

Kinetics, Isotherms and Mechanisms of Cr (VI) Adsorption onto Activated Date Palm Trunk (DPT)

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Abstract

Carbonization of raw date palm trunk (CDPT) is an attractive approach for improvement of Cr(VI) uptake from aqueous solutions. Cr(VI) adsorption significantly depends upon the initial concentration of Cr(VI), contact time, pH, and adsorbent dosage. The equilibrium was attained within ~30 min at optimum pH 1.5. 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}) agrees with the experimental value (14.75 mg g^{-1}). The equilibrium data were well fitted by the Langmuir isotherm model and reveal the maximum sorption capacity of CDPT (24.7 mg g^{-1}). Adsorption-desorption studies reveal that CDPT can be used as a potential adsorbent for waste water treatment containing Cr (VI).

Graphical abstract



Keywords: Adsorption, chromium(VI), date palm trunk, isotherms, kinetics.

1. INTRODUCTION

The increasing existence of toxic heavy metals in aquatic environment introduced by industrial pollution is a serious environmental problem. Among various heavy metal pollutants, chromium is one, commonly present as trivalent Cr(III) and hexavalent Cr(VI) forms in aqueous solution. Cr(VI) is 500 times more toxic and highly mobile than Cr(III)^[1] because it can diffuse as CrO_4^{2-} or HCrO_4^- through cell membranes and oxidize biological molecules, and has been reported as one of the top-priority toxic pollutants defined by the US Environmental Protection Agency (EPA)^[2]. 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^[3]. 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.

Among various water treatment and recycling methods, adsorption is a fast and less expensive method. The development of low-cost adsorbents has led to the rapid growth of research interests in the field of wastewater treatment. The use of agricultural wastes as adsorbents is an eco-friendly technique and reduces solid waste.

The purpose of this study is to explore the use of chemically activated date palm trunk for the removal of Cr(VI) from wastewater. The low temperature ($150 \pm 5 \text{ }^\circ\text{C}$) chemical carbonization has the potential to further reduce the cost of producing activated carbon from agricultural wastes/by-products. For the preparation of carbonized adsorbent, CDPT, an agricultural waste, was of particular interest in this study.

2. EXPERIMENTAL

2.1. Preparation of CDPT

Raw date palm trunk (DPT) was obtained from rural area(s) around Kanpur (India), cut into a length of approximately 1cm, washed thoroughly with distilled water (DW) to remove water soluble materials, dried overnight at $100 \pm 2^\circ\text{C}$ in a hot air oven and allowed to cool down to room temperature. It was ground and sieved to obtain the desired particles (125 to 105 μm). The DPT powder was mixed with concentrated sulphuric acid (1:1, w/v) for chemically carbonization and activation with constant mixing for 30 min. The black slurry was kept in a hot air oven at $150 \pm 5^\circ\text{C}$ for 24 h. This carbonized material was stirred with distilled water and centrifuged. The washed carbon was dried in hot air oven at $110 \pm 2^\circ\text{C}$, ground and sieved (125 to 105 μm), labelled as CDPT and stored in desiccator.

2.2. Batch Adsorption Experiments

Batch adsorption experiments were carried out in Erlenmeyer flasks (100 mL) containing 50 mL of Cr(VI) solution (10-50 mg L^{-1}). pH (1~7) was adjusted using NaOH or HCl solution before the addition of adsorbent. Adsorbent (0.1g) was added and the flasks were shaken in a rotator shaking machine (160 rpm) at room temperature (30°C) 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.^[4] 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 equations. (1) and (2), respectively.

$$\% R = \left(\frac{C_i - C_e}{C_i} \right) 100 \quad (1)$$

$$q_e (\text{mg/g}) = \left(\frac{C_i - C_e}{M} \right) V \quad (2)$$

where, C_i and C_e (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).

3. RESULTS AND DISCUSSION

3.1 Effect of pH

Figure 1 shows the Cr(VI) adsorption efficiency of the CDPT as a function of initial solution pH. As pH increased, decrease the adsorption capacity (14.75 to 4.2 mg g^{-1}) of the CDPT. Cr(VI) in aqueous solution exists in various anionic species : $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^{2-} , etc. Adsorption of Cr(VI) below pH 3.0 suggested that the dominant species (HCrO_4^-) of Cr(VI) required one exchange site from CDPT for the adsorption. The maximum uptake of Cr(VI) took place at $\text{pH} \sim 2$. At lower pH, H^+ ions were adsorbed on the CDPT surface and developed positively charged active sites. At pH 1.5 to 2, the dominant form of Cr(VI) is HCrO_4^- which interact electrostatically with positively charged CDPT active sites. As the solution pH increased (1-7), the concentration of HCrO_4^- also decreased. Therefore the adsorption of Cr(VI) also decreased with the increase solution pH^[5].

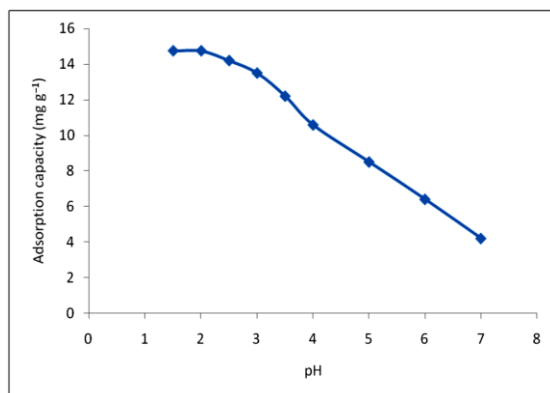


FIG. 1 Effect of pH on the adsorption of Cr(VI) on to CDPT: $C_i = 30 \text{ mg/L}$, dose = 2 g L^{-1} , and temperature = 30°C .

3.2 Effect of Contact Time, Initial Concentration and Adsorbent Dosage

The higher initial Cr(VI) concentration results in enhancing the adsorption process (Figure 2 a, b). The equilibrium adsorption capacity of CDPT increases (4.99 to 23.47 mg g⁻¹) as the initial Cr(VI) concentration increases (10-50 mg L⁻¹).

The adsorption capacity of Cr(VI) onto CDPT 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 within ~30 min, indicating that CDPT possess superior adsorption performance with high adsorption kinetics (Figure 3c).

The effect of CDPT 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.

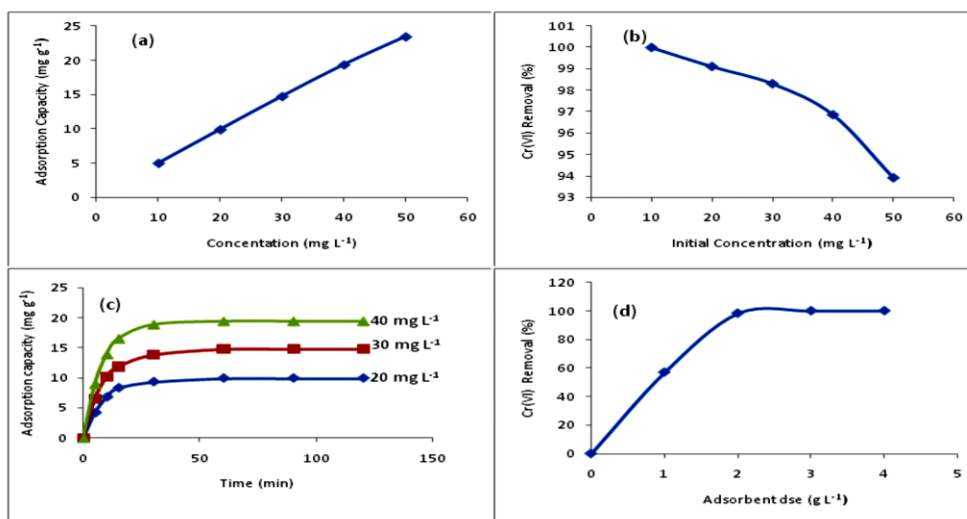


FIG. 2 (a, b) Effect of initial concentration (c) Effect of contact time and (d) Effect of adsorbent dose on the adsorption of Cr(VI) on to CDPT: pH = 1.5, C_i = 30 mg L⁻¹ and temperature = 30 °C.

3.3 Adsorption Isotherms

Langmuir sorption isotherm equation was used [6]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_M} + \frac{C_e}{Q_M} \quad (3)$$

where, q_e is the amount of Cr(VI) adsorbed on CDPT (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/bQ_m) of the linear plot of C_e/q_e versus C_e (Figure 3a) and are given in Table 1. The linearity of plots revealed that the adsorption followed Langmuir isotherm model. The essential characteristic of the Langmuir isotherm can also be evaluated by dimensionless adsorption intensity R_L given by:

$$R_L = \frac{1}{1 + bC_i} \quad (4)$$

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 is given by the following equation ^[7]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

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 3b, Table 1).

TABLE 1. Langmuir and Freundlich adsorption isotherm for adsorption of Cr(VI) onto CDPT.

Langmuir Isotherm		Freundlich Isotherm	
Constants	Values	Constants	Values
Q_m (mg g^{-1})	24.7	K_F (mg g^{-1})	17.35
b (mg^{-1})	4.93	n	3.6
R^2	0.993	R^2	0.992
R_L	0.019- 0.004		

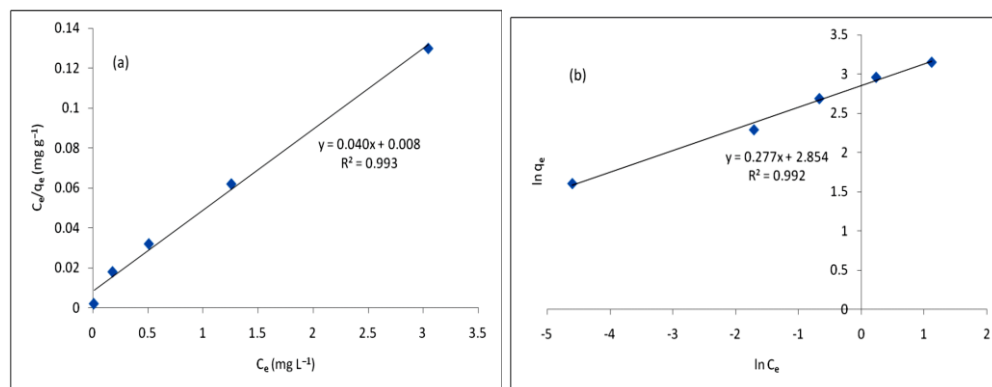


FIG. 3 (a) Langmuir isotherm plots for adsorption of Cr(VI) on to CDPT (b) Freundlich isotherm plots for adsorption of Cr(VI) on to CDPT.

3.4 Adsorption Kinetics

The pseudo-first-order rate model of Lagergren is based on solid adsorbent capacity and generally expressed as follows ^[8]:

$$\log(q_e - q_t) = (\log q_e) - \left(\frac{k_1}{2.303} \right) t \quad (6)$$

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 concentrations are summarized in Table 2 (Figure not shown). The correlation coefficient values were low and the calculated q_e values were not in good agreement with the experimental one.

The pseudo-second order model can be expressed as ^[9]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (7)$$

where, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) 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 4) shows a

linear relationship. The value of q_e (mg g^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}$) are determined from the slope and intercept of the plot, respectively. The results are summarized in Table 2. It can be seen that the calculated coefficient of determination (R^2) 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.

TABLE 2. Pseudo-first and pseudo-second order for adsorption of Cr(VI) onto CDPT.

Constants	Initial concentration [mg L^{-1}]		
	20	30	40
$q_{e \text{ exp.}}$ (mg g^{-1})	9.91	14.75	19.37
Pseudo-first order			
$q_{e \text{ (cal)}}$ (mg g^{-1})	4.31	6.47	8.37
k_1 (min^{-1})	0.011	0.016	0.017
R^2	0.791	0.760	0.874
Pseudo-second order			
$q_{e \text{ (cal)}}$ (mg g^{-1})	10.41	15.63	20.40
k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.018	0.012	0.011
R^2	0.998	0.999	0.999

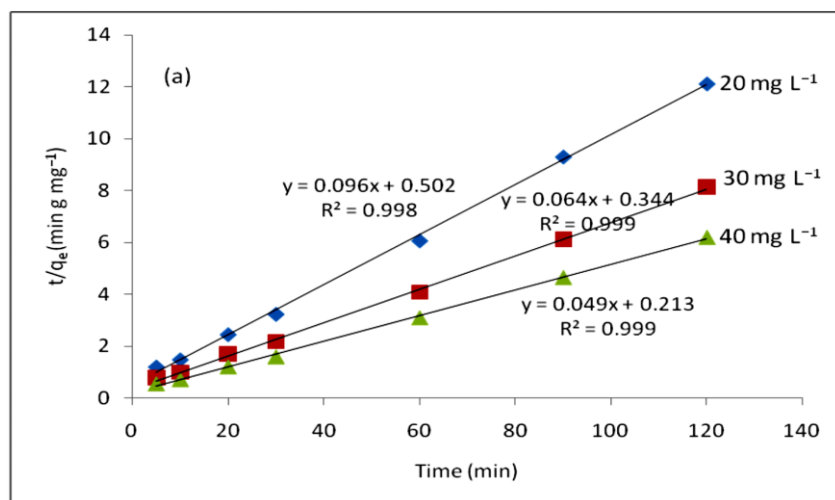


FIG. 4 Pseudo-second order plot for adsorption of Cr(VI) on to CDPT.

3.5 FTIR Analysis

FTIR spectra of DPT, CDPT and Cr(VI) loaded CDPT are shown in Figure 5. In the FTIR spectrum of DPT, the absorption peaks at 3396 , 2921 , 1738 and 1247cm^{-1} are due to $-\text{OH}$, C-H , C=O and C-O stretching vibrations, respectively. The absorption peaks at 1730 and 1207cm^{-1} in the FTIR spectrum of CDPT are due to CHO formed during charring process. FTIR spectrum of CDPT (Figure 5 b) shows a band at 3401cm^{-1} assigned to $-\text{OH}$ stretching vibration. Two weak bands at 2922 and 2854cm^{-1} may be assigned to aliphatic group stretching vibrations but their intensities are lower than the spectrum of DPT (Figure 5 a) leading to the decrease in aliphaticity in CDPT by increasing temperature. A peak at 1207.8cm^{-1} indicates the presence of $-\text{SO}_3\text{H}$ group and is shifted to 1169cm^{-1} in the spectrum of Cr(VI) loaded CDPT (Figure 5 c). The peak at 618cm^{-1} may be assigned to stretching vibration of S-O group and is shifted to 575.7cm^{-1} in the spectrum of Cr(VI) loaded CDPT.

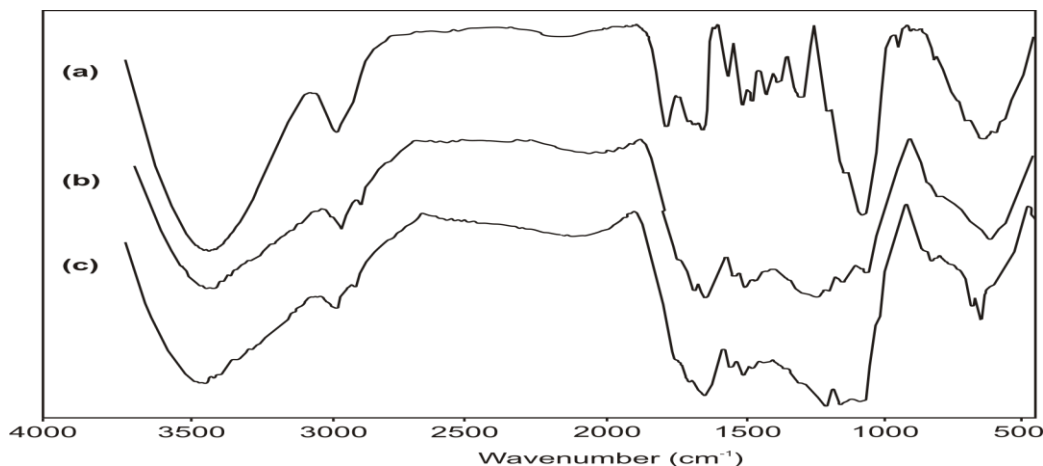
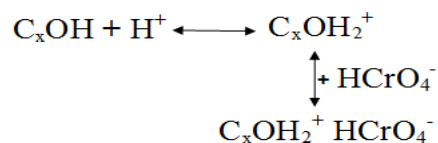


FIG. 5 FTIR spectra of (a) DPT (b) CDPT (c) Cr(VI)-loaded CDPT.

3.6 Adsorption Mechanism

The functional groups present on the CDPT surface greatly influence the Cr(VI) removal mechanism. The OXO-functional groups (denoted by C_xOH) including $-OH$ and $-COOH$. In Figure 5 (b, c) FTIR spectra of CDPT also resulted the presence $-OH$ and $-COOH$ by the absorption peaks at 3401 , 1730 and 1207 cm^{-1} . At low pH values, in the presence of adequate H^+ ions, the surface of the CDPT 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:



3.6 Desorption

The adsorbed Cr(VI) on CDPT was recovered using $0.1N$ NaOH as an eluting reagent. Further more, in order to investigate the reproducibility of CDPT, 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 CDPT was 99.95% for Cr(VI). This study reveals that the prepared adsorbent is capable of four cycles of adsorption/ desorption. The recovered chromium is benefit for industry.

4. CONCLUSIONS

The results obtained in this study indicate the potentiality of CDPT for the removal of Cr(VI). Maximum Cr(VI) adsorption (14.75 mg g^{-1}) occurred at $pH \sim 2$. Adsorption process revealed that the initial uptake of Cr(VI) up to 15 min was rapid (85%) and equilibrium was achieved within 60 min. 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. The desorption percentage was 99.5% using $0.1M$ NaOH as an eluting reagent. This study demonstrates that the CDPT can be used as a potential adsorbent for the treatment of wastewater containing Cr(VI).

REFERENCES

- [1] V. Sarin and K.K. Pant, *Biores Technol.* 97, 15 (2006).
- [2] B. Gulay and M.Y. Arica, *Chem Eng J.* 139, 20 (2008).
- [3] B.A. Hosseini, M.S. Hosseini, G.M. Sarw, S. Zowghi, E. Hosseini and B.H. Hosseini, *Chem Eng J.* 160, 190 (2010).
- [4] A.M. Yusof and N.A.N.N. Malek, *J Hazard Mater.* 162, 1019 (2009).
- [5] L.C. Qingqiang Meng, J. Zheng, X. Wei and Z. Ye, *Vacuum.* 89, 1 (2013).
- [6] Moussavi, G., and Barikbin, B. (2010) *Chem Eng J.* 162: 893.
- [7] Freundlich, H. (1907) *Z. Phys. Chem.*, 57: 385-470.
- [8] Lagergren, S. (1898) *Handlingar*, 24(04): 1-39.
- [9] Ho, Y. S., and McKay, G. (2000) *Water Res.*, 34: 735-742.