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Assessment of samarium biosorption from aqueous solution by brown macroalga *Turbinaria conoides*

K. Vijayaraghavan^{a,*}, S. Rangabhashiyam^b, T. Ashokkumar^a, Jesu Arockiaraj^c

^a Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India

^b Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, Germany

^c Division of Fisheries Biotechnology & Molecular Biology, Department of Biotechnology, Faculty of Science and Humanities, SRM University, Kattankulathur 603 203, Chennai, Tamil Nadu, India

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ABSTRACT

In the present research, a brown marine macroalga (*Turbinaria conoides*) was employed as a novel biosorbent for the sequestration of samarium ions from aqueous solutions. The influence of solution pH, initial Sm(III) concentration and contact time on Sm(III) removal were investigated. The biosorbent was characterized through Fourier transform infrared spectroscopy, potentiometric titration, scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis. Equilibrium experimental results were fitted to isotherm models such as the Langmuir, Freundlich and Redlich–Peterson to obtain the characteristic parameters of each model. The pseudo-first-order and pseudo-second-order kinetic models were used to analyze the experimental kinetic data. The Langmuir and Redlich–Peterson isotherms were found to best fit the equilibrium data and the biosorption kinetics followed the pseudo-second-order model. From the Langmuir isotherm model, the maximum biosorption capacity was found to be 151.6 mg/g at the solution pH 4.0. Desorption experiments revealed that 0.1 M HCl was efficient with good recovery of Sm(III) ions with desorption efficiency of 99.2%.

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1. Introduction

Rare earth metals are widely used in the metallurgy of materials, microelectronics, laser materials, high temperature superconductors, optical, magnetic, catalysts, chemical reagent, secondary batteries and green energy sectors [1,2]. Owing to these extensive applications in various fields, there is an increasing demand for rare earth metals in the international markets [3]. An efficient way to combat this demand is to recover rare earth metals from wastewater generated from rare earth industrial applications. Also, recovery of rare earth metal is vital to prevent its toxic effect on the environment [4].

Many conventional treatment processes such as ion exchange, precipitation, membrane filtration, reverse osmosis, evaporative recovery, coagulation, advanced oxidation, reduction and adsorption by activated carbon are generally employed to remove and recover metal ions from wastewater. Nevertheless, most of these conventional methods have several drawbacks and these includes secondary pollution, high cost, low selectivity, ineffectiveness at low metal concentrations, incomplete removal, high energy or chemi-

cal requirements, etc. [5,6]. Biosorption is a biological process that utilizes the potential of dead or inactive biomass for the removal of metal ions from the solutions. The merits of the biosorption process includes cost-effectiveness, efficiency at very low metal concentrations, eco-friendliness and unaltered performance over wide range of operating conditions [7,8]. A variety of biosorbents like *Sargassum fluitans* [9], *Sargassum polycystum* [10], *Pseudomonas aeruginosa* [11], *Saccharomyces cerevisiae* [12], *Platanus orientalis* leaf [13], *Pseudomonas* sp. [14], corn style [15], chitosan [16], *Pinus brutia* leaf [17], etc., have been reported for efficient removal of rare earth metals from aqueous solutions. However, it should be pointed out that compared to heavy metals, the studies devoted to identify biosorbents for rare earth metals are limited.

Among various biosorbents, the merits of employing dead algal biomass in metal biosorption includes higher capacities, easy handling, free from both aseptic conditions and growth media requirements, economical and easy source material procurement, etc. [18]. The distribution of biomolecules such as polysaccharides, proteins and lipids in the algal cell wall surface containing the functional groups such as hydroxyl, carboxyl, amino and sulfate, etc., offers binding sites for metal ions. The metal ion binding onto the biomass cellular membrane is often associated with the phenomenon like adsorption onto the surface and pores, chemisorption, ion-exchange, coordination, complexation, chelation, van der

* Corresponding author.

E-mail addresses: cevijay@iitm.ac.in, erkvijay@yahoo.com (K. Vijayaraghavan).

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Waals' attraction and entrapment in the spaces of the polysaccharides arrangement [19,20].

The objective of the present study was to investigate the potential of brown macroalgae (*Turbinaria conoides*) for the removal of Sm(III) ions from aqueous solution. *Turbinaria conoides* is a very common brown algal species found throughout the Pacific and Indian Ocean [4]. It comprises of tough thallus and is known for its rigidity; however the seaweed is believed to have less commercial importance. Hence, utilization of the seaweed as biosorbents will decrease the disposal cost as well as add value to the seaweed. The effects of various parameters such as solution pH, contact time and initial Sm(III) ion concentration on Sm(III) removal were investigated. The biosorbent was characterized using Fourier transform infrared spectroscopy (FT-IR), potentiometric titration, Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS). The Langmuir, Freundlich and Redlich–Peterson models were used to describe the biosorption equilibrium isotherm data. On the other hand, the pseudo-first-order and pseudo-second-order models were used to describe biosorption kinetics data. The efficacy of desorbing agents in stripping biosorbed Sm(III) ions from algal biomass was also examined.

2. Materials and methods

2.1. Preparation of the biosorbent material

Brown marine algae, *Turbinaria conoides* biomass (TCB) were collected from the beaches of Mandapam region (9°16'47"N 79°7'12"E) in Tamilnadu, India. The collected algal biomass were rinsed thoroughly with deionized (DI) water in order to get rid of any adhering debris and further dried overnight in an oven at 70 °C. The dried TCB was crushed and sieved to obtain biosorbent size in the range of 0.71–1.18 mm. For the removal of remaining dust on the sieved TCB surface, the sample was washed with DI water and oven dried at 70 °C for 48 h. The dried TCB samples were stored in an airtight container until further biosorption experiments.

2.2. Samarium stock solution

All the chemicals used for this study were of analytical (AR) grade. Stock solution (1000 mg/L) of Sm(III) were prepared by dissolving samarium(III) nitrate hexahydrate (Sigma–Aldrich, India) in DI water. All desired concentrations were prepared by diluting the stock solution using DI water. Initial pH of samarium solutions was adjusted and subsequently maintained by adding 0.1 M solutions of HCl or NaOH.

2.3. Characterization studies

Infrared spectra of the TCB samples were recorded in the 4000–400 cm⁻¹ region using Bruker-ATR IR (ACPHA) Fourier transform infrared spectrophotometer, Germany. The surface morphology of TCB was investigated through Scanning electron microscopy (Hitachi S4800, Japan). The elemental composition of the TCB was analyzed using Energy-dispersive X-ray spectroscopy.

In the case of potentiometric titration, 0.2 g of dry TCB was contacted with 100 mL of 1 mM NaCl solution in a beaker. Titrations were performed by adding 0.1 M NaOH. The suspension was stirred and continuously purged with nitrogen. After each addition of NaOH, the system was allowed to equilibrate until a stable pH value was obtained.

2.4. Biosorption experiments

Batch biosorption studies were performed to investigate the influence of parametric factors such as solution pH, contact time and

initial Sm(III) concentration on Sm(III) removal by TCB. In general, the experiments were carried out in 250 mL Erlenmeyer conical flask containing 0.1 g of TCB with 50 mL of the aqueous Sm(III) solutions. The suspensions were agitated in a thermostated incubator at 32 ± 1 °C and agitation speed of 160 rpm till the attainment of equilibrium. After the biosorption system reached equilibrium, the suspension was filtered using 0.45 μm PTFE membrane filter and the Sm(III) concentration in the filtrate was analyzed using an inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 5300 DV). Using the optimum biosorption conditions, the isotherm study was performed by varying initial Sm(III) concentration from 50 to 500 mg/L. Similarly, biosorption kinetic experiments were conducted by withdrawing samples at the regular intervals of time.

The amount of Sm(III) ions adsorbed per unit weight of TCB (q in mg/g) was calculated using the following expression:

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

where C_i and C_e represent the initial and equilibrium Sm(III) concentrations in the solution (mg/L), respectively, V is the initial volume of the solution (L) and m is the mass of the TCB (g). The parameters of the biosorption kinetics and isotherms were evaluated by non-linear regression using the Sigma Plot (version 4.0, SPSS, USA) software. The best fitting models of biosorption

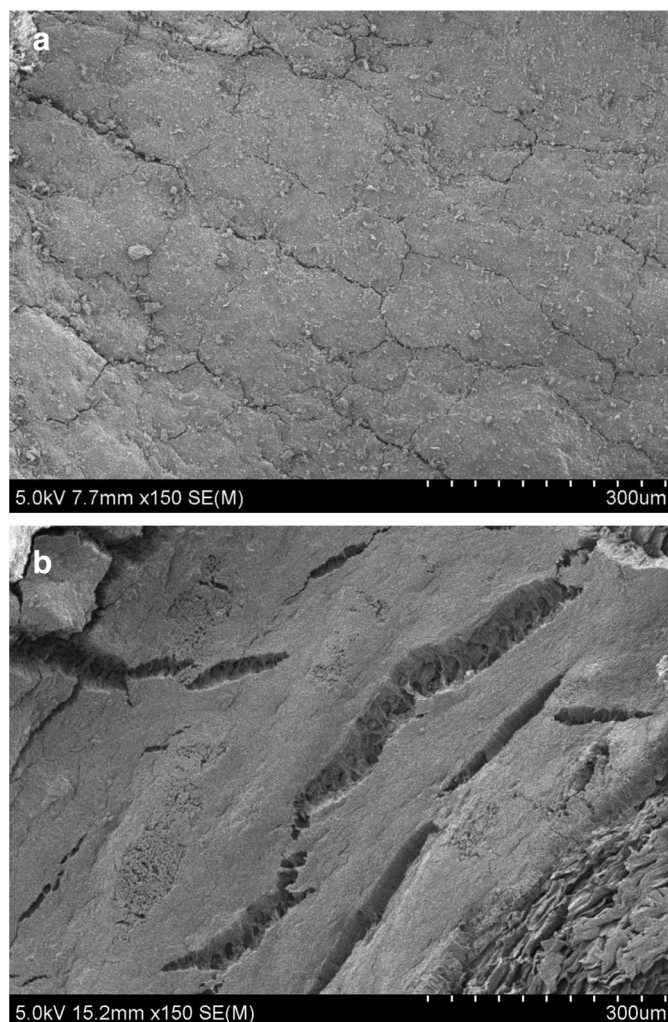


Fig. 1. SEM images of TCB (a) before and (b) after Sm(III) biosorption.

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