Efficient Removal of Cr(VI) from Aqueous Solution onto Palm Trunk Charcoal: Kinetic and Equilibrium Studies

Sunil Kumar Yadav1 and Dixit AK*1

1Department of Chemistry, HB Technological Institute, Kanpur, Uttar Pradesh, India
2Department of Chemistry, VSSD College, Kanpur, Uttar Pradesh, India

Abstract

In the present study, carbonization method using mineral acids at elevated temperature. The potential of chemically carbonized palm trunk charcoal (PTC) for the effective removal of Cr(VI) ions from aqueous solution has been investigated in batch experiments. The sorption kinetics at pH=1.5 and the sorption isotherms at different pHs were studied. Chromium concentration was analyzed spectrophotometrically using 1,5-diphenylcarbazide. In order to the maximal adsorption at pH 1.5 was 24.7 mg g⁻¹. The equilibrium adsorption capacity of PTC increases (4.99 to 24.7 mg g⁻¹) as the initial Cr(VI) concentration increases (10-50 mg L⁻¹). The adsorption behavior of Cr(VI) is best described by the pseudo-second order model and the calculated equilibrium capacity (15.6 mg g⁻¹) agree with the experimental value (14.75 mg g⁻¹). The equilibrium data were well fitted by the Langmuir isotherm model by revealing the maximum sorption capacity of PTC (24.7 mg g⁻¹). The mechanism of adsorption was also studied using Fourier transform infrared (FTIR) spectroscopy. The bond of Cr(VI) to the functional groups of charcoal seems to be irreversible in the case of dried Cr(VI) saturated charcoals.

Keywords: Adsorption; Chromium(VI); Palm trunk; Isotherms; Kinetics

Introduction

The increasing existence of toxic heavy metals in aquatic environments introduced by industrial pollution is a serious environmental problem. It is well recognized that heavy metal residues in polluted habitats may bioaccumulate in microorganisms and aquatic flora and fauna, which may be consumed by humans and cause health problems [1]. Among various heavy metal pollutants, chromium is one, commonly present as trivalent Cr(III) and hexavalent Cr(VI) forms in aqueous solution. Most common and stable oxidation states of chromium are Cr(III) and Cr(VI). Cr(VI) is 500 times more toxic and highly mobile than Cr(III) [2], because it can diffuse as CrO₄²⁻ or HCrO₄⁻ through cell membranes and oxidize biological molecules [3], and has been reported as one of the top-priority toxic pollutants defined by the US Environmental Protection Agency (EPA), and the Chinese Environmental Protection Board (EBP) [4,5]. The maximum permissible limits of Cr(VI) for discharge into potable water and industrial wastewater are 0.05, and 0.25 mg L⁻¹, respectively [6]. The industries should treat their effluents in order to reduce Cr(VI) ions concentration in wastewaters to the permissible limits before discharge into the municipal sewers. The sorption kinetic studies provide information about the Cr(VI) removal from wastewater, which include adsorption, biosorption, coprecipitation, electrocoagulation, chemical precipitation, membrane filtration, solvent extraction, and reosmosis and ion exchange [7-19].

Among various water treatment and recycling methods, adsorption is a fast and less expensive method. The conventional methods are not preferred due to their high cost and disadvantages like slow process, incomplete removal low selectivity, high-energy consumption, and generation of toxic sludge. The development of low-cost adsorbents has led to the rapid growth of research interests in the field of wastewater treatment. A variety of reported low-cost agro-waste adsorbents studied for the removal of Cr(VI) from wastewater include date palm trunk, wheat shell, ricinus communis seed shell, coir pith, grape waste, charcoal, and olive stone [20-26]. The use of agro-waste as adsorbents is an eco-friendly technique and reduces solid waste. The purpose of this study is to explore the use of chemically activated palm trunk for the removal of Cr(VI) from wastewater. Palm trunk is one of the main agro-waste generated by the palm oil industries. Oil palm wood has been used as raw material for preparations of activated carbon [27]. The activated carbon prepared from date palm trunk has been reported for the removal of Cu(II) [28] and methylene blue [29]. The major components of palm trunk and petiole are cellulose 44.17%, hemicelluloses 21.95%, and lipids 0.39%. Cellulose and hemicellulose contain large amount of easily available hydroxyl groups, and these active hydroxyl groups can easily make a series of chemical reaction for polymeric ion exchanger preparation [30,31]. The objective of this study is to exploit and utilize the modified date palm trunk as an adsorbent for treatment of wastewater containing Cr(VI). The low temperature (150±5 °C) chemical carbonization has the potential to further reduce the cost of producing activated carbon from agro-waste. Therefore, a low temperature chemical activation method was employed in this study for the generation of carbonized date palm trunk, to exploit and utilize the agro-waste for the effective removal of Cr(VI) from wastewater. For the preparation of carbonized adsorbent, PTC, an agricultural waste, was of particular interest in this study. Examined the various effects during experiment such as solution pH, initial Cr(VI) concentration, contact time and explore the Cr(VI) removal mechanism by PTC.

Experimental Methods

Reagents

All the primary chemicals used in this study were of analytical grade. The stock solution of Cr(VI) (1000 mg L⁻¹) was prepared by

*Corresponding author: Dixit AK, Department of Chemistry, VSSD College, Kanpur-208 002, Uttar Pradesh, India, Tel: +919415040226; Fax: 0512-2563842; E-mail: dixit_arvind2@yahoo.co.in

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dissolving 2.83 g K₂Cr₂O₇ in 1000 mL deionized water (DIW). Sodium hydroxide or hydrochloric acid solution (0.1M) was used for pH adjustment and pH was measured using pH meter (El Digital pH meter 111, Chandigarh, India).

Preparation of palm trunk charcoal (PTC)

Raw palm trunk (PT) was obtained from rural area(s) around Kanpur (India), cut into a length of approximately 1 cm, washed thoroughly with DIW to remove water soluble materials, dried overnight at 100 ± 2°C in a hot air oven (Shivam Instruments, Delhi, India), and allowed to cool down to room temperature. It was ground and sieved to obtain the desired particles (125 to 105 μm). In preparation of PTC, the crushed palm trunk powder (10 g) was mixed in concentrated sulphuric (11 mL, 98% m/m). After 10 min reaction time, concentrated nitric acid (6.6 mL, 65% m/m) was added. The mixture was heated in a hot air oven at 150 ± 2°C for 24 h and the reaction was allowed to run until the equilibrium was reached (60 min). After equilibrium, the adsorbent was separated from the solution using Whatman No.4 filter paper and the remaining concentration of Cr(VI) ions in the filtrate was analyzed spectrophotometrically using 1,5-diphenylcarbazide [32]. The percentage of Cr(VI) removal ‘R’ and q_e (mg g⁻¹) amount of Cr(VI) adsorbed per unit mass of the adsorbent were determined using the Eqs. (1) and (2), respectively.

\[
\% R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

\[
q_e (\text{mg g}^{-1}) = \left( \frac{C_0 - C_e}{M} \right) V
\]

where, C₀ and Cₑ (mg L⁻¹) are the initial and equilibrium Cr(VI) concentrations, respectively, V is the solution volume (L) and M is the weight of the adsorbent (g).

FTIR and SEM analysis

The functional groups present in PT, PTC and Cr(VI) loaded PTC were investigated using the Fourier transforms infrared (FTIR) spectrophotometer (Bruker FTIR Vertex 70, Germany). The spectra were recorded in the region from 400 to 4000 cm⁻¹. Scanning electron microscopy (SEM) observation was carried out on a Supra 40 VP, Zeiss, Germany.

Desorption studies

To explore the possibility of recycling of the PTC, consecutive adsorption-desorption experiments were repeated using the same adsorbent. Desorption was done by 0.1 N NaOH as stripping solution.

Results and Discussion

FTIR and SEM analysis

FTIR spectra of PT, PTC and PTC-Cr(VI) are shown in Figure 1a, 1b and 1c. In the FT-IR spectrum of PT, the absorption peaks at 3,400, 2,925, 2,854, 1,710 and 1,247 cm⁻¹ are due to –OH, C–H, –CH₂, C=O, and C–O stretching vibrations, respectively. In PTC, at the peak 3427 cm⁻¹ assigned –OH stretching vibration. Two week bands at 2923 and 2850 cm⁻¹ may be assigned to aliphatic groups stretching vibrations but their intensities are lower than the spectrum of PT, leading to the decrease in aliphaticity in PTC by increasing temperature. This is also associated by the C=O peak is shifted from 1710 cm⁻¹ to 1702. The adsorption peak at 1657 cm⁻¹ in FTIR spectrum of PT appears due to –COO– group and shifted to 1618 cm⁻¹ in PTC, which may suggest a change in structure of PT while converted into PTC. These observations indicate that carbonization of PT. After adsorption of Cr(VI), –COO– peak is shifted from 1618 cm⁻¹ to 1609 cm⁻¹ and 1602 cm⁻¹ in PTC. Larger shifting shows strong complex formation of Cr(VI) and hence, higher adsorption capacity.

The SEM micrograph clearly states the porous structure of the PTC (Figure 1d and 1e). There are holes and cave-type openings on the surface of the specimen which would definitely increase the surface area available for adsorption. It is clearly seen on the surface of PTC after adsorption in Figure 1b that the caves, pores and surfaces of adsorbent are covered by adsorbate. It was evident that the adsorbent structure changed upon adsorbing the Cr(VI) ions studied.

Effect of pH

In Figure 2 shows the Cr(VI) adsorption efficiency of the PTC as a function of initial solution pH. As pH increased, decrease the adsorption capacity (experimental: 14.75 to 4.99 mg g⁻¹) of the PTC. Cr(VI) in aqueous solution exists in various anionic species : Cr₂O₇²⁻, HCrO₄⁻, CrO₄³⁻, etc. Adsorption of Cr(VI) below pH 3.0 suggested that the dominant species (HCrO₄⁻) of Cr(VI) required one exchange site from PTC for the adsorption. The maximum uptake of Cr(VI) took place at pH ~ 2. At lower pH, H⁺ ions were adsorbed on the PTC surface and developed positively charged active sites. At pH 1.5 to 2, the dominant form of Cr(VI) is HCrO₄⁻ which interact electrostatically with positively charged PTC active sites. As the solution pH increased (1-7), the concentration of HCrO₄⁻ also decreased. Therefore the adsorption of Cr(VI) also decreased with the increase solution pH [33].

Effect of initial concentration, contact time and adsorbent dosage

The higher initial Cr(VI) concentration results in enhancing the adsorption process (Figure 3a and 3b). The equilibrium adsorption capacity of PTC increases (4.99 to 24.7 mg g⁻¹) as the initial Cr(VI) concentration increases (10-50 mg L⁻¹). An increase in Cr(VI) concentration results an increase the mass gradient between Cr(VI) solution and PTC increases with the increased concentration of Cr(VI).

The adsorption capacity of Cr(VI) onto PTC at concentration 30 mg L⁻¹ depicts that the adsorption is quite rapid initially, gradually slows down, and then reaches the equilibrium. It is interesting to note that the equilibrium was achieved with in ~30 min, indicating that PTC possesses superior adsorption performance with high adsorption kinetics (Figure 3c).

The effect of PTC dosage on adsorption of Cr(VI) shows that the percentage of Cr(VI) removal from aqueous solution increases from 57 to 98.3% when adsorbent dosage increases from 1.0 to 4.0 g L⁻¹ (Figure 3d). This may be due to an increased adsorbent surface area and availability of more adsorption sites or more functional groups resulting from the increased dosage of the adsorbent.
Adsorption isotherms

Langmuir isotherm model: Langmuir adsorption isotherm was applied to equilibrium adsorption assuming monolayer adsorption onto the surface with a finite number of identical sites. The following Langmuir sorption isotherm equation was used [34]:

\[ \frac{C_e}{q_e} = \frac{1}{Q_m} + \frac{C_e}{Q_m} \]

where, \( q_e \) is the amount of Cr(VI) adsorbed on PTC (mg g\(^{-1}\)) at equilibrium, \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)) of the Cr(VI) in solution, \( Q_m \) is the monolayer adsorption capacity (mg g\(^{-1}\)) and \( b \) is the Langmuir constant (L mg\(^{-1}\)) related to the free energy of adsorption. The values of \( Q_m \) and \( b \) were calculated from the slope (1/Q_m) and intercept (1/bC_e) of the linear plot of \( C_e/q_e \) versus \( C_e \) (Figure 4a) and are given in Table 1. The linearity of plots revealed that the adsorption followed Langmuir isotherm model. The Langmuir parameter, \( Q_m \) values obtained in this work were compared with the results reported in literature (Table 2) [35-39]. The essential characteristic of the Langmuir isotherm can also be evaluated by dimensionless adsorption intensity \( R_L \) given by:

\[ R_L = \frac{1}{1 + bC_i} \]  (4)

where, \( C_i \) (mg L\(^{-1}\)) is the initial concentration of Cr(VI) and \( b \) (L mg\(^{-1}\)) is the Langmuir constant. \( R_L \) values represent the type of isotherm and its value between 0 and 1 indicates favorable adsorption. The \( R_L \) values evaluated from the \( b \) values for Cr(VI) at various concentrations (Table 1) were found to be between 0 and 1, further supporting the Langmuir model.

Freundlich isotherm model: The Freundlich isotherm is applicable to highly heterogeneous surfaces, and an adsorption isotherm lacking a plateau indicates a multi-layer adsorption. The linear form of the Freundlich isotherm is given by the following equation [40]:

\[ \ln q_e = \ln K_F + \frac{n}{n} \ln C_e \]  (5)

where, \( q_e \) is the amount of Cr(VI) adsorbed (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of Cr(VI) solution (mg L\(^{-1}\)), \( K_F \) and \( n \) are the Freundlich constants which indicate the capacity and the intensity of the adsorption, respectively. Thus a plot of \( \ln q_e \) versus \( \ln C_e \) should be a straight line with a slope of \( 1/n \) and an intercept of \( \ln K_F \) as shown in Figure 4b. The value of the Freundlich constant, \( n=3.6 \) (Table 1) shows that the adsorption process favorable with supporting R\(^2\) value near to linear (R\(^2\)=0.99) revealed that Freundlich model is also governing the adsorption (Figure 4b; Table 1).

Temkin isotherm model: The Temkin isotherm is expressed by the following equation [41]:

\[ q_e = \frac{B}{Q_m} \ln C_e + B \ln C_i \]  (6)

where, \( B=RT/b \), \( b \) is the Temkin constant (J mol\(^{-1}\)) related to adsorption heat, \( T \) is the absolute temperature (K), \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( A \) is the Temkin isotherm constant (L g\(^{-1}\)). \( B \) and \( A \) can be calculated from the slope and intercept of the plot of \( q_e \) versus \( \ln C_e \), respectively (Figure 4c). The Temkin constants \( B \), \( B \), and \( A \) together with the R\(^2\) values are shown in Table 1. The heat of adsorption of Cr(VI) in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions.

Adsorption kinetics

The adsorption kinetics of Cr(VI) onto PTC, has been investigated with the aid of three kinetic models, namely Lagergren’s pseudo-first order model, Ho and McKay’s pseudo-second order model and Weber and Morris’s intraparticle diffusion model to analyse the experimental data.

Pseudo-first order kinetic model: The pseudo-first-order rate model of Lagergren is based on solid adsorbent capacity and generally expressed as follows [42]:

\[ \log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]  (7)

where, \( q_e \) is the amount of solute adsorbed at equilibrium per unit weight of the adsorbent (mg g\(^{-1}\)), \( q_t \) is the amount of solute adsorbed at any time (mg g\(^{-1}\)) and \( k_1 \) (min\(^{-1}\)) is the adsorption rate constant. Values of \( k_1 \) calculated from the plots of \( \log (q_e-q_t) \) versus \( t \) at different initial
Figure 3: (a, b) Effect of initial concentration on the adsorption of Cr(VI), (c) Effect of contact time on the adsorption of Cr(VI) on to PTC: pH = 1.5, C_i = 30 mg/ L, dose = 2 g/ L, and temperature =30 °C. (d) Effect of adsorbent dose on the adsorption of Cr(VI) on to PTC: pH = 1.5, C_i = 30 mg/ L and temperature =30 °C.

Figure 4: (a) Langmuir isotherm, (b) Freundlich isotherm and (c) Temkin isotherm plots for adsorption of Cr(VI) on to PTC: pH = 1.5, C_i = 10-50 mg/ L, dose = 2g/ L, and temperature =30 °C.
concentrations are summarized in Table 3 (Figure not shown). The correlation coefficient values were low and the calculated qe values were not in good agreement with the experimental one. Hence, the pseudo-first-order model does not describe the adsorption kinetics of Cr(VI) onto PTC.

Pseudo-second order kinetic model: The pseudo-second order model can be expressed as [43]:

$$\frac{t}{q_t} = \frac{1}{k_2q_{e}^{2}} + \frac{1}{q_{e}}t$$

(8)

where, $k_2$ (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second-order equation, $q_{e}$ (mg g⁻¹) is the maximum adsorption capacity, and $q_{t}$ (mg g⁻¹) is the amount of adsorption at time t (min). The plot of $t/q_t$ versus t (Figure 5a) shows a linear relationship. The value of $q_{e}$ (mg g⁻¹) and $k_2$ (g mg⁻¹ min) are determined from the slope and intercept of the plot, respectively. The results are summarized in Table 3. It can be seen that the calculated coefficient of determination (R²) is very close to unity and that $q_e$ (cal) values agree with the experimental values. These results suggest that the pseudo-second-order model describes the adsorption kinetics of the present system, $k_2$ values decreased with the increased initial Cr(VI) concentration. This decrease in $k_2$ values at higher concentrations seems due to the repulsion between the adsorbed and the non-adsorbed Cr(VI).

Intraparticle diffusion: The intra-particle diffusion plays an important role in the extent of adsorption and can be expressed as [44]:

$$q_t = k_3t^{1/2} + C$$

(9)

where, $k_3$ is the intra-particle diffusion constant (mg g⁻¹ min⁻¹/²) and the intercept (C) reflects the boundary layer effect. The values of $k_3$ were calculated from slopes ($k_3$) of the plots of $q_t$ versus $t^{1/2}$ (Figure 5b) and are presented in Table 3. The plot of $q_t$ versus $t^{1/2}$ should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not the only rate limiting step, but also other kinetics models may control the rate of adsorption. The plots of $q_t$ versus $t^{1/2}$ (Figure 5b) do not pass through the origin, showing that intra-particle diffusion is not the only rate controlling step.

Adsorption mechanism

The functional groups present on the PTC surface greatly influence the Cr(VI) removal mechanism. Based on the results of the present study it could be assumed that at low pH values, in the presence of adequate H⁺ ions, the surface of the PTC becomes positively charged via protonation of the surface functional groups, which adsorb negatively charged Cr(VI) species via electrostatic attraction according to the following mechanism:

$\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}^+ \rightarrow \text{C}_6\text{H}_{12}\text{O}_6^+ + \text{H}^\text{+}$

Desorption

The adsorbed Cr(VI) on PTC was recovered using 0.1N NaOH as an eluting reagent. Further more, in order to investigate the reproducibility of PTC, the adsorption-desorption cycles was repeated four times using the same adsorbent at the same optimum operating conditions. The obtained results show that in the first cycle, the removal efficiency by PTC was 99.95% for Cr(VI). From the second to fourth cycles, the PTC had slightly changed adsorption ability ranged from 97.0 to 91.6%. This study reveals that the prepared adsorbent is capable of four cycles of adsorption/desorption. The recovered chromium is benefit for industry.

Conclusion

The results obtained in this study indicate the potentiality of PTC for the removal of Cr(VI). Adsorption process revealed that the initial uptake of Cr(VI) up to 15 min was rapid (85%) and equilibrium was achieved within 60 min. The maximum capacity value calculated from Langmuir isotherm of PTC is high (24.75 mg g⁻¹) compared to most of the reported adsorbents (5.3-22.7 mg g⁻¹, Table 2). Experimental results indicate that the adsorption process follows a pseudo-second-order reaction kinetics. The isotherm studies show that the adsorption data correlate well with the Langmuir isotherm model. Active functional groups for the Cr(VI) adsorption process were identified by FTIR.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Constants</th>
<th>Values</th>
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<tr>
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<td>b (mol⁻¹)</td>
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<tr>
<td>Freundlich</td>
<td>K₂ (mg g⁻¹)</td>
<td>n</td>
</tr>
<tr>
<td>Temkin</td>
<td>B</td>
<td>B (J mol⁻¹)</td>
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</table>

Table 1: Parameters of Langmuir, Freundlich and Temkin adsorption isotherm constants for adsorption of Cr(VI) onto PTC.

Table 2: Comparison of adsorption capacity Cr(VI) onto PTC with various adsorbents.

<table>
<thead>
<tr>
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<th>Qm (mg g⁻¹)</th>
<th>Langmuir isotherm</th>
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</thead>
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<td>5.3</td>
<td>[35]</td>
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<tr>
<td>Biocomposite</td>
<td>1.0</td>
<td>5.4</td>
<td>[36]</td>
<td></td>
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<td>Sunflower head waste</td>
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<td>[37]</td>
<td></td>
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<tr>
<td>Bio-char</td>
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<td>6.1</td>
<td>[38]</td>
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<tr>
<td>Jatropha Seed</td>
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<td>22.7</td>
<td>[39]</td>
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<td>1.5</td>
<td>24.7</td>
<td>This study</td>
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Table 3: Pseudo-first-order, pseudo-second order and intra particle diffusion rate for adsorption of Cr(VI) onto PTC.
studies. The desorption percentage was 99.5% using 0.1M NaOH as an eluting reagent. This study demonstrates that the PTC can be used as a potential adsorbent for the treatment of wastewater containing Cr(VI). The method has also been tested successfully for removal of Cr(VI) from chrome plating wastewater. The treated water is almost free from Cr(VI) and recovered chromium can be reused for industrial applications.

References


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