REMOVAL OF CHROMIUM (VI) IN AQUEOUS SOLUTION AND INDUSTRIAL WASTEWATER USING DRY PODS OF PROSOPIS SPICIGERA

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ABSTRACT
The study involves the batch biosorption process for the removal of Chromium in the aqueous solution using the dried pods of Prosopis spicigera. Factors influencing the biosorption are pH, contact time, adsorbent dose and initial metal ion concentration. Characterization of the biosorbent is carried out to study the morphology by using Scanning Electron Micrograph (SEM). The maximum biosorption occurred at pH 3, contact time 120 min, Biosorbent dose 2 g/l and initial metal ion concentration of 200 mg L⁻¹. Kinetic models were also described and fit good in Pseudo second order. The equilibrium data was also analyzed using Langmuir and Freundlich isotherms.

KEY WORDS
Chromium, Prosopis spicigera, SEM, Kinetic models, Langmuir and Freundlich isotherms.

INTRODUCTION
Increasing awareness of water pollution during recent years and its far reaching effects has prompted concerted efforts towards pollution abatement. Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters [1]. Hexavalent Chromium is released into the environment by large number of processes such as electroplating, leather tanning, wood preservation, pulp processing, steel manufacturing etc. and it is also highly soluble in water and carcinogenic to humans. According to the IS: a Bureau of Indian standard (BIS), industrial effluent permissible discharge level of Chromium is 3.0 mg L⁻¹ [2, 3]. In aqueous solutions, chromium frequently occurs as Cr (VI) or Cr (III) [4]. Hexavalent chromium which is primarily present in the form of chromate CrO₄²⁻ and dichromate Cr₂O₇²⁻, has significantly higher levels of toxicity than the other valence states [5]. Generally chromium is removed from wastewater by different methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, ion-exchange, Reverse Osmosis, solvent extraction etc [6] and these methods are not cost effective, unaffordable for large scale to remove chromium from the wastewater.

An attractive process has emerged for removing noxious substances from wastewater is Biosorption which has major advantages over conventional treatment methods include low cost, high efficiency of metal removal from dilute solutions, minimization of chemical biological sludge, no additional nutrient requirement and regeneration of biosorbent and possibility of metal recovery [7].

In the present study the dried pods of Prosopis spicigera is used for the removal of Chromium in the aqueous solution. The pod is straight, edible, smooth, 10 to 15 cm long, 0.6 cm thick which grows in dry and arid region. Different parameters have been studied such as pH, contact time, adsorbent dose, initial metal ion concentration and size variation for the biosorption of chromium. The biosorption kinetics and equilibrium isotherms are also been investigated.

MATERIALS AND METHODS
Preparation of biosorbent: The pods of Prosopis spicigera belongs to Family Fabaceae was collected

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from Mysore district, Karnataka, India. The collected biosorbent was washed thoroughly with the distilled water several times to remove the impurities. Then the washed pods were sun dried for several days, grinded into different sizes from 100 µm to 400 µm and sieved. The fine powder of size 100 µm was selected and used as a biosorbent, kept in an air tight plastic jar until it is used for further experiments.

Preparation of Metal ion solution:
Stock solution of 1000 mg/L of chromium was prepared by dissolving 2.828 g Potassium dichromate A.R. grade in 1000ml of double distilled water and it was further diluted to required concentration. The pH of the solution is adjusted by using 0.01N HCl and 0.01N NaOH and the resultant final concentrations were analyzed by AAS.

Metal plating Wastewater:
The wastewater was collected from electroplating industry located in Mysore, Karnataka, India. The physico chemical characteristics were analyzed using standard methods and are presented in Table 1.

Characterization of Biosorbent:
The scanning electron micrograph was used to reveal the surface texture and morphology of the biosorbent by using ZEISS, EVO/LS 15-15-41, smart SEM version 5.05.

Biosorption Experiments:
Biosorption experiments have been carried for the removal of Chromium using pods of Prosopis spicigera. In the biosorption studies 20 ml of 1000 mg/L of Cr (VI) solution was taken in the Erlenmeyer flask and the solution was adjusted to desired pH using 0.01N HCl and 0.01N NaOH. The resulted solution was stirred for 20 min at rate of 180 rpm by centrifugation shaker and was separated by centrifugation at a rate of 6000 rpm for 30 min. The supernatant solution was analyzed by AAS.

The influence of pH on biosorption was carried by taking 20 ml of 1000 mg/L of chromium solution in pre cleaned conical flask containing 2 g of 100μm size P. spicigera and the pH was adjusted in the range of pH 2 to 6 by using 0.01N HCl and 0.01N NaOH.

In order to study the effect of size of adsorbent on biosorption, 20 ml of 1000 mg L\(^{-1}\) of Cr (VI) with particle size of adsorbent varying from 100-400 µm at pH 3. The mixture was shaken for 60 min in a mechanical shaker at a speed of 180 rpm, and then the resulting mixture was filtered.

In order to find out the effect of contact time of chromium biosorption by taking 20 ml of 1000 mg/L\(^{-1}\) of Cr (VI) in a Erlenmeyer flask containing 2 g 100 µm size biosorbent. The mixture was shaken at time intervals varying from 20 to 200 min in a mechanical shaker at a speed of 180 rpm.

The effect of biosorbent dosage was investigated by taking 20 ml of 1000 mg/L\(^{-1}\) fixed Cr (VI) concentration in a different 250 ml Erlenmeyer flask containing dosage from 0.2 to 3.0 g at a predetermined pH 6 with time intervals of 60 min. The effect of initial metal ion concentration from 25 to 250 mg/L\(^{-1}\) was studied by using predetermined optional pH, dosage, and size and equilibrium time at a room temperature.

The percent removal of chromium was calculated for each run using the following formula.

\[ R = \frac{(C_0 - C_f) \times 100}{C_0} \quad (1) \]

Where, \( C_0 \) and \( C_f \) are the initial and residual concentration of chromium respectively in solution (mg/L). The metal uptake capacity for initial and final concentration of chromium was calculated using the following formula:

\[ q_e (mg/g) = \frac{V (C_i - C_e)}{M} \quad (2) \]

Where, \( q_e \) is the chromium uptake (mg/g), \( C_i \) and \( C_e \) are the initial and final chromium concentration respectively in the solution (mg/l). \( V \) is the solution volume (L) and \( m \) is the mass of adsorbent (g).
Table I: Physico chemical parameters of Industrial effluent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Contents (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.50</td>
</tr>
<tr>
<td>Conductivity(µs/cm)</td>
<td>1765</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>1020</td>
</tr>
<tr>
<td>Calcium</td>
<td>103.13</td>
</tr>
<tr>
<td>Magnesium</td>
<td>44.89</td>
</tr>
<tr>
<td>Chloride</td>
<td>205.12</td>
</tr>
<tr>
<td>Sulphate</td>
<td>78.34</td>
</tr>
<tr>
<td>Sodium</td>
<td>65.3</td>
</tr>
<tr>
<td>Potassium</td>
<td>3.7</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>14.20</td>
</tr>
<tr>
<td>Chromium (VI)</td>
<td>45.82</td>
</tr>
</tbody>
</table>

Table II: Pseudo first–order and Pseudo second–Order constants for chromium biosorption by *P. spicigera*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_e (mg g⁻¹)</td>
<td>K_1 (min⁻¹)</td>
</tr>
<tr>
<td>chromium</td>
<td>1.561</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Table III: Langmuir and Freundlich isotherms for chromium biosorption by *P. spicigera*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (II)</td>
<td>q_max</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>18.9</td>
<td>0.528</td>
</tr>
</tbody>
</table>

Table IV: Comparison of biosorption capacity chromium (VI) with various adsorbents

<table>
<thead>
<tr>
<th>Biosorbents</th>
<th>Biosorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated saw dust of <em>Sal tree</em></td>
<td>9.5</td>
<td>[24]</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>13.4</td>
<td>[25]</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>17.7</td>
<td>[26]</td>
</tr>
<tr>
<td>Gulmohar’s fruit shell</td>
<td>12.28</td>
<td>[27]</td>
</tr>
<tr>
<td><em>Psidium guajava</em> (leaves powder)</td>
<td>4.7</td>
<td>[28]</td>
</tr>
<tr>
<td>Immobilized biomass</td>
<td>5.3</td>
<td>[29]</td>
</tr>
<tr>
<td>Bagasse fly ash—a sugar industry waste material</td>
<td>5.0</td>
<td>[30]</td>
</tr>
<tr>
<td><em>Cladophora crispata</em></td>
<td>6.20</td>
<td>[31]</td>
</tr>
<tr>
<td><em>Pilayella littoralis</em></td>
<td>6.55</td>
<td>[32]</td>
</tr>
<tr>
<td><em>Prosopis spicigera</em></td>
<td>18.9</td>
<td>Present study</td>
</tr>
</tbody>
</table>
Fig 1(a) SEM image of raw P. spicigera

Fig 1(b) SEM image of chromium loaded P. spicigera

Fig. 2 Effect of pH on biosorption of chromium by P. spicigera

Fig. 3 Effect of Biosorbent size on biosorption of chromium by P. spicigera

Fig.4 Effect of contact time on biosorption of chromium by P. spicigera
Fig. 5 Effect of Biosorption dose on biosorption of chromium by *P. spicigera*

Fig. 6 Effect of Metal ion concentration on biosorption of chromium by *P. spicigera*

Fig. 7 Pseudo first – order sorption Kinetics for chromium by *P. spicigera*

![Graph showing pseudo first-order sorption kinetics for chromium by *P. spicigera*]

Fig. 8 Pseudo second– order sorption Kinetics for chromium by *P. spicigera*

![Graph showing pseudo second-order sorption kinetics for chromium by *P. spicigera*]
RESULTS AND DISCUSSION

Characterization of Biosorbent:
SEM images of native and chromium loaded biosorbents are shown in Fig 1(a) and 1(b) at 1.14 X and 700 X magnifications. It has been observed that the uneven texture with a lot of irregular format in the native biosorbent. During the period of biosorption the morphology has undergone different changes as there is the opening of pores which results in large surface area and small dots like structure shows that the accumulation of metal on surface of the biosorbent.

Effect of Initial pH
Fig 2 shows the effect of pH on the percentage removal by P. spicigera. The pH of the solution influence both metal binding on the cell surface and the chemistry of metal in solution [8]. The maximum biosorption was recorded at pH 3 with percentage removal of 79.98%. The dominant form of chromium (VI) at pH 3 is HCrO₄ whereas increase in the pH will shift the concentration of HCrO₄ to other forms like, CrO₄^{2-} and Cr₂O₇. At lower pH Cr (VI) will be reduced to Cr (III) under acidic conditions. The resulting Cr (III) cations will not adsorb on the protonated surface of the biomass due to the repulsive force, it may cause decrease in the adsorption [26]. Beyond pH 6 the experiment was not conducted as precipitation may occur which interfere the biosorption process [9, 10]. Similar results coincide which is reported by using non-living biomass of Nostoc species, Treated saw dust of Indian Rose wood and Coconut tree saw dust [11, 13]

Effect of Particle size
In order to understand how particle size affects the adsorption, a series of experiments were conducted using P. spicigera. The average particle size was changed from 100 to 400 μm keeping the other variables constant. The experiment has revealed that the saturation capacity of metal ions adsorption of P. spicigera decreased by increasing the particle size (Fig. 3). This can be attributed to the relationship between the effective specific area of the adsorbent particles and their sizes. At 100 μm size the maximum adsorption was 79.98% and when the particle size increased from 100 to 400 μm the rate of adsorption decreases from 79.98% % to 45.7 %. This implies that
smaller particles have large surface area and hence the percentage of adsorption is more [14]

**Effect of contact time**

Fig 4 shows the effect of contact time on removal of Cr (VI) by P. spicigera with varied time from 20-200 min in a separate runs with constant pH 3. The result shows that the maximum percentage removal (79.98%) was attained at 120 min and further the rate of biosorption was static. At the initial stage the process of biosorption was high and became slower when it is approaching the equilibrium stage. This may be due to more number of vacant negatively charged sites available initially on the surface of the biosorbent and the sites are gradually filled up while approaching equilibrium [15]. Similar results were reported by using non living biomass of Nostoc species and Tamarindus indica pod shells [11, 12].

**Effect of Biosorbent dose**

Biosorbent dose is an important parameter for the removal of Cr (VI) was studied with varying biosorbent dosages from 0.2 - 3.0 g while keeping the metal ion concentration constant. Fig 5 shows the percent removal of metal ion increases rapidly with increasing the weight of the biomass. The maximum percent removal was attained at 2 g/L and the biosorption capacity of chromium on P. spicigera was 79.98% at fixed pH 3, contact time 120 min. It has been noted from the experiment that, as the biosorbent dose is increased the biosorption capacity also increase. The reason for this is, increase in surface area which in turn increases the binding sites for chromium [16]. The metal ion normally adsorbs one molecule thick layer over the surface. When this monolayer covers the surface the capacity of the adsorbent exhausted and causes the attainment of equilibrium [28]. The SEM reveals and shows the adsorption. As the metal ions are insufficient to cover all the binding sites of biosorbent the metal uptake is decreased. Similar trend of results were reported by using macro algae Cladophora species and immobilized fungal biomass [17, 18].

**Effect of Metal ion concentration**

The effect of metal ion concentration of Cr (VI) in the aqueous solution on the percentage removal is shown in the Fig 6. The removal of Cr (VI) decreased from 98% to 79.98% with increase in the concentration from 25 mg/L to 250 mg/L at a constant pH 3 with 2 g/L biosorbent at 120 min. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available sites on biosorbent. The results show that, with increasing metal ion concentration, the specific sites are saturated and vacant sites are filled and at low concentrations adsorption sites took up the available metal more rapidly or quickly while at higher concentrations metal ions need to diffuse to the biomass surface by intra particle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [15, 19, 20].

**Kinetics of Biosorption**

To investigate the biosorption mechanism and the its potential rate pseudo first order and pseudo second order kinetic models are used to check the equilibrium data and it was described traditionally by [21]. The pseudo first order equation is represented by following formula:

\[
\log q_e - \log q_t = \log K_1 \frac{t}{2.303}
\]  

Where, \( q_e \) is the amount of metal adsorbed (mg/g), \( q_t \) is the amount of metal adsorbed at time \( t \) (mg/g), \( K_1 \) is the rate constant of pseudo first order adsorption (min\(^{-1}\)). Values of adsorption rate constant \( K_1 \) for the metal adsorption onto P. spicigera were determined from the straight line plot of \( \log (q_e - q_t) \) against \( t \) (Fig 7). The pseudo first order equation parameters with correlation coefficient are represented in Table II

**Pseudo second order model:**

Pseudo second order equation is expressed as follows:

\[
d\frac{q_t}{dt} = K_2 (q_e - q_t)^2
\]  

Where, \( q_t \) and \( q_e \) are the amount of metal adsorbed at time \( t \) and at equilibrium (mg g\(^{-1}\)) and \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo second order rate constant for adsorption process. The integrated form of equation (4) can be expressed as

\[
t/q = 1/K_2 q_e^2 + 1/q_e t
\]  

The initial sorption rate, \( h \) (mg/g. min), at \( t = 0 \) is defined as

\[
h = K_2 q_e^2
\]  

Where, \( K_2 \) and \( h \) values were determined from the slope and intercept of the plots \( t/q \) against \( t \) (Fig 8).
Adsorption isotherms

In order to describe the adsorption mechanism of low-cost adsorbents used for water and waste water treatment experimental equilibrium data are most frequently modeled by the relationship developed by Langmuir isotherm [22] which is expressed as follows:

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

(7)

Where, \(C_e\) and \(Q_e\) are the residual and metal uptake capacity (mg/L) respectively, \(b\) is the adsorption equilibrium constant (mg/L) related to adsorption and \(q_m\) is the maximum monolayer capacity of the adsorbent (mg/g). A plot between \(C_e/Q_e\) and \(C_e\) is shown in (Fig. 9) and the values of \(q_{max}\) and \(b\) are 18.9 and 0.52 respectively as shown in (Table III).

And the linearized form of Freundlich isotherm [23] can be represented as:

\[ \log q = \log (K_f) + \frac{1}{n} \log C_e \]  

(8)

Where, \(q\) is the amount of metal adsorbed per unit weight of the adsorbent at equilibrium (mg/g), \(C_e\) is the Equilibrium of metal concentration (mg/L), \(K_f\) is the measurement of adsorption capacity (mg g\(^{-1}\)) based on Freundlich isotherm, \(n\) is the adsorption equilibrium constant. The results are shown in Table III and Fig 10.

Application to electroplating wastewater

In order to assess the performance of \(P.\) spicigera for the removal of Cr (VI) biosorption, experiment was conducted using Erlenmeyer flasks containing 100 ml of electroplating wastewater sample. To the wastewater sample 2 g/L of biosorbent was added adjusted to pH 3 at which the maximum biosorption was achieved, with agitation time 120 min in mechanical shaker at a speed of 180 rpm and the resultant solution was analyzed by AAS. The result showed that the biosorption of Cr (VI) from the electroplating wastewater was 65% which was less compare to the aqueous solution. The biosorption efficiency indicates that there is less competition of other ions present in the wastewater for binding sites on \(P.\) spicigera.

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CONCLUSION

The pod of \(P.\) spicigera can be used as low cost biosorbent for the removal of chromium due to its adsorption capacity \(q_{max}\) of 18.9 mg/g in the aqueous solution and also in electroplating wastewater. Maximum biosorption took place at pH 3, contact time 120 min. Pseudo second order fits well in the kinetic model than the pseudo first order model of \(R^2\) value 0.983. The adsorption isotherm was described by Langmuir and Freundlich model. However, Freundlich isotherm shows good agreement with equilibrium data.

REFERENCES

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