Equilibrium and Kinetic Parameters Determination of Cr(VI) Adsorption by Hogla Leaves (Typha elephantina Roxb.)

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Abstract

Equilibrium and kinetic parameters of Cr(VI) adsorption on Hogla leaves (Typha elephantina Roxb.) were determined in a batch process. Batch adsorption experiments were carried out as a function of pH, adsorbent dosage and initial metal ion concentration. Maximum metal adsorption was found to be 30.616 mg/g for initial Cr(VI) concentration of 400 ppm and optimum adsorbent dose of 10 g/L at 25°C. Compared to the Freundlich isotherm model, the Langmuir and Temkin model best fit the experimental data (R²>0.995). Batch adsorption models, based on the assumption of the pseudo first-order and pseudo second order mechanism were applied to examine the kinetics of the adsorption. The results of this study demonstrated that the pseudo-second order model was more suitable than pseudo-first order model for adsorption of Cr(VI) by Hogla leaves. At 25°C, with a contact time of 360 minutes and agitation rate of 180 rpm, the potential of Cr(VI) removal by Hogla leaves from industrial effluent was also investigated at optimized condition of pH 2.0, initial metal ion concentration of 400 ppm and adsorbent dose of 10 g/L and removal efficiency was found to be 44.8%.

Keywords: Hogla leaves; Adsorption; Adsorbent; Cr(VI)

Introduction

Heavy metals such as mercury, lead, cadmium, copper, chromium and nickel are extremely toxic even in minute quantities [1]. Chromium is more abundant in earth's crust and is widely used in electroplating, leather tanning, metal finishing and chrome plate preparation. It exists in two stable oxidation states Cr(III) and Cr(VI). Cr(VI) is of particular concern as because of its high toxicity, it may cause many adverse effects on human health such as epigastric pain, hemorrhage, severe diarrhea, vomiting, nausea, dermatitis by skin contact, ulcer, lung cancer and tissue necrosis. The allowable limit of Cr(VI) for the discharge of inland surface water is 0.1 ppm [2]. Therefore, it has become an essential to remove Cr(VI) from industrial waste water before discharging it into water body or on to land.

Conventional technology for the removal of metal ions from aqueous solution includes chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultrafiltration, etc. which have their own inherent limitations such as incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [3]. Adsorption is a physiochemical wastewater treatment process, which is gaining prominence as a means of producing high-quality effluents, which are low in metal ion concentrations. Natural materials which are available in large quantities or certain waste products from industries or agriculture have drawn attentions to researchers to be used as inexpensive adsorbents. Some of these are tea factory waste [4], eucalyptus bark [5], Hevea brasiliensis sawdust [6], beech sawdust [7], the agricultural byproduct of Lentinus edodes [8], non-living microbial biomass [9], fresh water algae [10], clay mineral [11], phosphate rock [12], etc. Among these adsorbents the ability of biological materials to adsorb metal ions has drawn considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment [4].

Hogla, local name for a bush-like small plant, Typha elephantina Roxb. of family Typhaceae. The plants look like grasses and may attain heights from two to five meters. The leaf blades are flattened and composed of aerenchymatous spongy tissue [13]. In Bangladesh Hogla is frequently seen in the North-Eastern part of the country especially along the banks of rivers and canals. Hogla grass is extensively used to make mats, baskets, ropes and different kinds of handicrafts. Beside these house hold applications, another application of Hogla leaves as low cost adsorbents can be explored. In many adsorption studies, activated carbon derived from many agricultural sources are being used as an adsorbent. Low cost and availability of Hogla leaves might be a suitable alternative of activated carbons. The objective of this study is to determine the equilibrium and kinetic parameters of Cr(VI) adsorption onto dried Hogla leaves by fitting the experimental data into various mathematical models such as Langmuir’s, Freundlich’s and Temkin’s models for sorption isotherms and pseudo first- and second- order rate equations for description of kinetics. And also to investigate the potential of Hogla leaves for removal of Cr(VI) from industrial effluents.

Materials and Methods

Adsorbents

Hogla leaves were collected from a village of Jessore, Bangladesh. After collection of dried leaves, it was then categorized into four subgroups NW (Normal Washed), NWP (Normal Washed Powder), AW (Acid Washed) & AW (Acid Washed Powder). NW category

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adsorbent was prepared by washing followed by drying. NWP was prepared by washing followed by drying and then grinding. AW was prepared by washing with 5% hydrochloric acid solution. After that it was dried. AWP was prepared by washing with 5% hydrochloric acid solution followed by drying and grinding. All washing was done by deionized water. Drying was carried out in a drying oven at 100–105°C.

**Preparation of Cr(VI) solution**

500 ppm of Cr(VI) solution was prepared by dissolving 1.414 g of potassium dichromate (K₂Cr₂O₇) in 1 L deionized water. Experimental solutions at the desired concentration were obtained by appropriate dilutions. Fresh dilutions were used for each experiment. The pH adjustments were carried out either by sulfuric acid and sodium hydroxide.

**Batch adsorption experiments**

Batch process was employed for adsorption studies. Pre weighted sample of the adsorbent and a measured volume of Cr(VI) solution were taken in 250 mL Erlenmeyer flask. The mixture was agitated at 180 rpm for 360 min to ensure equilibrium and then it was filtered through filter paper (Whatman 44). Cr(VI) concentration in the adsorbate was determined using an indirect UV–vis spectrophotometric method based on the reaction of Cr(VI) and diphenyl carbazide, which forms a red-violet colored complex. The absorbance of the colored complex was measured in a double beam spectrophotometer at 540 nm wavelength spectrometrically [14] Shimadzu UV-1800 UV – spectrophotometer. All the experiments were carried out at least three times.

**Results and Discussion**

**Selection of adsorbents**

The four category adsorbent prepared from hogla leaves were taken in equal amount in different 250 mL Erlenmeyer flask. The initial Cr(VI) ion concentration and pH of the solution were same at each flask and were shaken with adsorbent at the same rpm for the same period of time. It was found that AWP Hogla exhibits the highest removal of Cr(VI) then other three (Figure 1). Acid wash has sufficiently freed the active sites of the adsorbents and grinding increased the surface area promoting a great number of active sites to adsorb Cr(VI) from solution. Therefore, AWP Hogla adsorbent was chosen and all the experiments were conducted using this adsorbent.

**Fourier transform infrared spectroscopy (FTIR) analysis**

The functional groups before and after adsorption of Cr(VI) onto AWP Hogla and the corresponding infrared adsorption bands are shown in Table 1. The infrared spectra were obtained using Shimadzu IR Prestige-21 FTIR spectrophotometer. The FTIR spectra before and after adsorption of AWP Hogla are shown in Figures 2a and 2b respectively.

Metal ions are generally caught by carboxylic, phenolic, hydroxylic, carbonyl groups [15]. As shown in Figures 2a and 2b and Table 1, the spectra displayed a number of adsorption peaks which indicates the active functional groups present in AWP Hogla. These peak shifts indicated that the bonded OH stretching, alkane C–H stretching, O=C=O stretching, and C=C stretching were mainly responsible for the adsorption of Cr(VI) onto AWP Hogla [16].

**Effect of pH on Cr(VI) adsorption**

The effect of pH on Cr(VI) removal by AWP (acid washed powder) Hogla was investigated at constant adsorbent dose and contact time by varying pH from 2.0–12.0. Progressive increase in Cr(VI) adsorption was observed with decrease in pH from 12 to 2 and maximum adsorption was observed at pH 2 (Figure 3). AWP showed the maximum removal of 73.6% at pH 2.

The effect of pH on adsorption of Cr(VI) onto the adsorbent can be interpreted on the basis of the structure of the sorbent and the speciation of chromium. Chromium solution contains a larger number of CrO₄²⁻ ions and a smaller number of HCrO₄⁻ ions in the regions of lower pH and only Cr₂O₇⁻ ions above pH 8.0. In the pH range 3 to 6, the equilibrium shifts to dichromate according to the overall equilibrium [16]:

\[2\text{CrO}_4^{2-} + 2\text{H}^+ = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}.\]

A major fraction of negative sites are occupied by H⁺ ions via electrostatic attraction in the regions of lower pH and these positively charged sites of the adsorbent are occupied by Cr₂O₇⁻ ions [17]. Hence, the maximum chromium removal was observed at lower pH i.e., 2. Higher removal of chromium at low pH may also be due to the reduction of chromium (VI) to chromium (III) [18,19], which was then adsorbed by the adsorbent.
Effect of adsorbent dose

To investigate the effect of adsorbent dosage, the adsorption of Cr(VI) onto AWP Hogla was measured at five different adsorbent dosage (2.5, 5, 7.5, 10 and 15 g/L) for initial Cr(VI) concentration of 100 ppm and the percent removal were presented in (Figure 4). When the adsorbent dosage was increased from 2.5 to 15 g/L, the removal increased from 32.68% to 78.5%. It is obvious that the percent removal of heavy metals increases rapidly with increase in the adsorbent dose due to the greater availability of the exchangeable sites or surface area. However, very slow increase in removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at the existing operating conditions [20]. Higher adsorbent dose cause screening effect of a dense outer layer of cells, blocking the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [21]. The optimum dose for the removal of Cr(VI) was found to be 10 g/L with removal efficiency of 78.71%.

Effect of initial Cr(VI) concentration

The driving force to overcome the mass transfer restriction of molecules between aqueous and solid surface can be predicted by varying the initial metal ion concentration [22,23]. Effect of initial Cr(VI) ion concentration on its removal was carried out at optimized adsorbent dose, contact time and pH by varying the metal ion concentration from 150–400 ppm (Figure 5).

Figure 5 shows that the adsorption of Cr(VI) increases with increase in metal ion concentration from 150–300 ppm. This may be due to the interaction between the adsorbates and adsorbent, creating some new adsorption sites or the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the adsorbent [6]. The decrease in adsorption of Cr(VI) for initial metal concentration of 400 ppm is due to increase in number of metal ions competing for available binding sites and due to lack of free binding sites [24] or due to the development of a barrier by the adsorbed Cr(VI) molecule surrounding the molecular surface of the adsorbents.

Adsorption isotherm

An adsorption isotherm is characterized by certain constant values that express the surface properties and affinity of the adsorbent and can be used to compare the adsorptive capacities of the adsorbent for different pollutants [25]. The experimental data showed in Table 2a were applied to the Langmuir, Freundlich, D–R, Temkin, Frumkin, and Harkins–Jura isotherm, in order to determine the mechanism of Cr(VI) adsorption on AWP Hogla.

The constant parameters of the isotherm equations for this adsorption process were calculated by regression using a linear form of the isotherm equations. The constant parameters and correlation coefficient (R²) are tabulated in Table 2b.

**Langmuir isotherm model**

\[
\frac{1}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0}
\]  

(1)

Where, \(C_e\) – the equilibrium concentration, ppm, \(q_e\) – the amount absorbed at equilibrium, mg/g, \(Q_0\) and \(K_L\) – the Langmuir constants related to adsorption capacity and energy of adsorption.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \(R_L\) that is used to predict if an adsorption system is “favorable” or “unfavorable”. The separation factor, \(R_L\) is defined by Equation (2):

\[
R_L = \frac{1}{1 + KC_o}
\]  

(2)

Where, \(C_o\) – the initial Cr(VI) concentration, ppm, \(K\) – the
Table 2a: Experimental data for adsorption isotherm.

<table>
<thead>
<tr>
<th>C₀, Initial Cr(VI) Conc. (ppm)</th>
<th>Cₑ, Equilibrium Conc. (ppm)</th>
<th>qₑ, amount absorbed at equilibrium (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>34.272</td>
<td>11.573</td>
</tr>
<tr>
<td>200</td>
<td>44.676</td>
<td>15.532</td>
</tr>
<tr>
<td>300</td>
<td>64.26</td>
<td>23.574</td>
</tr>
<tr>
<td>400</td>
<td>91.29</td>
<td>30.871</td>
</tr>
</tbody>
</table>

Table 2b: Isotherm constants for adsorption of Cr(VI) on AWP Hogla.

<table>
<thead>
<tr>
<th>Isotherm Model</th>
<th>Qₒ, mg/g</th>
<th>Kₑ, L/g</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>416.667</td>
<td>0.0008</td>
<td>0.995</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>0.327</td>
<td>1.015</td>
<td>0.992</td>
</tr>
<tr>
<td>Temkin isotherm</td>
<td>0.0505</td>
<td>20.055</td>
<td>0.995</td>
</tr>
</tbody>
</table>

The Langmuir adsorption equilibrium constant, L/g.

The isotherm is unfavorable when Rₑ>1, the isotherm is linear when Rₑ=1, the isotherm is favorable when 0<Rₑ<1 and the isotherm is irreversible when Rₑ=0. Rₑ values are 0.893, 0.862, 0.806 and 0.757 while initial Cr(VI) concentrations are 150, 200, 300 and 400 ppm respectively. The values of Rₑ for adsorption of Cr(VI) on AWP Hogla studied at different concentrations were between 0 and 1 indicating favorable adsorption of chromium on AWP Hogla.

Freundlich isotherm model

\[ qₑ = Kᵥ Cₑⁿ \]  
(3)

Where, \( qₑ \) – the amount absorbed at equilibrium, mg/g, \( Cₑ \) – the equilibrium concentration, ppm, \( Kᵥ, n \) – the Freundlich model constants.

Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has generally been applied in the following form. Temkin isotherm model is shown in Equation (4):

\[ qₑ = \frac{RT}{b} \ln(Aₑ) \]  
(4)

\[ qₑ = B \ln Aₑ + B \ln Cₑ \]  
(5)

Where, \( B = (RT/b) \), \( qₑ \) – the amounts absorbed at the equilibrium concentration, mg/g, \( Cₑ \) – the amounts absorbed at the equilibrium concentration, ppm, \( T \) – the absolute temperature, \( K \), \( R \) – the universal gas constant, 8.314 J/(mol⋅K). The constant \( b \) is related to the heat of adsorption [26,27].

From Table 2b (based on correlation coefficient) and Figures 6-8, it was seen that the adsorption of Cr(VI) onto AWP Hogla best fits into the Langmuir and Temkin isotherm model (R²>0.995). The experimental data also fits quite well into the Freundlich isotherm model (R²>0.992).

As seen from Figure 6, the Langmuir isotherm for adsorption of Cr(VI) onto AWP Hogla was found to be linear and the correlation coefficient was extremely high as tabulated in Table 2b. It was seen from Figure 8 that the Temkin isotherm for Cr(VI) adsorption by AWP Hogla was also found to be linear and the correlation coefficient was as high as that of Langmuir isotherm, as seen in Table 2b. Since the Temkin isotherm constant (B) is related to the heat of adsorption, the adsorption of Cr(VI) onto AWP Hogla could think of as an endothermic adsorption [22]. From Figure 7, it was seen that the Freundlich isotherm also fits quite well for Cr(VI) adsorption by AWP Hogla. The correlation coefficient was also high as shown in Table 2b. The value of \( n \) was found to be greater than 1 as shown in Table 2b,
indicating favorable adsorption of Cr(VI) by AWP Hogla.

Adsorption kinetics

Using pseudo first-order and pseudo second-order kinetic models, the rate constants were calculated. The pseudo first-order expression is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$  \hspace{1cm} (6)

Where, $$q_t$$ – amount of adsorbed Cr(VI) on the adsorbent at time t, mg/g; $$k_1$$ – the rate constant of first-order adsorption, min$$^{-1}$$.  

A straight line of log ($$q_e - q_t$$) versus t suggests the applicability of this kinetic model. $$q_e$$ and $$k_1$$ can be determined from the slope and intercept of the plot respectively [28].

The pseudo second-order kinetic model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (7)

Where, $$k_2$$ – the rate constant of second order adsorption, g/(mg-min). The pseudo second-order kinetics will be applicable if the plot t/q$$_t$$ versus t gives a straight line. Then $$q_e$$ and $$k_2$$ can be determined from the slope and intercept of the plot respectively.

Again:

$$h = k_2 q_e^2$$  \hspace{1cm} (8)

Where, h – the initial sorption rate, mg/(g min) [29].

The pseudo first-order rate constants $$k_1$$, pseudo second-order rate constants $$k_2$$, the initial sorption rate h, calculated equilibrium sorption capacity $$q_{e,\text{theo}}$$ (theoretical), experimental equilibrium sorption capacity $$q_{e,\text{exp}}$$ (experimental) and regression coefficients R$$^2$$ at various initial Cr(VI) concentrations and at fixed temperature (25°C) are given in Table 3. A comparison of $$q_{e,\text{theo}}$$ and $$q_{e,\text{exp}}$$ results for various initial Cr(VI) concentration is shown in Figure 9.

From Table 3, it was seen that the regression coefficients for pseudo first- order kinetic model were much below than 0.96 which indicated a bad correlation. On the other hand, all the regression coefficients for the pseudo second- order kinetic model were found to be greater than 0.96 and thus indicated a good correlation. From Table 3 and Figure 9, the $$q_t$$ values estimated from the first order kinetic model gave different values compared to experimental values, except for the case of 200 and 300 ppm and the correlation coefficients were also found to be fairly lower except for 400 ppm. However, for the case of the pseudo-second-order kinetic model the calculated $$q_{e,\text{exp}}$$ values were quite close to $$q_{e,\text{exp}}$$ values at various initial Cr(VI) concentrations. Moreover, from Table 3 it was seen that the rate constants $$k_1$$, for the pseudo second-order model decreases with increasing of initial Cr(VI) concentration, while the initial sorption rate h, increases with increasing initial Cr(VI) concentration. Comparing the values of regression coefficients R$$^2$$, it was seen that the values for pseudo first- order model were pretty lower than those of pseudo second- order model for all the sorption process and therefore it can be said that the pseudo-second order- the model was better obeyed than the pseudo first- order model. The kinetic study was done by other researchers for the adsorption of Cr(VI) also supports the previous statement [6,30].

Comparison of AWP Hogla with other adsorbents

The metal uptake capacity of various adsorbents is different from one another. This is because of the properties of each adsorbent such as structure, functional groups, and surface areas. A comparison of adsorption capacity of Cr(VI) by AWP Hogla with other reported adsorbents is shown in Table 4. It can be seen that for almost every case pH 2.0 was the optimum condition for Cr(VI) adsorption whatever the adsorbent was. When compared with other adsorbents reported in literature elsewhere, the adsorption capacity of Cr(VI) by AWP Hogla was found to be higher with three exceptions.

Industrial feasibility of adsorbent

The industrial feasibility of AWP Hogla was studied for the removal of Cr(VI) from tannery effluent at optimized conditions obtained from experiments on a synthetic solution in batch mode. The removal efficiency of the adsorbent was reduced from 78.7% to 44.8%. This reduction in percent removal may be due to the presence of co-metal ions and dyes present in industrial effluents [31-37].

Conclusion

The adsorption of Cr(VI) by AWP Hogla was dependent on pH, adsorbent dose, and initial metal ion concentration. The adsorption capacity was highest at pH 2.0. The optimum dosage for Cr(VI) adsorption by AWP Hogla was found to be 10 g/L. Using Langmuir, Freundlich and Temkin isotherm, the adsorption of Cr(VI) onto AWP Hogla were described. Langmuir and Temkin model showed better correlation coefficient than the other model in the studied concentration. Freundlich model also showed quite good correlation coefficient. The pseudo first- order and pseudo second- order kinetic model were used to analyze the data obtained for the adsorption of Cr(VI) onto AWP Hogla. The pseudo second- order equation was found to have the best correlation for the adsorption data. The AWP
Hogla was found quite not suitable for the removal of Cr(VI) from its industrial effluents. This adsorbent can be applied after appropriate dilution of the industrial effluent for the removal of Cr(VI) or after removing the co-metals present in the effluent.

### References


### Table 4: Comparison of adsorption capacity of Cr(VI) with others.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>q, mg/g</th>
<th>pH</th>
<th>Max. conc., ppm</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eucalyptus bark</td>
<td>45.00</td>
<td>2.0</td>
<td>250</td>
<td>[5]</td>
</tr>
<tr>
<td>Hevea brasiliensis sawdust activated carbon</td>
<td>42.64</td>
<td>2.0</td>
<td>200</td>
<td>[6]</td>
</tr>
<tr>
<td>Beech sawdust</td>
<td>16.10</td>
<td>1.0</td>
<td>200</td>
<td>[7]</td>
</tr>
<tr>
<td>Waste acorn of Quercus ilabuernensis</td>
<td>31.48</td>
<td>2.0</td>
<td>400</td>
<td>[16]</td>
</tr>
<tr>
<td>Maghemite nanoparticles</td>
<td>19.20</td>
<td>2.5</td>
<td>200</td>
<td>[31]</td>
</tr>
<tr>
<td>Chlorella vulgaris</td>
<td>23.00</td>
<td>2.0</td>
<td>100</td>
<td>[32]</td>
</tr>
<tr>
<td>Scenedesmus obliquus</td>
<td>15.60</td>
<td>2.0</td>
<td>100</td>
<td>[32]</td>
</tr>
<tr>
<td>Synechocystis sp.</td>
<td>19.20</td>
<td>2.0</td>
<td>100</td>
<td>[32]</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>13.40</td>
<td>2.0</td>
<td>500</td>
<td>[33]</td>
</tr>
<tr>
<td>Sugar beet pulp</td>
<td>17.20</td>
<td>2.0</td>
<td>500</td>
<td>[33]</td>
</tr>
<tr>
<td>Coconut shell carbon</td>
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