Evaluation of the marine alga *Sargassum glaucescens* for the adsorption of Zn(II) from aqueous solutions

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**ABSTRACT**

The objective of this research was to study the efficacy of the marine brown alga *Sargassum glaucescens* in batch removal of Zn(II) from wastewater and seawater. For these experiments, a dried biomass was used to adsorb Zn(II) from aqueous solutions. The effects of varying pH, biomass weight, retention time and initial concentration of Zn(II) were studied. The maximum efficiency of Zn(II) removal obtained was 90.00%. The experimental adsorption data were fitted to the Freundlich adsorption model. A pseudo-second-order model was found to offer the best analysis of Zn(II) uptake. Kinetic studies showed that a biomass formed of marine-dried *S. glaucescens* exhibited high biosorption capacity. A solution pH of 5.0 was found to be optimal for adsorption. Results showed that removal of Zn(II), increased to 90.00% with increasing contact time, increasing pH (to 5.0) and decreasing adsorbent amount. The equilibrium adsorption data are fitted to the Freundlich isotherm model and pseudo-second-order kinetic models. Therefore, brown algae *Sargassum glaucescens* was an economical adsorbent.

**Key words** | aqueous solutions, biosorption, heavy metals, isotherm models, *Sargassum glaucescens*

**INTRODUCTION**

Heavy metal contamination in soils and fresh water environments is one of the world’s major environmental problems, posing risks to human health as well as to ecosystems. Ion exchange resins, electroflotation and reverse osmosis have been used for the removal of heavy metals from industrial effluents and waste waters (Hashim & Chu 2004), but can be costly. Employing a solid solution interface for adsorption is a useful method of reducing pollution from metallic industrial effluents. Such systems use complexation, chelation, adsorption, chemical precipitation, membrane separation, adsorption and microprecipitation (Freundlich 1906; Guibal et al. 1992). Heavy metals in wastewater are also toxic to the biosludge of the biological treatment process (Davis et al. 2003). Biosorption is a property of certain types of inactive, non-living microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution. Biomass of *Rhizopus arrhizus* exhibits this property, acting just as a chemical substance would as an ion exchanger of biological origin (Kalyani et al. 2004). Charged groups such as carboxylate and hydroxyl present in the biopolymers of biomass cells are believed to be responsible for the sequestration of metal ions. The use of the biomass of marine algae such as *Durvillaea potatorum*, *Ecklonia radiata* (Matheickal & Yu 1996) and *Ascophyllum nodosum* (Volesky 1990) for heavy metal removal has been reported. The present research investigates batch removal of Zn(II) from wastewater, natural seawater and synthetic seawater using a dried marine brown alga, *S. glaucescens*.

**MATERIALS AND METHODS**

**Preparation of biomass**

The brown marine alga *Sargassum glaucescens* was collected from Queshm Island in the Persian Gulf, off the
southern coast of Iran. Dirt and sand particles were removed by rinsing it several times with tap water. After being sun-dried for 5 days, the resulting dry biomass was milled to a particle size of 2–5 cm.

Chemicals

A zinc stock solution was prepared by dissolving 3.02 g of ZnSO₄·2H₂O (Merck) in 1000 mL of deionized water. Varying concentrations of the solution were then prepared by dilution of the stock solution with deionized water to 50, 100, 200, 300 and 350 mg/L. So in this experiment, we used control for removal.

Adsorption studies

The effect of pH on adsorption was investigated employing varying concentrations of Zn(II) and weights of dry biomass. The initial pH value of 4.0 was adjusted with diluted NaOH and HCl solutions. The suspensions were placed in conical screw-cap flasks and shaken at room temperature (23 ± 2°C) for 10, 20, 30, 40, 50, 60 and 120 min to determine the minimum contact time required to reach equilibrium. All adsorption experiments were carried out using an agitation speed of 150 rpm. An AA240 Varian atomic adsorption spectrometer was used to measure initial and final concentrations of metal ions in the solution of each flask.

Zinc uptake capacities and adsorption isotherms

Adsorption equilibrium isotherms were studied using zinc ion concentrations of 50 to 350 mg/L per gram of alga, starting with a pH of 4.0. The Zn(II) uptake was calculated by comparing the difference between the quantity of metal added to the biomass and the metal content of the supernatant. The following equation was used:

$$q_e = \frac{(C_0 - C_e)V}{M}$$  \hspace{1cm} (1)

where $q_e$ is the metal uptake (mg metal adsorbed per g adsorbent), $C_0$ and $C_e$ are the initial and equilibrium metal concentrations in solution (mg/L), $V$ is the volume of the solution (mL) and $M$ is the weight of the dry biomass (g). Langmuir and Freundlich adsorption isotherm models were employed for data analysis (Langmuir 1916).

Freundlich adsorption model

The Freundlich model (Freundlich 1906) is generally better suited for analyzing adsorption from liquids. It can be expressed as follows:

$$q_e = k_f C_e^{1/n}$$  \hspace{1cm} (2)

In this model, the rate of adsorption is determined by the constants $1/n$ and $K_f$ (L/g). For a good adsorbent, $0.2 < 1/n < 0.8$; a smaller value of $1/n$ indicates better adsorption and formation of a stronger adsorbent-adsorbate bond. This is a popular model for interpreting adsorption data in myriad systems (Ho & McKay 1999; Golder et al. 2006; Padmesh et al. 2006).

Langmuir adsorption model

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. It is assumed that there are a finite number of binding sites homogeneously shared over the adsorbent surface. These sites have the same adsorption as a single molecular layer, and there is no interaction between adsorbed molecules. The saturated monolayer isotherm can be represented as follows:

$$q_e = \frac{b \cdot q_{max} \cdot C_e}{1 + b \cdot C_e}$$  \hspace{1cm} (3)

where $q_e$ is metal ions absorbed (mg/g), $b$ is an affinity constant, $q_{max}$ is the maximum adsorption capacity, and $C_e$ is the equilibrium concentration (mg/L), whereas $q_{max}$ represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in comparison of adsorption performance, in cases where the adsorbent did not reach its full saturation in experiments and $b$ is constantly related to the affinity of the binding sites (Matheickal & Yu 1996).
Adsorption kinetic studies

The adsorption kinetics, or rate of zinc ion uptake onto alga prepared from *S. glaucescens*, is described as follows. These kinetic models include the first-order and second-order equations.

**Pseudo-first-order model**

The following equation shows the pseudo-first-order rate expression used by Ho & McKay (1999):

\[
dq_t/dt = k_1(q - q_t)
\]

where \( q_t \) is zinc adsorbed (mg/g) and \( k_1 \) is the rate constant (1/min). The integrated form of Equation (4) becomes

\[
\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t
\]

where \( q_e \) is zinc adsorbed at equilibrium per unit weight of adsorbent (mg/g).

A plot of \( \log(q_e - q_t) \) versus \( t \) indicates a straight line of slope \((k_1/2.303)\) and an intercept of \( \log(q_e) \). The adsorption rate constants are shown in Table 1. For strict surface adsorption, the rate fluctuation should be proportional to the initial solute concentration. When pore diffusion limits the adsorption process, the relationship between initial concentration and rate of adsorption will be non-linear. The kinetic model was found to fit nicely for the first 200 mg/L, but at higher concentrations the results deviated from the theory. Thus, although the model cannot be applied to the overall adsorption process, it does apply at the initial stages of rapid adsorption. Ho and McKay reported that the sorption data were represented well by the Lagergren second-order model only for the rapid initial phase that occurs for a contact time of 10–120 min (Matheickal & Yu 1996). This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for Zn(II) onto dried brown alga for the entire sorption period. The predicted \( q_e \) differed greatly from the experimental \( q_e \) for activated carbon as well as dried brown alga, which demonstrates that the pseudo-first-order model is not adequate for predicting the \( q_e \) or describing the overall process.

**Pseudo-second-order model**

The rate law for a pseudo-second-order model can be expressed as follows:

\[
dq_t/dt = K_2(\frac{q_e}{q_t})^2
\]

where \( q_t \) is the adsorption capacity at time \( t \), \( K_2 \) is the equilibrium rate constant (g/mg min) and \( q_e \) is the adsorption capacity at equilibrium (Ho & McKay 1999). Integrating Equation (5) gives

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2t
\]

which has the linear form

\[
t/\frac{q_t}{q_e} = 1/K_2\frac{q_e^2}{q_e} + (1/q_e)t
\]

A plot of \( t/\frac{q_t}{q_e} \) versus \( t \) shows an intercept of \( 1/K_2 \), \( q_e^2 \) and a straight line of slope \( 1/q_e \) (Sag & Aktay 2002). The adsorption kinetics has been elucidated by Ho & McKay (1999). In our study the pseudo-second-order rate constant decreased as the initial alga concentration increased. The calculated \( q_e \) values agreed very well with the experimental values, and the regression coefficients were above 0.99, which showed that the pseudo-second-order model could be applied for the entire adsorption process (Table 1).

### Table 1 | Kinetic model parameters for biosorption of Zn

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Zn ion concentration (mg/L)</th>
<th>First-order kinetic model</th>
<th>Second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td></td>
<td>( K_1 )</td>
<td>( K_2 )</td>
</tr>
<tr>
<td>1 g</td>
<td>50</td>
<td>0.0010</td>
<td>0.9202</td>
</tr>
<tr>
<td>1 g</td>
<td>100</td>
<td>0.0013</td>
<td>0.9312</td>
</tr>
<tr>
<td>1 g</td>
<td>200</td>
<td>0.002</td>
<td>0.9088</td>
</tr>
<tr>
<td>1 g</td>
<td>300</td>
<td>0.0018</td>
<td>0.9507</td>
</tr>
<tr>
<td>1 g</td>
<td>350</td>
<td>0.0015</td>
<td>0.9201</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The present study shows that preparation of brown marine alga *S. glaucescens* has the ability to remove Zn(II) from contaminated water. The investigation showed the marine alga used to be effective for removal of Zn(II) from both wastewater and saltwater. The degree of adsorption of metal ions is affected by the type of alga, the concentration of metal ions, the retention time and the pH of the metal solution. In all experimental data, we used standard arrow bars for figures. Also statistics was run on the data in all figures.

Effect of pH

Figure 1 shows that the biosorption of Zn(II) increased from pH 3.0 to 5.0 and then decreased from 5.0 to 7.0; the optimum pH was determined to be approximately 5.0. Formation of anionic hydroxide complexes are the most likely explanation for the lower uptake at higher pH values. Kalyani *et al.* (2004) have reported on biosorption at different pHs. This study investigates further the effects of pH on adsorption and bioreduction. The initial pH of the metal solution was observed to be an important parameter affecting adsorption of metal ions. The removal of Zn(II) increased with an increase in pH from 3.0 to 5.0 and then decreased to 7.0, with an optimum pH of about 5.0 observed. The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes. Because of this effect at higher pH values the ligands such as carboxylate and sulfonate groups could uptake fewer metal ions (Volesky 1990).

In another study, on the other hand, at low and high pHs, Ni(II) had a higher redox potential and favored Ni(II) bioreduction (Esmaeili *et al.* 2012). In addition, reductions on the biomass such as carbohydrate and protein could supply electrons for Ni(II) bioreduction, with partial release of soluble organics or final oxidized product (Park *et al.* 2004).

Effect of metal ion concentration

Figure 2 represents the effect of increasing the concentration of Zn(II), which resulted in decreased percentages of removal for both adsorbents resulting from saturation of the adsorption sites. The maximum uptake for Zn(II) with initial concentration of 200 mg/L at pH 4.0 was 80.0%.

Figure 2 shows that with a concentration of 200 mg/L of Zn(II) there was a decreased percentage of removal from the higher 90% at 100 mg/L. Because of this effect at 200 mg/L the ligands such as alginate groups could uptake fewer metal ions (Kalyani *et al.* 2004).

Effect of retention time

Figure 3 indicates that removal ability increased with increasing contact time before equilibrium was reached. Other limits such as dose of adsorbent, pH of solution and initial concentration were kept at optimum.

Figure 3 shows that with the temperature kept at 23 ± 2 °C, Zn(II) removal efficiency increased as contact time was increased to 30 min, and after that decreased rapidly.
Optimum contact time for both adsorbents was found to be 30 min. A previous study by this researcher had similar findings in evaluation of *Gracilaria corticata* for adsorption of Cu(II) from wastewater (Esmaeili *et al.* 2013).

**Effect of adsorbent dose**

The concentration of metal ions is a strong factor in overcoming the mass transfer resistance of metal ions from the aqueous to the solid phase. Our results indicated that the equilibrium concentration of Zn(II) increased at 200 mg/L. For both adsorbents, increased concentration of metallic ions resulted in a decrease in percentage removed, as a result of the saturation of the sorption sites (Esmaeili *et al.* 2008).

**Adsorption isotherm**

Adsorption isotherms can be used to effectively describe the interaction and equilibrium between an adsorbent and an adsorbate. Equilibrium studies of adsorption isotherms utilize constants to express the adsorbent affinity and surface properties. Equilibrium between adsorbent and adsorbate is usually given as the ratio of the amount adsorbed to the amount remaining in solution at a set temperature. This study employed two models to analyze the adsorption isotherm.

**Langmuir and Freundlich isotherms**

We used the Langmuir adsorption isotherm theory model, which assumes that adsorption takes place at specific homogeneous sites within the adsorbent. We also employed the Freundlich isotherm model, which is based on adsorption on a heterogeneous surface. The same set of experimental data was used for both models. This study demonstrated that the data could be well modeled using the Freundlich adsorption isotherm (Figure 4).

The Freundlich constant ($q_{max}$) is dependent on experimental conditions such as solution pH. Another important factor in evaluating adsorbent performance is the initial gradient of the adsorption isotherm, since it indicates the adsorbent affinity at low metal concentrations.

The isotherm experimental results showed that the data could be well modeled according to the Langmuir adsorption isotherms. The Langmuir constant ($q_{max}$) is dependent on experimental conditions such as solution pH. Another important factor in evaluating sorbent performance is the initial gradient of the adsorption isotherm, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant. The Langmuir isotherm assumes that adsorption takes place along a uniform adsorbent surface. In analyzing the applicability of the empirical Freundlich isotherm, the experimental results showed that the data could be analyzed according to this model. In the Freundlich equation, the initial gradient corresponds to the affinity constant ($b$).

**Kinetic modeling**

The Lagergren first-order rate constant ($k_{1,ads}$) and $q_e$ determined from the model indicated that this model failed to
estimate $q_e$ since the experimental values of $q_e$ differed from those estimated in Table 1. The rate of uptake of Zn(II) onto the biomass quickly increased up to 30 min, and no further adsorption was recorded.

Marine algae are biological resources which are available in large quantities in many parts of the world. Surface adsorption is qualifying to be an important basis for the treatment of toxic nickel contaminated water (Ziegler & Goswami 2005).

The pseudo-second-order rate model gave the best description of Zn(II) uptake by the biosorbents. The pseudo-second-order model is based on the supposition that biosorption follows a second-order mechanism, which means that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Nuhoglu & Oguz 2003; Kalyani et al. 2004). In literature evaluating adsorption of Ni(II) using active carbon prepared from Gracilaria alga it has been observed that the second-order kinetics model is followed in the adsorption (Esmaeili & Ghasemi 2009).

Recently, green algae have been attractive as they are ubiquitous in the natural environment, have large surface area-to-volume ratio and high binding affinity to pollutants (Gong et al. 2005). S. glaucescens cell walls are porous and allow the free passage of molecules and ions in aqueous solutions. The constituents of the cell wall provide an array of ligands with different functional groups capable of binding various heavy metals (Chong et al. 2000; Jeyakumar & Chandrasekaran 2014).

The studies were conducted using synthetic seawater, natural seawater and wastewater. Salinity had no effect on the adsorption of Zn(II); there appeared to be no interaction between the salt and either the solute or the surface of the adsorbent. High concentrations of Zn(II) ions may cause them to be more easily absorbed by the adsorbent. These results indicate that dried S. glaucescens can be used to remove Zn(II) from various aqueous solutions, including wastewater.

**CONCLUSION**

The present study demonstrates the feasibility of batch removal of Zn(II) from seawater and wastewater using brown marine alga S. glaucescens. A dried form of this indigenous marine alga has been isolated as an effective adsorbent for removal of Zn(II) ions from various aqueous solutions. Second-order kinetic models can be used to describe the adsorption kinetic data. Metal ion adsorption depends on both the concentration and pH of the metal ion solution, as well as retention time. The dosages of adsorbent indicated that the equilibrium concentration of Zn(II) increased at 200 mg/L. Removal of Zn(II) increased with an increase in pH from 3.0 to 5.0, with the optimum pH observed to be 5.0. The equilibrium adsorption data are correlated by the Freundlich isotherm equation. These environmentally friendly methods may be suitable for small-industry effluent discharges.

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