2011). The REEs market has been a sort of monopoly since China has been known to control over 90% of their production (Binnemans et al., 2013).

Rare Earth Elements comprise the series of the lanthanides (Ln) as well as scandium (Sc) and yttrium (Y) and are usually separated into light rare earths (LREE), medium rare earths (MREE) and heavy rare earths (HREE) according to their atomic weight. Yttrium is included in the HREEs due to the similarities with the rest of the group (Samson and Wood, 2004). The specific characteristics of the REEs allow their implementation in a vast array of industries such as the magnet, metallurgy and catalyst industries. In the glass, ceramics and phosphor industries, and electronic consumer instruments REEs are nearly irreplaceable (Barakos et al., 2016; Cardoso et al., 2019). As such, the development of technologies for the recycling of REEs from wastewaters and end-of-life products has been proposed as a solution for decreasing the dependence of importation of these elements. Among the new emerging technologies for recycling of REEs, sorption has been shown to be a promising alternative. Sorption is a chemical process where a bond between one substance at liquid or gaseous state and a solid surface is established. If the sorbent is of biological origin, the process is then

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known as biosorption (Fomina and Gadd, 2014). From the vast array of biological materials to be used as sorbents, algae biomass has been shown to be capable of removing metals from contaminated solutions (Zeraatkar et al., 2016). The ability to bind metals to its structure is a result of factors such as the presence of a diversity of functional groups as well as the high number of available binding sites on the algae's surface (Lacher and Smith, 2002). Sorption by algae biomass is dominated by processes like ion exchange, complexation and electrostatic interactions (Michalak and Chojnacka, 2010). Dried algae biomass has already been shown to be a promising sorbent for elements with high economic value such as rare earths (Ramasamy et al., 2019). However, few studies have focused on the sorption abilities of living macroalgae (Henriques et al., 2017, 2015a; Jacinto et al., 2018). Henriques and co-authors (Henriques et al., 2015a) have revealed the potential of living *Ulva lactuca*, *Fucus vesiculosus* and *Gracilaria gracilis* for the bioremediation of metal contaminated waters through adsorption and accumulation of mercury from solution. Regarding the sorption of REEs, to the best of our knowledge, the study of Jacinto and co-authors (Jacinto et al., 2018) is the only one that studies the ability of a living macroalga, *Gracilaria gracilis*, to remove REEs from a contaminated solution, although some studies have explored this potential using dried algae biomass (Vijayaraghavan et al., 2010, 2011). Because living macroalgae may uptake toxic elements into the cells, their use may be limited by toxicity effects (Zeraatkar et al., 2016), which are dependent on concentration and speciation of each particular element. Furthermore, other factors such as growth rate, salinity, pH and temperature influence the accumulation of these elements and, consequently, the removal conditions should be optimised (Kamala-kannan et al., 2008).

This study aims to assess the removal of rare earth elements by six living macroalgae species, *Ulva intestinalis, Ulva lactuca, Fucus spiralis, Fucus vesiculosus*, *Gracilaria* sp. and *Osmundea pinnatifida* from spiked solutions, and to identify the species with higher potentialities for biotechnological applications.

2. Material and methods

2.1. Reagents

All the laboratory material was washed at least during 24 h with 25% (v/v) nitric acid solution (Merck, suprapure, 65%) and rinsed with ultrapure water (Milli-Q, 18 MΩ/cm). Mono-elemental solutions of REEs in nitric acid solutions (HNO_3 1–7%) were obtained from certified suppliers: Alfa Aesar (Y, Pr, Tb, Dy), Inorganic Ventures (Nd, Ce), Plasma Cal (La, Eu) and Sigma Aldrich (Gd). Salt used in the preparation of artificial saline solutions was from Tropic Marine Centre (Tropic Marin) with a composition described by Atkinson and Bingmann, 1997.

2.2. Macroalgae

The macroalgae species selected for this study were: *Ulva intestinalis, Ulva lactuca, Fucus spiralis, Fucus vesiculosus*, *Gracilaria* sp. and *Osmundea pinnatifida.* Biomasses were collected in January and February 2019 at the lower part of the Aveiro lagoon, located in the NW coast of Portugal (Lopes et al., 2013). Salinity in sampling sites was lower than in seawater and fluctuated with the tide (Lopes et al., 2013). After collection, macroalgae were transported to the laboratory, washed with lagoon water from each sampling site, and left for 48 h in aquaria with synthetic seawater (salinity 30) in order to acclimate to the light, pH and salinity conditions of study. Subsequently, live macroalgae were used in the laboratory experiments.

2.3. Design of the experiments

Experiments run in 1.5-L transparent plastic bottles, containing 1 L of contaminated saline water (salinity 30) and 3 g L^{-1} of macroalgae (fresh weight). Each macroalgae species was exposed to mono-elemental solutions of REEs: yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), europium (Eu), gadolinium (Gd), terbium (Tb) and dysprosium (Dy). Exposure ran for 72 h under aerated conditions, and constant pH (8.5) and temperature (20 °C). Three concentrations were chosen, corresponding to low (10 μg L^{-1}) and high (500 μg L^{-1}) contaminated effluents (Åström, 2001), and a third equimolar value of 1 μmol L^{-1}, being equivalent to 89, 139, 140, 141, 144, 153, 157, 159 e 163 μg L^{-1} of Y, La, Ce, Pr, Nd, Eu, Gd, Tb and Dy, respectively.

Spiked saline solutions were prepared and left in plastic bottles for 24 h before the addition of the macroalgae biomass. To 1 L of each mono-elemental contaminated solution, 3 g of small rectangular pieces of each macroalgae were added. In general the size of the rectangles were: 1 × 5 cm^2 for *F. spiralis, F. vesiculosus*, *Gracilaria* sp. and *O. pinnatifida*, 5 × 5 cm^2 for *U. lactuca,* and 5 × 0.2 cm^2 for *U. intestinalis*. Different sizes resulted from morphological specificities of each macroalgae. Aliquots of 5–10 mL of the spiked solutions were sampled immediately before the addition of the biomass (time 0), 1, 3, 6, 9, 24, 48 and 72 h. Then 25 μL of HNO_3 (65% v/v) were added to the samples to guarantee a pH < 2. Acidified samples were stored at 4 °C until the analysis. Samples of each macroalgae that were used in the experiment were collected and stored at −80 °C for REEs analysis. All the experimental conditions were run in duplicate and controls, without the presence of macroalgae, were performed at the same conditions to assess possible loss of each element. This experimental procedure was previously used in (Jacinto et al., 2018).

2.4. Characterization of macroalgae

Prior to the experiments, a portion of each fresh macroalgae was weighted and air dried to constant weight. Water content of each species was calculated by the difference between fresh and dry weights divided by the fresh weight and expressed as percentage. The external contact area of each macroalgae species was assessed with the Fiji software. Samples were scanned with a resolution of 200 ppi, which served to set the scale and the file was saved as TIFF format to store the information of scale with the image. Fourier Transform Infrared (FTIR) of the macroalgae was performed before being exposed to the spiked solutions to identify the main functional groups potentially involved on the removal processes. A PerkinElmer Spectrum BX spectrometer coupled to a horizontal attenuated total reflectance (ATR) cell using 256 scans at a resolution of 4 cm^{-1} was used and the spectra were recorded as transmittance from 4000 to 500 cm^{-1}.

2.5. Quantification of rare earth elements in solution and accumulated in macroalgae

Concentrations of REEs were measured in saline solution through Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of Quadrupole Thermo Scientific X Series. Calibration curves were built with 5 multi-element standards, previously diluted from a certified standard in HNO_3 1%, with concentrations ranging from 0.1 to 10 μg L^{-1}. Curves with correlation coefficients lower than 0.999 were rejected and the error of each standard was always below 10%. The concentration of the lowest standard was considered the limit of quantification. The acceptable coefficient of variation between sample replicates was 5%.

Elements in spiked seawater samples were measured directly or after dilution with HNO_3 2%. Macroalgae biomass was solubilised through acid digestion: 0.2 g (dry weight) was placed into previously acid washed Teflon tubes together with 1 mL of HNO_3, 2 mL of H_2O_2 and 1 mL of Milli-Q water; tubes were then sealed and subjected to increasing temperature and pressure programme in a CEM Mars 5 microwave of 5 min ramp time to 160 °C, another 5 min at the same temperature, and cooled down. Then solutions were collected in 25 mL tubes and the remaining volume was completed with Milli-Q water.

2.6. Quality control

A Certified Reference Material (NCS DC73348) was always digested in parallel with the macroalgae samples to guarantee the validation of the obtained results. Recovery of the quantified elements varied within the acceptable range of 80–120 % and sample results were not corrected with the CRM recovery. To study the variation of the element concentrations in spiked solutions, value at each time t (C_t) was divided by the initial value (C_0). This procedure minimises slight differences occurring among solutions at time zero. Fig. 1 illustrates the changes of Gd concentrations in saline solutions at each time t (C_t) normalised to the initial conditions (C_0) along 72 h in the controls. Ratios C_t/C_0 remained between 1.0 and 0.9 for the three initial concentrations of Gd (10, 157 and 500 μg L^{-1}). Similar patterns with relatively constant ratios were also observed for Y, La, Pr, Nd, Eu, Tb and Dy. Concentration stability of the elements indicates that loss or contamination during the experiments were negligible. Cerium was the exception, since concentrations in the controls decreased after 12 h of exposure, and at 72 h the ratios C_t/C_0 were approximately 0.8.

All the experiments ran in duplicate. Differences between the pair of ratios C_t/C_0 in duplicates (DP) were calculated as

$$DP = (D1 - D2)*100 / D_1 \quad (1)$$

Where D_1 and D_2 were the ratios in the higher duplicate and lower duplicate, respectively. DP was calculated for 54 pairs of values (six macroalgae *versus* nine elements). Median, percentile 25 and percentile 75 of the ratios C_t/C_0 for those set of values were 4.9, 2.1 and 8.9, respectively. These values indicate small differences between values of the pair, and hence it was selected the duplicate of lower ratios C_t/C_0 in each experiment.

2.7. Kinetic modelling

Sorption kinetics of REEs by the macroalgae were analysed by fitting curves based on 3 kinetic models, namely Lagergren pseudo-first-order model (Lagergren, 1898), Ho's pseudo-second order model (Ho and McKay, 1999) and the Elovich model (Ho, 2006) to the experimental data.

The pseudo-first-order model (PFO) is given by the equation:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (2)$$

The pseudo-second-order model (PSO) is given by the equation:

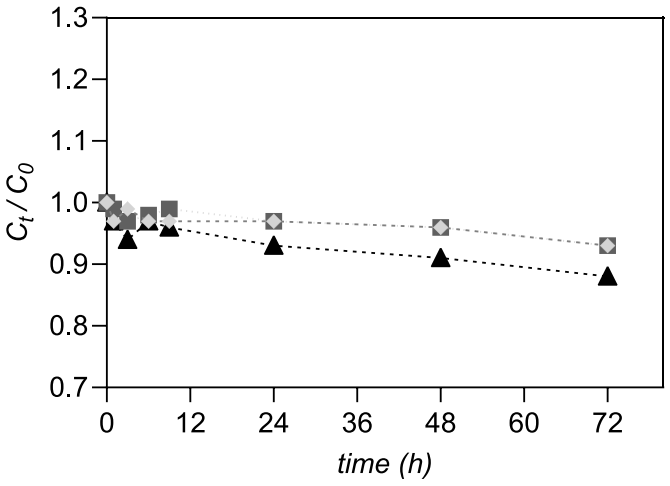

Fig. 1. Concentration of Gd in the controls, normalised to the initial concentration (C_t:C_0), along the 72 h of experiment. Controls corresponding to three initial concentrations were considered: 10 ( ), 157 (■) and 500 (▲) μg L^{-1}.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (3)$$

The Elovich model is given by the equation:

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \quad (4)$$

In these equations, q_t corresponds to the concentration of each element in the algae tissue after a certain time t has passed, and it is calculated through mass balance:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (5)$$

where C_0 and C_t (μg L^{-1}) are the element concentration in solution at the beginning and after a certain time t has passed, V (L) is volume of solution, and M (g) is the algal mass in dry weight. q_e is the value of the concentration at the equilibrium given by the model, k_1 is the pseudo-first-order constant (expressed in h^{-1}), k_2 is the pseudo-second-order constant (expressed in g μg^{-1} h^{-1}), α is the Elovich initial sorption rate (expressed in μg/g h) and β is the Elovich desorption constant (expressed in g/μg).

3. Results

3.1. Variation of macroalgae biomass during experiments

In each experiment, macroalgae was weighted at the initial time and after 72 h of exposure in order to assess possible changes in biomass. Variation of biomass (VB) was calculated by the expression:

$$VB = (B_{72} - B_0) \times 100/B_0 \quad (6)$$

where B_0 is the biomass weight (dry weight) at initial time and B_{72} the biomass weight (dw) after 72 h of the experiment. VB varied slightly and without a pattern among the three spiked conditions of 10 μg L^{-1}, 1 μmol L^{-1} and 500 μg L^{-1}. For each element, it was encompassed data from the six macroalgae species exposed to three initial concentrations. Medians of VB varied from −1 to +1 for La, Ce, Gd, Tb and Dy, which means that the presence of these elements in solution had negligible effects on macroalgae biomass. Slight variations were also found for Y (−1.8), Pr (3.3), Nd (−1.7) and Eu (2.5). However, combining VB values by macroalgae including the nine element experiments considerable differences were encountered (Table 1). In particular, the medians of VB for *U. intestinalis* (−35) and *U. lactuca* (−14) were far below zero, pointing the loss of biomass during the 72 h of exposure. On the contrary, median for *Gracilaria* sp. (9) suggest a slight increase of biomass. VBs of *F. spiralis* (−1), *F. vesiculosus* (4), and *O. pinnatifida* (2) were closer to zero, meaning that element concentrations had no effect on the biomass of these species.

3.2. Water content and external contact area of macroalgae

Table 2 presents the water content and the external contact area of each macroalgae used in the experiments. *U. intestinalis, Gracilaria* sp. and *O. pinnatifida* exhibited water content statistically ($p < 0.05$) higher than *U. lactuca*, *F. spiralis* and *F. vesiculosus*. Broad variation was found in the external contact area among macroalgae. Significant ($p < 0.05$) differences were obtained among: *U. lactuca* > *U. intestinalis* > *Gracilaria* sp. > *O. pinnatifida*, *F. spiralis* and *F. vesiculosus*. The noteworthy external contact areas of *U. lactuca* and *U. intestinalis* provide larger surfaces of contact with the solution, which may facilitate the removal of elements from the contaminated waters.

3.3. Fourier Transform Infrared in macroalgae

FTIR was performed in macroalgae before exposure to spiked

Table 1
Variation of macroalgae biomass (VB) calculated by equation (5) along the 72-h experiment; median, percentile 25th and percentile 75th encompassing duplicated of nine elements experiments (n = 18).

VB	*U. intestinalis*	*U. lactuca*	*F. spiralis*	*F. vesiculosus*	*Gracilaria* sp.	*O. Pinnatifida*
Median	−35	−14	−1	4	9	2
P25	−59	−26	−7	−2	6	−1
P75	−24	2	3	7	14	5

Table 2
Mean (±standard variation) of water content (%) and external contact area ($cm^2\ g^{-1}$) of the six macroalgae.

Macroalgae	*U. Intestinalis*	*U. lactuca*	*F. spiralis*	*F. vesiculosus*	*Gracilaria* sp.	*O. pinnatifida*
water content (%)	91 ± 0.58	83 ± 0.46	82 ± 3.1	80 ± 5.4	88 ± 5.5	89 ± 1.2
External contact area ($cm^2\ g^{-1}$)	148 ± 45	264 ± 31	29 ± 11	30 ± 8.9	79 ± 9.3	33 ± 1.8

solutions. Spectra provide information on major functional groups that can be involved in the possible removal of elements (Fig. 2). Most of the spectra exhibited five common vibration regions: the characteristic overlapping peak of O–H and N–H stretching vibrations at 3280-3290 cm^{-1} (Barboza et al., 2018; Rodrigues et al., 2015), the band at 2900 cm^{-1} attributed to the asymmetric C–H bonds (Figueira et al., 2011), the asymmetric and symmetric bands of C═O presented at 1630 and 1410 cm^{-1}, respectively (Omar et al., 2018), and the strong stretch at 1000-1100 cm^{-1} related with the alcohol groups (Murphy et al., 2009).

However, differences among the macroalgae species were registered. Green algae demonstrated a peak at around 847 cm^{-1} corresponding to the glycosidic C–H deformation and the O–H bending ring vibration. Additionally, the peak at 1032 cm^{-1} is also characteristic of cellulose (Jmel et al., 2019). The brown algae, *F. spiralis* and *F. vesiculosus* demonstrate peaks around 1740 and 1240 cm^{-1} which correspond to C═O and C—0 vibrations of carboxyl groups, present in the guluronic and mannuronic acids of alginate (Murphy et al., 2009), a compound present in the cell wall of *phaeophyta*. The peaks verified around 800 cm^{-1} correspond to the S═O vibration of sulphate groups, present in sulfated polysaccharides, namely fucoidan, a compound also specific to this group (Rupérez et al., 2002). In the red algae *Gracilaria* sp. and *O. pinntifida* peaks were detected at around 800 and 2930 cm^{-1}, corresponding to the vibration of sulphate groups of galactose present in carrageenan, a sulfated polysaccharide common in *rhodophyta that* may also be responsible for the amide group vibrations detected at around 1547 cm^{-1} (Rodrigues et al., 2015).

3.4. Baseline REEs concentrations in macroalgae used in experiments

Determination of REEs in the biomasses prior to their exposure to spiking solutions showed very low concentrations: Y, Pr, Gd, Eu and Tb in the six macroalgae were below 1.3 μg g^{-1}, and slightly higher concentrations of La (4.3 μg g^{-1}), Ce (9.0 μg g^{-1}), Nd (3.6 μg g^{-1}) in *U. intestinalis* and of Ce (2.4 μg g^{-1}) in *Gracilaria* sp.

3.5. Removal of rare earth elements by macroalgae

The ratios C_t/C_0 decreased with time in all the experiments although at different rates. Fig. 3 shows the decline with time of the normalised-Y concentrations in three spiked saline solutions containing the six macroalgae (plots A to F). At each plot it is compared the pattern when the macroalgae is exposed to 10, 89 and 500 μg L^{-1} initial concentrations. Despite this range of concentrations, differences among C_t/C_0 ratios for each sampling time were lower than 20% and clear-cut patterns were observed. Small differences were also observed for the other eight quantified REEs, pointing similar removal of REEs from solution (data presented as Supplementary Figs. S1, S2, S3, S4, S5, S6, S7 and S8).

3.6. Selectivity of macroalgae to remove rare earth elements

In this study, the best performance of the macroalgae to decrease the REEs concentrations in solution was evaluated based on the removal efficiency after 72 h of exposure (R), according the following expression:

$$R = (C_0 - C_{72}) \times 100/C_0 \quad (7)$$

where C_0 is the initial concentration and C_{72} the REE concentration that remains in solution after 72 h of the macroalgae exposure. Relatively constant concentrations in controls (except Ce) indicate that decrease in solution resulted from removal by the macroalgae.

Decrease of Y ratios with time were much more pronounced in the experiment with *U. lactuca* than with *U. intestinalis, F. spiralis*, *F. vesiculosus* and *O. pinnatifida* (Fig. 3). Whereas only 20–30% of the initial quantity of Y was in solution after 72 h in contact with *U. lactuca,* 70–80 % remained using the others macroalgae. An intermediate situation was observed for *Gracilaria* sp., with the residual quantity being 50–65 %. These results proved that removal efficiency of Y may vary within a broad range according to the macroalgae species.

Removal of the other REEs by *U. lactuca* was also relatively high, although *Gracilaria* sp. was more efficient in the removal of La, Ce and Pr. Fig. 4 compares the removal of the nine REEs by the six macroalgae at the same initial molar concentration (1 μmol L^{-1}). Species presenting the highest removal of REEs from mono-elemental spiked solutions were: *U. lactuca* for Y (>80 %), Nd, Eu, Gd, Tb (>70 %) and Dy (>60 %) and *Gracilaria* sp for La, Ce and Pr (>80 %).

3.7. Rare earth elements more easily removed by macroalgae

Assuming 60 % as the lower limit for removal with potential biotechnological application, data used in Fig. 4 were simplified to identify the elements efficiently removed by the macroalgae (Table 3). La and Ce were more easily removed from spiked saline solutions (1 μmol L^{-1}) by all tested species except *F. spiralis*, then Pr, Nd, Eu and Gd by two species (*U. lactuca* and *Gracilaria* sp. or *F. vesiculosus* in the case of Eu), and Y and Tb only by *U. lactuca.*

3.8. Sorption kinetic models

Adjustments of three kinetic models (PFO pseudo-first order, equation (2); PSO pseudo-second order, equation (3); Elovich, equation (4)) were applied only to the experimental results of the two species that presented better removal performance (*U. lactuca* and *Gracilaria* sp). All parameters related to the fittings accomplished by the models are presented in the Supplementary Table S1. Fig. 5 illustrates the fitting curves of the three models for La, Pr, Eu and Tb, for the initial concentration of 1 μmol L^{-1}, where all elements are at the same molar condition. Values of R^2 obtained for all the elements and the two macroalgae are given in

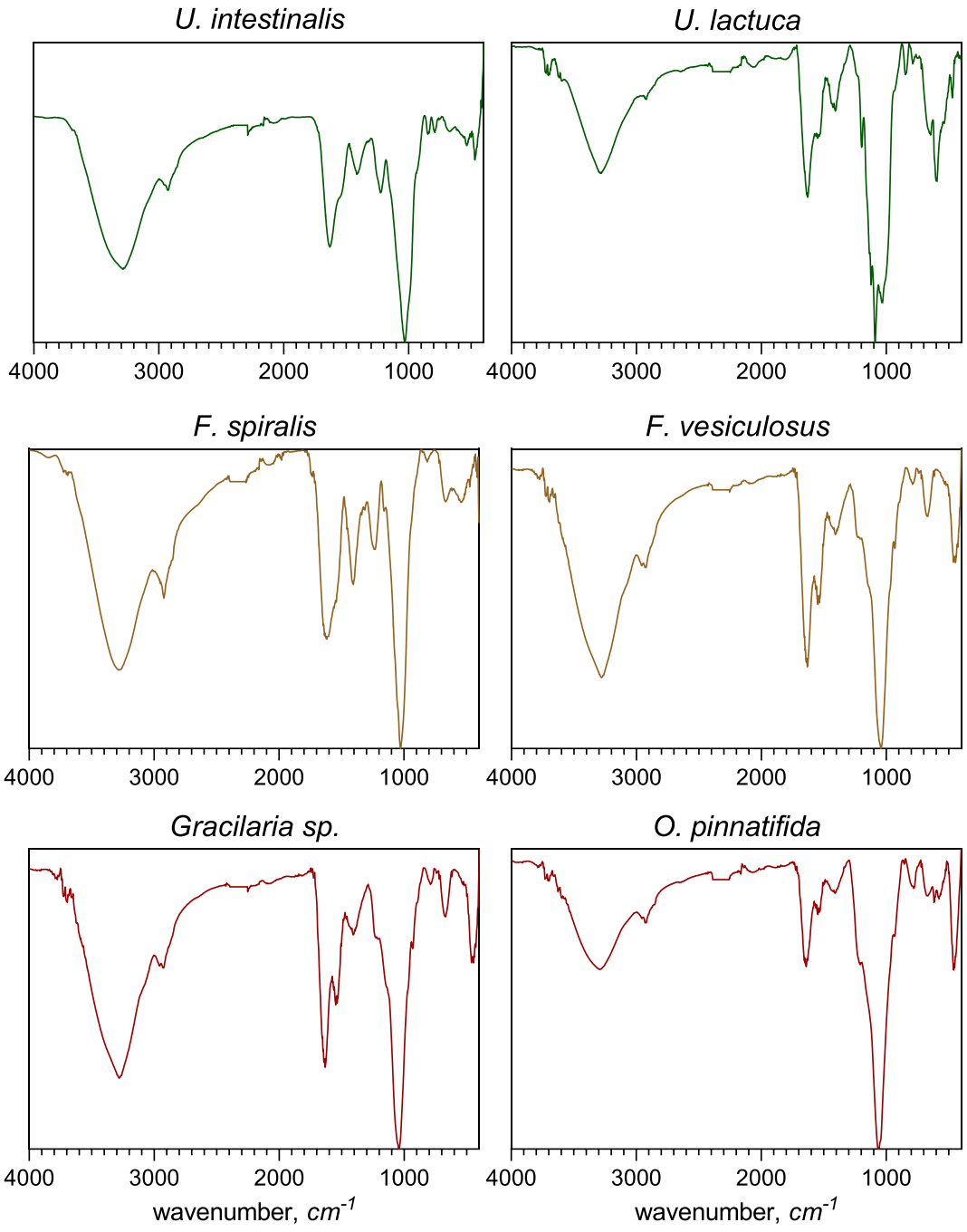

Fig. 2. FTIR spectra of the pristine macroalgae collected from the environment.

Table 4. Model adjustments were considered "good" in case of $R^2 >$ 0.980. The best fitting curves for both *U. lactuca* and *Gracilaria* sp. were obtained with the PSO model and Elovich model. Poorer adjustments were found for the heavy REEs Y, Tb and Dy.

4. Discussion

The present study showed the different ability of *U. intestinalis, U. lactuca, F. spiralis, F. vesiculosus*, *Gracilaria* sp. and *O. pinnatifida* to remove Y, La, Ce, Pr, Nd, Eu, Gd, Tb and Dy from contaminated seawater during a short period of 72 h. Because experiments run in mono-contaminated waters, interactions and competition between REEs to the binding sites of the macroalgae surface were not considered. Dissolved organic matter in the artificial seawater prepared for the experiments should be virtually absent. However, after the initial time it should not be excluded the possibility of macroalgae have exudate ligands, namely in response to the high concentration of REEs in solution. It is documented that some algae species such as *F. vesiculosus* are capable of releasing ligands that complex with metals, such as copper in an attempt to reduce its toxicity (Gledhill et al., 1999). To the best of our knowledge the possibility of REEs have this type of impact on macroalgae is not documented. If macroalgae-derived ligands would form stable compounds with REEs, competition with the sorption process may be effective. Despite the simplicity of the experimental design, the obtained results point to relevant information regarding the potential use of living macroalgae in biotechnological application towards the recovery of REEs. Only scarce information is available on the removal of REEs by living macroalgae (Jacinto et al., 2018).

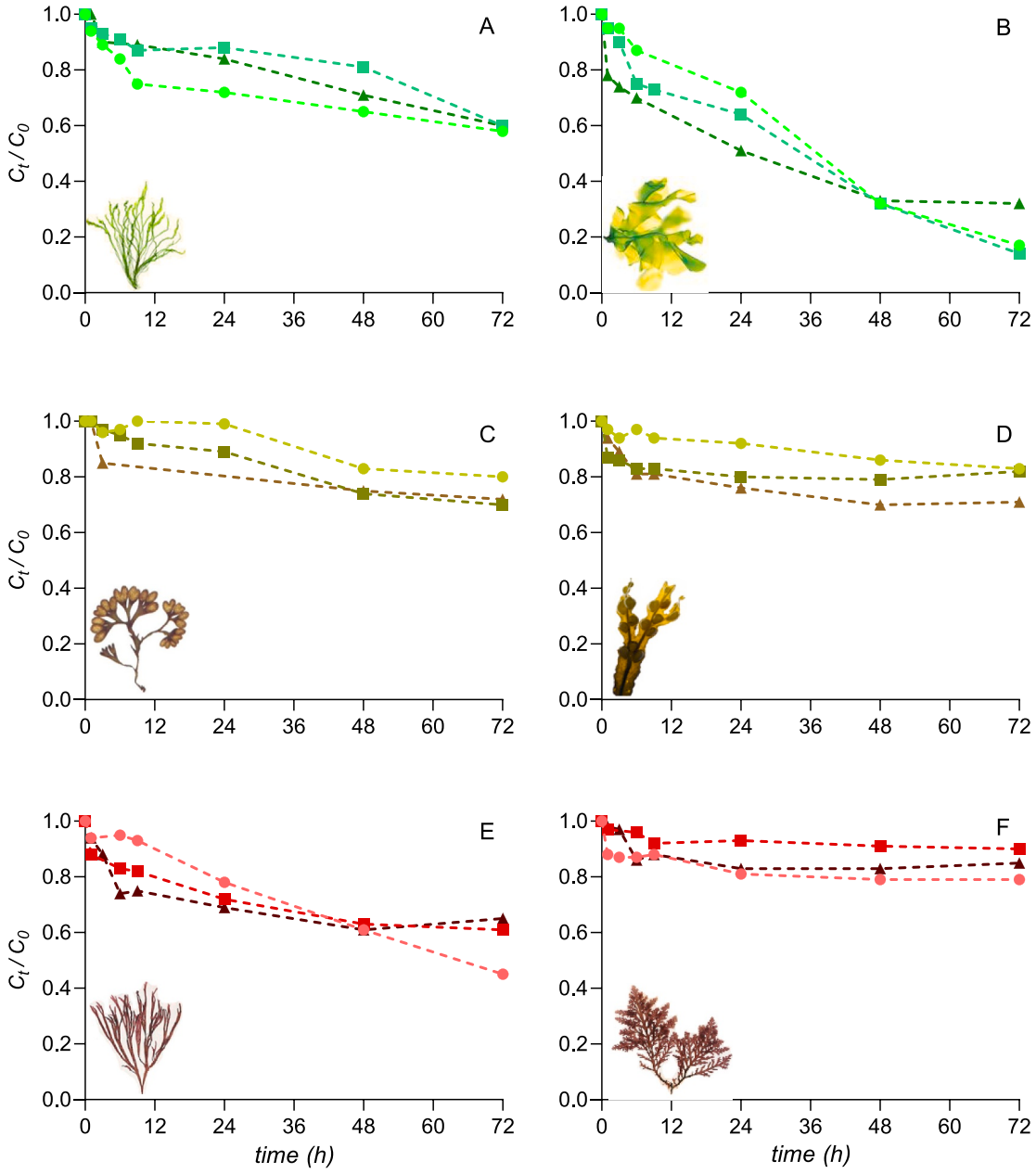

Fig. 3. Normalised concentrations of Y (C_t/C_0) during the 72 h of contact with the macroalgae *U. intestinalis (A), U. lactuca (B), F. spiralis (C), F. vesiculosus (D), Gracilaria* sp. *(E)* and *O. pinnatifida* (F) exposed to the initial concentrations of 10 (circles), 89 (squares) and 500 (triangles) μg L^{-1}.

4.1. Best macroalgae species to remove rare earth elements

Rare earth elements removed by 3 g L^{-1} of macroalgae (fresh weigh) from solutions containing between 10 and 500 μg L^{-1} fluctuated within narrow percentages. Intervals varied among the macroalgae, although a relative constancy of the values was found even for species with smaller external contact areas (Table 2). This result implies a minor influence of the initial concentration of the element on the removal process at least until 500 μg L^{-1}, the highest contamination scenario tested. Presumably, there are plenty of binding sites on the macroalgae surface with respect to the cations of REEs present in solution.

Among the six tested macroalgae *U. lactuca* exhibited the ability to remove all the studied elements at high percentages. After 72 h of contact time with the contaminated solutions, 63–86 % of the initial quantities of REEs were transferred to *U. lactuca*. Large external contact area of *U. lactuca* (264 ± 31 cm^2 g^{-1}) in comparison to *U. intestinalis* (148 ± 45 cm^2 g^{-1}), to *Gracilaria* sp. (79 ± 9.3 cm^2 g^{-1}) and to the other studied species (29–33 cm^2 g^{-1}) provides a higher number of binding sites for elements in solution. The availability of binding sites facilitates the sorption onto the macroalgae surface. A relevant question related to the use of living macroalgae as biosorbents is whether removal of REEs affect the wellbeing of the species. Interestingly, *U. lactuca* and *U. intestinalis*, the species that presented larger eternal contact areas, showed a decrease of 14% and 35% of biomass, respectively, during the experiments. These values contrast with the small variation of the biomass observed for the other species (medians of −1 to 9 %). Despite the high performance of *U. lactuca* for all the REEs studied, the highest removal of La, Ce, Pr was however obtained with *Gracilaria* sp., which indicates that the external contact area is not the major factor determining the sorption process. The functional groups present in the

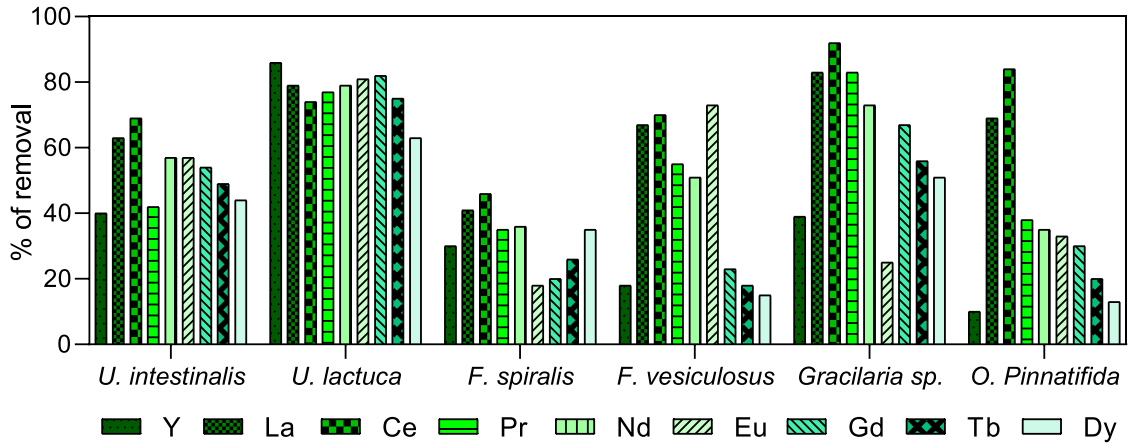

Fig. 4. Removal of rare earth elements (%) by six macroalgae species after 72 h of exposure at the initial concentration of 1 μmol L^{-1}.

Table 3
Macroalgae species with high removal efficiency (>60%) for rare earth elements (experiments with 1 μmol L^{-1} of REEs and 3 g of macroalgal biomass).

REEs	Macroalgae (removal >60 %)					
	U. lactuca	*Gracilaria* sp	*U.intestinalis*	*F. vesiculosus*	*O.pinnatifida*	*F. spiralis*
Y	x					
La	x	x	x	x	x	
Ce	x	x	x	x	x	
Pr	x	x				
Nd	x	x				
Eu	x			x		
Gd	x	x				
Tb	x					
Dy	x					

macroalgae that have high affinity to REES might have a major influence. In fact, *Gracilaria* sp. differentiate from macroalgae of other groups by the presence of sulfated polysaccharides, such as carrageenan in their cell wall (Fig. 2). The presence of sulphur groups, as shown by the FTIR analysis, may be active binding sites and contribute to the sorption of lighter rare earths (Ramos et al., 2007).

4.2. Decoupling of rare earth elements on removal processes

In environmental papers it is often referred that lanthanides have common properties (Johnson, 1980) and are treated as elements of similar behaviour in the aquatic environment. However, in technology it is well documented the individual application of REEs, namely in high-tech industries (Dutta et al., 2016). Decoupling of REEs by their preference for macroalgae species were clearly demonstrated in the present study. Indeed, different removal percentages of individual REEs were recorded for the six species. For example, La and Ce were the elements more easily uptaken, with removals above 60 % being achieved for *U. intestinalis, U. lactuca, F. vesiculosus*, *Gracilaria* sp. and *O. pinnatifida.* Ramasamy and co-authors (2019) using dried algae biomass also observed a preference towards the sorption of light REEs in comparison to heavy REEs, although this selectivity changed in a multi-element matrix. In contrast, when using living algae, Jacinto and co-authors (Jacinto et al., 2018) noted an increase in the sorption capabilities of the algae in a multi-element system composed of La, Ce, Nd and Eu. This difference emphasises the complex aspects behind the removal processes of REEs by living biosorbents.

4.3. Sorption or bioaccumulation

Cations in solution tend to diffuse to surfaces that are free of these elements and be sorbed if binding sites are available (Henriques et al., 2015b). On living algae elements may remain on the surface or may cross the cell wall and be accumulated. Examples of nutritive elements and toxic elements that are accumulated in algae are well documented (Chu et al., 2019; Intwala et al., 2008; Tai et al., 2010). Transport across the membrane is influenced by parameters such as molecular sizes and polarity (Hao et al., 1997; Tan et al., 2017). The present study was not designed to distinguish between elements associated with functional groups on the macroalgae surface and elements that crossed the cell wall. However, due to the short duration of the experiments the adsorption of REEs should be greater comparatively to their accumulation into macroalgae. Although (Minoda et al., 2015) showed that *Galdieria sulphuraria* is capable of accumulate La, Nd and Dy inside algae cells, understanding of the interaction between REEs and living organisms is still in the early stages. In this study it was assumed that REEs were preferentially sorbed on the macroalgae and the models PSO, PFO and Elovich were tested. Application of the pseudo-first order model showed poorer adjustments for both, *U. lactuca and Gracilaria* sp.. Association of the majority of the elements to the macroalgae are not explained by a simple sorption (Jacinto et al., 2018). Better adjustments with the Elovich model suggest that association of REEs with the macroalgae involves more complex mechanisms of chemical nature (e.g. complexation, coordination and chelation).

4.4. REEs-loaded macroalgae biomass as raw material source

The typical process of extraction of REEs from ores like apatite involves the grinding of the ore, followed by an acid leaching, solvent extraction, precipitation and calcination of the REE oxalate (Battsengel et al., 2018). All of these processes involve not only the consumption of large amounts of reagents and energy, but are also highly pollutant due to emission of gases, sludge and other effluents (Vahidi and Zhao, 2017). The use of macroalgae capabilities to recover and concentrate REEs from

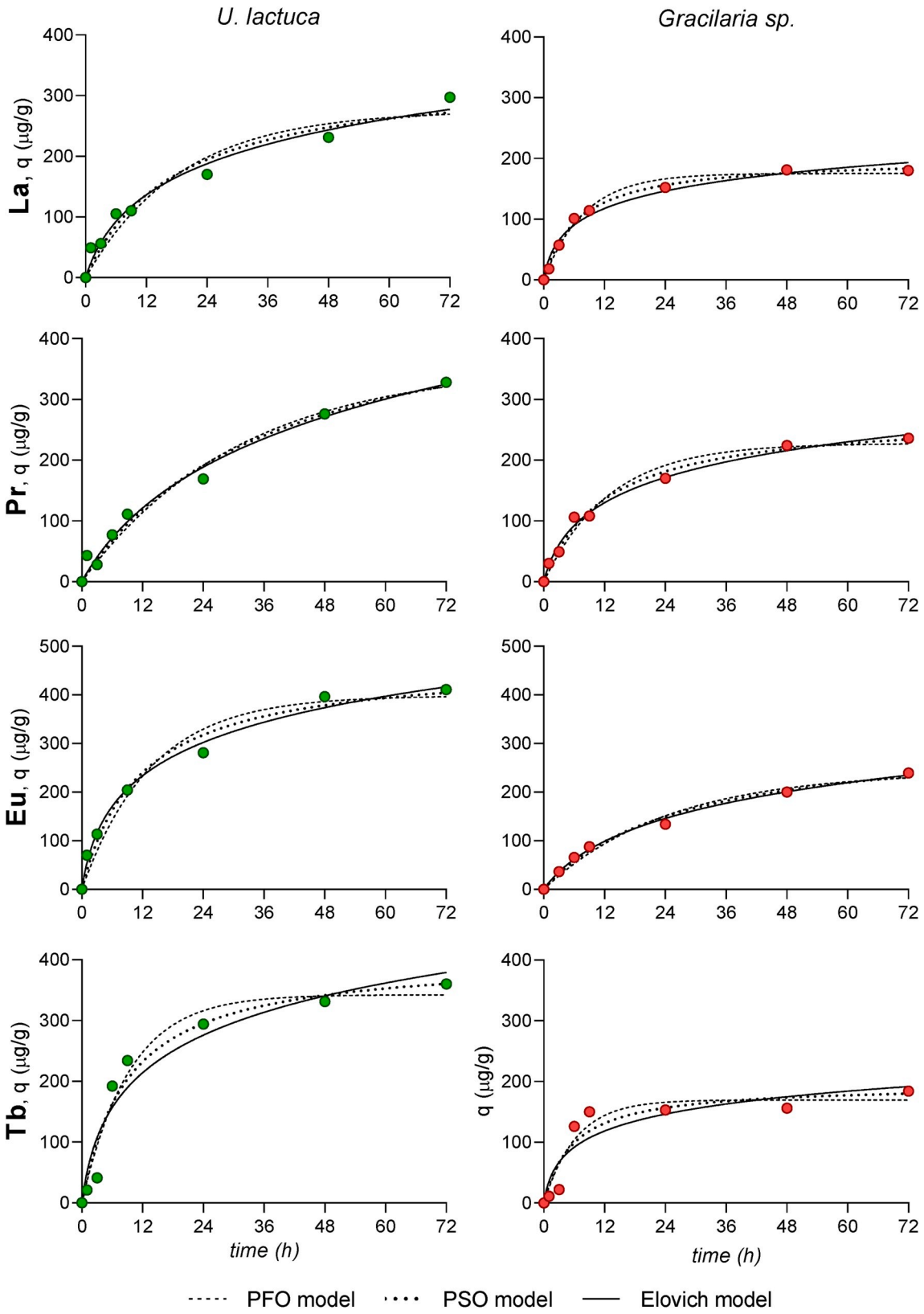

Fig. 5. Fitting curves of the PFO, PSO and Elovich models to the removal of 1 µmol L^{-1} of La, Pr, Eu and Tb by *U. lactuca* and *Gracilaria* sp..

diluted solutions may constitute a greener method to obtain REEs, as source of raw material for industry. Contaminated waters such as neutralized acid mine drainage (Ayora et al., 2016) or wastewaters from the lamp industry (Čížková et al., 2019) could be used as a source of REE for *U. lactuca*. Indeed, the REEs concentrations in algal biomass (from equation (6); Table 5), after 72 h of exposure to the highest contamination scenario, 500 µg L^{-1}, particularly for *U. lactuca*, *U. intestinalis* and *Gracilaria* sp., exceeded 1 mg g^{-1} for most elements, which is a value

Table 4
Values of R^2 obtained in the adjustment of each kinetic model for the sorption of rare earths by *U. lactuca* and *Gracilaria* sp. $R^2 > 0.980$ are in grey.

Element	Species	PFO model	PSO model	Elovich model
Y	*U. lactuca*	0.958	0.964	0.970
	Gracilaria sp	0.978	0.987	0.985
La	*U. lactuca*	0.936	0.958	0.975
	Gracilaria sp	0.989	0.995	0.979
Ce	*U. lactuca*	0.987	0.991	0.993
	Gracilaria sp	0.992	0.996	0.991
Pr	*U. lactuca*	0.987	0.990	0.993
	Gracilaria sp	0.977	0.989	0.991
Nd	*U. lactuca*	0.963	0.973	0.981
	Gracilaria sp	0.978	0.988	0.992
Eu	*U. lactuca*	0.962	0.980	0.992
	Gracilaria sp	0.981	0.990	0.996
Gd	*U. lactuca*	0.965	0.977	0.986
	Gracilaria sp	0.977	0.986	0.993
Tb	*U. lactuca*	0.965	0.959	0.938
	Gracilaria sp	0.913	0.892	0.849
Dy	*U. lactuca*	0.956	0.971	0.982
	Gracilaria sp	0.958	0.975	0.989

Table 5
Concentrations of rare earths in macroalgae biomass (q_{72}; from equation (6); μg g^{-1}) after 72 h of exposure to mono-elemental rare earths spiked solutions, with initial concentration of 500 μg L^{-1}).

q_{72} (μg g^{-1})	Y	Ce	Pr	Nd	Eu	Gd	Tb	Dy
U. lactuca	1047	938	1004	899	855	1101	1193	597
U. intestinalis	767	1097	1184	818	1295	990	1022	636
F.spiralis	261	219	451	515	318	283	367	352
F.vesiculosus	261	380	492	485	292	255	270	317
Gracilaria sp.	536	1187	1420	623	1034	905	876	861
O. pinnatifida	210	734	694	570	395	335	288	259

similar to those found on standard apatite ore (Sano et al., 2002). This means that those macroalgae were able to concentrate REEs in their tissues up to 2500 times, comparing to REEs initial concentration in solution (Bioconcentration factors, Table S2). Also, REEs may be easily recovered from algal biomass into a more concentrated solution, by the dissolution of the algal tissue (Henriques et al., 2019) through digestion, using a small volume of acid, as described in Material and Methods section. Assuming the REEs concentrations in algal biomass, the levels in digested *U. lactuca*, *U. intestinalis* and *Gracilaria* sp. (Table S3) are comparable to those found on a typical nitric acid leachate of apatite, around 70 mg L^{-1} (Li et al., 2006).

These results show that this technology has the potential to effectively recover REEs from contaminated effluents. The use of living algae can also help to reduce the carbon footprint left by the REEs industry as photosynthesis (and consequent consumption of carbon dioxide) is promoted under growth conditions.

5. Conclusions

The results obtained in this study highlight the capabilities of living algae to act as a biosorbent for the recovery of REEs present in contaminated waters in concentrations up to 500 μg L^{-1}. The removal of these elements is mainly dependent on the formation of chemical bonds between them and the algae surface, with the process being time-dependant: faster removal occurs in the first 24 h of contact, but an equilibrium is not reached even after 72 h. Different algae species showed different performances, with *U. lactuca* being the only species capable of efficiently remove all elements tested. Although the intracellular accumulation of certain elements was not possible to assess in the present study, it may justify higher removal of certain elements. Lack

of mortality and low variation of biomass during the experiments reveal that the algae could maintain their metabolism in the presence of the REEs. To evaluate the viability of these species on REE removal, multi-element matrix is proposed as future work.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

João Pinto: Investigation, Validation, Formal analysis, Writing - original draft, Writing - review & editing. **Bruno Henriques:** Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Supervision, Project administration, Writing - review & editing. **José Soares:** Investigation, Formal analysis. **Marcelo Costa:** Validation, Investigation, Formal analysis. **Mariana Dias:** Investigation, Formal analysis. **Elaine Fabre:** Investigation, Formal analysis. **Cláudia B. Lopes:** Methodology, Investigation. **Carlos Vale:** Validation, Writing - original draft. **José Pinheiro-Torres:** Project administration, Funding acquisition. **Eduarda Pereira:** Methodology, Validation, Resources, Supervision, Funding acquisition, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2020.110376.

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