Equilibrium and Kinetic Studies on the Biosorption of As (III) and As (V) by the Marine Algae Turbinaria conoides

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ABSTRACT
The potential of pre-treated Turbinaria conoides algal biomass to adsorb As (III) and As (V) from aqueous solutions was investigated in batch biosorption experiments. The process parameters studied include the solution pH, initial metal ion concentration, rate of agitation and sorbent dosage. It was seen that lower pH favours more adsorption for both the arsenic species (40 mg g⁻¹ of As (III) and 42 mg g⁻¹ of As (V) at pH 2 and the maximum uptake of the metal ions by the algae is obtained at lower concentration of metal ions and higher sorbent dosages. Also, the metal uptake was maximum at an agitation speed of 150 rpm and decreased beyond it. Equilibrium studies reveal that Langmuir isotherm model (Q_e = 20.2421 mg g⁻¹ for As(III) and 25.9747 mg g⁻¹) provides the greatest accuracy in describing the adsorption when compared to Freundlich and Redlich Peterson models. The sorption kinetics of arsenic could be modelled well by the Elovich equation than the Lagergren and Intraparticle diffusion models.

Key words: Biosorption, arsenic, isotherms, kinetics

INTRODUCTION
Pollution of water by toxic and heavy metals resulting from human technological activities is a major and challenging concern to deal with. Arsenic is a toxic pollutant which is brittle natured grey or white coloured metalloid. The adverse health effects of arsenic are vascular disorders, such as dermal pigments, skin and lung cancer (Haque et al., 2007). The elevated levels of arsenic in the environment are related to anthropogenic activities such as agriculture, manufacturing, mining and smelting (Haque et al., 2007). Arsenic is present both as organic and inorganic compounds of which inorganic form is highly toxic in nature. This heavy metal is usually present as trivalent molecules (arsenite, H₃AsO₃) and pentavalent anions (arsenate H₃AsO₅⁻, HAsO₄²⁻) in ground water in the normal pH range of 6-9. As the pentavalent arsenic is found in anionic forms in this pH range it can be more easily removed from water than trivalent arsenic by processes like ion exchange, reverse osmosis and electron diffraction that treat ions. However, as the trivalent species of arsenic is predominantly found in ground water it is essential to transform trivalent arsenic to pentavalent form by adding some oxidants to make use of the aforementioned processes in removing arsenic from water.

Removal and recovery of this metal by biosorption using microbial biomass (live or dead cells) and agricultural waste biomass (Singh et al., 2005) has proved to be a promising and potential...
alternative to existing technologies such as precipitation, ion exchange, solvent extraction, etc. from industrial wastewater in terms of performance, efficiency, maintenance cost and simplicity (Haque et al., 2007). Moreover, these chemical methods involve consumption of reagents in order to precipitate, coagulate and flocculate the contaminants.

Biosorption of the metal ions onto the biomass is accomplished by binding of the adsorbate to the carboxylate, hydroxyl, sulphate, phosphate, amide and amino groups in the biosorbents. These functional groups are present in the cell wall as polysaccharides, proteins and lipids. The polysaccharides of the algal cell wall could provide amino and carboxyl groups along with sulphate. The amino groups on the proteins of the cell wall and the nitrogen and oxygen of the peptide bond could also be available for binding metallic ions. Such bond formation could be accompanied by the displacement of protons dependent in part on the extent of protonation as determined by pH. Metallic ions could also be bounded electrostatically to unprotonated carboxyl oxygen and sulphate (Aksu and Kutsal, 1998). The performance of biosorption process depends upon external factors such pH, temperature metabolic products of cells and other ions in solution which may be in competition (Haque et al., 2007). Various adsorbent materials have been tested for their ability to remove the two inorganic arsenic species found in water, arsenite (As III) (Singh and Pant, 2004; Thirunavukkarasu et al., 2005) and arsenate (As V) (Xu et al., 2002; Dousava et al., 2003; Zhang et al., 2003; Dambies et al., 2002; Wang and Wai, 2004; Mohan and Pittman, 2007).

The objective of the present study was to analyze the sorption capacity of arsenic (III) and (V) by the brown algae Turbinaria conoides. In this study the effect of process parameters such as pH, agitation speed, initial concentration of adsorbent and adsorbent dosage are investigated. Also, the fit of the experimental data to equilibrium (Langmuir, Freundlich and Redlich-Peterson isotherms) and kinetic (Lagergren equation, Elovich equation and intraparticle diffusion equation) models are tested.

MATERIALS AND METHODS

**Biosorbent pre-treatment:** The dead marine alga, Turbinaria conoides, collected from the coasts in Mandapam (Tamilnadu, India) was washed several times with distilled water to remove the soluble materials and particulate matters and then sun-dried. It was then ground to particles of size less than 0.1 mm diameter. The biomass was then sieved using stainless sieves and soaked in 0.1 M HCl for 4 h for protonation. After washing in distilled water the algal matter was dried at 60°C overnight. After pre-treatment the biomass was witnessed with a weight loss of approximately 15%. This biomass is termed as Treated Non-Immobilized Biomass (TNIB) and used for all the experimentation.

**Chemicals:** The chemicals used for the study are of analytical grade and are obtained from Sd fine chemicals Ltd. (India). Stock solutions of As (III) and As (V) were prepared by dissolving sodium arsenate hydrate and sodium arsenite, respectively in deionized water and diluted further with distilled water to specified concentrations. Nitric acid solutions were used to maintain the pH at desired levels.

**Methods:** Initially the experimental investigations for optimization of process conditions namely pH, agitation rate, initial concentration of adsorbent and sorbent dosage are carried out followed by experiments pertaining to equilibrium and kinetic modelling. The dependence of pH on the biosorption onto the biomass was studied in batch experiments by interacting 50 mL of arsenic (III)
and (V) solutions each (100 mg L⁻¹) with 0.5 g of TNIB for 20 h under different pH conditions viz., 2 to 6. The impact of the initial concentrations of As (III) and As (V) solutions (50-300 mg L⁻¹) on their removal by sorption was investigated by agitating with 0.5 g of the TNIB at an agitation rate of 200 rpm. The effect of agitation rate on the removal of As (III) and As (V) was studied by agitating 50 mL of the metal solutions (100 mg L⁻¹) with 0.5 g of the sorbent at different speeds of rotation from 0 to 300 rpm. The influence of adsorbent dosage on the sorptive capacity was studied by agitating 50 mL of the metal solutions (100 mg L⁻¹) with different dosage levels from 0.5 to 4 g of adsorbent for 20 h. All these experiments were carried out at room temperature and a pH of 2. The experiments were run in duplicates and the mean value of the results for a specific experimental condition is used. The analysis for residual arsenic concentration was accomplished by the atomic absorption spectrophotometer (Perkin Elmer model 373, Life and analytical sciences inc., USA). The measurements do not account for speciation of As(III) and As(V) and provided only the total arsenic concentration. The amount of arsenic adsorbed by algae was calculated from the differences between the amount added to the biomass and the arsenic content after adsorption using the following equation:

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

(1)

where, Q is the arsenic uptake (mg g⁻¹), C_f and C_t are the initial and final arsenic concentrations in the solution respectively (mg L⁻¹), V is the solution volume (l) and M is the mass of biosorbent (g).

The development of a technology based on biosorption implies the use of mathematical models for the quantitative description of the process.

These models should be capable of predicting metal removal, reflecting the mechanism of the uptake, ionic strength and the influence of process parameters. In this context, an attempt has been made in predicting suitable equilibrium and kinetic models to describe the sorption performance and rate. The equilibrium studies are carried out with 0.5 g of the biomass in Erlenmeyer flasks containing 50 mL of each of the metal solutions in the concentration range of 20-500 mg L⁻¹ and at a pH of 2 with the agitation rate maintained at 200 rpm. To study the kinetics of the biosorption 5 g of the biomass and 1 L of arsenic solution (100 mg L⁻¹) are agitated in Erlenmeyer flasks at room temperature with the pH maintained at 2. The left out arsenic in the samples collected using 20 cc syringes at predetermined intervals were assayed after filtering through glass fibre prefilters.

**Modeling**

**Equilibrium isotherm models:** To predict the equilibrium adsorption of As (III) and As (V) metal ions by the TNIB, three different models, namely, Langmuir, Freundlich and Redlich-Peterson were tested for their validity in describing the sorption. The Langmuir isotherm which is the most commonly used model in biosorption assumes that all sites have the same affinity and the secondary effects between sorbed species are negligible. This model is given by the equation (Langmuir, 1918):

\[ Q = Q_{\text{max}} b C_f / (1 + b C_f) \]  

(2)

where, C_f is the final arsenic concentration (mg L⁻¹), Q_{max} is a Langmuir constant that expresses the maximum metal uptake (mg g⁻¹) and b is also a Langmuir constant related to the energy of adsorption and affinity of the sorbent. The Freundlich isotherm is an exponential equation and
therefore, assumes that the concentration of adsorbate on the adsorbent surface increases with the adsorbate concentration. This equation is widely applied in heterogeneous systems and formulated as:

\[ Q = K C_r^{1/n} \]  

(3)

where, K (L g\(^{-1}\)) and n are the Freundlich constants characteristic of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

The Redlich-Peterson isotherm is represented as (Redlich and Peterson, 1959):

\[ Q = K_{sp} C_r/(1+a_{sp}(C_r^\beta)) \]  

(4)

where, \(K_{sp}\) (L g\(^{-1}\)), \(a_{sp}\) (L mg\(^{-1}\)) \(\beta\) are Redlich-Peterson isotherm constants and \(\beta\) the exponent, lies between 0 and 1. This equation reduces to a linear isotherm in the case of low surface coverage and to a Langmuir isotherm when \(\beta = 1\).

**Kinetics of the metal uptake:** The knowledge of the kinetics of any adsorption process is crucial in order to enable industrial scale separation processes. In this perspective three kinetic models namely Langergren equation, Elovich equation and intraparticle diffusion equation were used to test the experimental data. Langergren model is a simplified first order rate equation given by the expression:

\[ \log (Q_t/Q) = \log Q_e - k_{ad} t/2.303 \]  

(5)

where, \(Q\) and \(Q_e\) (mg g\(^{-1}\)) are the amount of arsenic adsorbed at equilibrium and at time t (min), respectively and \(k_{ad}\) (min\(^{-1}\)) is the adsorption rate constant.

The Elovich equation is of general application to chemisorption kinetics. The equation has been applied satisfactorily to some chemisorption processes and has been found to cover a wide range of slow adsorption rates (Perez-Marin et al., 2007). The same equation is often valid for systems in which the adsorbing surface is heterogeneous and is given as:

\[ dQ/dt = \beta e^{-\beta t} \]  

(6)

where, \(\beta\) (mg/g min) is the initial adsorption rate and \(\beta\) is related to the extent of surface coverage and the activation energy involved in chemisorption (g mg\(^{-1}\)).

The intraparticle diffusion equation is given as:

\[ Q = k t^{1/2} \]  

(7)

where, k (mg/g min\(^{1/2}\)) is the intraparticle diffusion rate constant.

**RESULTS AND DISCUSSION**

**Effect of pH:** The results of the study of influence of pH on bicsorption of As (III) and As (V) for initial concentrations of 100 mg L\(^{-1}\) each are displayed in Fig. 1. It can be seen that the uptake
capacity of the alga at pronounced pH values shows negative effect favoring acidic environment for effective removal of As ions in both trivalent and pentavalent states. It was observed that the maximum metal uptake of As (III) was 40 mg g$^{-1}$ at the pH of 2. This trend is in accordance with the investigation of Hansen et al. (2006) wherein, they reported the maximum uptake of As (III) as 45 mg g$^{-1}$ using the algae Lessonia nigrescens at a pH of 2.5. Also, Haque et al. (2007), reported that initial pH above 5 is found to be unfavorable for biosorption of As (III) by sorghum biomass. This behavior is attributed to the chemical nature of the dominant species which remained uncharged in this range of pH, the lone pair of electrons in the arsenic atom may induce the formation of coordinate bonding with the protonated substrate (Rahaman et al., 2007). The removal of As (V) ions by the NIDB showed decreasing trend with increasing pH in the range studied showing maximum uptake of 42 mg g$^{-1}$ at the pH 2. This is because lower pH values assure the protonation of the amide groups for effective binding of negatively charged anions. This decreasing tendency is also due to the fact that acidic environment provides sufficient protonated sites to the substrate facilitating more positive charges to the sorbent and hence enabling more interaction with the negatively charged arsenic species. At higher pH values the substrate becomes negatively charged and cause repulsive force towards the arsenic ions resulting in poor uptake values. Niu et al. (2007) and Rahaman et al. (2007) reported the same trend in their investigations pertaining to the removal of As (V) ions using acid washed crab shells and fish scale, respectively.

**Effect of initial concentration of metal ions:** The initial concentration of the metal ions is found to have a negative influence on the biosorption performance by the NIDB as portrayed in Fig. 2. The removal of arsenic ions at lower initial concentration is predominant and a drastic decline in the uptake is observed beyond 200 mg L$^{-1}$. The logical reasoning behind the lower uptake levels of As (III) and (V) is the dominance of repulsive forces towards the adsorbent at higher initial concentrations of the metal ions. Similar observations were reported for removal of As(III) using Cambogia biomass (Kamala et al., 2005).

**Effect of agitation rate:** The agitation rate on the sorption performance of the alga is found to have positive impact as shown in Fig. 3. The maximum value of the adsorption capacity is observed at the speed of 150 rpm with the uptake of 17.5 mg g$^{-1}$ of As (V) and 15 mg g$^{-1}$ of As (III) ions. The adsorption capacity decreased considerably at agitation rates greater than 150 rpm. The best
Fig. 2: Effect of initial metal ion concentration for biosorption of Arsenic on *Turbinaria conoides*

Fig. 3: Effect of Agitation on Arsenic uptake

homogeneity of the mixture suspension provided at moderate speed is the reason for higher adsorption values. At higher speed, vortex formation and possible cell disruption makes the adsorption difficult leading to lesser uptake of the metal ions. This trend was reported for the removal of Cd and Zn removal using *Aspergillus niger* (Liu *et al.*, 2006).

**Effect of sorbent dosage:** Pronounced magnitude of active sites and the consequent functional groups enhance the uptake of metal substrate by the increased level of sorbents in the biosorption phenomenon. This fact is portrayed in the Fig. 4 wherein the adsorption percentage increases with the sorbent dosage level. Also the adsorption efficiencies for As (III) and As (V) ions were found to have lesser influence at dosage levels greater than 2.5 g L⁻¹ as the increment in the uptake percentage of both the ions was very meagre (around 4 to 5%). The reason behind this is the saturation adsorption levels for arsenic concentrations in the range investigated (Basu *et al.*, 2006). Similar results were obtained by Kamala *et al.* (2005) in their investigation of the removal of arsenic metal ions using fresh and immobilized plant biomass.

Fig. 4: Effect of sorbent dosage on Arsenic Biosorption

Fig. 5: Different isotherm models for Arsenic (As(III)) biosorption

**Adsorption isotherms:** Experimental and estimated uptake values of the arsenic metal ions from various isotherm models are displayed in Fig. 5, 6. Table 1 represents the values of the various parameters of the three isotherm models and the corresponding regression coefficients. The results of the equilibrium studies show that the adsorption of As (III) and As (V) ions by the NIDB follows the Langmuir isotherm model at its best with the maximum regression coefficient of 0.9872 when compared to the other two models. The maximum uptake capacities of As (III) and As (V) by the algae were found to be 20.2421 and 25.9747 mg g⁻¹ according to Langmuir model. This is in accordance with the value of maximum uptake of both the trivalent (Q_{max} = 19.8321 mg g⁻¹) and pentavalent arsenic (Q_{max} = 23.9854 mg g⁻¹) using *Laminaria japonica* (Ghimire et al., 2008). This shows that the surface of the sorbent is homogeneous and sorption stops at one monolayer.

On the other hand, the higher values of Freundlich constants shown in Table 1 reveal the easy separation of arsenic ions from aqueous medium indicating favourable adsorption. The same trend is observed by Liu et al. (2006) in the removal of Cd and Zn using *Aspergillus niger*. The Redlich
Fig. 6: Different isotherm models for Arsenic (As(V)) biosorption

Table 1: Adsorption isotherm parameters for As (III) and As (V) biosorption on Turbinaria conoides

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Experimental</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>Redlich-Peterson model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q_{ex} (mg g^{-1})</td>
<td>Q_{eq} (mg g^{-1})</td>
<td>b</td>
<td>R^2</td>
</tr>
<tr>
<td>As (III)</td>
<td>17</td>
<td>30.242</td>
<td>0.0123</td>
<td>0.9872</td>
</tr>
<tr>
<td>As (V)</td>
<td>19</td>
<td>25.974</td>
<td>0.0135</td>
<td>0.9823</td>
</tr>
</tbody>
</table>

Table 2: Kinetic model parameters for As (III) and As (V) biosorption on Turbinaria conoides

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Experimental</th>
<th>Lagergren model</th>
<th>Elovich model</th>
<th>Intraparticle-diffusion Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q_e (mg g^{-1})</td>
<td>K_d (l/mg min)</td>
<td>Q_{eq} (mg g^{-1})</td>
<td>R^2</td>
</tr>
<tr>
<td>As (III)</td>
<td>28</td>
<td>0.0018</td>
<td>36.6185</td>
<td>0.9683</td>
</tr>
<tr>
<td>As (V)</td>
<td>34</td>
<td>0.0020</td>
<td>45.6097</td>
<td>0.9677</td>
</tr>
</tbody>
</table>

Peterson isotherm shows that the value of β approaches unity (0.96 for As (III) and 0.98 for As (V)) indicating that the Redlich Peterson isotherm tends towards the Langmuir isotherm. The magnitude of Q_{Bmax} obtained from this model was within the range of values obtained by several authors under similar conditions (Perez-Marín et al., 2007; Reddad et al., 2002; Ko et al., 2004).

**Kinetic studies:** The kinetic profile of biosorption of As (III) and As (V) at pH 2 as shown in Fig. 7, 8 depicts that the rate of sorption is rapid in the first 17 h followed by a lesser rate and eventually constant after 25 h. Due to higher rate, high efficiency and economy can be ensured in the metal removal as the volume of the reactor required will be small (Loukidou et al., 2004). To fit the experimental data to theoretical equations three kinetic models namely Lagergren first order model, Elovich model and Intraparticle diffusion model are employed and the parameters of these models are represented in Table 2. From the values of the correlation coefficients it can be seen that the Elovich model proves to be the best fit with the R^2 value of 0.9879 for As (III) and 0.9874 for As (V) ions. This model assumes that the active sites of the sorbent are heterogeneous with α related...
Fig. 7: Different kinetic models for Arsenic (As (III)) biosorption at pH 2.0

Fig. 8: Different kinetic models for Arsenic (As(V)) biosorption at pH 2.0

to the rate of chemisorption and β to the surface coverage. Also it is based on a general second order reaction mechanism for heterogeneous adsorption processes (Cheung et al., 2001).

Equilibrium uptake values predicted from Lagergran models (36.6185 for As (III) and 45.6667 for As (V)) deviate more from the experimental values (28 for As (III) and 34 for As (V)). Also, Intraparticle diffusion model did not provide better results when compared to the prediction from Elovich model.

CONCLUSION

The results obtained in the sorption studies of As(III) and As(V) from aqueous solutions using Turbinaria conoides show that the metal uptake is strongly influenced by the process conditions such as pH, initial metal ion concentrations, sorbent dosage and agitation rate. It was observed that
lower pH enables higher adsorption efficiency for both the arsenic species (with $Q_{\text{max}}$ of 40 mg g$^{-1}$ of As(III) and 42 mg g$^{-1}$ of As(V) at pH 2. The sorption capacity is found to decrease with increase in the initial metal ion concentrations in the range studied. The removal capacity of arsenic increases with the increase of sorbent dosage. The agitation speed significantly influences the metal uptake and maximum uptake is obtained at 150 rpm. The isotherm studies show that the biosorption process can be best described by Langmuir isotherm model ($Q_{\text{max}} = 20.2421$ mg g$^{-1}$ for ss (III) and 25.9747 mg g$^{-1}$) than the Freundlich and Redlich Peterson models. For both the arsenic ions the sorption kinetics is best followed by the Elovich equation.

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