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

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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 chemical 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...
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:

\[ q = \frac{(C_i - C_f)V}{m} \]

where \( C_i \) and \( C_f \) 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.](image-url)
isotherm and kinetics models used in the present study was evaluated using coefficient of determination ($R^2$) and % error.

2.5. Desorption experiments

The regeneration of the TCB after biosorption process is an important aspect from economical point of view. Desorption study was carried out with the eluting agents like HCl and NaOH, each used with two different concentrations of 0.1 M and 0.01 M. The desorption experiments were performed in a similar way as that of biosorption studies. In brief, Sm(III)-loaded TCB previously exposed to 100 mg/L Sm(III) solutions at pH 4.0 was separated and subsequently dried. It was then contacted with 25 mL of desired desorbent for 60 min in a rotary shaker (160 rpm and 32 ± 1°C). After filtration, the concentration of Sm(III) in the filtrate was determined using ICP-OES.

3. Results and discussion

3.1. Characterization of TCB

The morphology of TCB before and after biosorption of Sm(III) was examined using SEM and presented in Fig. 1a and b, respectively. Fig. 1a shows the irregular and rough superficial structure of the TCB. After Sm(III) biosorption (Fig. 1b), the surface of TCB appeared to be smoother, shiny and whitish structure, which demonstrates that Sm(III) ions trapped onto the rough TCB surface. In addition, the EDS analyses were performed to determine qualitative elemental composition of TCB before (Fig. 2a) and after Sm(III) biosorption (Fig. 2b). The EDS spectrum observed from Fig. 2a illustrates that TCB comprises of elements such as carbon, oxygen, sulphur, potassium and magnesium. After biosorption, peaks of Sm(III) ions were noticed on the TCB surface along with other surface elements (Fig. 2b). By evaluating the EDS spectra of TCB before and after Sm(III) biosorption, the presence of Sm(III) peaks provided the confirmation for the specific biosorption of Sm(III) ion onto the TCB surface.

The FT-IR analysis was used to study the vibrational frequency changes in the functional groups of the TCB. The FT-IR spectra of TCB and Sm(III)-loaded TCB are presented in Fig. 3a and b, respectively. A number of peaks in Fig. 3a indicate the complex nature of TCB. The broad and strong vibration band centered at about 3426 cm$^{-1}$ is an indicative about the existence of –OH groups stretching in the TCB. The peak at 2923 cm$^{-1}$ can be assigned to the asymmetric and symmetric C–H stretching modes of the aliphatic groups. A band at 1444 cm$^{-1}$ correspond to the stretching vibrations of –NH$_2$+ , –NH$^+$ and –NH groups of the TCB. The strong bands at 1626 and 1422 cm$^{-1}$ were attributed to the asymmetric and symmetric stretching vibration of carboxyl groups (–C=O), respectively. The band observed at 1059 cm$^{-1}$ corresponds to the C–O stretching of alcohols and carboxylic acids, which proves the lignin based structure of TCB. The band at 676 cm$^{-1}$ fits in the fingerprint region and could be attributed to the phosphate groups [21–23].

After biosorption of Sm(III), several modifications were observed in the FT-IR spectra of TCB sample. For instance, the band corresponds to the stretching vibrations of –NH$_2$+ , –NH$^+$ and –NH groups were shifted to the band region at 2196 cm$^{-1}$. This behavior reveals the interaction between the amino groups and the Sm(III) ions. On the other hand, a new peak assigned at 1244 cm$^{-1}$ corresponding to SO$_3$ stretching of sulfonic acids of polysaccharides [24,25]. In general, FT-IR analysis demonstrate that some of the peaks were shifted and new peaks were identified in the Sm(III)-loaded TCB sample, which confirms the interaction of Sm(III) ions with TCB functional groups.

The acid-base titration curve of TCB is given in Fig. 4. The titration curve shows at least two inflection points at approximately pH 4.5 and 8.9, which corresponds to pk$\alpha$ values of two groups. From previous published reports [26,27,28], it can be inferred that
these two groups may be carboxyl and saturated amine (or saturated thiols). These groups present in TCB were likely to be involved in biosorption of Sm(III) ions. For pH values greater than the pKa, the sites were mainly in dissociated form and can exchange H+ ions with Sm(III) ions in solution; while at pH values lower than pKa, complexation phenomenon can also occur [28].

The number of carboxyl (weak acid) groups per gram of TCB ([COOH]_{total}, mmol/g) can be calculated by the estimation of inflection points (V_{eq}, mL) in the titration curve, using the following equation [27]:

\[
[\text{COOH}]_{\text{total}} = \frac{V_{\text{eq}} \times [\text{NaOH}]}{M}
\]  

The number of weak acid groups was calculated as 4.1 mmol/g.

3.2. Effect of solution pH

The solution pH is a vital parameter in the biosorption study, since it controls the biosorbent surface charge, degree of functional group dissociation on the biosorbent active sites and the speciation of metal ions [29]. The influence of solution pH on biosorption of Sm(III) onto TCB was studied at various solution pH values of 2.0, 3.0, 4.0, 4.5 and 5.0 at an initial Sm(III) concentration of 100 mg/L. The effect of solution pH on the biosorption capacity were measured and presented in Fig. 5. With an increase in solution pH from 2.0 to 4.0, the biosorption capacity of TCB increased from 34.1 to 49.7 mg/g and the percentage removal of Sm(III) increased from 68.2% to 99.4%. Further increase in solution pH resulted in slight decrease in the biosorption performance of TCB. At strong acidic solution pH, the biosorption of Sm(III) ions onto TCB was inhibited. These observations can be explained through the following facts: at lower solution pH of 2.0, the majority of binding sites of TCB were protonated with H+ ions and Sm(III) may not be able to compete with these ions in occupying the TCB sites. An increase in solution pH up to 5.0 resulted in decrease of H+ ions concentration, consequently favored the electrostatic interactions between positively charged Sm(III) ions and negatively charged TCB binding sites. As pointed out earlier (Section 3.1), TCB comprise of negatively charged functional groups such as carboxyl with pKa value of 4.5. On the other hand, samarium exists as Sm(III) ions at pH values less than 5.0. Under these conditions, the negatively charged functional groups attract positively charged Sm(III) through ion-
exchange mechanism [30,31]. Biosorption experiments beyond pH 5.0 was not considered, since precipitation of Sm(III) ions as insoluble hydroxide could interfere with the biosorption process [9,32]. Therefore, the subsequent experiments were conducted using the optimum solution pH 4.0.

3.3. Kinetic modeling

Kinetic studies are vital for the prediction of biosorption rate, which provides essential information for designing full-scale batch and fixed-bed biosorption process. In order to analyse and evaluate kinetics behavior of the biosorption process, experiments were conducted using different initial Sm(III) concentrations as depicted in Fig. 6. The results revealed that the uptake capacity of TCB increased with enhancing Sm(III) concentration. For example, the uptake amount of Sm(III) by TCB enhanced from 24.9 to 99.3 mg/g as the initial Sm(III) concentration increased from 50 to 200 mg/L. This increase in biosorption capacity was due to high driving force developed owing to changes in initial solute concentration, which enable the solute to overcome the mass transfer resistances of the metal ions between the solid and aqueous phases. Results also portrayed that the biosorption equilibrium attainment was not strongly dependent on the initial Sm(III) concentration, under the concentration ranges tested. The experimental kinetic data revealed that more than 90% Sm(III) removal was achieved within first 60 min of contact for all Sm(III) concentrations considered. The experimental kinetics data were fitted to the pseudo-first-order and pseudo-second-order kinetic models.

<table>
<thead>
<tr>
<th>Model</th>
<th>50 mg/L</th>
<th>100 mg/L</th>
<th>200 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_e (\text{mg/g}) )</td>
<td>24.1</td>
<td>48.1</td>
<td>97.1</td>
</tr>
<tr>
<td>( k_1 ) (min(^{-1}))</td>
<td>0.081</td>
<td>0.061</td>
<td>0.060</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.974</td>
<td>0.983</td>
<td>0.992</td>
</tr>
<tr>
<td>% error</td>
<td>1.34</td>
<td>1.79</td>
<td>1.31</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_e (\text{mg/g}) )</td>
<td>25.6</td>
<td>51.3</td>
<td>103.9</td>
</tr>
<tr>
<td>( k_2 ) (g/(mg.min))</td>
<td>0.0054</td>
<td>0.0019</td>
<td>0.0009</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.995</td>
<td>0.995</td>
<td>0.993</td>
</tr>
<tr>
<td>% error</td>
<td>0.09</td>
<td>0.43</td>
<td>0.72</td>
</tr>
</tbody>
</table>

3.3.1. Pseudo-first-order kinetic model

The pseudo-first-order model [33], in its non-linear form, can be represented as follows:

\[
q_t = q_e (1 - \exp (-k_1 t))
\]

where \( q_t \) and \( q_e \) are the amounts of Sm(III) biosorbed (mg/g) at equilibrium time and at any time, \( t \), respectively, and \( k_1 \) (1/min) denotes the rate constant of the pseudo-first-order biosorption process. The calculated parameters of pseudo-first-order kinetic model \( q_e \) and \( k_1 \) along with coefficient of determination and % error are presented in Table 1. The calculated biosorption capacity \( (q_{e,cal}) \) values using the Lagergren kinetic model did not agree well with the experimental \( q_e \) values \( (q_{e,exp}) \) and the \( R^2 \) values were found to be comparatively lower (Table 1). Several authors observed that the pseudo-first-order equation did not fit well over the entire contact time range and is generally applicable over the initial periods of the biosorption process [34].

3.3.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic model [35] is based on the assumption that the biosorption capacity is proportional to the number of active sites occupied on the biosorbent and follows chemisorption process [36]. The non-linear expression of pseudo-second-order kinetic model can be expressed as below:

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]

where \( k_2 \) (g/mg min) is the rate constant for pseudo-second-order kinetic model. The pseudo-second-order kinetic model parameters and the corresponding \( R^2 \) and % error values are reported in Table 1. It can be observed that the \( R^2 \) values were relatively higher and % error values were lower than the pseudo-first-order model. Moreover, the biosorption capacity calculated using the pseudo-second-order kinetic model \( (q_{e,cal}) \) were in good agreement with experimental biosorption capacity \( (q_{e,exp}) \). Thus,
the results showed that biosorption of Sm(III) by TCB follows the pseudo-second-order kinetic model than the pseudo-first-order kinetic model (Fig. 6).

3.4. Isotherm and modeling

Biosorption isotherm represents the relationship between metal concentration biosorbed by unit mass of biosorbent with metal concentration in the solution at a constant temperature. Fig. 7 shows the isotherm curve obtained through Sm(III) biosorption onto TCB. The curve was concave and favorable. It also exhibited steep slope, which implies high affinity of biosorbate to the biosorbent. The experimental maximum uptake was observed as 154.8 mg/g. The experimental isotherm curve was described using the Langmuir, Freundlich and Redlich–Peterson models [37,38].

3.4.1. Langmuir isotherm model

The Langmuir isotherm model is based on the assumption that all the biosorption sites have equal biosorbate affinity and biosorption at one site does not affect the biosorption at an adjacent site of biosorbent [39]. The Langmuir isotherm model provides information on the maximum biosorption capacity, which may not be achievable though experiments. The non-linear form of the Langmuir isotherm model is expressed using the following equation,

\[ q_e = \frac{Q_0 b_l C_e}{1 + b_l C_e} \]  \hspace{1cm} (5)

where \( C_e \) is the equilibrium concentration of the Sm(III) (mg/L), \( q_e \) indicate the amount of Sm(III) biosorbed on the unit mass of the TCB at equilibrium (mg/g), \( Q_0 \) and \( b_l \) are the Langmuir model parameters related to the biosorption capacity (mg/g) and equilibrium constant (L/mg), respectively.

The Langmuir model parameters were calculated using the equilibrium isotherm data and are listed in Table 2. The maximum biosorption capacity of TCB for Sm(III) was found to be 151.6 mg/g and the Langmuir equilibrium constant was calculated as 1.20 L/mg. High \( R^2 \) value and low % error value indicated that the Sm(III) equilibrium biosorption closely follow the Langmuir isotherm model. Table 3 compares the maximum sorption capacity of TCB for Sm(III) ions obtained in the present research with other sorbents reported in the literature. From Table 3, it can be concluded that TCB showed relatively high Sm(III) sorption capacity compared to other sorbents.

3.4.2. Freundlich isotherm model

The Freundlich isotherm model [40] is an empirical equation, based on the biosorption on heterogeneous surface. The Freundlich isotherm is represented as follows:

\[ q_e = K_f C_e^{1/n_f} \]  \hspace{1cm} (6)

where \( K_f \) (mg/g) (L/mg)\(^{1/n_f} \) and \( n_f \) are the Freundlich isotherm model parameters, corresponds to the biosorption capacity and biosorption intensity, respectively. The Freundlich isotherm model parameters values are presented in Table 2. The value of \( 1/n_f \) was less than unity, which pointed out the favorability of the Sm(III) biosorption onto TCB. However, low \( R^2 \) value and high % error value indicate the unsuitability of the Freundlich model for the present system.

3.4.3. Redlich–Peterson isotherm model

The Redlich–Peterson isotherm model [41] contains three parameters, as well as incorporates the features of both Langmuir and Freundlich isotherm models. This model may be used to represent biosorption equilibrium over a wide range of sorbate concentration. The non-linear expression of Redlich–Peterson isotherm model can be presented as follows:

\[ q_e = \frac{K_{RP} C_e^{\beta_{RP}}}{1 + a_{RP} C_e^{\beta_{RP}}} \]  \hspace{1cm} (7)

where \( K_{RP} \) (L/g) and \( a_{RP} (L/mg)^{\beta_{RP}} \) are Redlich–Peterson isotherm model constants and \( \beta_{RP} \) is the Redlich–Peterson model exponent. The value of model exponent (\( \beta_{RP} \)) lies between 0 and 1. The Redlich–Peterson equation behaves as the Langmuir form for the condition \( \beta_{RP} = 1 \) and as Henry’s law form, for \( \beta_{RP} = 0 \). The Redlich–Peterson isotherm model parameters for the Sm(III) biosorption by TCB are shown in Table 2. Higher value of \( R^2 \) and lower % error value ascertained the model applicability for Sm(III) biosorption. The value of the exponent was determined to be closer to unity, which confirms that the equilibrium isotherm is more of the Langmuir form. On comparison of all the three biosorption isotherm models based on \( R^2 \) and % error values, both the Langmuir and Redlich–Peterson isotherm model better described Sm(III) biosorption onto TCB.

**Table 2**

Biosorption isotherm model parameters along with coefficient of determination and % error values for Sm(III) biosorption onto TCB.

<table>
<thead>
<tr>
<th>Model</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td>( Q_0 ) (mg/g)</td>
<td>151.6</td>
</tr>
<tr>
<td>( b_l ) (L/mg)</td>
<td>1.20</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.993</td>
</tr>
<tr>
<td>% error</td>
<td>3.55</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
</tr>
<tr>
<td>( K_f ) (mg/g) (L/mg)^{1/n_f}</td>
<td>70.9</td>
</tr>
<tr>
<td>( n_f )</td>
<td>6.10</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.837</td>
</tr>
<tr>
<td>% error</td>
<td>19.2</td>
</tr>
<tr>
<td>Redlich–Peterson</td>
<td></td>
</tr>
<tr>
<td>( K_{RP} ) (L/g)</td>
<td>199.7</td>
</tr>
<tr>
<td>( a_{RP} (L/mg)^{\beta_{RP}} )</td>
<td>1.45</td>
</tr>
<tr>
<td>( \beta_{RP} )</td>
<td>0.978</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.993</td>
</tr>
<tr>
<td>% error</td>
<td>4.38</td>
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</table>

**Table 3**

Comparison of adsorption capacities for Sm(III) removal with different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum adsorption capacities (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parachlorella</td>
<td>1.29</td>
<td>[3]</td>
</tr>
<tr>
<td>Oxidized multiwalled carbon</td>
<td>89.28</td>
<td>[41]</td>
</tr>
<tr>
<td>nanotubes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soy hull</td>
<td>33.3</td>
<td>[44]</td>
</tr>
<tr>
<td>Cactus fibres</td>
<td>90.0</td>
<td>[45]</td>
</tr>
<tr>
<td>Sargassum sp.</td>
<td>97.73</td>
<td>[46]</td>
</tr>
<tr>
<td>Turbinaria conoides</td>
<td>151.6</td>
<td>Present study</td>
</tr>
</tbody>
</table>
3.5. Desorption study

Desorption studies were performed by subjecting Sm(III)-loaded TCB to either HCl or NaOH. Two different eluant concentrations (0.1 and 0.01 M) were used. The performance of NaOH as desorber for Sm(III)-loaded TCB was mediocre with only 8.2 and 9.4% desorption efficiencies were observed for 0.01 and 0.1 M NaOH, respectively. On the other hand, HCl performed well with 96.5% and 99.2% desorption efficiencies were observed for 0.01 M HCl and 0.1 M HCl, respectively. This superior performance of HCl further confirms the involvement of ion-exchange mechanism and participation of negatively charged binding sites such as carboxyl during biosorption process. During desorption, due to involvement of ion-exchange process, H⁺ ions supplied by desorber exchanged with bounded Sm(III) ions resulted in desorption. Also, the biomass weight loss after the 0.1 M HCl desorption process was less than 3.2%. It is well known that T. conoides is a rigid seaweed with tough structure [42], hence the highly acidic desorber apparently had no effect on the biomass structure. Based on desorption studies results, it can be concluded that higher concentration of HCl was effective for efficient desorption of Sm(III) from metal-loaded TCB.

4. Conclusions

The present work investigated the biosorption of Sm(III) onto the biomass of Turbinaria conoides. Experiments were performed as a function of different biosorption parameters like solution pH, contact time and initial Sm(III) concentration. It was observed that solution pH presented a strong effect on Sm(III) removal process and the optimum solution pH was found to be 4.0. Equilibrium data were best described by the Langmuir and Redlich–Peterson isotherm models. Using the Langmuir isotherm model the maximum biosorption capacity of TCB towards Sm(III) was predicted as 151.62 mg/g. The kinetic data of the biosorption process were best fitted with the pseudo-second-order kinetic model. During desorption studies, it was observed that 99.2% desorption efficiency was attained using 0.1 M HCl. Thus, the current study revealed that the cheap and eco-friendly Turbinaria conoides biomass exhibited excellent biosorption capacity towards Sm(III) and should be further explored for its removal performance in Sm(III) bearing industrial effluents.

Acknowledgements

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