Recovery of rare earth elements from aqueous solution obtained from Vietnamese clay minerals using dried and carbonized parachlorella

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Abstract

The ongoing development of new advanced technologies, created increasing demands for rare earth elements (REEs) in the international market. The available conventional technologies for concentration and recovery of REEs are expensive making biosorption an efficient and low-cost technology for the recovery of REEs from aqueous solution. Thus, the biosorption and desorption of multi-component solution containing Y(III), La(III), Sm(III), Dy(III), Pr(III), Nd(III), Gd(III) were investigated using dried or 250°C and 350°C carbonized parachlorella. Evaluating the effect of pH with respect to contact time indicated

a dependency of the system with those parameters. The optimum pH for dried and 250°C carbonized parachlorella was 7 whereas 350°C reaches its maximum uptake at pH 4. Rapid adsorption within the first 5 min of contact followed by a slight variation the following 20 min characterized the sorption processes onto parachlorella by-products. The mechanism of the biosorption is explained by a combination of complex reactions occurring simultaneously in the biosorption process.

In addition, desorption process has been investigated using various concentrations of HCl, HNO₃, and H₂SO₄ at different temperatures. It was found that the reversible process is rapid, less temperature and pH dependent with high desorption percentage. Moreover, only light REEs were desorbed regardless of the kind of acid and the solution temperature. Parachlorella is found to be good and low-cost biosorbent for the recovery of above REEs from aqueous solutions.

Key-words: Rare earth, biosorption, recovery, carbonization, parachlorella

1. Introduction

Rare earth elements (REEs) are often referred as the “seeds of technology” because of their uses in high-tech strength permanent magnets, lasers, automotive catalytic converters, fiber optics/superconductors, electronic devices, and green energy sectors [1, 2]. Due to the ongoing development of new advanced technologies, there is an over-increasing demand for REEs in the international markets, with emphasis on identifying new resources to ensure adequate supply for present and future use.

The designation “rare earths” refers to the 15 elements of the periodic table known as “lanthanides” with yttrium and scandium, further divided as a function of their atomic number into two categories. Light rare earth elements (LREE), which accounted for 66.8% of global demand in 2010 [2] referred to lanthanum, cerium, praseodymium, neodymium, promethium and samarium. Heavy rare earths elements (HREE), less common and more valuable, referred to the rest of lanthanides elements with yttrium. The 17 REEs are found in all REE geological deposits because they share many similar properties but their distribution and concentrations vary [2]. REE mineral deposits are usually rich in either LREE or HREE, but rarely contain both in significant quantities [2]. The term “rare earth” is actually a misnomer, because these elements are more abundant in the earth's crust compared to silver, gold or the platinum-group metals and are part of more than 200 rock-forming minerals [1, 3]. They are “rare” because they do not naturally occur in metallic form, only as mixed and scattered in minerals and are difficult to separate from each other due to very similar physico-chemical properties [1].

Several expensive methods exist to recover REEs from ores such as pyrometallurgy, hydrometallurgy etc processes in case of REEs rich ores. In addition, different methods have been proposed for separation and preconcentration of REEs such as precipitation, liquid-liquid extraction, solid-liquid extraction, super critical extraction, electro-winning, electro-refining, etc [4-7] but, those methods are inefficient or required a large volume of solvent or intensive labor [7-9]. Thus, find a low-cost and efficient technology for the concentration and recovery of REEs led to the choice of biosorption. Some biomasses such as *pseudomonas aeruginosa*, *saccharomyces cerevisiae* etc have been tested [10-11] and

found efficient for the recovery of Dy(III), Sc(III), La(III), Pr(III), Nd(III), Eu(III). However, due to the large number of candidate biomasses, biosorption of REEs need to be deepened and more biomasses need to be tested.

Therefore, in this study parachlorella, an alga used by PANAC Co. Ltd to enhance the bio-energy production efficiency, was used as biosorbent. In addition, a solution of REEs containing a mixture of Y(III), La(III), Sm(III), Dy(III), Pr(III), Nd(III) Gd(III) under various concentrations was prepared from Vietnamese rare earth ore and used for the experiment. Thus, In order to improve the sorption efficiency of parachlorella, the alga is carbonized at 250°C and 350°C and the REEs uptake of carbonized parachlorella is compared to the dried one. Desorption process was also evaluated and the mechanism clearly described.

2. Materials and Methods

2.1 Equipments

Thermo gravimetric differential thermal analysis (TG-DTA) (Thermo plus EVO TG 8120/ Rigaku) was carried out under nitrogen condition. The carbonization of parachlorella was made out using electric furnace (HPM-0G/AS ONE). The surface texture of the biosorbent before and after experiment was investigated using SEM (Scanning electron microscope JSM-6510LA/JEOL). The zeta potential was measured by electrophoresis analysis (LS-2000E/ Photal OTSUKA Electronic). The reciprocal shaking bath (FTB-01/AS ONE) was used for the batch experiment process. The pH of the solution was measured with pH meter (HM-25R/ TDA DK) previously calibrated. The REEs content in

treated solution was analyzed using ICP-OES (Inductively coupled plasma-optimal emission spectrometer /Perkin Elmer/Optima 5300). In order to point out the structure of the biosorbents and the functional group involved in the adsorption process Fourier transform infrared spectrometer (FT/IR 4100/DR410/ATR PRO 450-S) was used.

2.2 Biosorbents preparation

Parachlorella was received from Panac. Co. Ltd in dried form (the sample was subject to spray dried for 3 days). One part of the material is subjected to the thermal decomposition analysis under N₂ atmosphere (decomposition rate 10°C/min) on TG-DTA in order to point out the optima temperatures at which the carbonization should be made up. As results, the dried parachlorella was carbonized at 250°C or 350°C in the electric furnace, for 30 min. The heated was done under N₂ atmosphere (gas flow: 15L/min) to avoid any oxygenation during the carbonization. Then the carbonized materials are desiccated until there are completely cooled. The sample was then sieved to obtain a fraction of fine particles all passing 0.6 mm.

2.3 Batch experiments

A solution containing the mixture of Y(III), La(III), Sm(III), Dy(III), Pr(III), Nd(III), Gd(III) rare earth ions and others elements as Mg, Si, K, Ca, Mn, and Fe in diverse concentrations and initial pH= 5.63 at 30°C is shown in Fig. 1. This solution was prepared by dissolving the Vietnamese rare earth ore in 2 wt% of ammonium sulfate aqueous solution. The mixture was kept for 60h under room conditions. This aqueous solution (Fig.1) was used as an initial one for the batch experiments.

Batch studies were conducted to investigate the parametric factors such as pH, solution temperature, biosorbent dosage and contact time for both biosorption and desorption processes. The pH of the solution was adjusted using 1 mol/L of HCl or NH₃ aqueous solution. The biosorbent was then mixed with REEs aqueous solution, resulting to the concentration of 5 g/L. The mixture was then shaken in the bath at 30°C and 150 rpm. The sample was filtered with 0.2 µm filter and the filtrate was analyzed using ICP-OES in terms of remaining REEs and others elements concentration. The amount of REEs or others elements adsorbed q (mg/g) was calculated by using the following equation

$$q = \frac{V(C_{init} - C_{fin})}{M} \quad (1)$$

V Volume of the solution (L)

M Mass of the biosorbent used (g)

C_{init} Initial REEs or others common ions concentration (mg/L)

C_{fin} Final concentration of rare earth ions or others common ions in solution (mg/L)

The percentage of removed rare earth ions or others was interpreted as:

$$\text{Removal}(\%) = \frac{C_{init} - C_{fin}}{C_{init}} \quad (2)$$

Samples for desorption experiments were prepared by putting 2g of biosorbents and 100 mL of REEs solution into contact for 2 hours (to saturate as much as possible the available biosorbents sites with rare earth ions) . The biosorption process was conducted at pH 7 and 30°C until equilibrium was reached. The solution was analyzed using ICP-OES

and equation (1) helps to determine the desorption density at equilibrium q_o for the selected biosorbents. The REEs loaded samples, which will be subjected to desorption experiment were dried in the oven at 80°C for 72 hours.

0.05 g of the prepared sample was mixed with 10 mL of HCl, HNO₃, H₂SO₄ (various concentration of acid have been used) and shaken at various temperatures depending on the parameter study. The solution obtained was analyzed using ICP-OES and the results obtained were interpreted in terms of total REE recovery

$$q(X) = \frac{C.V(X)}{M_a} \quad (3)$$

X represents HCl, HNO₃, or H₂SO₄

$V(X)$ volume of HCl, HNO₃, or H₂SO₄ solution

C concentration of REE in the solution after desorption process was achieved

M weight of the de-sorbent used

The desorbed amount of rare earth ions using solution X (*Desorbed % (X)*) was expressed as

$$Desorbed \% (X) = \frac{q(X)}{q_o} \cdot 100 \quad (4)$$

3. Results and discussions

3.1 Biosorbents characteristics

As organic material, parachlorella is mainly composed of hemicelluloses, cellulose, lignin and others minerals [12]. The thermal decomposition of parachlorella can therefore be attributed to the decomposition of these macromolecules, which is accompanied by the release of volatile matters from the raw material.

Generally, carbonization also called slow pyrolysis or conventional pyrolysis, is characterized by a slow heating rate (6-60°C/min), and the formation of pyrolysis product occurs in the temperature range of 275-675°C [13]. The first stage of biomass decomposition, also called prepyrolysis stage, occurs at 120-200°C. During this stage, some internal molecular rearrangements such as water elimination, bond breakage, appearance of free radicals, and the formation of carbonyl, carboxyl and peroxide (ROOR') groups take place [13]. The second stage mainly involves the decomposition of solid biomass, which is associated with high rate of transformation and formation of pyrolysis product. During the third stage, the char decomposes at a very slow rate, forming a carbon-rich residual solid [13].

Many researchers have worked on the thermal decomposition of cellulose, hemicelluloses and lignin. For instance, it was previously reported that the decomposition of cellulose occurs in a flexible range of 200-400°C, lignin decomposed in the range of 150-750°C (900°C as maximum). Characterized by low thermal stability, hemicellulose is decomposed in the range 180-240°C [14-15].

The weight loss measurement of parachlorella can be well understood by considering the rate of raw material transformed (burned) with increasing temperature calculated from equation 5.

$$\alpha = \frac{W_T}{W_b} \quad (5)$$

where, W_T , W_b are respectively the weight of solid (dried) burned at temperature T and the total weight of solid burned during the pyrolysis process.

In other world, α represents the rate of volatile matter release from the raw material with increasing elementary temperature. α was calculated from the weight loss data obtained with TG-DTA analysis. Fig. 2 shows the experimental results of α vs. T .

It should be noted that, due to TG-DTA machine program setting, thermograms of α vs. T in Fig. 2 show two curves which were due to the machine programming system. The machine is settled to burn once time and re-burns at the same temperature that justifies the two curves. The highest curve represents the amount of volatile matters release from the material after the first thermal decomposition and the lowest one deal with the second burning operation. Moreover, α increases to a peak at around 300°C and then decreases with increasing temperature until 400°C whereby stability is observed.

Furthermore, Fig. 2 highlights that the prepyrolysis states of dried parachlorella occurred in the range 0-200°C were weight loss was comparatively low. From 200°C, the decomposition increased rapidly to a maximum at 300°C. Thus, parachlorella, decomposition of macromolecules may occur within 200°C-300°C. Beyond 300°C, however, the transformation rate decreased progressively until 400°C, implying that carbon-rich material may be formed in the range of 300-400°C with slow rate of gasification. Hence, there seems to be an optimal decomposition temperature at which carbon rich material is formed. Then the carbonization temperatures have been set at 250°C

or 350°C to better understand the transformation occurring before and after the main peak of Fig. 2. Further experiments were carried out using three kinds of biosorbents: dried parachlorella (PA); 250°C carbonized parachlorella (PA250); 350°C carbonized parachlorella (PA350).

PA, PA250 and PA350 were subjected to FT-IR analysis in order to understand the functional groups governing the biosorbents. Results are summarized in Fig. 3. Fig.3 shows that PA, PA250, and PA350 present different shapes. This should be due to the carbonization process that shifts the functional group of the original dried biosorbent to others more active functional groups [16]. The presence of carbonyl groups on the surface of the biosorbents at the wave numbers 1676 cm⁻¹ and 1707 cm⁻¹ for PA, 1707 cm⁻¹, 1710 cm⁻¹ and 1711 cm⁻¹ for PA250 and 1688 cm⁻¹ for PA350 cm⁻¹ may be helpful in the biosorption processes. In the carbonyl group, oxygen is more electronegative than carbon and then, can picks over electron density from carbon to increase the bond polarity. Thus, the carbon of the carbonyl group becomes electrophilic (able to react with anions in solution). In the same way, electronegative oxygen can react with cations. Moreover, phosphorus compound, which main element is phosphorous, is recognized as a highly electronegative group reacted as nitrogen since they belong to the same chemical group.

In addition, X-ray fluorescence (XRF) was used to determine the chemical composition of dried and carbonized parachlorella. The results are shown in Table 1. XRF analysis detects the presence of chemicals except C, O and H. Parachlorella by-products are mainly composed on P, S, K, Ca and Mg. The presence of cations K⁺, Mg²⁺ and Ca²⁺ may be helpful in ion exchange process [17].

Furthermore, the scan electromagnetic images of dried and carbonized parachlorella have been carried out and shown in Fig. 4. Dried parachlorella compared to carbonized one looks like a block. This block has been altered by the temperature since small pores appeared. Carbonization may increase the porosity of parachlorella by opening new pores or deepen existing pores [18].

3.2 Effect of pH on REEs removal

pH is one of the most important and predominant factors to be considered when assessing the biosorption capacity of a biosorbent as it influences the biomass adsorptive sites as well as the solution chemistry of REEs. The pH of the system controls the sorption capacity due to its influence on the surface properties and metal speciation [19]. The sorption experiments were carried out in the pH range 1-10 while keeping other parameters constant. 1mol/L of HCl or ammonia (because of the use of ICP-OES which does not show reliable results when Na concentration is high in the analysis solution) solution were used for the pH adjustments. Precipitation of the solution of rare earth ions, with rapid deposit is observed at pH higher than 7 due to the formation of hydroxide forms of rare earth ions which become dominant. Consequently, the pH effect on parachlorella by-products was conducted in the batch in the pH range 1-7 for 1hour. Results are shown in Fig.5. Zeta potential of PA, PA250, and PA350 were also investigated and results are shown in Fig.6.

Fig.5 indicated that, at strong acidic pH (pH range 1-3), rare earth ions uptake is inhibited for PA, PA250 and PA350 as shown by earlier researchers [20-22]. The low uptake observed at strong acidic values may be explained by the protonation of biosorbents

sites with H^+ ions. Fig. 6 justifies this assumption. Consequently, the majority of binding sites were occupied and rare earth cations may not be able to compete with hydronium cations in occupying sites due to the repulsion forces created between same positively charged ions [23].

As pH increased, surface positive charges decrease, leading to interaction between positively charged rare earth ions and negatively charged biosorbent sites [20] (Fig.6). PA and PA250 reached their maximum uptake of rare earth ions at pH 7 whereas PA350 increases until pH around 4 and decreases again.

As we described in the precedent sections, carbonyl functional group may be presents in 350°C carbonized parachlorella. The maximum uptake of rare earth ions observed at pH 4 using PA350 may be explained by the reaction of carbonyl functional group which pKa values lies around 4.8 [24]. Moreover, the point of zero charge of PA350 is close to pH 4.5 (Fig. 6). We can conclude that Y^{3+} , La^{3+} , Sm^{3+} , Dy^{3+} , Pr^{3+} , Nd^{3+} , Gd^{3+} are the dominant species at pH less than 4.5. Those species shift to hydrolyzed forms as $Y(OH)^{2+}$, $La(OH)^{2+}$, $Sm(OH)^{2+}$, $Dy(OH)^{2+}$, $Pr(OH)^{2+}$, $Nd(OH)^{2+}$, $Gd(OH)^{2+}$ or dihydrolyzed rare earth ions $Y(OH)_2^+$, $La(OH)_2^+$, $Sm(OH)_2^+$, $Dy(OH)_2^+$, $Pr(OH)_2^+$, $Nd(OH)_2^+$, $Gd(OH)_2^+$ or trihydrolyzed rare earth ions $Y(OH)_3$, $La(OH)_3$, $Sm(OH)_3$, $Dy(OH)_3$, $Pr(OH)_3$, $Nd(OH)_3$, $Gd(OH)_3$ or the mixture of the three hydrolyzed forms [21, 25].

For PA and PA250 the maximum uptake of rare earth ions observed at pH 7 may be explained by the electrostatic interaction between rare earth trivalent ions and biosorbent surface charge which is negatively charged (Fig.6).

Moreover selectivity in terms of ions uptake and type of biosorbent is observed at optimum pH. Consequently, PA and PA250 are found to be more efficient for biosorption of Sm and La than PA350. PA is more efficient for Pr and Nd than others biosorbents. PA250 is the best biosorbents for Dy, Gd, and Y. Then, the following experiments are done base on the optimum pH observed for PA and PA250, means pH 7.

3.3 Effect of contact time and possible biosorption mechanism

REEs uptake onto PA, PA250 and PA350 was investigated with respect to contact time in the range of 0-120 min, while keeping other parameters constant. Fig.7 shows the effect of contact time for PA, PA250 and PA350 at pH 7, keeping the biosorbent dosage to 5 mg/L. For all the biosorbents, a rapid uptake of REEs ions was observed during the first 5 min followed by a slight variation of uptake rate until 20 min. As expected, PA and PA250 show the best results compared to PA350. It is difficult to distinguish the best biosorbent in this experiment since selectivity is observed depending on the sorbate. For example, PA is good biosorbents for Nd than PA250 whereas PA250 is efficient for La than PA. This should be due to the affinity of each sorbate to react with each biosorbents than others. For better understanding of the mechanism of the biosorption system, kinetics of the others ions such as Si, Fe, Mn, Mg, K and Ca present in the Vietnamese ores solution was evaluated. Those concentrations have been compared to their initial ones. Results are shown in Fig.8. Fig. 8 shows that concentrations of Si, Fe, Mn and Ca were stable before and after biosorption process. However, Mg and K concentrations increased after sorption for PA and PA250 and only concentration of K increases after sorption for PA350 meaning that

only rare earth ions are adsorbed on parachlorella species selectively during the biosorption processes. As the XRF results of parachlorella by-products have shown, Mg, K are also presents in the sorbents. Then the increase of Mg and K concentration in the solution may be due to the dissolution of those elements present on the surface of biosorbents during the biosorption process. Authors suspect a kind of ion exchange between rare earth ions in the solution and Mg, K present on the surfaces of biosorbents. Then, mechanisms involved in biosorption of Vietnamese ores solution using parachlorella should be a complex process composed of many reactions occurring simultaneously in the system biosorbent-sorbates: electrostatic forces between rare earth ions and surface charges, biosorption of the tested rare earth ions onto the active functional groups of biosorbents, and ion-exchange process as described by Das et al. [26]. In addition, since the presence of hydroxide forms of rare earth ions were pointed out, sorption of REEs onto parachlorella species may also due to surface complexation reactions of parachlorella species forming $M-O-Ln^{2+}$. M designated the biosorbents used (PA, PA250, and PA350) and Ln represents rare earth ions.

3.3 Adsorption kinetics

Adsorption kinetics describes the solute uptake rate as a function of residence time of adsorbate at the solid-liquid phase including the diffusion process [16]. The kinetic rate of REE ions was investigated using the pseudo first-order and pseudo second-order model [27]. The agreement between experimental data and models as depicted by the values of their correlation coefficients (R^2) are summarized in Table 2. The pseudo first-order kinetic model is described by (Eq.6)

$$\log(q_e - q_t) = \log q_e - t \cdot k_1/2.303 \quad (6)$$

The pseudo second-order kinetic model is expressed as (Eq.7):

$$\frac{t}{q_t} = \frac{1}{[k_2 q_e^2]} + \frac{t}{q_e} \quad (7)$$

- K_1 Pseudo first-order kinetic equilibrium rate constant
- K_2 Pseudo second-order kinetic equilibrium rate constant (mg/g/min)
- q_e Amount adsorb per gram of the biosorbent at equilibrium (mg/g)
- q_t Amount adsorb per gram of the biosorbent at time t (mg/g)
- t Contact time (min)

Fig.9 represents the plots t/q_t vs. t of PA at the indicated experimental conditions. Table 2 shows the values of the kinetics. The correlation coefficients for the pseudo second-order kinetic model shows a much better fit compared with the coefficients derived from the pseudo first-order kinetic model, suggesting that the biosorption of REE ions onto PA, PA250 and PA350 follow the pseudo second-order kinetic model. Moreover, the experimental values of the biosorbents densities at equilibrium q_e are compared to the calculated values of the equilibrium densities q_{e1calc} and q_{e2calc} (Table 2) respectively the equilibrium density calculated using equations (6) and (7). The close or small difference between the values of q_e and q_{e2calc} further confirmed the fitness of pseudo second-order kinetic model with experimental data. The biosorption reaction rate is then limited to the rate of the rare earth ions diffusion in the pores.

3.5 Adsorption activation energy and enthalpy of activation

The Arrhenius equation for calculating activation energy is known as (Eq.8):

$$K_2 = k \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

The parameters k and E_a called Arrhenius parameters characterized (Eq.8). The pre-exponential factor K or the frequency factor indicates the rate at which collisions occur. The activation energy E_a is the minimum kinetic energy required for the reaction during the molecular collision [28].

k The pre-exponential factor or frequency factor (g/mg/min)

E_a The activation energy of sorption (J/mol)

R The gas constant (8.314 J/mol/K),

T The solution temperature (K)

Arrhenius equation parameters were evaluated using the pseudo second-order kinetic constant obtained based on temperature controlled data (30°C, 50°C, 70°C). Sorption of REEs onto parachlorella species increases with temperature showing the temperature dependency of the process. The value of activation energy is obtained by using the pseudo second-order kinetic equilibrium rate constant k_2 obtained at each temperature. A plot of $\ln k_2$ vs. $1/T$ yields a straight line with a slope $-E_a/R$. Generally, the value of activation energy is used to distinguish physical and chemical sorption. Physical sorption is characterized by low energy whereas chemical sorption involves stronger forces needed for the formation of external bonding [16].

In the present study the values of activation energy E_a , and enthalpy of activation ΔH° (Eq.9) as well as the nature of the reaction occurring have been shown in Table 3.

$$\Delta H^\circ = E_a - RT \quad (9)$$

It can be concluded from Table 3 that Y^{3+} , La^{3+} , Sm^{3+} , Dy^{3+} , Pr^{3+} , Nd^{3+} , and Gd^{3+} are chemically adsorbed onto dried and carbonized parachlorella and the tested rare earth ions are adsorbed under endothermic reactions. However, the real nature (chemisorption and endothermic) of the systems (Dy, PA); (Dy, PA250) and (Y, 250) was not clearly determined due to their low adsorption densities.

3.6 Adsorption isotherms

Sorption density of PA, PA250 and PA350 as a function of biosorbent dosage was investigated in the biosorbent dosage range of 1-250 g/L while keeping REE initial concentration constant. The amount of adsorbed REE ions increased with increasing biosorbent dosage, emphasizing the dependency of biosorption density of the system on the biosorbent dosage.

In order to describe the interactive relationship between biosorbent and adsorbate and design the biosorption system, Langmuir model was examined using (Eq.10)

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{C_e}{q_{max}} \quad (10)$$

C_e REE concentration in solution at equilibrium (mg/L)

q_e Amount adsorb per gram of the biosorbent at equilibrium (mg/g)

b Langmuir constant (L/mg)

q_{max} Maximum adsorption capacity (mg/g)

Langmuir isotherms (Eq. 10) deal with monolayer coverage formed by adsorbed molecules. As can be seen in Table 4, Langmuir isotherm model fitted well the experimental data and the best densities with carbonized materials were observed with 250°C carbonized materials demonstrating the importance of low carbonization temperature on parachlorella. Results obtained in this work are lower compared to the ones of Oliveira et al. [17]. Many parameters affect the biosorption process that creates a discrepancy in experimental results. In multi-components solution, all sorbates compete for a single population of surface sites and interact each other. In that case competitive Langmuir adsorption occurs [29] . For example in a solution containing only one sorbate, the relation between the biosorption density at equilibrium and the maximum one is expressed as:

$$\frac{q_e}{q_{max}} = \frac{bC_e}{1+bC_e} \quad (11)$$

Generalizing the above result to the case where j sorbates compete for the site we obtained:

$$\frac{q_{ei}}{q_{max}} = \frac{b_i C_{ei}}{1 + \sum_{all j} b_j C_{ej}} \quad (12)$$

(Eq. 12) explained the low q_{max} obtained for the rare earth elements ions studied in the present work. The numerator of (Eq. 12) is the same of the one of (Eq. 11), and the denominator of (Eq. 12) depends on the number of sorbates present in the system. Then each additional sorbate in the solution increases the denominator of (Eq. 12) then decreases the amount of i adsorbed. As would be expected, the larger the activity of the competing sorbates and the greater their tendency to adsorb, and the larger is their effect on sorption [29]. Oliveira et al. used a mono-component and binary component solution for their experiments explaining their results.

3.7 Recovery of REES

The recovery of adsorbed REEs is an important step to obtain the metals in their pure forms. Desorption process may help to decrease the operating cost and diminish the dependency to continual supply of the biosorbents. Thus, more the desorption percentage is high more the process is efficient and biosorbent useful [30-32]. Desorption processes has been studied using various concentrations (0.1, 0.5, 1mol/L) of HCl, HNO₃, H₂SO₄ at different temperatures (30°C, 50°C, 70°C). Results are shown in Tables 5 and 6.

Since biosorption occurs at weak alkali pH, desorption of REEs from parachlorella by-products may occur at acidic pH. Variation of acid concentration affected the solution pH. Results have proved that pH (Table 5) as well as temperature (Table 6) have slight effect on the desorption percentage. However selectivity is observed. Dysprosium and gadolinium were not desorbed by acid neither with variation of pH nor with increasing temperature. Coppin et al.[33] related this behavior to the “lanthanide contraction” in the ionic radii going from light to heavy REEs. The effective ionic radii from lighter to heavier REEs are 90, 103.2, 99, 98.3, 95.8, 93.5, 91.2 pm respectively for Y³⁺, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺, and Dy³⁺. According to the results obtained in Table 5 and 6 we can then conclude that desorption is more due to the molecular weight than the ionic radii. The lighter metals are easy to be desorbed than the heavier.

Moreover, the kinetics of REEs extraction were very fast (Fig.10) for all three biosorbents used. Within 5 min, equilibrium was reached regardless of the acid type. These

results are quite related with the ones obtained by Moldoveanu [1]. The high and rapid desorption rate obtained demonstrates the good efficiency of the method and since low-cost biosorbents are used, the process is low-cost and can be employed to recover REEs from ores aqueous solutions or sewage.

4. Conclusions

The present study investigated the biosorption/desorption of, Y(III), La(III), Sm(III), Dy(III), Pr(III), Nd(III), Gd(III) present under various concentration in Vietnamese ores aqueous solution, onto dried and 250°C and 350°C carbonized parachlorella. Experiments performed as function of solution pH and contact time revealed that biosorption of above cited rare earth are highly dependent on those parameters. Moreover the uptake of rare earth ions was inhibited at low pH due to the protonation of the biosorbents sites. Selectivity of rare earth ions for one biosorbent than others characterized the biosorption process which was found rapid. The mechanism of the biosorption processes is explained by the combination of four reactions; electrostatic interaction between rare earth ions and biosorbent charges, biosorption onto functional groups of the biosorbents, ion exchange between rare earth ions and Mg and K present on the biosorbent sites and, surface complexation within hydroxide forms of rare earth ions and biosorbents; occurring simultaneously. In addition the sharing of the same biosorbent adsorptive sites by all the rare earth ions tested results in the low maximum biosorption density observed.

Moreover, pH and temperature had slight effect on desorption process of rare earth ions resulting on high desorption percentage. The kinetics of REEs desorption were fast

with less than 10 min to reach terminal extraction regardless of acid type via bath agitation. The extraction efficiency of REEs from parachlorella biosorbents adsorbed sites at 30°C using HCl, H₂SO₄, HNO₃ followed the order HNO₃ > H₂SO₄ > HCl with dried and 350°C carbonized parachlorella and HNO₃ ≥ HCl > H₂SO₄ when using 250°C carbonized parachlorella.

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Fig.1. Vietnamese rare earth aqueous solution composition

Fig.2. Thermal decomposition of parachlorella under nitrogen flow (15L/min)

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Fig.4. Scan Electromagnetic images of a/ dried (PA) and b/ 250°C (PA250) or c/ 350°C (PA350) carbonized parachlorella.

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Fig.6. Zeta potential of on dried (PA) and 250°C (PA250) or 350°C (PA350) carbonized parachlorella

Fig.7. Effect of contact time on REEs: Adsorbent dosage: 5g/L; Solution temperature 30°C; initial pH+ 6.94.

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Fig.10. Effect of contact time on desorption process using 250°C carbonized parachlorella

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Table 1: X-Ray fluorescence of dried (PA) and 250°C (PA250) or 350°C (PA350) carbonized parachlorella

Weight percentage of atoms (%)			
Atom	PA	PA250	PA350
Mg	1.12	0.89	0.965
Al	1.11	2.20	0.0862
Si	7.17	3.62	1.735
P	29.45	18.30	22.35
S	13.55	6.70	3
Cl	0.54	0.18	0.105
K	35.20	64.55	70
Ca	3.46	1.69	1.17
Fe	3.23	1.90	0.655
Cu	3.17	-	-
Zn	0.68	-	-
Ag	0.38	-	-

Table 2: Kinetics parameters of dried (PA) and 250°C (PA250) or 350°C (PA350) carbonized parachlorella

Ads.	Chem. elem.	Pseudo1 st order parameters				Pseudo2 nd order parameters		
		q_e (mg/g)	K_1	q_{e1calc}	R^2	K_2	q_{e2calc}	R^2
PA	Y	1.57	0.03	0.44±0.26	0.04	0.21	1.54±0.16	0.98
	La	8.06	0.03	2.10±1.21	0.14	0.05	7.95±0.66	0.99
	Pr	2.32	0.05	0.41±0.34	0.19	0.33	2.31±0.09	0.99
	Nd	6.70	0.05	0.98±0.89	0.15	0.14	6.66±0.24	0.99
	Sm	1.23	0.05	0.20±0.15	0.21	0.67	1.23±0.05	0.99
	Gd	0.71	0.04	0.13±0.09	0.08	0.90	0.70±0.04	0.99
	Dy	0.50	0.05	0.08±0.09	0.01	2.31	0.49±0.02	0.99
PA250	Y	2.66	0.07	0.97±0.17	0.95	0.13	2.68±0.10	0.99
	La	7.17	0.03	1.82±0.83	0.27	0.06	7.08±0.58	0.99
	Pr	1.95	0.05	0.67±0.24	0.68	0.17	1.95±0.11	0.99
	Nd	5.86	0.08	2.01±0.66	0.86	0.07	5.91±0.16	0.99
	Sm	1.18	0.06	0.42±0.13	0.79	0.30	1.19±0.05	0.99
	Gd	0.89	0.06	0.32±0.11	0.75	0.38	0.90±0.05	0.99
	Dy	0.80	0.07	0.30±0.11	0.80	0.43	0.80±0.03	0.99
PA350	Y	0.97	0.09	3.97±3.53	0.68	0.76	0.98±0.02	0.99
	La	3.12	0.09	1.74±0.49	0.46	0.18	3.17±0.05	0.99
	Pr	0.96	0.02	39.29x10 ⁴ ±41.25x10 ⁷	0.65	0.09	0.96±0.25	0.91
	Nd	3.07	0.02	63.89±93.04x10 ¹	0.39	0.03	2.98±0.93	0.88
	Sm	0.52	0.04	55.22x10 ⁵ ±11.09x10 ⁹	0.74	0.24	0.52±0.08	0.97
	Gd	0.33	0.04	74.38x10 ⁵ ±17.86x10 ⁹	0.61	0.57	0.33±0.03	0.99
	Dy	0.25	0.03	1.65x10 ¹⁴ ±1.67x10 ²²	0.51	0.50	0.25±0.04	0.96

Table 3: Thermodynamics parameters of dried (PA) and 250°C (PA250) or 350°C (PA350) carbonized parachlorella

Adsorbents	REEs	Ea(KJ/mol)	$\Delta H(KJ/mol)$	Nature of the reaction
PA	Y	28.56	26.04	Chemisorption and endothermic
	La	14.34	11.82	Chemisorption and endothermic
	Pr	18.05	15.53	Chemisorption and endothermic
	Nd	287.13	284.61	Chemisorption and endothermic
	Sm	0.22	-	Chemisorption
	Gd	92.16	89.64	Chemisorption and endothermic
	Dy	-	-	
PA250	Y	-	-	
	La	9.28	6.76	Chemisorption and exothermic
	Pr	18.27	15.75	Chemisorption and endothermic
	Nd	20.59	18.07	Chemisorption and endothermic
	Sm	44.69	42.17	Chemisorption and endothermic
	Gd	32.42	29.90	Chemisorption and endothermic
	Dy	-	-	
PA350	Y	24.40	21.88	Chemisorption and endothermic
	La	37.80	35.28	Chemisorption and endothermic
	Pr	63.62	61.10	Chemisorption and endothermic
	Nd	76.64	74.12	Chemisorption and endothermic
	Sm	128.73	126.21	Chemisorption and endothermic
	Gd	114.20	111.68	Chemisorption and endothermic
	Dy	60.84	58.32	Chemisorption and endothermic

Table 4: Langmuir parameters of dried (PA) and 250°C (PA250) or 350°C (PA350) carbonized parachlorella

Adsorbents	Chemical elements	q_{max} (mg/g)	Langmuir b	R^2
PA	Y	1.15	0.89	0.99
	La	6.08	0.08	0.99
	Pr	2.38	0.26	0.97
	Nd	6.49	0.07	0.99
	Sm	1.29	0.40	0.99
	Gd	0.57	1.67	0.99
	Dy	0.68	0.23	0.96
PA250	Y	4.73	0.03	0.98
	La	8.52	0.04	0.98
	Pr	2.02	0.22	0.98
	Nd	5.53	0.08	0.99
	Sm	1.53	0.25	0.99
	Gd	1.05	0.51	0.99
	Dy	1.39	0.36	0.99
PA350	Y	1.14	0.02	0.99
	La	3.47	0.02	0.99
	Pr	1.08	0.10	0.99
	Nd	2.84	0.03	0.98
	Sm	0.68	0.30	0.96
	Gd	1.05	0.06	0.95
	Dy	0.20	5.09	0.99

Table 5: Desorption: effect of acid concentration; : Solution temperature 30°C; adsorbent: adsorbate rate 0.05g/10mL; contact time 1h.

Samples	Desorption, (%)									
	HCl concentration (mol/L)				H ₂ SO ₄ concentration (mol/L)			HNO ₃ concentration (mol/L)		
	C.E	0.1	0.5	1	0.1	0.5	1	0.1	0.5	1
PA	Y	98.81	75.76	81.20	70.46	59.46	45.27	78.37	75.04	84.53
	La	100.00	100.00	100.00	100.00	94.18	82.26	100.00	100.00	100.00
	Pr	100.00	91.95	98.21	91.03	83.03	70.51	97.65	96.89	100.00
	Nd	100.00	100.00	100.00	100.00	94.51	81.95	100.00	100.00	100.00
	Sm	74.13	59.76	65.63	58.56	50.90	38.39	64.27	64.28	76.43
	Gd	7.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.21
	Dy	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PA250	Y	78.96	80.60	83.34	69.77	67.81	58.18	78.34	77.04	77.75
	La	94.61	92.60	96.52	85.53	83.64	73.22	94.76	92.89	95.07
	Pr	83.36	81.82	86.03	74.47	73.79	62.48	84.59	85.80	88.35
	Nd	97.89	96.12	100.00	88.72	87.47	75.84	98.68	100.00	100.00
	Sm	47.93	48.28	51.77	40.51	39.54	29.28	48.66	52.06	55.32
	Gd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Dy	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PA350	Y	78.44	67.73	64.54	64.93	48.14	40.88	68.42	62.86	64.55
	La	100.00	93.31	88.47	92.40	79.36	74.00	93.48	88.23	93.07
	Pr	79.32	71.84	67.47	72.50	61.82	57.84	71.68	69.37	74.43
	Nd	94.34	86.95	81.70	86.95	75.30	71.41	86.54	83.81	89.63
	Sm	42.56	33.71	29.81	34.89	23.65	19.15	34.07	31.01	36.81
	Gd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Dy	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

C.E: Chemical element

Table 6: Desorption: Effect of temperature: adsorbate rate 0.05g/10mL; acid concentration 1mol/L; contact time 1h.

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