BIOSORPTION OF CHROMIUM (VI) BY USING TAMARIND (Tamarindus indica L.) POD SHELL

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ABSTRACT
The use of Tamarind pod shell (Tamarindus indica L.) for effective removal of chromium (VI) from aqueous solutions in a batch system was studied. The FTIR study of acid treated biosorbent showed that the possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. The SEM represents a porous structure with large surface area. The effects of operational factors including solution pH, biosorbent dose, initial chromium (VI) concentration, contact time and temperature were studied. The equilibrium data were well described by typical Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin adsorption isotherms. A detailed analysis has been conducted by testing kinetic models such as pseudo-first-order, pseudo second-order, Elovich equation and Weber & Morris intra-particle diffusion rate equation. Thermodynamic study revealed that the adsorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. Tamarind pod shell (Tamarindus indica L.) used successfully for removal of chromium (VI) from aqueous solutions can have promising application in industrial wastewater treatment.

Key Words: Effective removal, chromium (VI), tamarind pod shell (Tamarindus indica L.) leaves, adsorption isotherms, adsorption kinetics, thermodynamic study

INTRODUCTION
The serious problem of heavy metal pollution in the environment due to industrial activities needs to be solved. Heavy metals tend to persist indefinitely circulating and eventually accumulating throughout the food chain which results in ecological and health hazard (Selomulya et al., 1999, Geleel et al., 2013). Chromium occurs frequently as Cr (VI) and Cr (III) in aqueous solutions (Dakiky, 2002). Hexavalent chromium, which is primary present in the form of chromate (CrO$_4^{2-}$) and dichromate (Cr$_2$O$_7^{2-}$) possesses significantly higher level of toxicity than the other valence states (Smith et al., 1972). Cr (VI) discharge into the environment can be due to various large numbers of industrial functions like dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, etc (Patterson et al., 1985). Major diseases caused by toxic hexavalent chromium ions are bronchial asthma and lung cancer. Therefore, there is an urgent need to seek alternative treatment methods which is cost effective and environmentally friendly for removal of Cr (VI) from wastewater.

Biosorption of heavy metals is very effective, versatile, powerful, most efficient and cost effective technologies involved in the removal of heavy metals from industrial effluents. Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals ions. Use of low cost adsorbent for biosorption study of heavy metals is very advantageous (Maind et al., 2012). Among the various resources in biological waste, both dead and live
biosorbent, exhibit particularly interesting metal-binding capacities. A variety of adsorbents, including leaf mould, pongamia leaf, algae, bacteria, tamarindus indica seeds, activated carbon rice husks, quarternised rise husk, hazelnut shell, almond shell, corn cob, quarternised wood, groundnut husk, coconut husk and palm pressed fibers, coconut shell, coconut jute, coconut tree sawdust, native and immobilized sugarcane bagasse, synthetic material, inorganic materials, have been used for chromium (VI) removal.

Natural materials that are available in large quantities or certain waste products from industrial and agricultural operations may have potential as inexpensive sorbents. The (Tamarindus indica L.) tamarind pod shell being one of the inexpensive materials.

The (Tamarindus indica L.) tamarind pod shell was selected because of a low cost, possibility of higher adsorption capacity and availability of various function groups such as hydroxyl, carbonyl, carboxylic etc., which favours biosorption of heavy metals.

The main objective of this work was to evaluate the adsorption capacity of (Tamarindus indica L.) tamarind pod shell for the effective removal of Cr (VI) from aqueous solutions by varying solution pH, biosorbent dose, initial Cr (VI) concentration, contact time and temperature. Equilibrium adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) for adsorption of Cr (VI) onto (Tamarindus indica L.) tamarind pod shell were described. Kinetic models (pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intra-particulate mixing equation) were employed to understand the probable adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard free energy change ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$) and standard entropy change ($\Delta S^\circ$).

MATERIALS AND METHODS

Chemicals and reagents
All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute sulphuric acid and dilute sodium hydroxide.

Preparation of Cr (VI) solution
The stock solution of 1000 ppm of chromium (VI) was prepared by dissolving 0.7072 g of potassium dichromate (K$_2$Cr$_2$O$_7$) in 250 ml of double distilled water and further desired test solutions of chromium (VI) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent
The Tamarind pod shell (Tamarindus indica L.) was collected and washed with several times with distilled water. The washed biosorbent was then dried at sunlight andgrounded in a mechanical grinder to form a powder. The powder was sieved and a size fraction in the range of 100-200 µm will be used in all the experiments. For further use, the powder biomass was stored in air tighten plastic bottle to protect it from moisture.

Instrumentation and data analysis
The concentration of Cr (VI) in the solutions before and after equilibrium was determined by measuring absorbance using digital UV-visible spectrophotometer (EQUIP-TRONICS, model no. Eq-820) and ICP-AES. The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode.
The following equation was used to compute the percentage adsorption (% Ad) of Cr (VI) by the adsorbent,

\[
\% \text{ Ad} = \left(\frac{C_i - C_e}{C_i}\right) \times 100
\]  

(1)

where \(C_i\) and \(C_e\) are the initial concentrations and equilibrium concentrations of the Cr (VI) in mg/L.

RESULTS AND DISCUSSION

Effect of pH

The adsorption capacity of the adsorbent and speciation of metals in the solution is pH dependent. The optimization of pH was done by varying the pH in the range of 1-8 for biosorption of chromium (VI) and pH trend observed in this case is shown in Figure 1. It was found that at pH 4 the adsorption process was maximum with 85.77 % and after increasing pH, adsorption was decreases.

Effect of biosorbent dose

Effect of biosorbent dose of metal ions biosorption onto biosorbent which is an important parameter was studied while conducting batch adsorption studies. The sorption capacity of chromium (VI) on to the Tamarind pod shell (Tamarindus indica L.) by varying adsorbent dose from 1.0 mg/ml to 15.00 mg/ml is as shown in Figure 2. From the results it was found that adsorption of chromium (VI) increases with increase in adsorbent dosage and is highly dependent on adsorbent concentration.

Effect of initial chromium (VI) concentration

The effect of initial chromium (VI) concentration from 10 mg/L - 300 mg/L on the removal of chromium (VI) from aqueous solutions at adsorbent dose 10 mg/ml and at optimum pH 4.0 at 40°C temperature was studied and shown in Figure 3. On increasing the initial chromium (VI) concentration, the total chromium (VI) ions uptake decreased appreciably when chromium (VI) concentration increases from 10 mg/L - 300 mg/L.
Effect of chromium (VI) concentration on chromium (VI) biosorption by *Tamarindus indica L.* (tamarind pod shell) (pH: 4, biosorbent dose concentration: 5 mg/L, contact time: 180 minute, temperature: 40°C)

**Effect of contact time**

Contact time plays an important role in affecting efficiency of adsorption. Contact time is the time needed for adsorption process to achieve equilibrium when no more changes in adsorptive concentration were observed after a certain period of time. The contact time which is required to achieve equilibrium depends on the differences in the characteristics properties of the adsorbents. In order to optimize the contact time for the maximum uptake of chromium (VI), contact time was varied between 10 minute – 240 minute on the removal of chromium (VI) from aqueous solutions in the concentration of chromium (VI) 10 mg/L, adsorbent dose 5 mg/ml, optimum pH 4.0 and 40°C temperature (Figure 4). The results obtained from the adsorption capacity of chromium (VI) onto Tamarind pod shell (*Tamarindus indica L.*) showed that the biosorption increases with increase in contact time until it reached equilibrium.

![Figure 3: Effect of chromium (VI) concentration on chromium (VI) biosorption by *Tamarindus indica L.* tamarind pod shell (pH: 4, biosorbent dose concentration: 5 mg/L, contact time: 180 minute, temperature: 40°C)](image)

![Figure 4: Effect of contact time on chromium (VI) biosorption by *Tamarindus indica L.* tamarind pod shell (pH: 4, biosorbent dose concentration: 5 mg/L, initial chromium (VI) concentration: 10 mg/ml, temperature: 40°C)](image)
**Adsorption isotherms**

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

![Adsorption isotherm models](image)

Figure 5: Adsorption isotherm models (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for biosorption of Cr (VI) by *Tamarindus indica L.* tamarind pod shell (pH: 4.0, biosorbent dose concentration: 5 mg/ml, contact time: 180 minute, temperature: 40°C)

**Langmuir adsorption isotherm** [I. Langmuir]:

The Langmuir equation:

\[
q_e = \frac{q_m b C_e}{1 + b C_e}
\]

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e}
\]

![Langmuir adsorption isotherm](image)
The values of $q_m$, $b$, and regression coefficient ($R^2$) are listed in Table 1. $R_i$ expressed as in the following equation:

$$ R_i = \frac{1}{1+bc_i} $$

(5)

Langmuir model for surface area of biosorbent surface has been represented in the following equation:

$$ bC_i = \frac{\theta}{1-\theta} $$

(6)

Freundlich adsorption isotherm [H. M. F. Freundlich]:

Freundlich equation is represented by:

$$ q = kC^{1/n} $$

(7)

Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$ \log q_s = \log K + \frac{1}{n} \log C_s $$

(8)

The values of $K$, $1/n$ and regression coefficient ($R^2$) are listed in Table 1.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm:

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as:

$$ \ln q_s = \ln q_m - \beta \varepsilon^2 $$

(9)

$$ \varepsilon = RT \ln \left(1 + \frac{1}{C_s} \right) $$

(10)

$$ E = \frac{1}{\sqrt{2\beta}} $$

(11)

Temkin adsorption isotherm [V. J. Temkin]:

Linearized Temkin adsorption isotherm is given by the equation:

$$ q_s = \frac{RT}{b_T} \ln (A_T C_s) $$

(12)

The values of $A_T$, $b_T$, and regression coefficient ($R^2$) are listed in Table 1.

Table: Adsorption isotherm constants for biosorption of Chromium (VI) by (Tamarindus indica L.) Tamarind pod shell

<table>
<thead>
<tr>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
<th>DKR parameters</th>
<th>Temkin parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$</td>
<td>$B$</td>
<td>$R^2$</td>
<td>$K$</td>
</tr>
<tr>
<td>35.21</td>
<td>0.037</td>
<td>0.986</td>
<td>1.208</td>
</tr>
</tbody>
</table>

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Adsorption kinetics

Figure 6. Adsorption kinetic models (a) pseudo-first-order equation, (b) pseudo-second-order equation, (c) Elovich equation and (d) Weber and Morris intraparticulate mixing equation, for biosorption of Cr (VI) by (*Tamarindus indica* L.) tamarind pod shell (pH: 4.0, biosorbent dose concentration: 5 mg/ml, Cr (VI) concentration: 10 mg/L, temperature: 40°C)

the pseudo-first-order equation, the pseudo-second-order equation, Elovich equation, Weber and Morris intraparticle diffusion equation are presented below.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \tag{13}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}
\]
Biosorption of Chromium (VI) by using Tamarind Pod Shell

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \]  \hspace{1cm} (15)

\[ q_t = k_t t^{0.5} + c \]  \hspace{1cm} (16)

Table 2: Adsorption kinetic data for biosorption of Chromium (VI) by (Tamarindus indica L.) Tamarind pod shell

<table>
<thead>
<tr>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
<th>Elovich model</th>
<th>Intra-particle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_e )</td>
<td>( q_e )</td>
<td>( k_t )</td>
<td>( k_z )</td>
</tr>
<tr>
<td>0.4737</td>
<td>1.7226</td>
<td>0.002</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

Thermodynamic study

\[ \ln K_c = -2809.5x + 10.806 \]

\[ R^2 = 0.6698 \]

The effect of temperature on removal of Cr (VI) from aqueous solutions in the Cr (VI) concentration 10 mg/L and adsorbent dose 5 mg/ml with optimum pH 4.0 was studied. Experiments were carried out at different temperatures from 20°C-40°C. The samples were allowed to attain equilibrium. Sorption slightly increases from 20°C-40°C. The equilibrium constant at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:
The values of $\Delta H^0$ and $\Delta S^0$ were determined from the slope ($\Delta H^0/R$) and the intercept ($\Delta S^0/R$) from the plot of $\ln K_c$ versus $1/T$ (Figure 6). The values of equilibrium constant ($K_c$), standard Gibbs free energy change ($\Delta G^0$), standard enthalpy change ($\Delta H^0$) and standard entropy change ($\Delta S^0$) calculated in this work were presented in Table 3.

Table 3: Thermodynamic parameters of biosorption of Chromium (VI) by (Tamarindus indica L.) Tamarind pod shell

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$K_c$</th>
<th>$-\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.9416</td>
<td>2.628</td>
<td>23.358</td>
<td>89.841</td>
</tr>
<tr>
<td>298</td>
<td>4.5710</td>
<td>3.765</td>
<td></td>
<td></td>
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<tr>
<td>303</td>
<td>5.4557</td>
<td>4.273</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>5.4935</td>
<td>4.432</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSIONS

The present investigation revealed that Tamarind pod shell (Tamarindus indica L.) used as inexpensive, excellent biosorbent for the removal of chromium (VI) from aqueous solutions. The optimal parameters such as solution pH, biosorbent dose, initial chromium (VI) concentration, agitation speed, contact time and temperature determined in the experiment were effective in determining the efficiency of chromium (VI) onto Tamarind pod shell (Tamarindus indica L.). Sorption equilibrium exhibited better fit to Freundlich isotherm than Langmuir isotherm, Temkin isotherm and Dubinin-Kaganer-Redushkevich (DKR) isotherm. The maximum chromium (VI) loading capacity ($q_e$) of Tamarind pod shell (Tamarindus indica L.) determined from Freundlich adsorption isotherm was found to be 35.211 mg g$^{-1}$. The pseudo-second-order kinetic model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of chromium (VI) onto Tamarind pod shell (Tamarindus indica L.) is spontaneous, endothermic and increasing randomness of the solid
solution interfaces. From these observations it can be concluded that Tamarind pod shell 
(Tamarindus indica L.) has considerable biosorption capacity, available in abundant, non-
hazardous material can be used as an effective indigenous material for treatment of 
wastewater stream containing chromium (VI).

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