Removal of Hexavalent Chromium from Contaminated Waters By Mangifera indica Seed Powder (Biosorption)
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Abstract— Industrialization & urbanization of developing cities in unplanned manner has resulted in long term ecotoxicological impact on environment and human health. Certain metals such as chromium, mercury, lead, cadmium, etc., in wastewater are hazardous to the environment because of their toxicity and pollution impacts on our ecosystem. Among the different heavy metals, hexavalent chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters. The Hexavalent Chromium discharged from various industries as solid or liquid waste has great potential to contaminate drinking water sources due to its more solubility and is one of the most important environmental problems due to its health impacts on human. Water quality regulatory authorities (WHO, BIS, ICMR) have recommended the maximum limit of 0.05 mg/L for drinking purposes. Adsorption is one of the effective techniques for hexavalent chromium removal from wastewater. In the present study, adsorbent has been prepared from Mangifera indica seed powder and studies are carried out for chromium (VI) removal. The parameters investigated in this study are contact time, adsorbent dosage, temperature, variable initial chromium (VI) concentration and pH using Diphenyl carbizide as color developing reagent and taking the absorbance at 540 nm spectrophotometrically. The adsorption process of chromium (VI) is tested with Linear, Langmuir and Freundlich isotherm models. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 23.25 mg/g at a solution pH of 7 having Cr (VI) concentration 50 mg/L and biosorbent dose 1g/L. The adsorption of chromium (VI) was found to be maximum 97.66% at low pH values of 2 having Cr (VI) concentration 50 mg/L and biosorbent dose 1g/L. The contact time of 60 min resulted to the 40.42% adsorption of metal in 50mg/L solution using adsorbent dose of 1g/L and can used for removal of chromium (VI) from the polluted water as a very low cost biosorbent. The scanning electron microscopy carried out shows the change in biosorbent surface significantly on edge of particles after hexavalent chromium adsorption.

Key Words: Hexavalent chromium; Removal; Biosorption, Mangifera indica seed powder,

I. INTRODUCTION
Chromium is an essential element for dietary requirement for number of organisms in trivalent state; however the presence of chromium (VI) in the surface and ground water is hazardous to the environment because of its high toxicity. Due to its high potentiality to contaminate drinking water sources [1], possible human health risk occurs and it finally pollutes our ecosystem. In recent years, increasing awareness of water pollution 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 [2]. The two major sources of contamination are tanneries (trivalent chromium), electroplating and metal finishing industries (hexavalent chromium). Chromium occurs most frequently as Cr (VI) or Cr (III) in aqueous solutions [3]. Both valence of chromium are potentially harmful but hexavalent chromium possesses a greater risk due to its water soluble nature and high penetrating power to enter into the living cells [3], which leads to its carcinogenic properties. Hexavalent chromium, which is primarily present in the form of chromate CrO₄²⁻ and dichromate Cr₂O₇²⁻ depending on pH and redox potential, has significantly higher levels of toxicity than the other valence states [4]. Metals are generally removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation, etc. [5]. However, these methods are cost intensive and are unaffordable for large scale treatment of wastewater which is rich in chromium (VI). Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular [6, 7]. Other commercial adsorbents are recently reported to have been used in industries, although their versatility and adsorption capacity are generally less than those of activated carbon [8]. Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction [9], reduction followed by chemical precipitation [10], adsorption on the activated carbon [11], solvent extraction [12], cementation, freeze separation, reverse osmosis [13], ion-exchange [14] and electrolytic methods [15]. These methods have found limited application because they often involve high capital and operational costs. Biosorption is an effective and versatile method for removing chromium. Natural materials which are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed off without expensive regeneration. Most of the low cost biosorbents have the limitation of low sorptive capacity and thereby for the same degree of treatment, it generates more solid waste (pollutant laden sorbent after treatment), which possess disposal problems. Therefore, there is need to explore low cost biosorbent having high
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contaminant sorption capacity. Several recent publications utilized locally available adsorbents [16, 17] and agricultural byproducts [18] for heavy metal removal. However, the literature is still insufficient to cover this problem and more work and investigations are needed to deal with other locally available and cheap biosorbents to eliminate Cr (VI) discharged by industrial wastage.

Mangifera indica is a very common tree in tropical countries. It is grown mainly for its fruits, pulp and prickle. Mango (Mangifera indica) seed kernel contains inorganic ions, amino acid composition, tannin and fatty acid composition. Mango seed kernel had 44.4% moisture content, 6.0% protein, 12.8% fat, 32.8% carbohydrate, 2.0% crude fiber, 2.0% ash and 0.39% tannin [19]. Literature survey reveals that in most of the peer reviewed journals the adsorption study of Cr (VI) with Mangifera indica seed powder as biosorbent yet has not been investigated, and this is the first such study undertaken by the authors. Based on their efficacy, Mangifera indica seed powder was selected for further study. The effect of pH, contact time, temperature, initial hexavalent chromium concentration, variable adsorbent doses and adsorption equilibrium were investigated. The SEM of adsorbent and chromium adsorbed adsorbent was also carried out for adsorption studies.

II. METHODS & MATERIALS

All the chemicals used were of analytical reagent grade. The standard stock Cr(VI) solutions was prepared by weighing 2.8287 g of Potassium dichromate in one liter double distilled water and it was further diluted to desired concentrations containing 1,2,4,5,6,8,10,20, 40, 50, 60, 80, 100, and 200 mg/L of chromium (VI) in aqueous phase standard solutions. The estimation of hexavalent chromium in the solution at different conditions and time interval was carried out by using Diphenyl carbazide method as per standard methods [20]. Shimadzu UV-VIS Spectrophotometer at 540 nm was used for measurement. The Cr (VI) loadings on sorbents were computed based on on mass balance through loss of metal from aqueous solution. The pH of solution was maintained using 0.5 N HCl and 0.5 N NaOH solutions. The temperature of the solutions was maintained by using temp. regulatory oven. The SEM of the sorbent (Mangifera indica seed powder) and chromium loaded was carried out for absorption studies.

A. Preparation of Biosorbent (Mangifera indica seed powder)

The sorbents used was powder of Mangifera indica seed powder. The material was obtained from local area. There after it was washed, dried and then pulverized in pulverizer and air-dried in the sun for five days. After drying, the powder was kept in air tight plastic bottles. The powdered material was used as such and no pretreatment was given to the materials. The particle size was maintained in the range of 212–300 μm (geometric mean size: 252.2 μm).

B. Screening of Biosorbent

The experiments were carried out in 125 mL borosil conical flasks by agitating a pre-weighed amount of powdered adsorbent of Mangifera indica seed powder with 10 - 100 mL of the aqueous chromium (VI) solutions for a predetermined period at 10-40°C in an ice bath / oven. The biosorbent doses were maintained 1-5 g/L for different experiments. The adsorbent is filtered with whatman filter paper no 41 from aqueous solution for analysis of hexavalent chromium on spectrophotometer. Adsorption isotherm study is carried out with 50 mg/L concentrations of chromium (VI) and the adsorbent dosage of 1-5 g/L. The effect of pH on Cr (VI) biosorption was studied at 30°C with chromium (VI) concentration of 50 mg/L and an adsorbent dosage of 1 g/L. The effect of adsorbent dosage is studied by varying the adsorbent amount from 1 g/L to 5 g/L with chromium (VI) concentration of 50 mg/L. The effect of temperature varying from 10- 40°C was studied at Cr (VI) concentration of 50 mg/L and biosorbent dose of 1 g/L. The time duration 10-300 min was studied on Cr (VI) concentration of 5 mg/L and biosorbent dose of 1 g/L.

The equilibrium concentration of free chromium (VI) ions at different experimental conditions with suitable time interval in the solution was determined by filtering the adsorbent loaded with hexavalent chromium through whatman filter paper followed by developing a purple-violet color in the filtrate with 1, 5-diphenyl carbazide in acidic medium as complexing agent spectrophotometrically. The absorbance of the purple-violet colored solution was read at 540 nm after 20 min.

III. RESULTS AND DISCUSSION

In the present study, Mangifera indica seed powder has been used for chromium (VI) removal from aqueous solutions. Table-1 shows the adsorbent capacity of various adsorbents.

The comparatively study with other non-conventional adsorbents reveals that present study of adsorbent prepared from Mangifera indica seed powder has better adsorption capacity in many cases (maize cob, sugar cane bagasse, biomass residual slurry, Fe (III)/Cr (III) hydroxide, waste tea, walnut (shell); comparable adsorption capacity with palm pressed-fibers, Mangifera indica bark and lower adsorption capacity with activated carbon, Syzygium cumini bark, Ficus racemosa bark & saw dust for chromium (VI) ions [15, 21-29].

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbent Capacity (mg/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walnut shell</td>
<td>1.33</td>
<td>[25]</td>
</tr>
<tr>
<td>Fe (III)/Cr (III) hydroxide</td>
<td>1.43</td>
<td>[26]</td>
</tr>
<tr>
<td>Waste tea</td>
<td>1.55</td>
<td>[25]</td>
</tr>
<tr>
<td>Biomass residual slurry</td>
<td>5.87</td>
<td>[15]</td>
</tr>
<tr>
<td>Tamarind seeds</td>
<td>11.08</td>
<td>[24]</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>13.4</td>
<td>[22]</td>
</tr>
<tr>
<td>Maize cob</td>
<td>13.8</td>
<td>[22]</td>
</tr>
<tr>
<td>Palm pressed-fibers</td>
<td>15.0</td>
<td>[23]</td>
</tr>
<tr>
<td>Mangifera indica</td>
<td>19.64</td>
<td>[28]</td>
</tr>
<tr>
<td>Mangifera indica seed powder</td>
<td>23.25</td>
<td>[Present Study]</td>
</tr>
<tr>
<td>Ficus racemosa bark</td>
<td>25.9</td>
<td>[29]</td>
</tr>
<tr>
<td>Syzygium cumini bark</td>
<td>31.51</td>
<td>[27]</td>
</tr>
<tr>
<td>Sawdust</td>
<td>39.7</td>
<td>[22]</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>57.7</td>
<td>[21]</td>
</tr>
</tbody>
</table>

Table 1: Summary of adsorbent capacity of various adsorbents
A. Effect of Contact Time on Chromium (VI) Adsorption
The effect of contact time up to 300 min. on chromium VI adsorption was studied using biosorbent dose of 1 g/L and hexavalent Chromium concentration of 50 mg/L. (Fig. -1). The extraction process was carried out with standard Cr (VI) 100 mL solution of 50 mg/L in 125 mL conical flask with biosorbent dose of 1g/L and the concentration of hexavalent chromium in the solution was recorded by filtration through whatman filter paper followed by development of color using Diphenyl carbazide at 540 nm in time interval of 10, 20, 30, 60, 120, 180, 240 and 300 minutes. Most of the adsorption takes place in first hour of contact and longer contact time has negligible effect on extraction of chromium (fig-1).

B. Effect of Increasing Concentration of Cr (VI) on Adsorption
Standard Cr (VI) solutions of 100 mL having initial concentration of 10, 20, 30, 40 and 50 mg/L were treated with biosorbent 0.1 g dose in each solution. The concentration of Cr (VI) in the solution was determined using the standard methods. The percentage adsorption increases up to 94.8 for 10 mg/L Cr (VI) concentration there after it decreases (figure-2).

C. Effect of Temperature on Cr (VI) biosorption
The 100 mL samples of 50 mg/L hexavalent chromium concentration in 125 mL conical flasks were treated with 0.1, 0.2, 0.3, 0.4, 0.5 g of Biosorbent (Mangifera indica seed powder) maintained at 10, 20, 30 & 40 °C. The solutions were kept for 120 min. with gentle shaking at periodical intervals and the concentration of Cr (VI) was measured in the solution after filtering through Whatman filter paper by developing the colour using Diphenyl carbazide at 540 nm spectrophotometrically. The percentage biosorption of Cr (VI) was found maximum at 40 °C and minimum at 10 °C showing an increasing trend with temperature. (Figure-3)

D. Effect of pH on Cr (VI) biosorption
The experiments using 100 mL of 50 mg/L Cr(VI) solutions for 60 min time and adsorbent dose of 0.1 g were carried out at pH 2, 4, 7, 10 and 12 and the biosorption of Cr(VI) is depicted in figure-4. The acidic medium (pH-2) has been found to show maximum biosorption up to 97% of initial chromium (VI) which decreases to 42% at neutral (pH-7) and further increases to 63% in basic medium (pH-12). (Figure-4)

E. Effect of Biosorbent Concentration on Cr (VI) Adsorption
The 100 mL samples of 50 mg/L hexavalent chromium concentration in 125 mL conical flasks were treated with 0.1, 0.2, 0.3, 0.4, 0.5 g of Biosorbent (Mangifera indica seed powder) maintained at room temperature 25 °C. The solutions were kept for 120 min. with gentle shaking at periodical intervals and the concentration of Cr (VI) was measured in the solution after filtering through Whatman filter paper and developing the colour using Diphenyl carbazide at 540 nm spectrophotometrically. The percentage biosorption of Cr (VI) was found maximum with biosorbent
dose of 0.5 g and minimum at 0.1 g showing an increasing trend with increasing biosorbent doses. (Figure-5)

F. Adsorption Isotherms

The equilibrium of the sorption is one of the important physico-chemical aspects for the evaluation of the sorption process as a unit operation. The sorption isotherm studies are conducted by varying adsorbent dosage of 1 to 5 g/L and the initial concentration of chromium (VI) from 50 mg/L and maintaining the temp. The adsorption isotherm (qe versus Ce) shows the equilibrium between the concentration of chromium (VI) in the aqueous solution and its concentration on the solid (mass of chromium (VI) per unit mass of Mangifera indica seed powder). It is evident that adsorption capacity increases with increasing equilibrium chromium (VI) concentrations. Fig.- 6 & 7 show that the adsorption capacity increases rapidly from 0 to 20.29 mg/g for the equilibrium concentration of 0 to 9.71 mg/L. Further a gradual increase in adsorption capacity is observed with the increase in equilibrium concentration and it reaches up to 23.25 mg/g for the equilibrium concentration of 26.75 mg/L. In order to model the sorption behavior, adsorption isotherms have been studied. The adsorption process of chromium (VI) is tested with Langmuir and Freundlich isotherm models. Langmuir and Freundlich equations are given in equation (1) and (2), respectively.

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

[where \( b \) - Langmuir constant (L/mg), \( C_e \) - Concentration of Cr (VI) at equilibrium (mg/L), \( q_e \) - Amount of Cr(VI) adsorbed by the adsorbent (mg/g) and \( q_m \) - Maximum adsorption capacity (mg/g)]

\[
\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e
\]

[where \( K_F \) - Freundlich constant (mg/g) and \( n \) - Freundlich constant (L/mg)]

The isotherm data has been linearized using the Langmuir equation and shown in Fig. 8 to 11. The regression constants are tabulated in Table-2. The high values of correlation coefficient (\( R^2 = 0.996, 0.998, 0.935, 0.994 \)) indicated a good agreement between the parameters. The constant \( q_m \), which is a measure of the adsorption capacity to form a monolayer, can be as high as 23.25 mg/g at pH 7. The constant \( b \), which denotes adsorption energy, varies from 0.041 to 0.130 L/mg. The same data also fitted with the Freundlich equation and shown in Fig. 12 & 13. The regression constants are listed in Table-2. The values of correlation coefficient (\( R^2 = 0.989, 0.961 \)) showed that the data confirm well to the Freundlich equation also.

<table>
<thead>
<tr>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constants</strong></td>
<td><strong>Corr Coef (R^2)</strong></td>
</tr>
<tr>
<td>( q_m ) (mg/g)</td>
<td>( b ) (L/mg)</td>
</tr>
<tr>
<td>23.25</td>
<td>0.041</td>
</tr>
<tr>
<td>21.74</td>
<td>0.120</td>
</tr>
<tr>
<td>48.83</td>
<td>0.046</td>
</tr>
<tr>
<td>22.68</td>
<td>0.130</td>
</tr>
</tbody>
</table>

Table. 2: Isotherm constants for adsorption of chromium (VI) on Mangifera indica seed powder.
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**G. Scanning Electron Microscopy of Mangifera indica seed and biosorbent with Cr (VI)**

The biosorbent Mangifera indica seed powder and Chromium (VI) loaded was studied using Scanning Electron Microscopy and the same is given in below figure 14 & 15. The microscopy shows that most of the hexavalent chromium is adsorbed on the corners of the biosorbent particles (fig-15).

**IV. CONCLUSIONS**

Following conclusions are made based on present study and scientific information derived from literature:

- Adsorbent prepared from Mangifera indica seed can be used for removal of chromium (VI) from aqueous solutions due to its significantly remarkable higher biosorption capacity of 23.25 mg/g at 30 °C.
- The adsorption rate of chromium (VI) on the adsorbate prepared from Mangifera indica seed in the present study from aqueous solutions (50 mg/L solution and adsorbent dose of 1 g/L) is maximum for the first hour (40%) thereafter it increases very slowly up to 45% in the next four hours. Since maximum adsorption of chromium (VI) on Mangifera indica seed powder takes place within first hour so the equilibrium time is found to be 60 min. in the present experimental conditions.
- The adsorption process of chromium (VI) can be described by Langmuir isotherm and Freundlich isotherm models. However, Langmuir isotherm model shows a good agreement with the equilibrium data.
- Adsorption of chromium (VI) on Mangifera indica seed yielded maximum adsorption capacity of 23.25 mg/g at...
solution pH of 7 and temperature 30 °C.

- Removal of chromium (VI) increases with increase of adsorbent dosage.
- The maximum adsorption of chromium (VI) took place in the pH range 1-3.
- The increase in temperature increases the biosorption up to 40 °C, showing the chemisorptions behavior.
- The maximum adsorption takes place in 60 minutes and further increase in duration of contact time has negligible effect.
- The adsorption efficiency is graphed in following figure -16

![Fig-16 Adsorption Efficiency of Different Biosorbents with Cr(VI)](image)

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