Batch and Column Removal of Total Chromium from Aqueous Solution Using Sargassum polycystum

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INTRODUCTION

The presence of heavy metal ions in surface water continues to be most pervasive environmental issues of present time. Chromium, one of the important heavy metal, occurs mainly as a result of human activities through production of waste waster in metal smelting, metallurgy, electroplating, leather, and dyes-tuff industries. Chromium exists in a wide range of valency states from $-4$ to $+6$, with the hexavalent species (Cr(VI)) predominant in natural aquifers and its trivalent counterpart (Cr(III)) prevailing in the municipal wastewater rich in organics [1]. Hexavalent chromium is more toxic than the trivalent form, in the order of 100-fold more toxicity [2]. This is because of their high-oxidation potentials and the ease with which they penetrate biological membranes. Chromium(VI) is known to be carcinogenic and mutagenic, and it induces dermatitis. Hence various technologies were employed to treat the chromium-bearing wastewaters at the point of source. Chemical precipitation with lime or caustic soda is one of the...
common conventional treatments, where recovery of metals or water is not a consideration. However, a large quantity of chemicals is necessary to effectively decrease metal concentration to acceptable levels, which in turn generates voluminous sludge [3]. Other available treatments such as ion exchange, activated carbon, electrolys, and reverse osmosis require high-capital investment and running costs [4]. Thus, there is a need for the development of low-cost-effective methods that are more environmentally benign.

In recent years, research attention has been focused on biological methods for the treatment of metal-bearing effluents [3, 5], some of which are in the process of commercialization. Among these, biosorption has been demonstrated to possess good potential to replace conventional methods for the removal of metal ions. In the case of Cr removal, several biosorbents under the class of bacteria [6, 7], fungi [8–10], and seaweed [11, 12] were identified as potential candidates.

*Sargassum*, popular brown marine algae, is known for its metal biosorption capacity [13]. Its cell wall content, alginate, is responsible for binding heavy metal ions. They are plentiful and fast growing; and sometimes threaten the tourist industry by spoiling the environment and fouling the beaches. Therefore, alternate solutions that utilize the potential of seaweeds are significant and beneficial to local communities. Thus, the objective of this study was to employ locally available seaweed (*Sargassum polycystum*) for the biosorption of Cr in batch and column mode of operation.

**MATERIALS AND METHODS**

**Materials**

The raw biomass of brown algae *S. polycystum* was collected from Mandapam (Tamil Nadu, India). The biomass was washed with copious quantities of deionized water to remove extraneous materials. The washed biomass were dried at 60°C overnight and the dried biomass was grounded to particle sizes of 0.7–1 mm. Stock solutions of chromium at various concentrations. In the batch kinetic experiments, the biomass was added to the solutions with varying Cr concentration, while in the biosorption isotherm experiments, the solution pH was varied and the same amount of biomass was added to the solutions with varying Cr concentrations. In the batch kinetic experiments, the biomass was added to the solutions of different initial Cr concentration and samples were taken at periodic time intervals and subsequently analyzed for chromium concentration. The total chromium uptake was calculated using the mass balance,

\[
Q = V(C_0 - C_f)/M
\]

where \(V\) is the solution volume (L), \(M\) is the amount of biomass (g), and \(C_0\) and \(C_f\) are the initial and final concentration of chromium in solution, respectively.

**Sorption Models**

Modeling of biosorption isotherm data is important for predicting and comparing biosorption performance. Two, three, and even four-parameter isotherm models are available for modeling biosorption data [14, 15]. In this study, the equilibrium data were analyzed using three isotherm models, which include Langmuir, Freundlich, and Redlich–Peterson isotherm expressions. They were represented by the following equations,

**Langmuir model** [16]:

\[
Q = \frac{Q_{	ext{max}}bC_f}{1 + bC_f}
\]

**Freundlich model** [17]:

\[
Q = K_F C_f^{1/n}
\]

**Redlich–Peterson model** [18]:

\[
Q = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{b_{RP}}}
\]

where \(Q_{	ext{max}}\) is the maximum metal uptake (mg/g), \(b\) is the Langmuir equilibrium constant (L/mg), \(K_F\) is the Freundlich constant (L/g)\(^{1/n}\), \(n\) is the Freundlich constant, \(K_{RP}\) is the Redlich–Peterson isotherm constant (L/g), \(a_{RP}\) is the Redlich–Peterson isotherm constant (L/mg)\(^{b_{RP}}\), and \(b_{RP}\) is the Redlich–Peterson model exponent. All the model parameters were evaluated by non-linear regression using Sigma Plot (version 4.0, SPSS, USA) software.

**Column Experiments**

Continuous flow sorption experiments were conducted in a glass column of 2 cm i.d. and 35-cm height. A known quantity of biomass was placed in the column to yield a desired bed height. A solution of 100 mg Cr/L was pumped upward through the column at a desired flow rate by a peristaltic pump (pp40, Miclins).
Samples were collected at the exit of the column at different time intervals and analyzed for total Cr concentration. Operation of the column was stopped when the effluent Cr concentration exceeded a value of 99.6 mg/L. All the experiments were carried out in duplicates, and the deviations were within 5%. The total quantity of metal mass biosorbed in the column ($m_{ad}$) is calculated from the area above the breakthrough curve (outlet metal concentration versus time) multiplied by the flow rate. Dividing the metal mass ($m_{ad}$) by the biosorbent mass ($M$) leads to the uptake capacity ($Q$) of the biomass.

The other column parameters were calculated as described later [19]:

Overall sorption zone:

$$\Delta t = t_e - t_b$$

Total amount of metal ions sent to column:

$$m_{total} = \frac{C_0 \cdot F \cdot t_e}{1000}$$

Total metal removal (%):

$$\text{Removal} (%) = \frac{m_{ad}}{m_{total}} \times 100$$

where $C_0$ is the inlet metal ion concentration (mg/L), $F$ the volumetric flow rate (mL/min), $t_e$ is the exhaustion time (h), and $t_b$ is the breakthrough time (h). The slope of the breakthrough curve from $t_b$ to $t_e$ was represented by $dc/dt$. All experiments were done in duplicates and the data presented are the average values of two replicate experiments.

RESULTS AND DISCUSSION

Effect of pH and Biosorption Isotherm

Preliminary experiments on the effect of equilibrium pH on the Cr removal revealed that strong acidic conditions are required to obtain maximum removal efficiencies. Maximum Cr removal efficiency was observed at pH 2. Further increase or decline in the pH resulted in reduced Cr removal efficiency. Hexavalent chromium exists as $\text{CrO}_4^{2-}$, $\text{HCrO}_4^-$, $\text{H}_2\text{CrO}_4$, $\text{Cr}_2\text{O}_7^{2-}$, or $\text{Cr}_2\text{O}_7^{3-}$, depending on the pH of the medium and the total Cr(VI) concentration [20]. However, only $\text{HCrO}_4^-$ and $\text{Cr}_2\text{O}_7^{2-}$ are prevalent when total chromium concentration is 2 mM in the pH range of 2–4. On the other hand, Sargassum biomass comprises of abundant carboxyl, sulfonate, and amino groups [13]. As the solution pH decreases, these functional groups become protonated, thus making the biomass more positively charged and hence creating an electrostatic attraction with Cr(VI) species. However, recently several researchers proposed that removal of anionic hexavalent chromium by brown marine algae is a complicated process, in which reduction, surface complex formation, and ion exchange is involved [11, 21]. Hexavalent chromium can form surface complexes with the protonated functional groups on the biosorbents. Simultaneously, the Cr(VI) anions can also oxidize the secondary alcohol groups on the biosorbents, while being reduced to Cr(III) cations. The Cr(III) cations that formed from the redox reactions are then able to undergo ion exchange reactions with cationic alkaline metal ions, which are initially bound onto the seaweed [21]. However, no attempts were made to identify the concentrations of Cr(III), as this was considered out of scope of this study.

To elucidate the complete biosorption potential of S. polycystum, isotherm experiments were conducted at pH ranges of 1.5–2.5. The nonlinear equilibrium data between the sorbed Cr ions on the alga ($Q$) and total Cr ions in the solution ($C_g$) are shown in Figure 1. Typical L-shaped isotherms were obtained at all pH conditions examined. This implies that the ratio between the total Cr concentration remaining in solution and that sorbed on the biomass decreased with increasing Cr concentration, providing a concave curve with a strict plateau. Among the pH conditions examined, isotherm obtained at pH 2 was found to be steep with highest uptake value.

Modeling of the Cr isotherm data was attempted using the Langmuir, Freundlich, and Redlich–Peterson models. The Langmuir model served to estimate the maximum uptake values where they could not be reached in the experiments. The constant $b$ represents affinity between the sorbent and sorbate. Both $Q_{max}$ and $b$ were found to be high at pH 2 (Table 1).

![Figure 1. Biosorption isotherms at different pH conditions for chromium (biosorbent dosage = 2 g/L).](image)

For good biosorbents, in general, high $Q_{max}$ and a steep initial isotherm slope (i.e., high $b$) are desirable. The Freundlich isotherm was originally empirical in nature, but was later interpreted as the sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. Table 1 demonstrates that the Freundlich model also describes the Cr biosorption data very well with high-correlation coefficients. High $K_F$ and $1/n$ values were observed at pH 2, suggesting that the binding capacity was maximized and the af-
finity between the algal biomass and metal ions was also raised. Also, a three parameter isotherm model, i.e., the Redlich–Peterson model was also used. The Redlich and Peterson model incorporated the features of the Langmuir and Freundlich isotherms. There are two limiting behaviors: Langmuir form for $b_{RP} = 1$ and Henry’s law form for $b_{RP} = 0$. The model able to describe the isotherm curves with high-correlation coefficients. All the Redlich–Peterson model parameters were found to be high at pH 2 (Table 1).

### Biosorption Kinetics

The prediction of batch sorption kinetics is necessary for the design of industrial sorption columns. The nature of the sorption process depends on physical or chemical characteristics of the biosorbent system and also on the system conditions. Figure 2 shows the plot of the total Cr uptake versus contact time at different initial metal concentrations. From the figure, it was observed that the Cr uptake increased with contact time at all initial Cr ion concentrations. It also observed that Cr uptake was rapid for the first 2 h and thereafter it proceeds at a slower rate and finally attains saturation. The higher sorption rate at the initial period (2 h) may be due to an increased number of vacant sites available at the initial stage, as a result there develops an increased concentration gradient between sorbate in solution and sorbate in the biosorbent surface. As time increases, this concentration gradient was reduced due to the accumulation of Cr ions in the vacant sites, leading to a decrease in sorption rate at later stages of 2–8 h.

The pseudo-first-order kinetic model has been widely used to predict the sorption kinetics [22, 23], which can be expressed as,

$$\ln\left(\frac{Q_e}{C_0} - \frac{Q_t}{C_0}\right) = -k_1t$$

Thus, the rate constant $k_1$ (1/min) can be calculated from the slope of the plot of $\ln(Q_e - Q_t)$ versus time $t$. The calculated $k_1$ values and the corresponding linear regression coefficient values are shown in Table 2. It was observed that at all concentrations examined, pseudo-first-order model underpredicted equilibrium uptake values.

The kinetic data were further analyzed using pseudo-second-order kinetics [23], which can be represented as,

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}t$$

where $k_2$ is the pseudo-second-order rate constant (g/mg min), $Q_e$ and $Q_t$ represent the metal uptake at equilibrium and at any time $t$, respectively. The rate constant $k_2$ and predicted $Q_e$ can be calculated from the plot of $t/Q_t$ versus time $t$ using the equation. The pseudo-second-order rate constants, equilibrium uptake values, and the linear regression coefficients are presented in Table 2. Based on the correlation coefficients, it was observed that the pseudo-second-order model better described the Cr biosorption kinetics compared with first-order model.

### Sorption Thermodynamics

Sorption isotherm data obtained at different temperatures were used to calculate the important thermodynamic properties such as standard Gibbs free energy ($\Delta G^\circ$), standard enthalpy ($\Delta H^\circ$), and standard entropy ($\Delta S^\circ$). Isotherm data obtained at 25, 30, 35, and 40°C were fitted with Langmuir isotherm model using nonlinear regression. The Langmuir constant $b$ (L/mg) was used to calculate the standard Gibbs free energy ($\Delta G^\circ$) according to the following equation,

$$\Delta G^\circ = -RT \ln b$$

Standard enthalpy ($\Delta H^\circ$) and standard entropy ($\Delta S^\circ$) were obtained from the plot of ($\Delta G^\circ$) versus temperature ($T$), as follows,
The values of $\Delta G^\circ$ were obtained as $-22.2$, $-22.9$, $-23.5$, and $-23.9$ KJ/mol at 25, 30, 35, and 40°C, respectively. The negative value of free-energy change indicates the feasibility of Cr biosorption process and confirms affinity of biosorbent toward Cr ions. The positive value of enthalpy ($\Delta H^\circ = 12.4$ KJ/mol) shows the Cr biosorption process was endothermic and the positive entropy value ($\Delta S^\circ = 0.12$ KJ/mol K) indicates the increasing randomness at the solid–liquid interface during the biosorption process [24].

Column Studies

Effect of Bed Height

Accumulation of metals in a packed bed column is largely dependent on the quantity of sorbent inside the column. To produce different bed heights, 21.1, 28.2, and 35.2 g of $S. polycystum$ were added to yield 15, 20, and 25 cm, respectively. The sorption breakthrough curves obtained by varying the bed heights from 15 to 25 cm at 5 mL/min flow rate and 100 mg/L initial Cr concentration are shown in Figure 3. The influence of bed height was well pronounced in terms of breakthrough time ($t_b$) and exhaustion time ($t_e$), as both increased with an increase in bed height (Table 3). The slope of the S-curve from $t_b$ to $t_e$ ($dc/dt$) decreased as the bed height increased from 15 to 25 cm, indicating that the breakthrough curve becomes steeper and the mass transfer zone ($\Delta t$) becomes shorter as the bed height decreases. Also, the metal uptake capacity and metal removal percentage of the seaweed increased with an increase in bed height due to the availability of more binding sites for sorption [25].

Bed-depth service time (BDST) is a simple model, which states that bed height ($Z$) and service time ($t$) of a column bears a linear relationship. The equation can be expressed as follows [26]:

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln \left( \frac{C_0}{C_b} \right) - 1$$  \hspace{1cm} (12)

where $C_0$ is the breakthrough metal concentration (mg/L), $N_0$ is the sorption capacity of bed (mg/L), $v$ is the linear velocity (cm/h), and $K_a$ is the rate constant (L/mg h). The plot of service time against bed height at a flow rate of 5 mL/min (figure not shown) was linear ($R^2 = 0.991$) indicating the validity of BDST model for the present system. The sorption capacity of the bed per unit bed volume, $N_0$, was calculated from the slope of BDST plot, assuming initial concentration, $C_0$, and linear velocity, $v$, as constant during the column operation. The rate constant, $K_a$, calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase [27]. The computed $N_0$ and $K_a$ were 12515 mg/L and 0.0042 L/mg h, respectively. If $K_a$ is large, even a short bed will avoid breakthrough, but as $K_a$ decreases a progressively longer bed is required to avoid breakthrough [27]. The BDST model parameters can be useful to scale up to the process for other flow rates without further experimental run.

Effect of Flow Rate

Flow rate is one of the important characteristics in evaluating sorbents for continuous-treatment of metal-laden effluents on an industrial scale. The effect of flow rate on Cr biosorption by $S. polycystum$ was studied by varying the flow rate from 5 to 15 mL/min, whereas the bed height and initial Cr concentration were held constant at 25 cm and 100 mg/L, respectively. The breakthrough curves of Cr biosorp-
tion at different flow rates are shown in Figure 3. Breakthrough and exhaustion occurred faster at higher flow rates (Table 3). Also as the flow rate increased, metal concentration in the effluent increased rapidly resulting in much sharper breakthrough curves. The flow rate also strongly influenced the Cr uptake capacity of *S. polycystum* as 29.1, 25.8, and 23.5 mg/g, were recorded at 5, 10, and 15 mL/min, respectively. This behavior may be due to insufficient time for the solute inside the column and the diffusion limitations of the solute into the pores of the sorbent at higher flow rates [19]. Even though more shortened mass transfer zone (usually preferable) was observed at higher flow rates, the total Cr removal percentage (a reflective of system performance) was actually recorded as 63.3, 63.1, and 57.5% at 5, 10, and 15 mL/min, respectively.

**Column Data Modeling**

To describe the column breakthrough curves obtained at different flow rates, two models were used. These include,

Thomas model:

\[
\frac{C_0}{C} = 1 + \exp \left( \frac{k_{TH} Q_0 M}{F} - C_0 V_{eff} \right) \tag{13}
\]

Modified dose-response model:

\[
\frac{C}{C_0} = 1 - \frac{1}{1 + \left( \frac{C_0 V_{eff}}{Q_0 M} \right)^a_{mdr}} \tag{14}
\]

where \(k_{TH}\) is the Thomas model rate constant (L/mg h), \(Q_0\) is the maximum solid-phase concentration of the solute (mg/g), \(V_{eff}\) is the volume of metal solution passed into the column, and \(a_{mdr}\) is the modified dose-response model constant.

The Thomas model is one of the most widely used methods to describe column biosorption data. The Thomas model, which assumes Langmuir kinetics of sorption–desorption and no axial dispersion is derived with the sorption that the rate driving force obeys second-order reversible reaction kinetics [28]. In this study, the Thomas model predicted the breakthrough curves well at all flow rates examined with very high-correlation coefficients (Table 4). Also, the predicted Cr uptake values coincided well with the experimental uptake values. The rate constant \(k_{TH}\), which characterize the rate of solute transfer from the liquid to the solid phase, increased with increase in flow rate.

Although very high-correlation coefficients were obtained using the Thomas model, it has a fixed value when the experimental time or bed volume is zero (Eq. 13), which is contrary to real conditions. Yan *et al.* [29] proposed a modified dose-response model, which minimizes the error that results from use of the Thomas model, especially with lower and higher breakthrough curve times. The model able to describe the breakthrough curves with even better correlation coefficients, compared with the Thomas model (Table 4). The maximum solid-phase of the solute \(Q_0\) predicted by the modified dose-response model exhibited the same trend as that of predicted by the Thomas model.

**CONCLUSIONS**

From this study on the biosorption of total Cr from aqueous solution, using *S. polycystum*, the following conclusions are suggested:

<table>
<thead>
<tr>
<th>Bed height (cm)</th>
<th>Flow rate (mL/min)</th>
<th>Uptake (mg/g)</th>
<th>(t_b) (h)</th>
<th>(t_e) (h)</th>
<th>(dc/dt) (mg/L h)</th>
<th>Cr removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>5</td>
<td>24.7</td>
<td>8.6</td>
<td>34.1</td>
<td>4.46</td>
<td>52.4</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>28.6</td>
<td>15.5</td>
<td>44.3</td>
<td>3.84</td>
<td>61.6</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>29.1</td>
<td>21.7</td>
<td>54.2</td>
<td>3.28</td>
<td>63.3</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>25.8</td>
<td>9.2</td>
<td>24.1</td>
<td>2.14</td>
<td>63.1</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>23.5</td>
<td>5.2</td>
<td>16.0</td>
<td>9.95</td>
<td>57.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Thomas model</th>
<th>Modified dose-response model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_0) (mg/g)</td>
<td>(k_{TH}) (L/mg h)</td>
</tr>
<tr>
<td>5</td>
<td>27.4</td>
<td>0.0022</td>
</tr>
<tr>
<td>10</td>
<td>22.1</td>
<td>0.0071</td>
</tr>
<tr>
<td>15</td>
<td>21.9</td>
<td>0.0092</td>
</tr>
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Environmental Progress & Sustainable Energy (Vol.29, No.3) DOI 10.1002/ep October 2010 339
• The solution equilibrium pH was found to severely affect the Cr biosorption capacity of *S. polycystum*, with pH 2 found to be optimal for biosorption.
• Biosorption isotherms obtained at pH 1.5, 2, and 2.5 were modeled using the Langmuir, Freundlich, and Redlich–Peterson models. *S. polycystum* exhibited Cr uptake of 69.4 mg/g at pH 2, according to the Langmuir model. Biosorption kinetics data at different initial Cr concentrations were better described by pseudo-second-order model.
• Column studies indicated that bed height and flow rate affected the biosorption characteristics of *S. polycystum*, with the highest bed height (25 cm) and lowest flow rate (5 mL/min) resulting in highest Cr uptake and removal efficiency.
• The breakthrough curves obtained at different flow rates were described using the Thomas and modified dose-response models.
• Thus, *S. polycystum* showed good potential for the removal of total Cr in both batch and column mode of operation. In addition, the low cost and easy availability makes this biosorbent an effective and practical solution for the chromium removal.

**LITERATURE CITED**