DEU FMD 21(63), 955-966, 2019

Dokuz Eylül Üniversitesi Mühendislik Fakültesi Fen ve Mühendislik Dergisi
Dokuz Eylul University Faculty of Engineering Journal of Science and Engineering

Basılı/Printed ISSN: 1302-9304. Elektronik/Online ISSN: 2547-958X

Biosorption of Eu(III) onto *Narcissus Tazetta L.* Leaf Powder

Eu (III) 'un *Narcissus Tazetta L.* Yaprak Tozu Üzerine Biyosorpsiyonu

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Geliş Tarihi / Received: 16.01.2019 *DOI:10.21205/deufmd.2019216324*
Kabul Tarihi / Accepted: 09.07.2019 *Araştırma Makalesi/Research Article*
Atıf şekli/ How to cite:İNAN, S., ÖZKAN, B., (2019), Biosorption of Eu(III) onto Narcissus Tazetta L. Leaf Powder, DEUFMD, 21(63), 955-966.

Abstract

In the present study, biosorption behaviours of novel biosorbent, *Narcissus Tazetta L.* leaf powder, were investigated for the separation of Eu(III) from aqueous solution. Batch experiments were conducted to examine the effect of various parameters such as contact time, initial pH, initial Eu(III) concentration, biosorbent dosage and temperature on the Eu(III) uptake. The biosorption process is fast, and equilibrium was established in 30 min. of contact time. It was found that the material has a significant biosorption capacity for europium in the pH range of 4-7. The results showed that the biosorption data fit Langmuir monolayer isotherm and pseudo-second order kinetic model well. Biosorption capacity of leaf powder was obtained as 122.0 mg g^{-1} according to the Langmuir isotherm at pH 7. Thermodynamic analysis indicates that the biosorption was spontaneous and endothermic in nature. Desorption efficiency(%) of 97.17 was achieved in single step using 0.1 mol L^{-1} HNO_3 solution. Surface area of the biosorbent and the average pore size were determined as 1.725 mg g^{-1} and 1.75 nm, respectively. The critical functional groups -CH, C-O, O-H, C=O and COO- which may have taken part for the biosorption were identified by infrared spectra data. It was deduced that *N. Tazetta* leaf powder can be used as an effective, costless, and eco-friendly biosorbent for the separation and recovery of Eu(III) from aqueous solution.

Keywords: *Narcissus Tazetta*, Europium, Rare Earths, Biosorption, Separation

Öz

Bu çalışmada, yeni bir biyosorbent olan *Narcissus Tazetta L.* yaprak tozunun sulu çözeltilerden Eu(III) iyonlarının ayrılmasında biyosorpsiyon davranışları incelenmiştir. Eu(III) alımında temas süresi, başlangıç pH'sı, başlangıç Eu(III) derişimi, biyosorbent dozajı ve sıcaklık gibi çeşitli parametrelerin etkisini incelemek için kesikli denemeler yürütülmüştür. Biyosorpsiyon prosesi hızlıdır ve 30 dakikalık temas süresi sonunda dengeye ulaşılmıştır. pH 4-7 aralığında materyalin Eu(III) için önemli bir biyosorpsiyon kapasitesine sahip olduğu bulunmuştur. Biyosorpsiyon verisi Langmuir tek tabaka izotermi ve yalancı ikinci derece kinetik model ile uyum göstermiştir. Yaprak tozunun biyosorpsiyon kapasitesi Langmuir izotermine göre pH 7'de 122.0 mg g^{-1} olarak bulunmuştur. Termodinamik analiz biyosorpsiyonun kendiliğinden gerçekleştiğini ve endotermik yapıda olduğunu göstermiştir. 0.1 mol L^{-1} HNO_3 çözeltisi ile tek kademede %97.17'lik desorpsiyon verimine ulaşılmıştır. Biyosorbentin yüzey alanı ve ortalama por çapı sırasıyla 1.725 mg g^{-1} ve 1.75 nm olarak tespit edilmiştir. Biyosorpsiyonda rol almış olabilen -CH, C-O, O-H, C=O ve COO- gibi kritik fonksiyonel gruplar kızıl ötesi spektroskopisi ile aydınlatılmıştır. Sulu çözeltilerden Eu(III) ayrılması ve kazanılmasında *N. Tazetta* yaprak tozunun etkili, maliyetsiz ve çevre dostu bir biyosorbent olduğu sonucuna varılmıştır.

Anahtar Kelimeler: *Narcissus Tazetta*, Evropyum, Nadir Topraklar, Biyosorpsiyon, Ayırma

1. Introduction

Rare earth elements (REEs) are a series of 17 elements having extensive and novel applications in metallurgy [1], ceramic industry [2], agriculture [3], medicine [4] and nuclear industry [5]. Among them, Europium (Eu) is an active metal that trace amount of europium may greatly enhance the properties of metals [6]. Europium ion exhibits excellent luminescent properties, especially as a sensitizer and an activator. Its unique fluorescence is widely used in industrial production [7, 8], as well as agriculture, medical and biological research [9, 10].

On the other hand, both radioactive and stable REEs can enter the food chain and therefore they can be intaken by humans. Due to the accumulation property of REEs and its relative toxicity towards living organisms [11, 12], an effective and economical treatment method is required for REE-containing solutions. As a consequence, separation and recovery of europium from nuclear [13] and industrial waste streams are very significant for environmental and economical reasons.

Several studies have been reported to separate and enrich rare earth elements, such as chemical precipitation [14], solvent extraction [14], ion exchange [15], membrane separation [16] and electrochemical deposition [17].

The traditional methods have some drawbacks, such as low selectivity, high amount of reagent consumption and energy, and high operational expenses [18]. There is a need to develop eco-friendly and cost effective method to recover and separate rare earth metals from aqueous environment.

Biosorption is a fast, reversible, economical and eco-friendly technology in comparison to other techniques for the separation and recovery of rare earth metals [19]. The utilization of inexpensive biosorbents is arousing an interest because of their abundant availability. Bacteria [20, 21], algae [22, 23], yeast [24], tree leaves [25], resin [26, 27] and activated carbon [28] have been using for the recovery of rare earth metals. However, there are few studies reported on Eu(III) biosorption using biosorbents such as crab shell particles [29], sargassum biomass [23, 30] malt spent rootlets [31] and brown marine alga [32].

Narcissus is the common name of the plant species from the *Amaryllidaceae* family of *Narcissus* genus. The homeland of these plants are Europe and the most species richness are found in Spain and Portugal [33]. *Narcissus Tazetta* is the name of the genus particularly grown in Karaburun district of Agean Region in Turkey. Flowers are harvested in winter period and afterwards, leaves coming out of bulbs starts to dry. During summer period they totally become dry. Dried leaves have no use and they are consdiered as biowaste. The utilization of this biowaste material has not been reported in elsewhere until now. It is of a great importance to investigate the recovery and separation potential of this novel bio-material for rare earth elements.

In the present study, dried leaves of *N. Tazetta* which are regarded as biowaste and available in large amounts were collected and grinded. Powdered form of leaves were used as a biosorbent for the separation of Eu(III) from aqueous solution. Equilibrium isotherms, kinetic models were applied and thermodynamic parameters were calculated to assess the biosorption behaviours. In addition, desorption studies were carried out.

2. Material and Method

2.1. Reagents

Europium nitrate pentahydrate ($Eu(NO_3)_3.5H_2O$), Eu ICP standart (1000 μg mL^{-1}), ammonia solution and nitric acid were purchased from Sigma-Aldrich. The stock solution of europium (1000 μg mL^{-1}) was prepared with dissolving 0.704 g of $Eu(NO_3)_3.5H_2O$ in 250 mL deionized water. Concentration of test solutions were obtained by diluting the stock solution in appropriate volumes. pH of the test solutions were adjusted to desired values by adding nitric acid and ammonia solutions.

2.2. Preparation of biosorbent

Dry *N. Tazetta* leaves were collected from a flower garden in Karaburun district (38°40'9.97"N, 26°26'24.61"E), İzmir province (Turkey) in June 2018. *N. Tazetta* leaves were kept in an oven at 50^{o}C for 72 h and were all crushed in a grinder.

2.3. Characterization studies

Infrared spectrum of *N. Tazetta* leaf powders were acquired before and after biosorption by Perkin Elmer Spectrum Two model FTIR-ATR spectrometer in the wavenumber range of 400-4000 cm^{-1}. Surface area and porosity of leaf powders were measured at 77 K by Micromeritics ASAP 2020 Surface area and porosity analyzer. Before measurements, powders were degassed at 323 K under vacuum for 72 h. Surface area and pore diameter of *N. Tazetta* leaf powders were calculated by the Brunauer-Emmett-Teller (BET) and BJH method, respectively.

2.4. Batch biosorption experiments

The effect of independent variables (Particle size, contact time, initial pH, initial Eu(III) concentration, biosorbent dosage and temperature) on biosorption of Eu(III) were investigated by batch tests. Test solutions (25-600 mg L^{-1}) were prepared by diluting the stock solution. For each run, liquid/solid contact was carried out using a GFL 1086 model thermostatically controlled shaker bath at 130 rpm in 100 ml erlenmeyer containing 50 mL of test solution. Desired amount of *N. Tazetta* leaf powder was added. The effect of each variable was determined by changing only one variable at a time while others kept constant.

After the equilibrium was established, the solid/liquid separation was done with blue ribbon filter paper. Eu(III) concentrations in the solution were measured before and after equilibrium by Perkin Elmer Optima 2000DV model ICP-OES. A Single element solution containing 1000 mg L^{-1} of Eu^{3+} in 2–3% (v/v) HNO$_3$ was used to obtain the calibration curve. The biosorption capacity (mg g^{-1}) and biosorption efficiency(%) were calculated as follows:

$$Capacity(Q) = (C_o - C_e) \times \frac{V}{m} \qquad (1)$$

$$Bisorption\ efficiency(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of Eu(III) ions in solution (mg L^{-1}), V is the solution volume (mL) and m (g) is the mass of the biosorbent.

2.5. Desorption experiments

Desorption potential of deionized water, HCl and HNO$_3$ solutions were used to investigate the reusability of the biosorbent. For this aim, biosorption–desorption tests were carried out. Biosorbent loaded with Eu(III) ions was contacted with desorption solutions at 130 rpm for 60 min. at 25^{o}C. Eu(III) ion concentrations in desorption solutions were measured by using Perkin Elmer Optima 2000DV model ICP-OES as described above. Desorption efficiency(%) was calculated by using Eq. (3):

$$Desorption\ (\%) = \frac{Amount\ of\ Eu(III)\ desorbed}{Amount\ of\ Eu(III)\ biosorbed} \times 100 \qquad (3)$$

3. Results

3.1. Characterization studies

3.1.1. FTIR analysis

Infrared spectra of *N. Tazetta* leaf powder before and after Eu(III) biosorption were shown in Figure 1. The peak observed around 3319 cm^{-1} was assigned to -OH stretching vibrations of hydroxylated functional groups and two peaks at 2920 and 2848 cm^{-1} were ascribed to -CH stretching vibrations [34]. A peak at 1733 cm^{-1} attributed to C=O stretching of COOH and ketones, and the peak at 1610 cm^{-1} associated to structural vibrations of asymmetrical C=O stretching of COO- groups [35]. The peak at 1250 cm^{-1} might be attributed to O-H stretching of phenolic –OH. In addition, the peak at 1025 cm^{-1} can be the indicator of C-O stretching [36]. There were no significant changes observed before and after the biosorption process except a slight alteration in the intensity of some peaks.

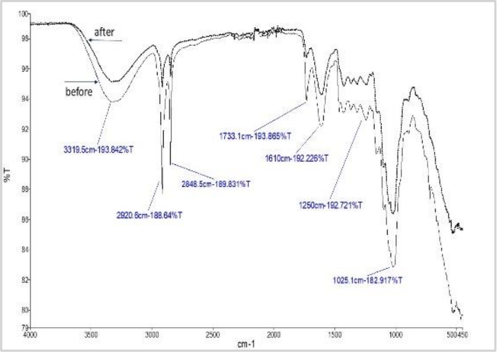
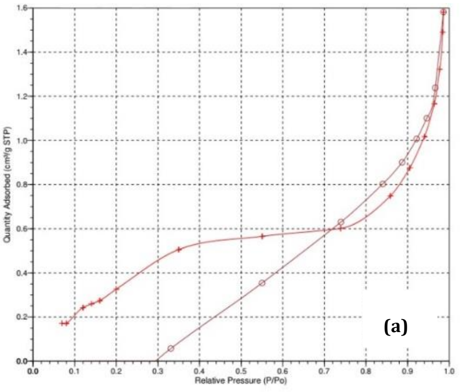


Figure 1. FTIR spectra of *N. Tazetta* leaf powders before and after Eu(III) biosorption

Leaves and stems of plants and trees contain lignin and cellulose which are mainly composed of hydroxyl, methoxyl and carbonyl groups. Despite the complexity of the biochemical properties of biosorbent [37], some studies have revealed that carboxyl and hydroxyl groups play a significant role in metal uptake [38].

3.1.2 Surface analyses

Surface area and porosity analysis were performed for a particle size of +125-250 µm. Adsorption-desorption isotherm plot was provided in Figure 2a. BET surface area and BJH adsorption cumulative pore volume of leaf powders were measured as 1.725 ± 0.0988 m^2 g^{-1} and 0.00252 cm^3 g^{-1}, respectively. *N. Tazetta* leaf powder has a pore volume of smaller than 3×10^{-3} cm^3 g^{-1}, which may explain the low surface area detected. The majority of pores have an average diameter of 1.75 nm however there are few pores with an average diameter between 5 and 100 nm (Figure 2b).



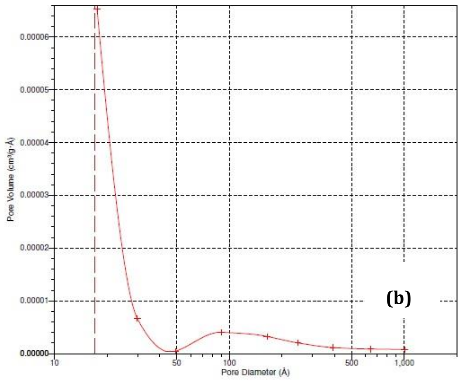


Figure 2. (a) Nitrogen adsorption-desorption isotherm, **(b)** BJH adsorption pore volume-pore diameter distribution

3.2. The effect of particle size

The effect of particle size in the range of 125–1000 µm on uptake capacity of Eu(III) was investigated. Experiments were conducted with initial Eu(III) concentration 200 mg L^{-1}, pH 6, 130 rpm for 60 min., at 25^{o}C and biosorbent dose 0.0500 g.

It was found that biosorption capacity was slightly higher for smaller particle size. About 4% decrease in the uptake of Eu(III) was determined with an increase in the particle size up to 1000 µm (Figure 3).

This can be explained as follows: the smaller particle size may provide an increment in the surface area, and thus, higher adsorption rates can be expected. Nadeem et al. [39], mentioned the similar behaviour. Since particles between 125-250 µm resulted in slightly higher uptake of Eu(III) ions from aqueous solution, it was used in further biosorption experiments.

3.3. The effect of time and biosorption kinetics

One of the most important features of sorbents utilized in solid phase separation processes is the time necessary to achieve sorption equilibrium. The effect of contact time on Eu(III) biosorption was investigated under varying metal ion concentrations from 50–200 mg L^{-1}. In the experiments contact time was varied from 1 to 120 min. Figure 4 illustrates the amount of Eu(III) sorbed onto *N. Tazetta* leaf powder as a function of contact time. From plots, it is clearly seen that uptake of Eu(III) increased in the first 15 min. and it became almost constant after 30 min. No significant change was observed after 30 min., therefore 30 min. was selected as equilibrium time for further experiments. Fast biosorption kinetics could be explained by the abrupt utilization of most of the easily accessible sites on the cell wall of the biosorbent.

The fast kinetics of this novel biosorbent can be consdiered as one of the key parameters for economical separation and recovery processes**.** As shown in the Figure 4, Eu(III) uptake increases with the increase in initial Eu(III) concentration. Biosorbent has an uptake capacity of 37.07, 64.78 and 82.65 mg g^{-1} for 50, 100 and 200 mg L^{-1} initial Eu(III) concentration, respectively.

According to Baral et al. [40], when the metal concentration increases there are more metal ions available in the aqueous solution. With this, it become easier to break through the mass transfer resistance of metal ions from solution to solid phase.

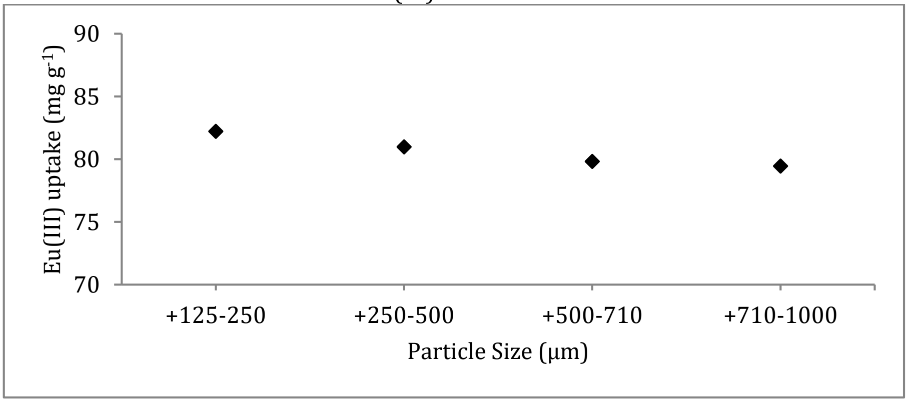


Figure 3. Effect of particle size on Eu(III) uptake (Contact time= 60 min., pH= 6, Eu(III) conc.= 200 mg L^{-1}, temperature= 25°C, biosorbent dosage= 1 g L^{-1}, shaking rate= 130 rpm)

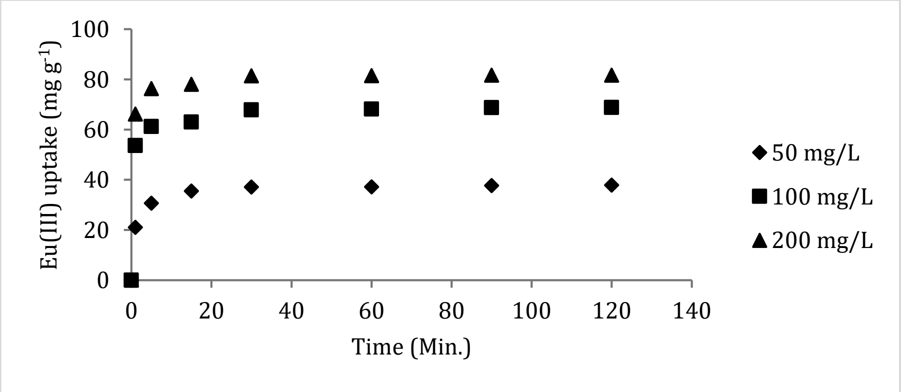


Figure 4. Effect of contact time at different initial Eu(III) concentrations (pH= 6, biosorbent dosage= 1 g L^{-1}, temperature= 25°C, shaking rate= 130 rpm)

It would be more possible for Eu(III) ions to contact with active sorption sites, thus higher uptake capacity will be obtained. The similar behaviour was also reported by Aksu and Tezer [41].

The experimental kinetic data were evaluated using the pseudo-first and pseudo-second order kinetic models. Pseudo-first order model is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

Integrated form of equation is:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (5)$$

where q_t and q_e are amount of metal ion adsorbed (mg g^{-1}) at time *t* and at equilibrium, respectively, k_1 is the rate constant (min^{-1}) [42, 43].

First order rate constant k_1 and q_e can be obtained from the slope and the intercept of plot.

The experimental data can not be explained well with pseudo-first order kinetic model due to the fact that R^2 values obtained are relatively low and the calculated qe values are not in accordance with the experimental data.

The pseudo-second order [44] is based on sorption capacity of solid phase.

$$\frac{dq_t}{d_t} = k_2(q_e - q_t) \qquad (6)$$

where k_2 is the second order rate constant (g mg^{-1} min^{-1}). Integrated linear form of equation is:

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

The kinetic plots of t/q_t versus t at different metal ion concentrations are presented in Figure 5. q_e and the second order rate constant k_2 can be calculated from the slope and the intercept of plots (Figure 5). High value of correlation coefficients (R^2) for all Eu(III) concentrations explain that data fit the pseudo-second order model well. The values of k_2 and q_e were calculated as 0.03, 0.01, 0.01 g mg^{-1} min^{-1} and 38.17, 68.97, 81.96 mg g^{-1} for 50, 100 and 200 mg L^{-1} Eu(III), respectively.

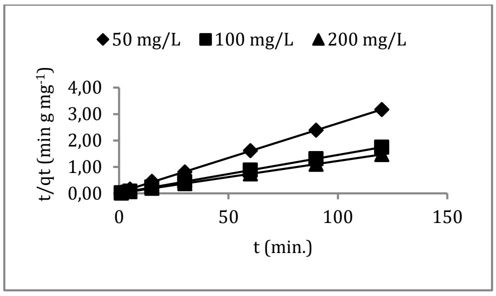


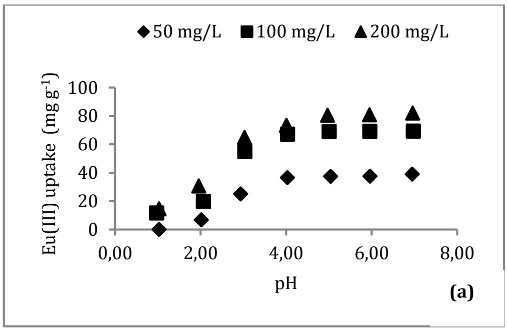
Figure 5. Pseudo-second order kinetic plots for Eu(III) biosorption

3.4. The effect of pH

pH is a key factor which determines the surface characteristics of the sorbent and the ionic form of the metal ion in solution [45]. Dissociation of active functional groups can also be altered by solution pH [45, 46].

Generally, metal biosorption is a complex phenomenon. Ion exchange, physical adsorption, chelation and ion entrapment in inter- and intra-fibrillar capillaries and pores of the biosorbents may take part in the sorption process separately or together [47, 48].

The effect of pH on the biosorption of Eu(III) ions onto *N. Tazetta* leaf powder was studied in the pH range 1–7. Experiments above pH 7 were not carried out due to the risk of europium hydrolysis. Biosorption capacity as a function of solution pH is presented in Figure 6a. At pH 1, sorption was not favored especially for the initial concentration of 50 mg L^{-1} Eu(III) which may be attributed to the protonation of adsorption sites. Similar results have also been reported in the literature for sorbents that contain carboxylic and amine groups as adsorptive sites [49, 50]. However, the biosorbent has an Eu(III) uptake capacity of 11.48 and 14.53 mg g^{-1} even at pH 1 when the Eu(III) initial concentration was 100 and 200 mg L^{-1}, respectively. The uptake capacity was increased from 30.65 mg g^{-1} to 81.91 mg g^{-1} at initial metal concentration of 200 mg L^{-1} when pH was increased from 2 to 7. At pH range of 4 to 7, the biosorption remained almost constant. The similar behaviour was observed for 100 and 200 mg L^{-1} Eu(III) concentration.



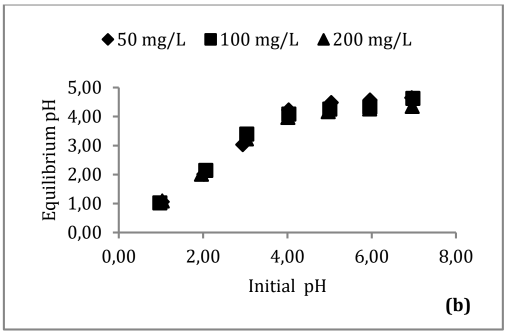


Figure 6. (a) Effect of pH on biosorption capacity at different initial Eu(III) concentrations, **(b)** The final pH of the system after biosorption (Contact time= 30 min., biosorbent dosage= 1 g L^{-1}, temperature= 25°C, shaking rate= 130 rpm)

The relation between initial pH and equilibrium pH is presented in Figure 6b. The equilibrium pH values were relatively close which can be explained that pH has not a significant impact on the equilibrium status of the system despite different initial Eu(III) concentration.

3.5. The effect of initial Eu(III) concentration

The effect of initial Eu(III) concentration at pH 5, 6 and 7 was investigated and data were presented in Figure 7. It was determined that Eu(III) uptake increased from 10.66 to 62.10 mg g^{-1} with an increase in the initial Eu(III) concentration from 25 to 200 mg L^{-1} at pH 5.0. Between 200-600 mg L^{-1} initial Eu(III) concentration range, the uptake capacity of biorsorbent reached a plateau and remained almost constant.

However, at initial pH 6.0 and 7.0 the similar behaviour could not be observed. As the initial Eu(III) concentration increases from 25 to 600 mg L^{-1}, the uptake capacity follows an increasing trend. Eu(III) uptake of biosorbent increased from 10.51 to 105.0 mg g^{-1} and 10.70 to 110.16 mg g^{-1} at pH 6.0 and 7.0, respectively. This result can be explained that the biosorption is more favourable at pH 6.0 and 7.0 and the active sites on the surface of the biosorbent could not be saturated in this initial concentration range.

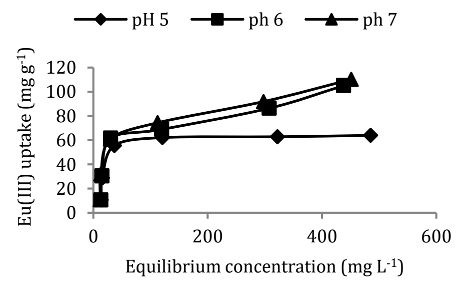


Figure 7. Effect of initial Eu(III) concentration at different initial pH values (Contact time= 30 min., biosorbent dosage= 1 g L^{-1}, temperature= 25°C, shaking rate= 130 rpm)

The sorption equilibrium data are interpreted by sorption isotherms. Isotherms clarify the relationship between the mass of the metal sorbed per unit mass of sorbent q_e and the metal concentration in the solution at equilibrium C_e.

Langmuir theory assumes that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in linear form [51] and is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (8)$$

where q_m is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer (mg g^{-1}), C_e is the equilibrium concentration of metal ion (mg L^{-1}), and b is a constant related to the sorption energy (L mg^{-1}). q_m and b can be calculated from the slope and intercept of linear plot between C_e/q_e and C_e. Langmuir plots at varying initial pH were shown in Figure 8.

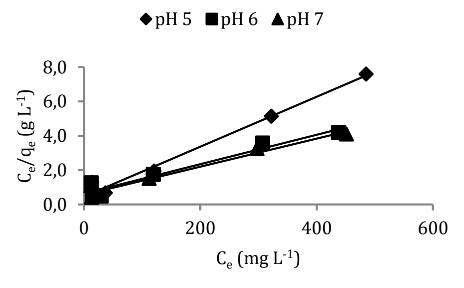


Figure 8. Langmuir plots at different initial pH values

q_m, b and correlation coefficient (R^2) values calculated from the isotherms are given in Table 1. q_m and b values were estimated to be 122.0 mg g^{-1} and 0.0147 (L mg^{-1}) at pH 7, respectively. High R^2 value of 0.961 indicates that the sorption data could be explained well by Langmuir model. The comparison of maximum Eu(III) uptake (q_m) with other biomass reported in literature is illustrated in Table 2.

Table 1 Langmuir, Freundlich and D-R isotherm parameters for Eu(III) biosorption on *N. Tazetta* leaf powder.

Models		pH 5	pH 6	pH 7
Langmuir	q_m (mg g^{-1})	68.49	116.3	122.0
	b (L mg^{-1})	0.0326	0.0136	0.0147
	R^2	0.985	0.950	0.961
Freundlich	K_f	8.37	6.56	7.07
	n	2.73	2.12	2.13
	R^2	0.610	0.714	0.733
D-R	q_m (mg g^{-1})	66.02	88.82	91.26
	E (kJ mol^{-1})	0.10	0.09	0.11
	R^2	0.926	0.924	0.894

Table 2 Comparison of maximum europium uptake (q_m) of various biosorbents.

Biosorbent	Maxiumum metal Uptake (mg g^{-1})	Reference
Crab Shell Particles	49.53	[29]
Malt Spent Rootlets	156.0	[31]
Brown Marine Alga	138.2	[32]
N. Tazetta Leaf Powder	122.0	Present Study

Freundlich adsorption isotherm [52] can be represented as:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{9}$$

It can be written in linear form as:

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \tag{10}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration of the metal in solution, K_f and n are constants related to adsorption capacity and intensity, respectively. The values of n and K_f for different pH values were calculated and are shown in Table 1. It can be inferred from R^2 values that biosorption data does not fit Freundlich isotherm well.

Dubinin-Radushkevich isotherm [53] as Eq. (11):

$$lnq_e = lnq_m - \beta\varepsilon^2 \tag{11}$$

ε is the Polanyi potential given by Eq. (12)

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \tag{12}$$

where β is a constant related to the mean free energy of adsorption (mol^2 J^{-2}), q_e is the amount of solute adsorbed at equilibrium (mg g^{-1}), q_m is the theoretical saturation capacity (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), R is the gas constant (R=8.314 J mol^{-1} K^{-1}) and T is the temperature (K). The adsorption mean free energy E (kJ mol^{-1}) can be calculated as follows:

$$E = \frac{1}{\sqrt{2\beta}} \tag{13}$$

When the E value is below 8 kJ mol^{-1}, sorption process can be considered as physical sorption. If the E value is between 8 and 16 kJ mol^{-1}, the sorption process follows a chemical mechanism. D-R isotherm constants and E values are summarized in Table 1. Adsorption mean energy values were obtained in the range of 0.09-0.11 kJ mol^{-1} at pH 5-7. These values indicate that physical sorption plays a dominant role in Eu(III) biosorption process.

3.6. The effect of biosorbent dosage

Biosorbent dosage is directly proportional to the number of available binding sites to remove metal ions. The effect of biosorbent dosage on the biosorption efficiency of Eu(III) at two different particle sizes was studied.

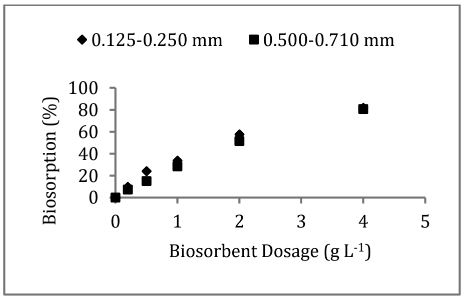


Figure 9. Effect of biosorbent dosage at different particle sizes (Contact time= 30 min., pH= 6, initial Eu(III) concentration= 200 mg L^{-1}, temperature= 25^{o}C, shaking rate= 130 rpm)

As shown in Figure 9, biosorption efficiency of Eu(III) increases with an increase in biosorbent dosage from 0.2 to 4.0 g L^{-1}. The efficiency of Eu(III) biosorption was increased from 9.72 to 81.78% and 7.26 to 80.67% for the particle size of 0.125-0.250 mm and 0.500-0.710 mm, respectively. The increase in bisorption efficiency could be explained by the increase in biomass surface area with the increase in biosorbent dosage. It is also clearly seen from Figure 9 that slightly higher efficiency was obtained when the particle size of the biosorbent is smaller.

3.7. The effect of temperature

Experiments were carried out at 303, 313 and 323 K. As shown in Figure 10, the biosorption capacity of the *N. Tazetta* leaf powder increased with the increase in temperature from 303 to 323 K. The uptake capacity increased from 29.01 mg g^{-1} to 38.32 mg g^{-1} with the increase in temperature from 303 to 323 K at 50 mg L^{-1} initial Eu(III) concentration. The same trend was observed both for 100 and 200 mg L^{-1} initial Eu(III) concentration.

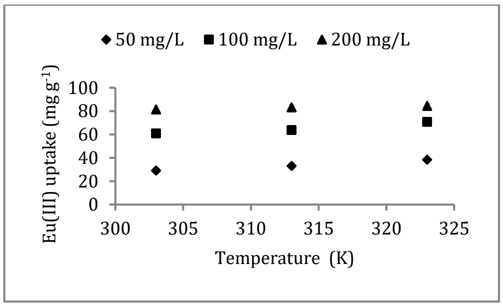


Figure 10. The effect of temperature on Eu(III) uptake under varying Eu(III) concentrations (Contact time= 30 min., pH= 6, biosorbent dosage= 1 g L^{-1}; shaking rate= 130 rpm)

Thermodynamic data provides information about the spontaneity of the biosorption process. Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and Gibbs free energy change (ΔG°) were estimated using the following Eqs. (14), (15) and (16) [54] :

$$K_D = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (14)$$

$$lnK_D = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (15)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (16)$$

Where K_D is the thermodynamic equilibrium constant (mL g^{-1}); *R* is the universal gas constant (8.314 J mol^{-1} K^{-1}); *T* is the temperature in Kelvin; *V* is the solution volume (mL) and *m* is the mass (g) of the biosorbent. The values of ΔH° and ΔS° were obtained from the slopes and intercepts of Van't Hoff plot (the plot between InK_D versus 1/T).

The calculated values of thermodynamic parameters for 100 mg L^{-1} initial Eu(III) concentration were shown in Table 3.

The Gibbs free energy combines the entropy and enthalpy of a system into one value. It describes the energy available to do work and thus can be used to determine the spontaneity of a reaction. If ΔG° is zero, the sorption reaction is at equilbrium. If ΔG° is negative the sorption is spontaneous in the forward direction and if ΔG° is positive the sorption is non-spontaneous.

The ΔG° values were found negative as -16.50, -17.50 and -18.50 kJ mol^{-1} at 303, 313 and 323 K indicating that the biosorption process of Eu(III) was spontaneous.

The positive value of ΔH° (13.80 kJ mol^{-1}) denoted that biosorption is an endothermic process. This behaviour can be explained by the increase in kinetic energies of europium ions with the increasing temperature. At lower temperatures, the kinetic energy is low and increase in temperature increases the mobility of the ions [55, 56].

The positive value of ΔS° (0,10 kJ mol^{-1} K^{-1}) indicates the increase in randomness at the solid-liquid interface during biosorption process.

Table 3 Thermodynamic parameters for the Eu(III) biosorption at 100 mg L^{-1} initial Eu(III) concentration.

Temperature (K)	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
303	13.80	0.10	-16.50
313			-17.50
323			-18.50

3.8. Desorption studies

The effect of deionized water, HCl and HNO_3 on the desorption of Eu(III) were investigated by preliminary tests. Deionized water has not any effect observed to desorb the adsorbed Eu(III). HNO_3 provided better results then HCl, so further investigation was performed by using HNO_3 solutions. As a first step, biosorbent was contacted with 100 mg L^{-1} Eu(III) solution at pH 6.0 for 30 min. V/m ratio was kept as 1000 (50 mL/0.0500 g).

Table 4 Desorption data for Eu(III) biosorption using HNO_3 solutions.

	HNO_3 Solutions				
	0.01 mol L^{-1}	0.1 mol L^{-1}	0.5 mol L^{-1}	1.0 mol L^{-1}	2.0 mol L^{-1}
Eu(III) Desorption Efficiency (%)	93.68	97.17	96.30	90.16	84.83

Desorption conditions; contact time= 60 min., V/m ratio= 50 mL/0.0500 g, temperature= 25°C, shaking rate= 130 rpm

At the equilibrium, biosorption efficiency(%) of Eu(III) was determined as 59.53%. HNO_3 solutions were used as desorption solutions in the concentration range of 0.01–2.0 mol L^{-1}. As it can be seen from Table 4, desorption of 97.17% of Eu(III) ions were achieved by using 0.1 mol L^{-1} HNO_3 in one stage batch contact.

Further increase in acid concentration up to 2.0 mol L^{-1} HNO_3 presented a slight decrease in the desorption efficiency of Eu(III) ions.

Acknowledgement

The authors would like to thank Mr. Ümit Emre KARTAL for his assistance in the laboratory.

4. Discussion and Conclusion

The utilization of biomaterials both for recovery of valuable metal ions and removal of the hazardous ions are of a great importance. In this context, biosorption potential of novel bio material *Narcisssus Tazetta* leaf powder towards Eu(III) ions were investigated under varying parameters such as contact time, initial pH, initial Eu(III) concentration, biosorbent dosage and temperature. Surface characteristics of the biosorbent were determined and the presence of key functional groups CH, C-O, O-H, C=O and COO- which might have taken part in the biosorption was approved by infrared analysis. Biosorption kinetics of the material is fast and the equilibrium was attained in 30 minutes. Kinetic data is compatible with pseudo-second order model. The biosorption of Eu(III) ions can be achieved effectively in a broad pH range of 4 to 7. Experimental equilibrium data can be explained with Langmuir isotherm. A monolayer Eu(III) uptake capacity of biosorbent was obtained as 122.0 mg g^{-1} at pH 7. The biosorption efficiency of Eu(III) was increased from 9.72 to 81.78% by the increase in biosorbent dosage from 0.2 to 4.0 g L^{-1}. Negative ΔG^o values and positive ΔH^o value obtained as a result of thermodynamic data evaluation, point out that the biosorption of Eu(III) was spontaneous and endothermic. In addition, it was found that 97.17% of biosorbed Eu(III) can be desorbed in a single step using 0.1 M HNO_3.

Overall results indicate that *Narcisssus Tazetta L.* leaf powder is a promising, costless and environmental friendly novel biosorbent for the separation and recovery of Eu(III) ions from aqueous solution.

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