Environmental Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tent20

Study of nickel and copper biosorption on brown algae Sargassum angustifolium: application of response surface methodology (RSM)
Salman Ahmady-Asbchin\textsuperscript{a}, Reza Tabaraki\textsuperscript{b}, Naser Jafari\textsuperscript{c}, Abdollah Allahverdi\textsuperscript{d} & Ashkan Azhdehakoshpour\textsuperscript{e}

\textsuperscript{a} Department of Biology, Ilam University, Ilam, Iran
\textsuperscript{b} Department of Chemistry, Ilam University, Ilam, Iran
\textsuperscript{c} Department of Biology, Mazandaran University, Babolsar, Iran
\textsuperscript{d} Division of Structural Biology and Biochemistry, School of Biological Sciences, Nanyang Technological University, Singapore
\textsuperscript{e} Offshore Fisheries Research Centre of Chabahar, Sub centre of Iranian Fisheries Research Organization (IFRO), Chabahar, Iran

Accepted author version posted online: 01 Feb 2013. Published online: 26 Feb 2013.


To link to this article: http://dx.doi.org/10.1080/09593330.2013.772643

PLEASE SCROLL DOWN FOR ARTICLE
**ORIGINAL ARTICLE**

**Study of nickel and copper biosorption on brown algae Sargassum angustifolium: application of response surface methodology (RSM)**

Salman Ahmady-Asbchin\(^a\), Reza Tabarakib, Naser Jafari\(^c\), Abdollah Allahverdid\(^d\) and Ashkan Azhdehakoshpoure\(^e\)

\(^a\)Department of Biology, Ilam University, Ilam, Iran; \(^b\)Department of Chemistry, Ilam University, Ilam, Iran; \(^c\)Department of Biology, Mazandaran University, Babolsar, Iran; \(^d\)Division of Structural Biology and Biochemistry, School of Biological Sciences, Nanyang Technological University, Singapore; \(^e\)Offshore Fisheries Research Centre of Chabahar, Sub centre of Iranian Fisheries Research Organization (IFRO), Chabahar, Iran

(Received 17 November 2012; final version received 27 January 2013)

This study has been focused on the batch culture removal of Cu\(^{2+}\) and Ni\(^{2+}\) ions from the aqueous solution using marine brown algae Sargassum angustifolium. Influences of parameters like pH, initial metal ions concentration and biosorbent dosage on nickel and copper adsorption were also examined using the Box–Behnken design matrix. For biosorption of Cu\(^{2+}\) the optimum pH value was determined as 5.0, optimum biosorbent concentration to 1.0 g/L and optimum initial concentration 0.15 mmol/L. For the biosorption of Ni\(^{2+}\), the optimal condition was the same but the optimum pH value was determined as 6.0. Desorption experiments indicated that CH\(_3\)COOH and EDTA were efficient desorbents for recovery from Cu\(^{2+}\) and Ni\(^{2+}\). The Langmuir isotherm model was applied to describe the biosorption of the Cu\(^{2+}\) and Ni\(^{2+}\) into S. angustifolium. The maximum uptake of Cu\(^{2+}\) and Ni\(^{2+}\) ions by the S. angustifolium biomass under the optimal conditions was approximately 0.94 and 0.78 mmol/g dry alga, respectively. Response surface models showed that the data were adequately fitted to a second-order polynomial model. Analysis of variance showed a high coefficient of determination value (\(R^2 = 0.993\) for Cu\(^{2+}\) and 0.991 for Ni\(^{2+}\)) and a satisfactory second-order regression model was derived. In addition, results reported in this research demonstrated the feasibility of employing S. angustifolium as biosorbent for Ni\(^{2+}\) and Cu\(^{2+}\) removal.

**Keywords:** copper; nickel; Sargassum angustifolium; isotherm; response surface methodology

1. Introduction

Heavy metals are major pollutants of the environment due to their toxicity and harm to human, animals and plants. Heavy metals are used in the operations of various industries, such as the semiconductor industry, electroplating and production of metal alloys. The resulting waste streams from the industries contain metal ions. Many studies have shown that they are highly toxic and can seriously damage the aqueous environment [1]. Copper ions are recognized to be one of the most widespread metal contaminants in the environment [2]. The EPA requires copper and nickel in drinking water not to exceed 1.3 and 0.04 mg/L, respectively [3]. The effects of heavy metals on functions of ecosystems vary considerably and relate to the economy and public health. Therefore, it is necessary to remove these pollutants from the ecosystem. The conventional technologies for metal removal from wastewater are precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, electrochemical treatment, and evaporation [4]. Application of the ion-exchange process is rather expensive due to the cost of synthetic ion-exchange resins. Furthermore, it is not always selective enough to allow an effective recovery of heavy metals present in the waste [4]. These approaches are either inefficient or expensive when heavy metals exist in low concentrations [4,5].

In the last two decades, biosorption has drawn attention due to its low cost, high efficiency and minimization of chemical or biological sludge. According to Gadd, biosorption may be simply defined as the removal of substances, including heavy metals, from solution by biological substance [6]. It is a property of both living and dead organisms and their components. Biosorbents exhibit this property, acting just as a chemical substance, as ion exchanger of biological origin. Also, biosorbents may be reused and the metals may be recovered [6].

Marine algae biomass is a good biosorbent due to its high uptake capacity and the ready abundance of biomass in many parts of the world [7,8]. The biosorption capability of algae is attributed mainly to the cell wall, which contains various polysaccharides and other highly complex organic compounds, such as alginic acid and fucoidan. Metal sorption performance depends greatly on the properties of the solutions [9]. Solution pH plays an important role since it can change the nature of metal speciation and thus affect the...
soption. In higher pH, cationic metal ion uptake is generally enhanced. Some species of the brown algae Sargassum have proved to be a highly effective biosorbent because of their capacity to remove high metals at a relatively rapid rate [10]. In Persian Gulf Iran, the genus Sargassum is an untapped resource that could be used for treating effluents from mining activity [11]. To develop a biosorption process by using Sargassum angustifolium for industrial applications, it is desirable to better understand the metal uptake process. The biomass of marine algae Sargassum species has shown a good capacity for heavy metals biosorption, highlighting its potential for effluent treatment processes. The use of marine algae for heavy metal removal has been reported by several authors (Table 1 [12–19]).

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>Ion</th>
<th>Capacity (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undaria pinnatifida</td>
<td>4.0</td>
<td>Cu²⁺</td>
<td>0.42</td>
<td>[12]</td>
</tr>
<tr>
<td>U. pinnatifida</td>
<td>4.7</td>
<td>Ni²⁺</td>
<td>0.66</td>
<td>[12]</td>
</tr>
<tr>
<td>Fucus serratus</td>
<td>5.5</td>
<td>Cu²⁺</td>
<td>1.73</td>
<td>[13]</td>
</tr>
<tr>
<td>F. serratus</td>
<td>5.5</td>
<td>Ni²⁺</td>
<td>0.95</td>
<td>[13]</td>
</tr>
<tr>
<td>Sargassum vulgare</td>
<td>4.5</td>
<td>Cu²⁺</td>
<td>0.93</td>
<td>[14]</td>
</tr>
<tr>
<td>Gracilaria sp.</td>
<td>3.5</td>
<td>Ni²⁺</td>
<td>0.27</td>
<td>[15]</td>
</tr>
<tr>
<td>Sargassum fluitans</td>
<td>4.5</td>
<td>Cu²⁺</td>
<td>0.80</td>
<td>[9]</td>
</tr>
<tr>
<td>Codium vermilare</td>
<td>6.0</td>
<td>Cu²⁺</td>
<td>0.27</td>
<td>[16]</td>
</tr>
<tr>
<td>Spirogyra insignis</td>
<td>6.0</td>
<td>Cu²⁺</td>
<td>0.30</td>
<td>[16]</td>
</tr>
<tr>
<td>Chondrus crispus</td>
<td>6.0</td>
<td>Cu²⁺</td>
<td>0.64</td>
<td>[16]</td>
</tr>
<tr>
<td>Palmaria palmata</td>
<td>6.5–7</td>
<td>Cu²⁺</td>
<td>0.10</td>
<td>[17]</td>
</tr>
<tr>
<td>P. palmata</td>
<td>6.5–7</td>
<td>Ni²⁺</td>
<td>0.5</td>
<td>[17]</td>
</tr>
<tr>
<td>Chondria armata</td>
<td>6.0</td>
<td>Cu²⁺</td>
<td>0.33</td>
<td>[16]</td>
</tr>
<tr>
<td>Sargassum glaucescens</td>
<td>6.0</td>
<td>Ni²⁺</td>
<td>0.94</td>
<td>[18]</td>
</tr>
<tr>
<td>Gelidium</td>
<td>5.3</td>
<td>Cu²⁺</td>
<td>0.21</td>
<td>[19]</td>
</tr>
<tr>
<td>Aspergillus armata</td>
<td>6.0</td>
<td>Ni²⁺</td>
<td>0.29</td>
<td>[16]</td>
</tr>
<tr>
<td>Sargassum sp.</td>
<td>5.0</td>
<td>Cu²⁺</td>
<td>0.99</td>
<td>[15]</td>
</tr>
<tr>
<td>Sargassum sp.</td>
<td>5.5</td>
<td>Ni²⁺</td>
<td>0.61</td>
<td>[15]</td>
</tr>
<tr>
<td>S. vulgare</td>
<td>4.5</td>
<td>Cu²⁺</td>
<td>1.01</td>
<td>[14]</td>
</tr>
</tbody>
</table>

The aim of the present investigation was to quantify the sorption of Ni²⁺ and Cu²⁺ ions to brown algae S. angustifolium. In addition the effects of initial metal ion concentration, exposure time, concentration of alga biomass and pH were studied. The results were also analysed in terms of an intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate controlling step in adsorption of Cu²⁺ and Ni²⁺ on S. angustifolium biosorbent. In the present study, RSM was used to optimize the uptake of metals (Cu²⁺, Ni²⁺) by S. angustifolium.

2. Materials and methods

2.1. Biosorbent

The biosorbent of brown macroalgae S. angustifolium used in this study was collected during January 2011 from the city of Chabahar in southeast Iran (Lat. 25°16’ 30” N, Long. 60°40’ 32” W). Raw material was washed twice with tap water, then twice with deionized water. After drying at 60°C, the algae were crushed, sieved, and the 0.355–0.5 mm particle size fraction was kept for the experiments. Copper and nickel solutions of different concentrations (0.01–0.44 mmol/L) were prepared by adequate dilution of the stock solution with deionized water. The stock copper and nickel solution was prepared by dissolving CuCl₂·2H₂O and NiCl₂·6H₂O (purchased from Merck & Co. Inc.) in deionized water.

2.2. Batch-culture experiments

The effect of pH, exposure time, initial metal ions concentration and adsorbent dosage were evaluated using batch-culture adsorption experimentation at room temperature, 25 ± 1°C. The S. angustifolium was added to the solutions while being shaken at 150 rpm in an orbital shaker. The pH of each solution was adjusted with HCl and NaOH solutions before mixing with the biosorbent. After the experiments, the supernatants were taken from each flask and filtered. Isotherm experiments were carried out in bottle flasks filled with 1000 ml of water thoroughly mixed with 0.1 g of S. angustifolium at 25 ± 1°C and initial pH close to 5.0. The initial concentrations of metal ions were in the range 0.01–0.44 mmol/L. Single-metal concentrations in the relevant samples were determined with an atomic absorption spectrophotometer (Chem. Tech. Analytical CTA 2000). The liquid phase was separated from the adsorbent by a filtration system using 0.45 μm membranes. The metal uptake
at equilibrium was calculated by the following equation:

$$q_e = \frac{V}{W}(C_i - C_e)$$  \hspace{1cm} (1)

where $q_e$ is the metal uptake (mmol Cu$^{2+}$ and Ni$^{2+}$ adsorbed per g adsorbent), $V$ (L) is the solution volume, $W$ (g) is the amount of sorbent, and $C_i$ (mmol/L) and $C_e$ (mmol/L) are the initial and equilibrium metal concentration in solution, respectively. The biosorption results were analysed using an intra-particle diffusion model (Weber–Morris). This is represented as:

$$q_t = k_{id}t^{0.5} + c$$  \hspace{1cm} (2)

where $q_t$ (mg/g) is the amount adsorbed at time $t$ (min), $k_{id}$ (mg/g min$^{0.5}$) is the rate constant of intraparticle diffusion. $c$ is the value of intercept, which gives indicates the boundary layer thickness: the larger the intercept, the greater the boundary effect.

In order to optimize the design of a sorption system for the removal of Cu$^{2+}$ and Ni$^{2+}$ ions from effluents, it is important to establish the most appropriate correlations for equilibrium curves.

### 2.3. Experimental design by RSM

RSM is a useful technique for development and optimization of the biosorption process [24,25]. One of the most appropriate applications of RSM is in situations where a large number of variables influence the system [26,27].

The generalized second-order polynomial model proposed for the response surface analysis is given as follows:

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + e$$  \hspace{1cm} (3)

where $Y$ is the predicted response, $\beta_0$, $\beta_j$, $\beta_{jj}$ and $\beta_{ij}$ are coefficients estimated from regression, representing the linear, quadratic and cross products of $x_1$, $x_2$ and $x_3$ on response. The three factor designed experiments were conducted with three replications of each experiment. Three parameters, algal amount ($x_1$), initial concentration copper/nickel ($x_2$) and pH ($x_3$), were studied using the Box–Behnken model with two levels (Table 2). The dependent variables were $q_{Ni}$ and $q_{Cu}$ (Table 3).

Statistical analysis was performed using the Minitab 15.1 (Minitab Inc., State College, PA, USA) software and fitted to a second-order polynomial regression model containing the coefficient of linear, quadratic and interaction terms. The data were subjected to analysis of variance and the coefficient of regression ($R^2$) was calculated to find out the goodness of fit of the model. An analysis of variance (ANOVA) with 95% confidence level was then carried out for each response variable in order to test the model significance and suitability. The significances of all terms in the polynomial models were analysed statistically by computing the $F$-value at a probability ($p$) of 0.0001, 0.01 or 0.05.

### 2.4. Desorption experiment

If the biosorption process were to be used as an alternative to the wastewater treatment scheme, the regeneration of the biosorbent may be crucially important for keeping the process costs down and in opening the possibility of recovering the metals extracted from the liquid phase. For the desorption study, contact made between 0.1 g dried biomass and a 100 ml Cu$^{2+}$ and Ni$^{2+}$ solution (3 mmol/L). After Cu$^{2+}$ ion sorption, the biomass was filtered, washed three times with distilled water to remove residual Cu$^{2+}$ on the surface, and kept in contact with the 100 ml desorbent solution: HNO$_3$, Ca(NO$_3$)$_2$, EDTA, CH$_3$COOH (0.1 and 1 mM) and distilled water. The mixtures were shaken in a rotary shaker for 16 h. The filtrates were analysed to determine the concentration of Cu$^{2+}$ and Ni$^{2+}$ after desorption.
2.5. Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was used to confirm the presence of the functional groups in samples of *S. angustifolium* and to observe the chemical modification after Cu\(^{2+}\) and Ni\(^{2+}\) ions adsorption in raw algae. Specimens of various biosorbents were first mixed with KBr at an approximate ratio of 1/100 (sorbent/KBr) and then ground in an agate mortar. Infrared spectra were recorded in the 500–3500 cm\(^{-1}\) region using a Thermo Nicolet instrument, model Hartman-Bomen device, to obtain information about the surface.

3. Results and discussion

3.1. Effect of pH on biosorption

The metal ion binding in biosorption could be attributed to several mechanisms, such as ion exchange, complexation, electrostatic attraction and micro precipitation. For algae biomass, ion exchange has been considered as a main mechanism responsible for metal sequestering [14]. The effect of pH on Cu\(^{2+}\) and Ni\(^{2+}\) biosorption on *S. angustifolium* biomass is studied at room temperature by varying the pH of Cu\(^{2+}\) and Ni\(^{2+}\) solution. Experimental results indicate that in the present of the biomass a chemical precipitation occurred since the Cu\(^{2+}\) began to precipitate after pH 6 (Figure 1). Uptake reduction of copper and nickel may be due to chemical precipitation in solution and nature of binding sites in *S. angustifolium* biomass. The pH is one of the most important parameters of biosorption and, regarding *Sargassum* sp., its high content of ionizable groups (carboxyl groups) makes it very liable to be influenced by the pH of the medium [28]. For *Sargassum* sp., carboxyl groups are chiefly responsible for binding metallic ions [9]. However, other functional groups may contribute to the process, such as the sulphonate and amine groups. However, the majority of copper ions precipitate at pH values over 5.5.

3.2. Kinetics of adsorption

Kinetics of Cu\(^{2+}\) and Ni\(^{2+}\) ions adsorption by *S. angustifolium* were accomplished to estimate the time required to reach the sorption equilibrium. Figure 2 shows the kinetics of Cu\(^{2+}\) and Ni\(^{2+}\) ions adsorption for an initial metal ions concentration of 4 mg/L. In general, about 80% of the total metal ion sorption was achieved within 40 min. Therefore, in subsequent equilibrium experiments 4 h was deemed more than sufficient to establish equilibrium.

3.3. Optimal conditions for copper and nickel biosorption process

The hierarchical quadratic model was used to represent the response surface in three-dimensional plots and to find the optimal conditions for copper and nickel ions removal by *S. angustifolium* biosorbent, biosorbent amount and pH interaction that had the most significant effect on copper and nickel uptake (Figure 3). At pH 5 and biosorbent amount of 1 g/L, the model predicted copper and nickel maximum uptake capacities by *S. angustifolium* close to 0.95 and 0.78 mmol/g, respectively. According to this figure, the solution pH considerably affects biosorption of copper and nickel by *S. angustifolium*. Various reasons might explain the metal adsorption behaviour of the biosorbent relative to solution pH. The cell wall of algae contains a large number of surface active sites. The metal biosorption mechanism depends on the surface of the biosorbent and the nature of the physicochemical interaction of ions.

Figure 2 illustrates that the uptake of copper and nickel is enhanced with increasing initial copper and nickel concentration for ranges of pH from 4 to 6 and amount of biosorbent from 0.5 to 1 mg/g, respectively. At higher concentration (0.15 mmol/L), a decline in copper and nickel biosorption occurred. This decrease at high concentration may be due to competition among metal ions for a smaller number of available binding sites and also saturation of most of the
binding sites. The initial concentration provides an important driving force to overcome all mass transfer resistance of copper and nickel between the aqueous and solid phases. Hence, a higher initial concentration of copper and nickel will increase the biosorption rate. Since cells offer a finite number of surface binding sites, removal showed saturation at higher metal ion concentrations.

The sorbent amount used for the treatment studies is an important parameter which determines the potential of biosorbent to uptake copper and nickel. The uptake increased with an increase in sorbent amount. The increase of metal ions sorption capacity of biosorbent with an increase in metals concentration is probably due to higher interaction between metal ions and the sorbent. A similar result has been reported by Rajasimman and Murugaiyan for nickel removal by red macroalgae (*Hypnea valentiae*) [29]. As shown in Figure 2, the removal of copper and nickel increased with an increase in sorbent amount. It was shown that the removal of nickel and copper increased up to 1.5 g/L (Figure 3).

The optimum values for initial concentration, pH, and algae amount were estimated to be 0.15 mmol/L, 5 and 1.5 g/L respectively.

### 3.4. Biosorption isotherms

Figure 4 shows the Cu$^{2+}$ and Ni$^{2+}$ uptake isotherms at pH 5.0. The experimental results were fitted with the Langmuir isotherm model, which fitted the equilibrium data better than the Freundlich isotherm. The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. This model is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent:

$$q_e = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e}$$  \hspace{1cm} (4)$$

where $q_e$ is the amount of metal ions adsorbed (mmol/g), $C_e$ is the equilibrium concentration (mmol/L), $q_{max}$ (mmol/g) is the maximum adsorption capacity and $b$ (L/mmol) is an affinity constant. For determining the equilibrium parameters, Equation (2) can be altered into a linear form as follows (Figure 5):

$$\frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m}$$  \hspace{1cm} (5)$$

Figure 3. Response surface plot for metal (Ni$^{2+}$, Cu$^{2+}$) removal by *S. angustifolium* biosorbent as (a) functional of initial nickel concentration and pH; (b) functional of biosorbent dose and pH; (c) functional of biosorbent dose and initial nickel concentration; (d) functional of initial nickel concentration and pH; (e) functional of biosorbent dose and pH; (f) functional of biosorbent dose and initial nickel concentration.
Figure 4. Sorption isotherm of a \( \text{Cu}^{2+} (\bullet, \circ) \) and \( \text{Ni}^{2+} (\blacksquare, \square) \) in deionized water and in tap water.

Figure 5. Sorption isotherm of a \( \text{Ni}^{2+} (\blacksquare) \) and \( \text{Cu}^{2+} (\bullet) \) in deionized water and \( \text{Ni}^{2+} (\square) \) and \( \text{Cu}^{2+} (\circ) \) in tap water by Langmuir linear form.

Table 4. Calculation parameters from Langmuir equation in deionized water.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( q_m ) (mmol/g)</th>
<th>( b_L ) (L/mmol)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>In deionized water</td>
<td>Cu(^{2+})</td>
<td>0.949</td>
<td>15.27</td>
</tr>
<tr>
<td></td>
<td>Ni(^{2+})</td>
<td>0.789</td>
<td>27.55</td>
</tr>
<tr>
<td>In tap water</td>
<td>Cu(^{2+})</td>
<td>0.197</td>
<td>52.87</td>
</tr>
<tr>
<td></td>
<td>Ni(^{2+})</td>
<td>0.551</td>
<td>44.34</td>
</tr>
</tbody>
</table>

The values of \( q_m \) (mmol/g) and \( b \) (L/mmol) were obtained from Equation (3). The linear correlation coefficient was 0.991 and \( q_m \) of Cu\(^{2+}\) was 0.94 mmol/g from calculation using the Langmuir equation (Table 4). For adsorption of Ni\(^{2+}\) correlation coefficient and \( q_m \) 0.993 and 0.78 were calculated, respectively.

Experimental fixation capacities obtained in tap water are much less described by the tested models and show a decrease in comparison with deionized water. The difference between them could be attributed to a competition mechanism between ions naturally present in tap water and Cu\(^{2+}\) and Ni\(^{2+}\) for the binding moieties present on \( S. \text{angustifolium} \) surface. This indicates that, in addition to the ion exchange mechanism, there are other reactions contributing to the heavy metal binding [30]. The adsorption study has highlighted an ion exchange mechanism responsible for metal uptake. With the release of calcium and magnesium on \( S. \text{angustifolium} \), the same amount of Ni\(^{2+}\) and Cu\(^{2+}\) is adsorbed. This release depends on the initial Cu\(^{2+}\) and Ni\(^{2+}\) concentration of the solution, which could lead to a fixation mechanism by ion exchange for 4 h. Because the isotherms of Cu\(^{2+}\) and Ni\(^{2+}\) adsorption and Ca\(^{2+}\) and Mg\(^{2+}\) desorption were similar, Cu\(^{2+}\) and Ni\(^{2+}\) ions seemed to be exclusively adsorbed by an ion exchange mechanism. Ion exchange is an important mechanism in biosorption, because it explains many of the observations made during heavy metal uptake experiments. Under certain conditions, the ions attracted to a solid surface may be exchanged with other ions in an aqueous solution. Both cations and anions exchange can occur, but in some natural material, cations exchange is the dominant process [31].

Several models of kinetics can be used in order to investigate the mechanism of biosorption and potential rate controlling steps such as mass transport and chemical reaction processes. The Weber–Morris plots for adsorption of Ni\(^{2+}\) and Cu\(^{2+}\) are given in Figure 6. It was observed that the Cu\(^{2+}\) and Ni\(^{2+}\) amounts biosorbed by \( S. \text{angustifolium} \) have a multi-linearity in that two or more steps occur. The first was attributed to the adsorption of metal ions over the surface of the biosorbent, and, hence, was the fastest sorption stage. The second is the gradual adsorption stage, where the intraparticle diffusion starts to slow due to extremely low solute concentration in the solution. The high \( R^2 \) values (Ni\(^{2+}\) 0.993, Cu\(^{2+}\) 0.994) show that the metal ions biosorption data has been very well fitted to the Weber–Morris model.

3.5. Desorption experiment

Figure 7 shows the percentage of Cu\(^{2+}\) and Ni\(^{2+}\) released by \( S. \text{angustifolium} \) after treatment with different desorbents. It was observed that the percentage of desorption
using distilled water was almost negligible. The desorption percentage decreased with a decreasing concentration of HNO₃ (Cu desorbed percentage: 1 mol/L HNO₃: 26%; 0.1 mol/L HNO₃: 16%; Ni desorbed percentage: 1 mol/L HNO₃: 24%; 0.1 mol/L HNO₃: 7%). Chelating agent (i.e. EDTA) was more efficient than HNO₃ and Ca(NO₃)₂, and 0.1 mol/L EDTA can remove 81% and 66% of Cu²⁺ and Ni²⁺ respectively bound to biomass. CH₃COOH was more efficient than other desorbents, and 1 mol/L CH₃COOH can remove 89% and 77% of Cu²⁺ and Ni²⁺ respectively bound to biomass. This is attributed to the high value of the conditional formation constant of the complex Cu²⁺-CH₃COOH (kₐ = 1.14 x 10¹⁰, pH = 5.0), which favours desorption of Cu²⁺ from the biomass. The high recovery percentage of Cu²⁺ by CH₃COOH and EDTA allows the recycling of Cu²⁺ Ni²⁺ from the biomass in industry, thus the algal biomass can be used as a disposable as well as allowing use more than once.

3.6. FT-IR spectroscopy analysis

In order to determine the main functional groups of S. angustifolium participate in Cu²⁺ and Ni²⁺ biosorption, FT-IR spectra of natural and metal loaded S. angustifolium (Figures 8 and 9) were recorded. There were clear band shifts and intensity change in four bands. These bands are the functional groups of S. angustifolium participate in Cu²⁺, Ni²⁺ biosorption (C=O, −NH, −SO₃ and −CN). The intensity of stretching C=O (carboxyl) group changed after adsorption of Cu²⁺, but wavenumber of −SO₃ and −CN groups shifted between 1209–1212 cm⁻¹ and 819–920 cm⁻¹, respectively. The bands at 1209 cm⁻¹ represent SO₃ stretching, which is mainly present in sulphonic acids of polysaccharides such as fucoidan [32,33]. The intensity of C=O group changed after adsorption of Ni²⁺, but the wavenumber of SO₃, −CN and −NH functional
groups shifted between 1208–1212 cm\(^{-1}\), 819–920 cm\(^{-1}\) and 1522–1542 cm\(^{-1}\), respectively.

4. Conclusion
This study indicates that brown marine algae \textit{S. angustifolium}, which is widely available at a low cost, can be used as an efficient biosorbent material for the treatment of Cu\(^{2+}\) and Ni\(^{2+}\) in aqueous solution. The adsorption isotherm of Cu\(^{2+}\) and Ni\(^{2+}\) by dried \textit{S. angustifolium} pieces could be adequately described by the Langmuir isotherm model. The maximum adsorption capacity was 0.94, 0.78 mmol/g for Cu\(^{2+}\) and Ni\(^{2+}\) respectively. Desorption experiments proved that CH\(_3\)COOH and EDTA were efficient and practical desorbents for the recovery of Cu\(^{2+}\) and Ni\(^{2+}\) from the biomass. The properties of the biosorbent were determined and the nature of biomass–metal ions interactions was evaluated by FT-IR analysis, which showed the participation of COOH, CN, SO\(_3\) and NH groups in the biosorption process.

The pH value that was selected for the experiments on the biosorption of Cu\(^{2+}\) and Ni\(^{2+}\) by \textit{S. angustifolium} was pH = 5 since it combined the best characteristics for the lowest chemical precipitation and the highest biosorption. The biosorption conditions of Cu\(^{2+}\) and Ni\(^{2+}\) ions on \textit{S. angustifolium} were optimized by using RSM. The relationship between the response and the independent variables was developed via the quadratic approximating function of Cu\(^{2+}\) and Ni\(^{2+}\) biosorption capacity of biosorbent at the end of 4 h biosorption. The optimum biosorption conditions were determined as initial pH 5.0, biosorbent amount/concentration 1.0 g/L and initial metal concentration 0.15 mmol/L. With advantages of high metal biosorption and desorption capacities, the biomass of \textit{S. angustifolium} has a promising application as a cost-effective biosorbent material for the removal of Cu\(^{2+}\) and Ni\(^{2+}\) from wastewater.

References


