

Study of Adsorption Isotherm Models on Rare Earth Elements Biosorption for Separation Purposes

Nice Vasconcelos Coimbra, Fábio dos Santos Gonçalves, Marisa Nascimento, Ellen Cristine Giese

Abstract—The development of chemical routes for the recovery and separation of rare earth elements (REE) is seen as a priority and strategic action by several countries demanding these elements. Among the possibilities of alternative routes, the biosorption process has been evaluated in our laboratory. In this theme, the present work attempts to assess and fit the solution equilibrium data in Langmuir, Freundlich and DKR isothermal models, based on the biosorption results of the lanthanum and samarium elements by *Bacillus subtilis* immobilized on calcium alginate gel. It was observed that the preference of adsorption of REE by the immobilized biomass followed the order Sm (II) > La (III). It can be concluded that among the studied isotherms models, the Langmuir model presented better mathematical results than the Freundlich and DKR models.

Keywords—Rare earth elements, biosorption, *Bacillus subtilis*, adsorption isotherm models.

I. INTRODUCTION

REE consist of elements of the periodic table located in the lanthanide series, divided into two categories namely the light rare earths (LRE) and the heavy rare earths (HRE). The former includes cerium (Ce), lanthanum (La), neodymium (Nd), praseodymium (Pr), samarium (Sm), and the latter include gadolinium (Gd), europium (Eu), terbium (Tb), dysprosium (Dy), thulium (Tm), ytterbium (Yb), lutetium (Lu), yttrium (Y), holmium (Ho) and erbium (Er). REE is a multi-applicable group which contributes to important sectors such as fluorescent lamps, high-tech technologies as batteries, lasers and super-magnets, high-temperature superconductivity, information storage, conservation and transport of energy [1], [2].

In recent years, with ever-increasing demand for high-purity REE and their compounds, purification of individual REE have gained considerable attention [2]. The high similarity of these elements, due to the nature of their electronic configurations, increases the difficulty and costs of the development of chemical processes of REE separation and recovery [3].

As an alternative to classical hydrometallurgical methods such as leaching and solvent extraction, the biosorption process has been described in the scientific literature as a process of ion exchange with potential for recovery of REE by different microbial species [4]-[9].

N. V. Coimbra, F. S. Gonçalves, and M. Nascimento are with the Center for Mineral Technology, Rio de Janeiro, CEP 21941-908 Brazil (e-mail: vasconcelos.coimbra@gmail.com, fabinho.solar@gmail.com, marisa@cetem.gov.br).

E. C. Giese is with the Center for Mineral Technology, Rio de Janeiro, CEP 21941-908 Brazil (corresponding author, phone: +55 21 3865-7377; e-mail: egiese@cetem.gov.br).

Different methods have been employed to separate lanthanides from aqueous solution, such as chemical precipitation, ion exchange, membrane filtration, coagulation and flocculation, electrochemical treatment, and solvent extraction [10]. However, these processes have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost, and difficult further treatment due to generation of toxic sludge [5].

Biosorption consists of a biological adsorption process that refers to the passive bonding of metal ions by living or dead biomass, which has been applied mainly at a high scale in effluent treatment processes [4]. However, studies have shown that it is possible to have better efficiency in the biosorption process when the microorganisms are immobilized in porous matrices [11]-[13].

Immobilized biosorbents have high metal ion adsorption capacity, due to the composition of their outer surface structure. Microorganisms immobilized in calcium alginate gel have been used in several biotechnological applications, e.g. biofuel, drugs, and vitamins production [14]; in bioremediation, bioleaching and acid mine drainage processes [15]; as well as in heavy metal and REE biosorption processes [11]-[13], [16].

The cell wall of the *Bacillus subtilis* bacterium has a specific binding site for REE, which has a lower affinity for LRE and higher affinity for HRE [17]. This preference occurs once REE bind to the active sites of *B. subtilis* surface cells forming complexes with phosphate groups, and HRE phosphoester bonds are having the highest coordination number than LRE phosphoester bonds [18].

The interaction between lanthanides and *B. subtilis* is reversible, where rare earths apparently bind to carboxylic groups in pH ranges less than 5 and to phosphoester bonds in higher pH values [19]. Among pH 2.5 and 4.5, *B. subtilis* has a specific binding site for REE, which has low affinity for La, Ce, Pr, Nd (LRE) and higher affinity for Tm, Yb, Lu (HRE) [20].

In alginate, it is especially the guluronic acid that offers these functional groups for ion exchange. As the alginate matrix is present as a gel phase, this material is easily penetrable for small metallic cations making it thus a suitable biosorbent with a high sorption potential [21].

This study aimed to evaluate the data of the equilibrium study of REE biosorption by *B. subtilis* biomass immobilized on calcium alginate gel by adjusting the Langmuir, Freundlich, and Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherms.

II. METHODOLOGY

A. Cell Immobilization

A colony of *B. subtilis* strain, from pre-existing Petri dishes, was transferred to 500 mL Erlenmeyer flasks containing 200 mL of culture medium (yeast extract, 5 g.L⁻¹; and tryptone from soybean, 30 g.L⁻¹), which were kept under constant stirring at 150 rpm for 72 h at 30 °C for the growth of the bacteria. After this period, the culture was stopped and distributed in 5mL Falcon tubes for centrifugation at 4000 rpm for 15 min at room temperature.

The sedimented biomass was pretreated with 1M NaCl solution for 1h. The cell immobilization step was performed from the blending of *B. subtilis* cells to 120 mL of 2% w.v⁻¹ sodium alginate solution. This mixture was dripped in a 125 mL Erlenmeyer flask containing 15 mL of 1M CaCl₂ solution.

B. Biosorption Experiments

Batch biosorption experiments were carried out in duplicate using synthetic solutions of La (III) and Sm (III) chlorides with single systems (La (III) or Sm (III), separately) and binary (La (III) + Sm (III)). Each Erlenmeyer containing about 1.10 g of *B. subtilis*-alginate biosorbent received 20 mL of REE solution. Biosorption experiments (Fig. 1) were carried under constant stirring at 100 rpm for 1 h and 30 °C.

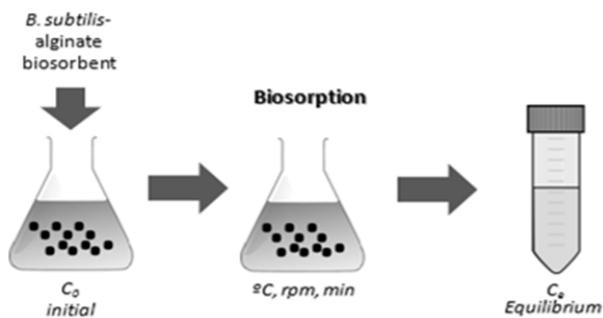


Fig. 1 Schematic diagram of batch biosorption equilibrium experimental procedure

For the studies of adsorption isotherm models, the following concentrations of REE were evaluated: 15, 30, 50, 75, 100, 150, 200, 300, 400 and 500 mg.L⁻¹. The biosorption experiments were carried out in three replicate and the average results were presented in this work. The determination of the final concentration of La (III) and Sm (III) in solution was performed using inductively coupled plasma optical emission spectrometry (ICP-OES).

The biosorption was expressed by the a) adsorption capacity (q) of the biosorbent *B. subtilis*-alginate, expressed in milligrams of REE adsorbed per gram of biosorbent dry mass (mg REE.g⁻¹) (1); and b) REE removal efficiency (%), expressed as (2) [22]:

$$q = \left(\frac{C_i - C_e}{m} \right) \cdot V \quad (1)$$

$$\% = \left(\frac{C_i - C_e}{C_i} \right) \cdot 100 \quad (2)$$

where C_i is the initial concentration of REE (mg.L⁻¹), C_e is the REE concentration at equilibrium (mg.L⁻¹), m is the mass of the biosorbent in the reaction mixture (g), and V is the volume of the reaction mixture (L).

III. RESULTS AND DISCUSSION

Under natural conditions, REEs exist in a mixed state. Therefore, it is necessary to investigate the selectivity of REEs on *B. subtilis*-alginate biosorbent. The adsorption of different concentrations of lanthanides on biosorbent was studied for La (III) and Sm (III) in the range of 15 to 500 mg.L⁻¹, keeping all other variables constant.

The results regarding the effect of initial concentration of REE ions are presented in Figs. 2 and 3. These results indicated that Sm (III) is preferably adsorbed in both mono- and binary systems, characterizing a higher affinity between the REE and *B. subtilis*-alginate biosorbent. Similar results were obtained for free cells from *Pseudomonas aeruginosa*, which was capable of adsorb selectively Eu (III) = Yb (III) > La (III) from aqueous solution [23].

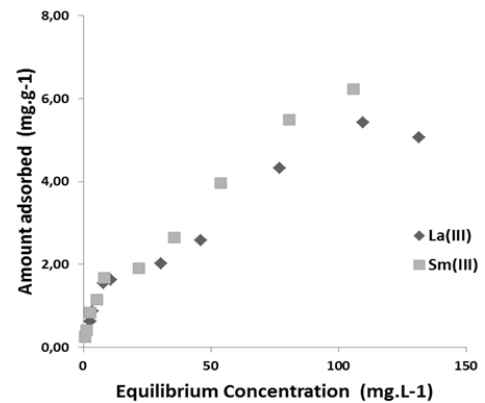


Fig. 2 Adsorption capacity of La (III) and Sm (III) species in single systems

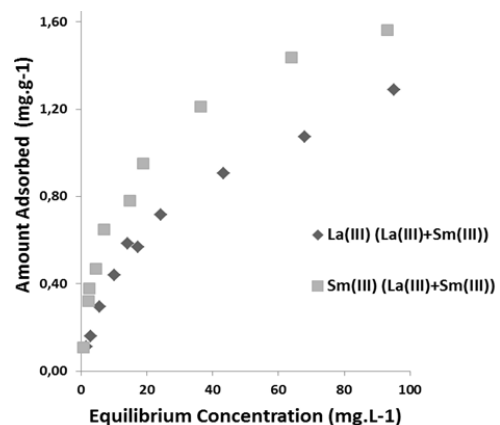


Fig. 3 Adsorption capacity of La (III) and Sm (III) species in binary systems

The adsorption of La(III) and Sm(III) exhibited similar behavior on these two systems. As the ion concentration increased, the adsorption rate increased in an approximately

linear manner. This behavior was also described for La(III) and Ce(III) adsorption by an immobilized gel doping sodium alginate with poly- γ -glutamate (PGA) [24]. In this context, it is important to utilize an appropriate immobilization technique because even if the free cells can provide valuable information in the laboratory [25], they are not suited for column packing in industrial applications.

Preliminary testing of biosorption systems are based in the investigation of equilibrium batch sorption tests described by fitting the experimental points with models. Traditionally, the adsorption process in biosorption systems can be described using the Langmuir and the Freundlich isotherms [26], [27]. The Langmuir model assumes that adsorption occurs at specific homogenous sites within the adsorbent, and it has been successfully applied in many monolayer adsorption studies. The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and that are not equally available [25].

The Langmuir isotherm is used for monolayer sorption on the surface of the particle, which contains some of free sites to perform the biosorption (3):

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (3)$$

where C_e is the adsorbate concentration at equilibrium (mg.L^{-1}), q_e is the amount adsorbed per gram of the adsorbent (mg.g^{-1}), Q_0 is the maximum monolayer coating capacity (mg.g^{-1}), and K_L is the Langmuir constant of the theoretical adsorption capacity in the monolayer (L.g^{-1}).

In the present paper, Langmuir isotherm model was suitably adapted to the experimental points for both the species treated alone and together, since they presented values for the correlation coefficients (R^2) between 0.98 and 0.99.

An indicative for favorable adsorption in the Langmuir model is when the R_L (separation factor) value is between 0 and 1. Equation (4) shows the calculation of the R_L value.

$$R_L = 1/(1 + K_L C_0) \quad (4)$$

where C_0 = initial concentration (mg.L^{-1}).

The value of R_L indicates the type of Langmuir isotherm as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$). From the values obtained for the present La (III) and Sm (III) sorption system, presented in Table I, it is quite evident that the adsorption is favorable, once the R_L values are between 0 and 1, and the adsorbate prefers the solid to the liquid phase [25].

The Freundlich isotherm is based on the sorption of heterogeneous surfaces (5):

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (5)$$

where, q_e is the amount adsorbed per gram of the adsorbent (mg.g^{-1}), and C_e is the adsorbate concentration at equilibrium (mg.L^{-1}). The constants associated with the Freundlich isotherm model are sorption capacity (K) and sorption intensity ($1/n$).

According to Table I, the Freundlich isotherm values of n was in the range $1 < n < 10$ (1.68-1.97), indicating that the strong affinity between *B. subtilis*-alginate and La (III) and Sm (III) in a favorable adsorption. The data obeyed both Langmuir and Freundlich models ($R^2 \geq 0.97$) indicating a multilayer adsorption of La (III) and Sm (III) onto the heterogeneous surface.

TABLE I
ADSORPTION ISOTHERMAL CONSTANTS FOR LA (III) AND SM (III)

Models	Parameters	La	Sm	La (La+Sm)	Sm (La+Sm)
Langmuir	Q_m (L.mg^{-1})	3.62	4.22	1.12	1.66
	K_L (L.g^{-1})	0.091	0.087	0.10	0.10
	R^2	0.98	0.99	0.98	0.99
	R_L	0.026	0.025	0.082	0.056
Freundlich	K	2.51	2.62	10.21	5.16
	N	1.87	1.69	1.68	1.97
	R^2	0.97	0.97	0.97	0.94
DKR	Q_s	2.52	2.56	1.50	1.17
	K	1.00E-06	6.00E-07	1.00E-06	5.00E-07
	E	1.00E+03	1.29E+03	1.00E+03	1.41E+03
	R^2	0.61	0.70	0.69	0.73

The DKR model is significant for calculating the apparent energy of adsorption, which predicts the type of adsorption, i.e. physisorption or chemisorptions. DKR isotherm [28] is used in the description of adsorption mechanisms considering a Gaussian distribution of energy and heterogeneous surfaces (6):

$$\ln q_e = \ln q_s - k\varepsilon^2 \quad (6)$$

where ε is the potential of Polanyi, q_e is adsorption capacity at equilibrium (mol.g^{-1}), q_s is the maximum theoretical adsorption capacity for the formation of a monolayer (mol.g^{-1}) and k constant associated with adsorption energy.

The k constant is associated with the average energy of adsorption E (kJ.mol^{-1}). If the E value is between 8 and 16 kJ/mol , the adsorption process follows by chemical ion exchange and if $E < 8$ kJ/mol , the adsorption process is of a physical nature [29].

Table I indicated that the nature of the adsorption of REE by *B. subtilis*-alginate biosorbent was physical, since its values, 1.0 - 1.41 kJ.mol^{-1} , are below 8.0 kJ.mol^{-1} . Physical adsorption of the metal ions onto the adsorbent surface implies more feasibility of the regeneration of the adsorbent [30], which, in turn, is a useful feature for employment of a biosorption process on a larger scale.

IV. CONCLUSION

Biosorption process proves to be a promising, effective and cost-effective method for the recovery of REE. This study has demonstrated the potential of application of *B. subtilis* bacterium cells immobilized in calcium alginate as an adsorbent for La (III) and Sm (III) ion separation in aqueous solutions. The low contact time (60 min.) and adsorbent dose (1.0 g.L^{-1}) together with high removal efficiency indicated that

B. subtilis-alginate biosorbent is a useful adsorbent for rapid and effective removal of Cr(VI) from aqueous solution.

From the studied isotherms models, Langmuir presented the best mathematical suitability, which probably suggests monolayer adsorption where each active site contains only one adsorbed molecule. On the other hand, the adsorption spontaneity was also determined by the equilibrium parameters R_L and n for the Langmuir and Freundlich models respectively. In both cases, the values determined do not indicate significant spontaneity in the adsorption process by the biomass. According to the DKR isotherm, the physical adsorption mechanism is consistent.

The adsorption preference follows the order Sm (III) > La (III), in the case of studies of the isolated species (single systems), as well as in experiments where the competition was promoted by the presence of both ions in solution (binary systems). This is a good indication that the biosorption process can represent a biotechnological innovation as well as a cost-effective excellent tool for the concentration, recovery, and separation of REE from aqueous solutions.

Future work must be focused on application of *B. subtilis*-alginate biosorbent on the recovery of REE from real leachate liquor. Moreover, batch equilibrium approaches should be accompanied by column studies for better understanding the mechanism and the behavior between the adsorbent and REE.

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