Equilibrium and kinetic study on chromium (VI) removal from simulated waste water using gooseberry seeds as a novel biosorbent

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ABSTRACT: Gooseberry seed (Phyllanthus acidus) was used as an adsorbent to determine its feasibility for the removal of chromium (VI). Various parameters such as pH, temperature, contact time, initial metal concentration and adsorbent dosage were investigated to determine the biosorption performance. Equilibrium was attained within 60 minutes and maximum removal of 96% was achieved under the optimum conditions at pH 2. The adsorption phenomenon demonstrated here was monolayer represented by Langmuir isotherm with $R^2$ value of 0.992 and the Langmuir constants k and $q_0$ was found to be 0.0061 (L/mg) and 19.23 (mg/g). The adsorption system obeyed Pseudo second order kinetics with $R^2$ value of 0.999. The results of the present study indicated that gooseberry seed powder can be employed as adsorbent for the effective removal of hexavalent chromium economically.

Keywords: Biosorption, Cr(VI), Equilibrium, Gooseberry seed, Isotherm, Kinetics, Removal

INTRODUCTION

Rapid industrialization and urbanization have resulted in exponential discharge of industrial effluents and toxic heavy metals in to aquatic and terrestrial ecosystem (Das et al., 2007; 2013). Chromium metal, which is currently explored in this research work, is present mainly in leather tanning, precious metal mining and electroplating industrial effluents, according to US EPA, Chromium is considered to be the topmost priority toxic pollutant. Chromium metal in its natural form is found to exist in two states: Cr(III) and Cr(VI). Hexavalent chromium is 100 times more toxic than trivalent chromium and due to its toxicological and carcinogenic consequences, it is likely to cause detrimental health hazards (Rao and Parbhakar et al., 2011). According to AWWA permissible level of Cr(VI) ion in surface and portable water are 0.1 and 0.05mg/L respectively (APHA, 2005). Thus, it becomes top priority to make effluents free from Cr(VI) before releasing into the environment.

Common technique involved in the handling of heavy metal remediation includes, precipitation (both physical and chemical), ion exchange (resin based), filtration achieved via physical means, chemical based coagulation, flocculation, and other electrochemical methods (Orhan and Buyukgungur, 1993). The major hurdles in adapting these techniques includes high operational cost coupled with higher energy requirements, further, generation of huge sludge deposition and finally operational complexities. Thus, the alternative of adsorption as a remediation tool has been considered the best and it is further augmented with it being economical and environmental friendly technique (Salman et al., 2014). Many agricultural waste residues had been extensively studied in the past to determine their adsorption efficiency. Bioresource material like agriculture waste residuals, showing maximal adsorption capabilities and metal selectivity had been...
suggested as suitable biosorbent for heavy metal sequestration (Nguyen et al., 2013). Currently locally available agricultural waste residues are an automatic choice for remediation of heavy metals, they are also being considered as an important source of biosorbents due to the presence of certain functional groups such as hydroxyl, ester, amino, carboxyl, carbonyl, sulphhydryl, and phosphor group to which heavy metal bind. In this context, Gooseberry seed powder (Phyllanthus acidus), a novel biosorbent was examined for Cr(VI) binding efficiency. In the present study, various parameters which influence Cr(VI) removal such as pH, initial metal ion concentration, contact time and adsorbent dosage were investigated in a batch mode. Analytical techniques such as FTIR and SEM were employed for biosorbent characterization. FTIR analysis was employed to determine the active site responsible for biosorption based on the changes in vibrational frequencies of the functional groups. The surface morphology and the porosity of the biosorbent were investigated by SEM analysis. Investigations on equilibrium isotherm and adsorption kinetics were also carried out to understand the adsorption mechanism. The present work was carried out at Coimbatore during the period of December 2014 to February 2015.

MATERIALS AND METHODS

Biosorbent material

Gooseberry seeds were procured locally (Coimbatore, India). The seeds were washed under running tap water and were subjected to drying in hot air oven at an optimum temperature of 40°C. Then the seeds were ground and sieved. The finely powdered biosorbent was subjected to washing. After washing with distilled water, the mixture was filtered and dried at 50°C for a period of 1 h. The dried powder was stored in an air tight container to prevent moisture. The dried powder was used as a biosorbent for the experiment.

Batch studies

The maximal adsorption efficiency of biosorbent was determined by varying several parameters which influence the adsorption phenomenon, such as pH, contact time, adsorbent dosage and initial metal concentration by fixing the volume of metal solution to 100ml. After agitating for 30 min in a temperature controlled orbital shaker at 120rpm, the solution was centrifuged. The residual concentration of chromium present in the supernatant was determined spectrophotometrically using 1, 5 Diphenyl carbazide reagent as a complexing agent at 540 nm (APHA method 3500-Cr).

Chromium removal analysis

Chromium removal was estimated using 1,5 Diphenyl carbazide as a complexing agent spectrophotometrically. Different standards containing less than 100 mg/L (20, 40, 60, 80, and 100) were prepared and maintained at pH less than 2. To 10 ml of standard, 0.2 ml of diphenyl carbazide was added as a complexing agent. The solution was incubated until red violet color was developed. The absorbance was noted at 540 nm using visible spectrometer (Systronics-106). A blank was prepared for Cr (VI) analysis. The amount of chromium present in the sample was determined from calibrated curve according to the standard method (APHA method 3500-Cr).

Removal efficiency

The percentage of Chromium removal (R %) was determined using the below equation:

$$\text{Removal efficiency (R %)} = \frac{C_i - C_0}{C_i} \times 100$$

where $C_i$ and $C_0$ represents the initial and final concentration of chromium metal in mg/L.

Adsorption isotherm

Adsorption isotherm aids in the evaluation of adsorption efficiency of any adsorbent and also facilitate in quantifying the correlation of equilibrium with the amount of adsorbate present in the solution and relate the quantum of adsorbate adsorbed in to any bioresource material at a given temperature.

Adsorption capacity is given by the empirical relation:

$$q_e = \frac{(C_i - C_0)}{m} \times \frac{V}{m}$$

Where $q_e$ is the adsorption capacity (mg/g), $C_i$ and $C_0$ are initial and final metal concentration (mg/L), $m$ is the mass of the adsorbent (g) and $V$ is the volume of the metal solution (L). In the present study, adsorption of Cr(VI) with the help of gooseberry seed powder was investigated by employing various adsorption isotherms.
Langmuir adsorption isotherm

This model is based on the assumption that metal uptake takes place on the homogeneous surface by monolayer adsorption. It involves uniform energies of adsorption. Langmuir adsorption isotherm is represented by the empirical equation:

\[
\frac{1}{q} = \frac{k}{q_0} + \frac{1}{q_y} \tag{3}
\]

Where \( q \) is the amount of solute adsorbed per amount of adsorbent (mg/g), \( K \) (L/mg) and \( q_0 \) (mg/g) are the Langmuir constants related to energy of adsorption and maximum monolayer capacity and \( y \) is the solute concentration in the solution (mg/L). By plotting \( 1/q \) versus \( 1/y \), Langmuir parameters were obtained (Langmuir, 1917).

Freundlich adsorption isotherm

Freundlich adsorption isotherm is theorized, that metal uptake takes place on the heterogeneous surface of an adsorbent by multilayer adsorption. It involves non uniform energies of adsorption. Freundlich adsorption isotherm is given by the empirical equation:

\[
\ln q_e = \ln k + \frac{1}{n} \ln y \tag{4}
\]

Where \( q_e \) is the amount of solute adsorbed per amount of adsorbent (mg/g), \( y \) is the solute concentration in the solution (mg/L), \( K \) and \( n \) are the Freundlich constants related to adsorption capacity and intensity. By plotting \( \ln q_e \) versus \( \ln y \), Freundlich constants \( k \) and \( n \) were obtained. It also determines the heterogeneity of surface pore distribution and the value of \( n \) indicates the favorability of adsorption (Freundlich, 1906).

Temkin adsorption isotherm

Temkin model is based on the concept that the heat of adsorption of all molecules decreases linearly with coverage due to adsorbate-adsorbent interaction. It involves uniform distribution of binding energies up to some maximum binding energy.

Temkin adsorption isotherm model is represented by the linearized form of equation:

\[
q_e = B_T \ln A_T + B_T \ln y \tag{5}
\]

Where, \( B_T = (RT)/b_T \), \( T \) is the absolute temperature in Kelvin and \( R \) is the universal gas constant. The constant \( b_T \) is related to heat of adsorption (J/mol), \( A_T \) is the equilibrium binding constant (1/L/min). By plotting \( q_e \) versus \( \ln y \), Temkin constants such as \( B_T \) and \( A_T \) were determined (Temkin and Pyzhev, 1940).

Adsorption kinetics

Studies on adsorption kinetics had been carried out to describe adsorption mechanism and diffusion process. The generated data were tested using Pseudo first order and second order kinetics equation.

Pseudo first order / lagerrgen kinetic model

This model was derived based on adsorption capacity. The overall adsorption rate is directly proportional to the driving force i.e., the difference between the initial and equilibrium metal concentration (Qu et al., 2009). The equation can be represented as follows:

\[
\frac{dq}{dt} = K_i \left( q_e - q_t \right) \tag{6}
\]

Where \( q_e \) is the amount of solute adsorbed at equilibrium per unit mass (mg/g), \( q_t \) is the amount of solute adsorbed at any time \( t \) (mg/g), \( K_i \) is the pseudo first order rate constant (1/min). Integrating the above equation under boundary conditions yields the following equation:

\[
\log (q_e - q_t) = \log q_e - \frac{K_i t}{2.303} \tag{7}
\]

Pseudo second order kinetic model

According to this model, the driving force \( (q_e - q_t) \) is proportional to the available fraction of active site. The equation can be expressed as follows:

\[
\frac{dq}{dt} = K_2 \left( q_e - q_t \right)^2 \tag{8}
\]

Integrating under boundary conditions such as \( q=0 \) to \( q>0 \) and \( t=0 \) to \( t>0 \) and further simplification yields the following equation:

\[
\frac{t}{q_e} = \frac{1}{V_0} + \frac{1}{V_o q_e} \tag{9}
\]

Where \( V_0 = k_2 q_e^2 \), \( V_o \) is the initial adsorption rate (mg/gmin) and \( k_2 \) is the pseudo second order rate constant (g/mg/min). Adsorption parameters such as \( V_0 \), \( q_e \), \( k_2 \) can be determined by plotting \( t/q_e \) versus \( t \) (Ho and McKay, 1999).
RESULTS AND DISCUSSION

**FT-IR analysis**

To understand the capability of gooseberry seeds as an efficient adsorbent for chromium removal, FT-IR analysis was carried out to determine the functional groups present in the adsorbent based on the changes in the vibrational frequencies. The functional groups representing each peaks and stretch are given in the Table 1. The shift in the peak from 3317.57 to 3417.66 \(1/cm\) indicated that stretching of -OH group was responsible for the binding of Cr(VI) ions onto the adsorbent. It was found that C=O, C-H, C-N stretch, N-H and C-H bend were also responsible for the effective removal of Cr(VI) ions as it can be elucidated from Fig. 1. Similar results were obtained by Muthukumaran and Beulah, (2010), where stretching of O-H group was responsible for the adsorption of Cr(VI) using chemically activated Syzygium jambolanum nut carbon.

**SEM analysis of Gooseberry seed powder**

Metal adsorption capacity of any biosorbent material can be comprehended by surface morphology analysis using SEM, where presence of many pores indicates the possibility of higher metal sorption. The Surface morphology of gooseberry seed powder (GSP) was found to be highly porous with different shape and size (Fig. 2). The SEM micrograph taken after sorption showed irregularities and decrease in pore size. The formation of white layer on the surface of the sorbent indicates that the sorbent is loaded with Cr(VI) ions (Aravind et al., 2013).

<table>
<thead>
<tr>
<th>IR Peak</th>
<th>Before adsorption (1/cm)</th>
<th>After adsorption (1/cm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3317.57</td>
<td>3417.66</td>
<td>-OH Stretch</td>
</tr>
<tr>
<td>2</td>
<td>2862.36</td>
<td>2854.65</td>
<td>CH Stretch</td>
</tr>
<tr>
<td>3</td>
<td>1728.22</td>
<td>1720.50</td>
<td>C=O Stretch</td>
</tr>
<tr>
<td>4</td>
<td>1527.62</td>
<td>1519.91</td>
<td>N-H Bend</td>
</tr>
<tr>
<td>5</td>
<td>1049.28</td>
<td>1058.99</td>
<td>C-N Stretch</td>
</tr>
<tr>
<td>6</td>
<td>609.51</td>
<td>617.22</td>
<td>C-H Bend</td>
</tr>
</tbody>
</table>
Studies on effect of pH

pH is the most important parameter in heavy metal biosorption. At aqueous phase, Cr(VI) exist in several anionic forms such as chromate CrO₄²⁻ (pH>6), dichromate Cr₂O₇²⁻ and HCrO₄⁻ (pH:1-6). It is observed from Fig. 3 that the removal percentage decreases with an increase in pH from 2 to 7. Maximum removal was obtained at pH 2 indicating the influence of pH in protonation and deprotonation of adsorbent. As the pH is lowered, the surface of the adsorbent becomes protonated and most of the chromium exists as anionic species. Therefore large number of protons in the adsorbent could easily coordinate with the metal ions present in the solution through electrostatic interaction, whereas the removal percentage sharply decreases with an increase in pH from 2 to 7 due to the deprotonation.
of adsorbent. The adsorbent surface becomes negatively charged and there exists electrostatic repulsion between anionic form of chromium and adsorbent. Similar results were obtained with Eucalyptus bark (Sarin and Pant, 2006).

**Effect of adsorbent dosage**

Adsorbent dosage plays a major role in adsorption process. From the result, as shown in the Fig. 4, it is understood that, with an increase in adsorbent dosage from 0.1 to 0.5 g, there exists an increase in percentage removal from 51 to 92% and the maximum removal was attained at the adsorbent dosage of 0.5 g. The observed trend may be due to greater availability of surface area and functional groups at higher adsorbent dosage (Suresh and Babu, 2008). As a result, electrostatic interaction occurs between the functional groups present in the active site of the adsorbent and the metal ions present in the solution, similar trends were reported by Devi et al., (2012).

**Effect of contact time**

Percentage removal of Cr(VI) ions was measured as a function of time to establish an appropriate contact time between adsorbent and adsorbate. 

**Effect of initial metal concentration**

The experiments were performed by varying the initial metal concentration from 20 to 100 mg/L, while the contact time was varied from 15 to 60 minutes at a constant adsorbent dosage of 0.5 g/100 ml at pH 2 and an agitation speed of 120 rpm. Cr(VI) removal as a function of contact time and initial metal concentration is given in the Fig. 6. From the Fig. 6, it is clear that with an increase in metal concentration from 20 to 100 mg/L, removal percentage decreases from 97 to 88 with an increase in adsorption capacity. The maximum removal was obtained within 15 minutes, after which there was
Fig. 5: Effect of contact time with 100mg/L metal concentration, 0.5g/100ml adsorbent dosage, and speed of 120 rpm at pH 2

Fig. 6: Effect of initial metal concentration with adsorbent dosage of 0.5g/100ml and speed of 120rpm at pH 2

negligible removal since the surface of the sorbent gets exhausted after the formation of one layer thickness of metal ions and then metal uptake rate is controlled due to the transport of ions from exterior to interior site of the adsorbent. Similar trend was observed with ternary biopolymeric microspheres.
Chromium removal using gooseberry seed powder

![Graph A: Langmuir isotherm](image)

\[ y = 0.117x + 0.051 \]
\[ R^2 = 0.992 \]

![Graph B: Freundlich isotherm](image)

\[ y = 0.4937x + 1.7416 \]
\[ R^2 = 0.9907 \]

![Graph C: Temkin isotherm](image)

\[ y = 4.484x + 5.847 \]
\[ R^2 = 0.990 \]

Fig. 7: (A; B; C): Equilibrium isotherms for Cr(VI) removal on gooseberry seed powder (pH 2, temperature 37°C, metal concentration 100 mg/L)

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The data generated due to effect of initial metal concentration helps in determining the equilibrium concentration ($C_e$), adsorption capacity ($q_e$), metal uptake rate and kinetic characteristics.

**Equilibrium isotherms**

Isotherms have been used to describe the equilibrium relationship between the amount of solute that is present in the solution and adsorbent (Aravind et al., 2013). In the present study, Langmuir, Freundlich and Temkin models were employed. The best equilibrium model was determined based on correlation coefficient. Fig. 7.A-7.C represents the investigations over various adsorption isotherms on Cr(VI) removal. Under the optimal conditions, the metal adsorption equilibrium was very well represented by Langmuir isotherm which accounts for existence of monolayer adsorption on homogeneous surface. Langmuir constants $q_0$ and $k$ evaluated from the slope and intercept are 19.23 (mg/g) and 0.0061 (L/mg) respectively with the correlation coefficient of 0.992. Higher $R^2$ value indicates the strong binding of Cr(VI) ions to the adsorbent. Gooseberry seed powder was found to have better adsorption capacity which indicates the favorability of Langmuir isotherm as shown in the Fig. 7.A. The slope and the intercepts evaluated from the Figs. 7A, B, C are given in Table 2.

**Adsorption kinetics**

Studies on adsorption kinetics were carried out in order to determine the metal uptake rate. The effect of initial metal concentration was investigated to determine the best kinetic model. Pseudo first order kinetics model were applied by plotting log ($q_e$-$q_t$) versus time as shown in the Fig. 8.A. The obtained $R^2$ value was found to be 0.994 and the results obtained were found to be in agreement with the results obtained from the biosorption of Cr(VI) using the husk of Bengal gram (Ahalya et al., 2005).

Pseudo second order kinetics model were applied by plotting $t/q_t$ versus time. From the Fig. 8.B, $R^2$ Value was observed to be high (0.999) which implies adsorption mechanism obeys Pseudo Second order. Various constants determined from kinetics study are given in the Table 3. The results obtained were similar when granular activated carbon was used as an adsorbent (Gholipour et al., 2011).

**Comparison of gooseberry seeds as an adsorbent**

In the present study the performance of gooseberry seeds as an effective and economical adsorbent material with other adsorbent available in

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>$K$ value</th>
<th>$n$ value</th>
<th>$K$ value</th>
<th>$q_0$ value</th>
<th>$A_T$ Value</th>
<th>$B_T$ Value</th>
<th>$R^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$K$ value</td>
<td>5.47(mg/g(L/mg)$^{1/n}$)</td>
<td>2.482</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.990</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$K$ value</td>
<td>0.0061(L/mg)</td>
<td></td>
<td>19.23(mg/g)</td>
<td></td>
<td></td>
<td></td>
<td>0.992</td>
</tr>
<tr>
<td>Temkin</td>
<td>$A_T$ Value</td>
<td>5.9(L/mg)</td>
<td></td>
<td>5.118(J/mol)</td>
<td></td>
<td></td>
<td></td>
<td>0.990</td>
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</table>

<table>
<thead>
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<th>Parameters</th>
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<th>$q_e$ Value</th>
<th>$K_2$ Value</th>
<th>$q_e$ Value</th>
<th>$R^2$</th>
</tr>
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<tr>
<td>Pseudo first order</td>
<td>$K_1$ Value</td>
<td>0.0483</td>
<td>18.57</td>
<td></td>
<td></td>
<td>0.994</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td>$K_2$ Value</td>
<td>0.0184</td>
<td>20.83</td>
<td></td>
<td></td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 2: Constants evaluated from various isotherms

Table 3: Constants evaluated from kinetics study
Table 4: Comparison of gooseberry seeds on chromium adsorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption Capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste tea</td>
<td>1.55</td>
<td>Orhan et al., (1993)</td>
</tr>
<tr>
<td>Formaldehyde modified saw dust</td>
<td>3.60</td>
<td>Baral et al., (2006)</td>
</tr>
<tr>
<td>Paper mill sludge</td>
<td>7.40</td>
<td>Calace et al., (2002)</td>
</tr>
<tr>
<td>Treated saw dust of Indian rosewood</td>
<td>10</td>
<td>Karthikeyan et al., (2005)</td>
</tr>
<tr>
<td>Coconut shell carbon</td>
<td>10.88</td>
<td>Karthikeyan et al., (2005)</td>
</tr>
<tr>
<td>Tamarind seeds</td>
<td>11.08</td>
<td>Suresh et al., (2006)</td>
</tr>
<tr>
<td>Sugarcane bagasse</td>
<td>13.4</td>
<td>Karthikeyan et al., (2005)</td>
</tr>
<tr>
<td>Rice bran</td>
<td>12.34</td>
<td>Singh et al., (2011)</td>
</tr>
<tr>
<td>Rice straw</td>
<td>12.17</td>
<td>Singh et al., (2011)</td>
</tr>
<tr>
<td>Hyacinth roots</td>
<td>15.28</td>
<td>Singh et al., (2011)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>11.39</td>
<td>Singh et al., (2011)</td>
</tr>
<tr>
<td>Neem bark</td>
<td>19.60</td>
<td>Singh et al., (2011)</td>
</tr>
<tr>
<td>Neem leaves</td>
<td>15.95</td>
<td>Singh et al., (2011)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>18.69</td>
<td>Singh et al., (2011)</td>
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<tr>
<td>Beech saw dust</td>
<td>16.1</td>
<td>Karthikeyan et al., (2005)</td>
</tr>
<tr>
<td>Hazelnut shell activated carbon</td>
<td>17.70</td>
<td>Cimino et al., (2000)</td>
</tr>
<tr>
<td>Gooseberry seed</td>
<td>19.23</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Fig. 8: (A; B): Adsorption kinetics of Cr(VI) removal on gooseberry seed powder at metal concentration of 100 mg/L at 37°C

\[ y = -0.0214x + 0.6295 \quad R^2 = 0.994 \]

\[ y = 0.0483x + 0.1253 \quad R^2 = 0.9997 \]
literature, on its ability to remove the chromium metal from the synthetic effluent. The gooseberry seeds were found to be effective and better than many adsorbent used for chromium removal (Table 4).

CONCLUSION
The gooseberry seed powder was found to be a better adsorbent based on its efficiency in the removal of chromium, with 96% efficiency, under optimum condition like pH of 2, dosage of 0.5g and equilibrium attained within 60 minutes. Langmuir isotherm was found to be the best fit with an adsorption capacity of 19.23 mg/g and the adsorption mechanism observed Pseudo second order kinetics. Hence the gooseberry seed powder can be claimed as good for removal of chromium from industrial effluents.

CONFLICT OF INTEREST
The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES


Chromium removal using gooseberry seed powder

How to cite this article: (Harvard style)