Interaction of Mercuric Ions with Different Marine Algal Species

K. Vijayaraghavan & Umid Man Joshi

Singapore-Delft Water Alliance, National University of Singapore, Singapore


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Interaction of Mercuric Ions with Different Marine Algal Species

K. Vijayaraghavan and Umid Man Joshi
Singapore-Delft Water Alliance, National University of Singapore, Singapore

ABSTRACT
The use of different seaweeds such as Sargassum sp., Turbinaria conoides, and Ulva sp. in removing mercury(II) from aqueous solutions were investigated. The initial experimental runs, conducted at different equilibrium pH conditions, demonstrated that brown seaweeds outperformed green seaweed in Hg(II) biosorption at all pH conditions. In particular, at pH 5, maximum biosorption capacities of 170.3 and 145.8 mg/g were recorded for the brown seaweeds T. conoides and Sargassum sp., respectively, compared with 138.4 mg/g for the green seaweed Ulva sp. Isotherm data were modeled and interpreted using the Langmuir, Freundlich, Redlich-Peterson, and Toth models, with the latter described the Hg(II) isotherms with high correlation coefficients and low % error values. The kinetic data indicate the rapidity of the biosorption process, with the equilibrium achieved within 90 min. Several models, including the Elovich, pseudo-first-order, and pseudo-second-order models, were examined for their suitability with the present data; the correlation coefficient and % error values, along with better prediction of equilibrium uptake values, favored the pseudo-first-order model. The desorption experiments were highly successful for T. conoides biomass with 0.05 M HCl, whereas for the other two seaweeds, 0.05 M HCl resulted in high biomass weight loss. Reusing T. conoides biomass in three successive sorption-desorption cycles resulted in only 8.8% reduction in Hg(II) biosorption capacity compared with its original uptake.

KEYWORDS
biosorption, isotherm, mercury, seaweeds, wastewater treatment

INTRODUCTION
Mercury has attracted considerable attention as a serious pollutant owing to its toxic and bioaccumulative properties. Mercury has a very high tendency for binding to proteins (Samanta et al. 2007; Nayak et al. 2007; Banerjee and Lahiri 2009) and it mainly affects the renal and nervous systems (Shokrollahi, Ghaedi, and Shamsipur 2009). Many countries have enforced legislation and written regulations with the aim of reducing mercury emissions to air, land, and water. The US Environmental Protection Agency (US EPA) classified mercury as a priority and hazardous pollutant and defines a maximum permissible concentration of inorganic mercury of as low as 2 μg/L for drinking water (US EPA 2011). Natural sources of mercury include the weathering...
of mercuriferous areas, the degassing of surface water and from the Earth’s crust through volcanic eruptions, naturally caused forest fires, and biogenic emissions (Morel et al. 1998). Mercury is also released into the environment from anthropogenic activities that include fossil fuel burning, battery production, chloralkali industries, wood pulping, paint, mining, and metallurgical processes (Boening 2000). Highly reactive Hg(II) salts are often converted by bacteria into the most toxic form of methylmercury, which pose a serious health risk to humans and other organisms through the aquatic food chain (Miretzky and Cirelli 2009; Dou and Chen 2011). Thus, it is necessary that wastewaters from industries should be properly treated to remove Hg(II), before being discharged into waterways and the biosphere. A number of approaches have been suggested in the past for the removal of mercury from aqueous solutions, which include adsorption, ion exchange, precipitation, coagulation, and reduction. In recent years, sorption by biological materials has shown a great potential as a low-cost, environmental friendly, and highly efficient technique for the removal of heavy metal ions from industrial effluents (Kratochvil and Volesky 1998; Nayak and Lahiri 2006; Vijayaraghavan and Yun 2008). Apart from a few studies (Nayak et al. 2002, 2003; Zeroual et al. 2003; Reategui et al. 2010), mercury has been less focused in biosorption research, especially for its interaction with seaweeds. Thus, this study aims to fill this knowledge gap by exploring the possibility of Hg(II) removal via interaction with three different marine algal species.

MATERIALS AND METHODS

Preparation of Biosorbents

The brown seaweed, Sargassum sp., was collected from the beaches of Labrador Park, Singapore. The other brown seaweed, T. conoides, was obtained from the beaches in the Mandapam region, Tamilnadu (India). The green seaweed, Ulva sp., was collected from the shores of Sentosa Island, Singapore. All seaweeds were initially sun-dried in the site itself. In the laboratory, all seaweeds were washed extensively with deionized water to remove sand and other impurities. The seaweed samples were then oven-dried overnight, ground in a blender, and then sieved to obtain an average particle size of 0.75 mm for use in biosorption experiments.

Biosorption Experimental Procedure

Biosorption experiments were conducted by adding 0.2 g of seaweed biomass to 100 ml of different Hg(II) test solutions at desired pH conditions in Erlenmeyer flasks (250 ml capacity). The solution pH was initially adjusted and maintained using 0.1 M HNO₃ or NaOH. The flasks were agitated in a rotary shaker at 160 rpm and 22°C ± 1°C for 3 h. After equilibrium, the content in the flask was filtered using a 0.45-μm polytetrafluoroethylene (PTFE) membrane filter and the filtrate was analyzed for metal concentrations on an inductively coupled plasma optical emission (ICP-OES) spectrometer (PerkinElmer Optima 3000 DV; California, USA).

For the desorption experiments, the seaweed biomass that was previously exposed to 100 mg/L of Hg(II) solutions at pH 5 was separated from the solution by filtration. The Hg-loaded seaweed biomass was then brought into contact with 50 ml of 0.05 M HCl for 1 h on a rotary shaker at 160 rpm. The remaining procedure was the same as that employed in the biosorption experiments.
Models to Fit Experimental Data

Four equilibrium isotherm models were used to fit the Hg(II) isotherm experimental data:

Freundlich model: \[ q = K_F (C_e)^{1/n} \] (1)

Langmuir model: \[ q = \frac{q_{\text{max}} b_L C_e}{1 + b_L C_e} \] (2)

Redlich-Peterson model: \[ q = \frac{q_{\text{max}} b_T C_e}{[1 + (b_T C_e)^{1/n_T}]^{n_T}} \] (3)

Toth model: \[ q = \frac{q_{\text{max}} b_T C_e}{[1 + (b_T C_e)^{1/n_T}]^{n_T}} \] (4)

where \( q \) is the metal uptake (mg/g), \( C_e \) is the equilibrium metal concentration (mg/L), \( K_F \) is the Freundlich model constant (mg/g) (L/mg) \( 1/n \), \( n \) is the Freundlich model exponent, \( q_{\text{max}} \) is the maximum metal uptake (mg/g), \( b_L \) is the Langmuir equilibrium constant (L/mg), \( K_{\text{RP}} \) is the Redlich-Peterson model isotherm constant (L/g), \( a_{\text{RP}} \) is the Redlich-Peterson model constant (L/mg), \( \beta_{\text{RP}} \) is the Redlich-Peterson model exponent, \( b_T \) is the Toth model constant (L/mg), and \( n_T \) is the Toth model exponent.

Three kinetic models were used to fit Hg(II) kinetic experimental data:

Elovich model: \[ q_t = \frac{1}{b} \ln(1 + abt) \] (5)

Pseudo-first-order model: \[ q_t = q_e (1 - \exp(-k_1 t)) \] (6)

Pseudo-second-order model: \[ q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \] (7)

where \( a \) is the initial adsorption rate (mg/(g·min)), \( b \) is the desorption constant (g/mg), \( q_t \) is the amount of metal sorbed at time \( t \) (mg/g), \( q_e \) is the amount of metal sorbed at equilibrium (mg/g), \( k_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)), and \( k_2 \) is the pseudo-second-order rate constant (g/mg·min). All the model parameters were evaluated by nonlinear regression using SigmaPlot (version 4.0; SPSS, Chicago, Illinois, USA) software. The average percentage error between the experimental and predicted values is calculated using

\[ \varepsilon(\%) = \frac{\sum_{i=1}^{N} (q_{\text{exp},i} - q_{\text{cal},i}/q_{\text{exp},i})}{N} \times 100 \] (8)

where \( q_{\text{exp}} \) and \( q_{\text{cal}} \) represent experimental and calculated metal uptake values, respectively, and \( N \) is the number of measurements. All experiments were conducted twice and the data presented were the average values of duplicate experiments.

FIGURE 1  Influence of equilibrium pH on Hg(II) biosorption by different seaweed biomass (initial Hg(II) concentration = 501 ± 2 mg/L; agitation rate = 160 rpm; temperature = 22°C ± 1°C).
RESULTS AND DISCUSSION

Interaction of Hg(II) Ions with Seaweeds at Different pH Conditions

The solution pH is one of the most important operating parameters that influence the biosorption performance of any biomass. In particular, pH strongly influences the biomass surface chemistry as well as metal speciation. Considering this, experiments were conducted at different pH conditions, from pH 2 to 7 (Figure 1). The results revealed that Hg(II) biosorption by all three seaweeds were severely affected at low-pH conditions. This is because of the competition from H\textsuperscript{+} ions in occupying the binding sites of the seaweed biomass. Thus, increasing the pH (Figure 1) reduces the competition of protons against mercury species for interaction with biomass. This pH effect was very high; for instance, the Hg(II) removal efficiency of \textit{T. conoides} increased from 23.1% to 57.8% as pH was increased from 2 to 5, with an overall increase of 2.5 times. In the case of \textit{Sargassum} sp. and \textit{Ulva} sp., 2.4- and 3.0-fold increases in Hg(II) removal, respectively, were observed when the pH was increased from 2 to 5. The influence of pH on Hg(II) biosorption was less pronounced above pH 5. This is possibly due to complete saturation of Hg(II) ions onto the binding sites of seaweed biomass at pH 5 and therefore further increase in pH resulted in no significant increase in uptake capacity. Similar results have been reported in the literature for different biosorbents during Hg(II) biosorption (Al Rmalli et al. 2008; Khambhaty et al. 2008).

In the present study, the Hg removal efficiency of \textit{Ulva} sp. was 42.5% at pH 5, compared with 58.1% and 49.1% by \textit{T. conoides} and \textit{Sargassum} sp., respectively. Thus, clearly both brown seaweeds outperformed the green seaweed in Hg(II) biosorption. The high performance of brown seaweeds in metal biosorption is due to the presence of alginate, which constitutes 10–40% of the dry weight of the algae (Davis, Volesky, and Mucci 2003). The alginic acids are linear carboxylated copolymers comprising different proportions of 1,4-linked \(\beta\)-D-mannuronic acid (M-block) and \(\alpha\)-L-guluronic acid (G-block). Among different functional groups in alginate, carboxyl groups were identified to be responsible for binding metal cations (Davis, Volesky, and Mucci 2003). It is worth noting that the pK\textsubscript{a} value of the carboxyl groups lies at about 4.8 (Palmieri, Volesky, and Garcia 2002); hence an increased binding of Hg(II) can be expected at or above this pH value. On the other hand, green seaweeds comprise of xylan (principally a \(\beta\)(1→3)-linked D-xylose) and mannan (a \(\beta\)(1→4)-linked D-mannose) (Davis, Volesky, and Mucci 2002).
In many studies in metal biosorption, brown seaweeds outperformed green seaweeds and the reason cited are its cell wall composition and the number of carboxyl groups (Romera et al. 2006; Vijayaraghavan and Yun 2008).

### Isotherms and Modeling

In order to explore the full biosorption potential of biomass, isotherm experiments were essential. It is a plot of equilibrium concentration versus uptake at a fixed operating condition. In the present study, this equilibrium distribution of the Hg(II) between the solid and liquid phases was obtained by varying the initial Hg concentrations in the range of 100–1000 mg/L at two pH of 3 and 5 (Figure 2). Conventional L-shaped isotherms, i.e., concave-shaped curves with strict plateau, were obtained for all three seaweeds at different pH conditions. All isotherms exhibited steep slopes, which generally indicates the degree of affinity of the sorbate towards sorbent. Comparing the curves at different pH conditions, it was clear that Hg(II) biosorption was optimal at pH 5. For instance, uptake capacity

<table>
<thead>
<tr>
<th>Model</th>
<th>Sargassum sp.</th>
<th>T. conoides</th>
<th>Ulva sp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 3</td>
<td>pH 5</td>
<td>pH 3</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>88.3</td>
<td>145.8</td>
<td>102.2</td>
</tr>
<tr>
<td>$b_L$ (L/mg)</td>
<td>0.011</td>
<td>0.022</td>
<td>0.014</td>
</tr>
<tr>
<td>$R^2$</td>
<td>.996</td>
<td>.998</td>
<td>.998</td>
</tr>
<tr>
<td>% error</td>
<td>0.73</td>
<td>0.68</td>
<td>0.28</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (mg/g) (L/mg)$^{1/n}$</td>
<td>11.7</td>
<td>26.0</td>
<td>16.3</td>
</tr>
<tr>
<td>$n$</td>
<td>3.41</td>
<td>3.80</td>
<td>3.71</td>
</tr>
<tr>
<td>$R^2$</td>
<td>.962</td>
<td>.965</td>
<td>.966</td>
</tr>
<tr>
<td>% error</td>
<td>3.63</td>
<td>4.81</td>
<td>3.26</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{RP}$ (L/g)</td>
<td>0.96</td>
<td>3.21</td>
<td>1.47</td>
</tr>
<tr>
<td>$a_{RP}$ (L/mg)$^{1/\beta_{RP}}$</td>
<td>0.011</td>
<td>0.023</td>
<td>0.014</td>
</tr>
<tr>
<td>$\beta_{RP}$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>$R^2$</td>
<td>.992</td>
<td>.998</td>
<td>.995</td>
</tr>
<tr>
<td>% error</td>
<td>1.89</td>
<td>0.85</td>
<td>0.57</td>
</tr>
<tr>
<td>Toth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>81.5</td>
<td>143.6</td>
<td>98.4</td>
</tr>
<tr>
<td>$b_T$ (L/mg)</td>
<td>0.009</td>
<td>0.021</td>
<td>0.013</td>
</tr>
<tr>
<td>$n_T$</td>
<td>0.71</td>
<td>0.93</td>
<td>0.85</td>
</tr>
<tr>
<td>$R^2$</td>
<td>.998</td>
<td>.998</td>
<td>.998</td>
</tr>
<tr>
<td>% error</td>
<td>0.44</td>
<td>0.49</td>
<td>0.21</td>
</tr>
<tr>
<td>Elovich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (mg/(g-min))</td>
<td>—</td>
<td>283.5</td>
<td>—</td>
</tr>
<tr>
<td>$b$ (g/mg)</td>
<td>—</td>
<td>0.059</td>
<td>—</td>
</tr>
<tr>
<td>$R^2$</td>
<td>—</td>
<td>.977</td>
<td>—</td>
</tr>
<tr>
<td>% error</td>
<td>—</td>
<td>3.73</td>
<td>—</td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>—</td>
<td>119.8</td>
<td>—</td>
</tr>
<tr>
<td>$k_1$ (min$^{-1}$)</td>
<td>—</td>
<td>0.15</td>
<td>—</td>
</tr>
<tr>
<td>$R^2$</td>
<td>—</td>
<td>.988</td>
<td>—</td>
</tr>
<tr>
<td>% error</td>
<td>—</td>
<td>0.26</td>
<td>—</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>—</td>
<td>130.8</td>
<td>—</td>
</tr>
<tr>
<td>$k_2$ (g/(mg-min))</td>
<td>—</td>
<td>0.002</td>
<td>—</td>
</tr>
<tr>
<td>$R^2$</td>
<td>—</td>
<td>.987</td>
<td>—</td>
</tr>
<tr>
<td>% error</td>
<td>—</td>
<td>0.22</td>
<td>—</td>
</tr>
</tbody>
</table>
increased 1.7-fold for *T. conoides* when pH was increased from 3 to 5. Among the seaweed species, both brown seaweeds out performed *Ulva* sp. in Hg(II) biosorption.

The experimental isotherms were modeled using the Freundlich, Langmuir, Redlich-Peterson, and Toth models. The Freundlich model was originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. As the Freundlich isotherm equation is exponential, it can only be reasonably applied in the low to intermediate concentration ranges (Liu and Liu 2008). A similar trend was observed in the present study, as the Freundlich equation was unable to describe the isotherm curve in high concentration ranges (Figure 2), which eventually resulted in low correlation coefficients and high % error values (Table 1). Considering the model constants, maximum values of $K_F$ and $n$ were obtained at pH 5 (Table 1). This implies that the binding capacity reaches the highest value and the affinity between the biomass and Hg(II) ions was also higher at pH 5. Applying the Langmuir equation to the present isotherm data significantly improved the degree of accuracy, with high correlation coefficients and low % error values (Table 1). The Langmuir model was originally developed to describe the gas-solid–phase adsorption of activated carbon. Later, however, the model was successfully used to quantify and contrast the performance of different adsorbents and biosorbents. In its formulation, the Langmuir model assumes binding to the surface was primarily by physical forces and all sites possess equal affinity for the sorbate. Coinciding with the experimental data, the Langmuir model predicted that maximum capacity ($q_{\text{max}}$) and high affinity ($b_L$) were observed at pH 5 for all the biomass of the three seaweed species. Since the Langmuir model is able to predict the maximum biosorption capacity of any biomass under controlled conditions, comparison among biomass performance towards the particular ion is possible. In that way, efforts were made to compare the Hg(II) biosorption performance of three seaweed species with other biomasses reported in the literature (Table 2). Results revealed that all the three seaweed biomasses performed comparatively better than most of the other biosorbents.

In an effort to further enhance the accuracy of prediction, the more complex three-parameter models were used. The Redlich-Peterson model incorporates the features of both the Langmuir and Henry models. The model exponent has two limiting behaviors: if $\beta_{RP}$ is equal to 1, Equation 3 reduces to the Langmuir equation, whereas in the case of $\beta_{RP}$ equals zero, Equation 3 reduces to the Henry’s equation. The Redlich-Peterson isotherm constants are presented in Table 1. The values clearly indicate the superior performance of *T. conoides* in Hg(II) biosorption over other seaweeds. Taking the exponent $\beta_{RP}$ into consideration, it is clear that the values were closer to unity, indicating that the isotherm data were more of the Langmuir form than Henry’s form. Next, the Toth model was examined for its compatibility with the present isotherm data. Very high correlation coefficients and very low % error values were obtained for all systems (Table 1). The Toth isotherm (Toth 1971), derived from potential theory, has proven useful in describing sorption in heterogeneous systems.

### TABLE 2 Comparison of Mercury(II) Uptake by Different Biosorbents

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>pH</th>
<th>Uptake capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Drepanocladus revolvens</em></td>
<td>5.5</td>
<td>94.4 (L)</td>
<td>Sari and Tuzen 2009</td>
</tr>
<tr>
<td><em>Ulva lactuca</em></td>
<td>7.0</td>
<td>149.3 (L)</td>
<td>Zeroual et al. 2003</td>
</tr>
<tr>
<td><em>Chlamydomonas reinhardtii</em> (Ca-alginate)</td>
<td>6.0</td>
<td>116.8 (L)</td>
<td>Bayramoğlu et al. 2006</td>
</tr>
<tr>
<td>Guava bark</td>
<td>9.0</td>
<td>3.4 (E)</td>
<td>Lohani et al. 2008</td>
</tr>
<tr>
<td><em>Phanerocochaete chrysosphorium mycelium</em></td>
<td>7.0</td>
<td>61.0 (L)</td>
<td>Sağlan et al. 1999</td>
</tr>
<tr>
<td>Tree fern</td>
<td>—</td>
<td>26.5 (L)</td>
<td>Ho and Wang 2008</td>
</tr>
<tr>
<td><em>Ricinus communis</em> L.</td>
<td>5.5</td>
<td>37.2 (L)</td>
<td>Al Rmalli et al. 2008</td>
</tr>
<tr>
<td><em>Aspergillus niger</em></td>
<td>3.0</td>
<td>40.5 (E)</td>
<td>Khambhayat et al. 2008</td>
</tr>
<tr>
<td>Crab carapace</td>
<td>3.0</td>
<td>13.0 (E)</td>
<td>Rae, Gibb, and Lu 2009</td>
</tr>
<tr>
<td><em>Lessonia</em> sp. kelp</td>
<td>6.0</td>
<td>270.0 (L)</td>
<td>Reategui et al. 2010</td>
</tr>
<tr>
<td><em>Turbinaria conoides</em></td>
<td>5.0</td>
<td>170.3 (L)</td>
<td>This study</td>
</tr>
<tr>
<td><em>Sargassum</em> sp.</td>
<td>5.0</td>
<td>145.8 (L)</td>
<td>This study</td>
</tr>
<tr>
<td><em>Ulva</em> sp.</td>
<td>5.0</td>
<td>138.4 (L)</td>
<td>This study</td>
</tr>
</tbody>
</table>

*Note.* (L) = uptake values predicted by Langmuir model; (E) = experimental uptake values.
It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e., most sites have sorption energy less than the mean value (Ho, Porter, and McKay 2002). The model was able to predict the whole set of isotherm data at both pH conditions for all three seaweeds (Figure 2).

**Kinetics and Modeling**

Sorption kinetics is crucial for any adsorption process because it plays an important role in determining the equilibrium time of sorption process and provides valuable insights into the reaction pathways. Since biosorption is a metabolism independent process, it would be expected to be a very fast process. Experimental Hg(II) kinetic data for all three seaweeds were rapid, with 95% of the total removal occurred within 20 min. This initial quick phase was followed by the slow attainment of equilibrium in 90 min. The first quick phase can be attributed to the easily accessible sites in the initial phases, which facilitates relatively easy ion exchange wherein Hg ions bind to carboxyl sites. As the time progresses, there develops a shortage of binding sites and repulsion among metal ions in occupying the same site, which hinder the kinetic rate and thus the second phase is relatively slow. On comparing the rate of Hg(II) biosorption by three seaweeds, no significant difference was observed (Figure 3). However, the extent of Hg(II) biosorption by three seaweeds was clearly distinguished.

To study the rate of biosorption and controlling mechanisms, three kinetic models were used. The kinetic data predicted by all three models are presented in Figure 3. Initially, the Elovich equation was used to describe the Hg(II) kinetic data. This equation is useful in describing metal adsorption on highly heterogeneous surfaces (Aharoni and Tompkins 1970), when the interactions are predominantly chemical in nature. The Elovich rate equation is commonly used to describe the sorption behavior with a rapid equilibrium rate in the early period, whereas it slows down the equilibrium at later periods of the sorption process. The constants \( a \) and \( b \) represent the rate of sorption and surface coverage, respectively. Of the different seaweeds, *T. conoides* exhibited high \( a \) value compared with others, whereas \( b \) values were in the order of *Sargassum* > *T. conoides* > *Ulva*. This is a contradictory result, as we would expect *T. conoides* to have a high \( b \) value owing to high efficiency. Also, values of \( R^2 \) were in the order of .951–.977; hence other kinetic models were tested for their suitability with the present systems. The data predictions by pseudo-first-order and pseudo-second-order
models are presented in Figure 3. Both models were able to describe the kinetic data very well with high correlation coefficients and low % error values. In particular, the pseudo-first-order model predicted the equilibrium uptake values with better accuracy compared with the pseudo-second-order model. The pseudo-second-order model overpredicted the equilibrium uptake values in all cases, whereas the pseudo-first-order model slightly underpredicted the $q_e$ values of *Sargassum* and *T. conoides* (Table 1).

### Elution and Regeneration of Biosorbents

Once the biosorbent is exhausted, efforts should be made to elute the bound metal ions and regenerate the biosorbent. In this manner, process costs as well as the dependency of the process on the continuous supply of biosorbent can be decreased. Considering that strong acidic conditions were unfavorable for Hg(II) biosorption by all three seaweeds, a reverse equilibrium would be expected under these conditions. Thus, HCl was used as a desorbing agent and the results were as expected when the eluant performed well in Hg(II) desorption. For 0.05 M HCl, high elution efficiencies in the order of 97.1–99.3% were observed in the case of all three seaweeds. When the concentration of HCl was reduced to 0.04 M, elution efficiencies decreased below 92%. Hence, 0.05 M HCl was identified as optimum and thus employed in the regeneration experiments. Also worth noting, the eluant volume used in the desorption process was only 50% of the original volume; hence the desorbed Hg(II) was in a highly concentrated form. The recovery of mercury from these concentrated solutions can be accomplished using another process, such as precipitation or electrowinning (Vijayaraghavan and Yun 2008). Further reduction in eluant volume to 40 ml affected desorption efficiency of 0.05 M HCl. For instance, the desorption efficiency of 0.05 M HCl onto Hg(II)-loaded *T. conoides* decreased from 99.3% to 82.7% when the eluant volume decreased from 50 to 40 ml. The exposure of seaweeds to acidic solution during the desorption process resulted in significant weight loss, especially for *Ulva* and *Sargassum* biomasses. Both *Ulva* and *Sargassum* biomasses were fragile compared with the highly rigid *T. conoides*. It is well known that acidic solutions could dissolve some of the organic matters and damage the structural integrity of the biomass (Kuyucak and Volesky 1989). The weight losses after the desorption process were in the order of 14.5%, 3.0%, and 20.5% for *Sargassum*, *T. conoides*, and *Ulva*, respectively.

The regeneration experiments explore the possibility of reusing the same biosorbent for three Hg(II) sorption-desorption cycles (Figure 4). Among the three seaweeds, *T. conoides* was able to retain its first-cycle
Hg(II) biosorption capacity throughout the three cycles examined. Also, the weight loss at the end of third cycle was only 7.5%. The percent decreases in the Hg(II) uptake in the third cycles compared with the first cycles were 26.2%, 8.8%, and 39.4% for Sargassum, T. conoides, and Ulva, respectively.

CONCLUSIONS

The interaction of different seaweed biomasses with Hg(II) ions was explored in the present study. Three seaweeds, Sargassum sp., T. conoides, and Ulva sp., exhibited high biosorption capacity towards Hg(II) ions. In particular, at pH 5, T. conoides recorded a high biosorption capacity of 170.3 mg/g in isotherm experiments. The kinetic experiments highlighted that Hg(II) biosorption by all three seaweeds were rapid, with equilibrium attained within 90 min. In order to model the Hg(II)-seaweed interactions, several isotherm and kinetic models were attempted. In view of the correlation coefficients and % error values, the Toth and kinetic models were attempted. In view of the correlation coefficients and % error values, the Toth isotherm model performed better compared with the Langmuir, Redlich-Peterson, and Freundlich models, whereas the pseudo-first-order model best described the kinetics compared with the pseudo-second-order and the Elovich models. Following sorption, Hg(II)-loaded seaweeds were regenerated successfully using 0.05 M HCl. However, the strong acidic nature of the desorbent damaged both Sargassum and Ulva biomasses, with weight losses of 14.5% and 20.5%, respectively, which affected their next-cycle sorption capacities. On the contrary, T. conoides was least affected by the desorbent and exhibited reasonably unaffected Hg(II) sorption capacities in the subsequent three cycles. Thus, our experiments indicated that seaweed-based biosorption technology possesses inherent advantages such as good removal efficiency, fast kinetics, and biomass reusability. Additionally, seaweeds are inexpensive and widely available, which make this technology practical for decontaminating Hg(II)-contaminated water.

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