

## **CHROMIUM(VI) REMOVAL FROM WASTEWATER BY BATCH ADSORPTION MODE USING DATE NUT CARBON**

### **ABSTRACT**

Water pollution has great impact on environmental degradation. Release of untreated wastewater containing toxic metal ions into natural waters is a threat to aquatic ecosystem and is attributed to affect the health of living things. Date nut carbon was analysed as an adsorbent for extracting Cr(VI) ions from wastewater using batch method. Investigations were done by varying the pH from 1 to 6, carbon dose from 0.1 g to 0.5 g and equilibration time from 1 to 24 hours. Cr(VI) removal of 93% occurred at an optimal pH of 2, carbon dose of 0.3 g/100mL, and equilibration time of 3 hours. The adsorption of Cr(VI) on Date nut carbon followed first order kinetics. The kinetic process of Cr(VI) adsorption onto Date nut carbon was tested by applying first order kinetics.

**Key words:** Date nut carbon, Adsorption, Chromium(VI) removal, Kinetics

### **1.Introduction**

Chromium is a chemical element in the periodic table that has the symbol Cr and atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. Chromium (III) occurs naturally in the environment and is an essential nutrient. Chromium (VI) and chromium (0) are generally produced by industrial processes. The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is  $0.05 \text{ mg L}^{-1}$ . Cr(VI) is mobile in the environment and is highly toxic. Cr(VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases. At short-term exposure levels above the maximum contaminant level, Cr(VI) causes skin and stomach irritation or ulceration. Long-term exposure at levels above maximum contaminant can cause dermatitis, damage to liver, nerve tissue damage, and death in large doses [1]. Conventional treatment methods such as electrochemical precipitation, ion exchange, membrane processing, solvent extraction, coagulation, and adsorption have been employed to remove chromium ions from

wastewater. Adsorption is an efficacious method. Up to now, activated carbon is the most widely used adsorbent due to its high efficiency and easy recovery, but its price is relatively high, which limits its use as an adsorbent in developing countries. In recent years, agricultural waste materials have become widely used as adsorbents due to their cheap prices, abundance in nature, large surface area and high adsorption capacity[2]. Various agricultural wastes like tea waste [3], moringa leaves [4], neem bark [5], Gliricidia sepium leaf powder [6], seeds of *Artimisia absinthium* [7], mosambi peel dust [8], litchi peel [9], palm kernel shell [10], longan seed [11], apple peels [12], mango kernel [13], rice husk [14], pine apple peel [15], walnut shell [16], potato peel [17] chat stem [18] sugarcane bagasse [19] etc have been used as adsorbents for the removal of Cr(VI) from aqueous solution

Date or date palm tree is cultivated for its edible sweet fruit called dates. The species grows in many tropical and subtropical regions worldwide. Date trees reach up to 30 metres in height, Slow-growing, they can reach over 100 years of age when maintained properly. Date fruits are very sweet and are enjoyed as desserts. The Date nut, a waste material has been explored as activated carbon for decontaminating Cr(VI) from wastewater.

## **2.MATERIALS AND METHOD**

### **2.1Chemicals and Adsorbent**

All reagents were of analytical grade and double distilled water was used for dilution purposes. Chromium (VI) solution (1000 mg/L) was prepared by dissolving 0.7071 g of potassium dichromate in water and diluting to 250 mL. For standard chromium (VI) solution (10 mg/L) appropriate volume of the stock solution (1000 mg/L) was diluted with water to provide a solution containing 10 mg/L of Cr(VI). Chromium determination was done by Spectrophotometry [20].

Date nuts collected were cleaned and dried before carbonization. High temperature Date nut carbon was prepared by modified dolomite process [21]. Fifty grams of Date nut were placed between a bed of  $\text{CaCO}_3$  of 1 cm thickness and subjected to pyrolysis at 600 °C for 1h. The char was maintained at 900 °C for 30 min for activation by  $\text{CO}_2$ . The activated material soaked in 10 % HCl, washed with distilled water, dried at  $105 \pm 5$  °C. The carbon was designated as Date Nut Carbon (DNC).

### **2.2 Batch Studies**

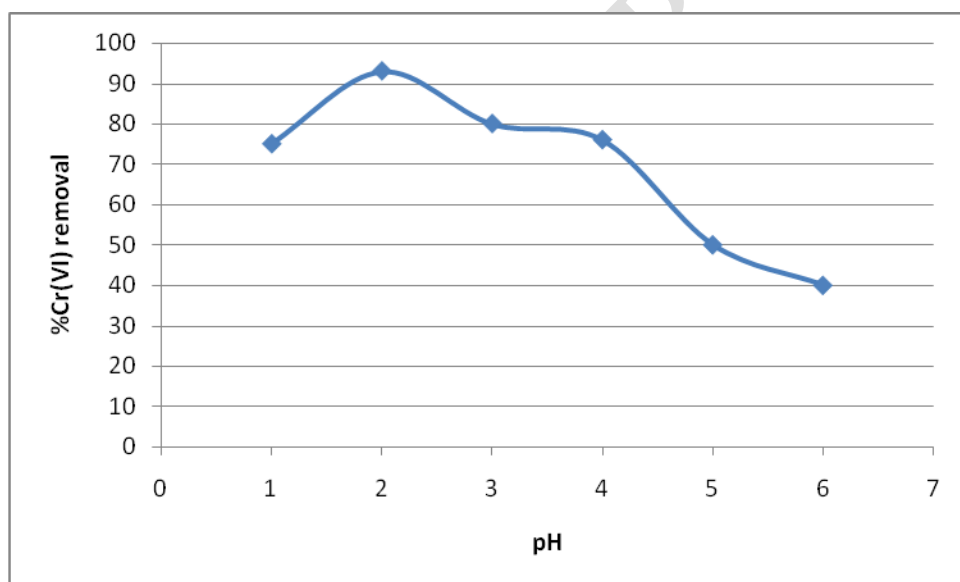
Batch experiments were conducted in polythene bottles of 300 mL capacity provided with screw caps. One hundred millilitre of the solution containing 10 mg/L of Cr(VI) under investigation

was taken in the bottles. After the addition of known amount of carbon, the bottles were equilibrated for a predetermined period of time in a mechanical shaker. The adsorbent is separated using a filter paper. Diphenyl carbazide method (DPC) was used to establish the Cr(VI) content spectrophotometrically at 540 nm. Adsorption studies were carried out in the pH range of 1.0-6.0 (contact time = 24 hrs, adsorbent dose = 0.5g, and room temperature) with 100 mL of 10 mg of Cr(VI)/L solutions. Effect of carbon dose at optimum pH and effect of equilibration time at optimum pH and carbon dose were also evaluated.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of pH

The maximum removal of chromium(VI) was at pH 2 (Figure 1). Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cation.

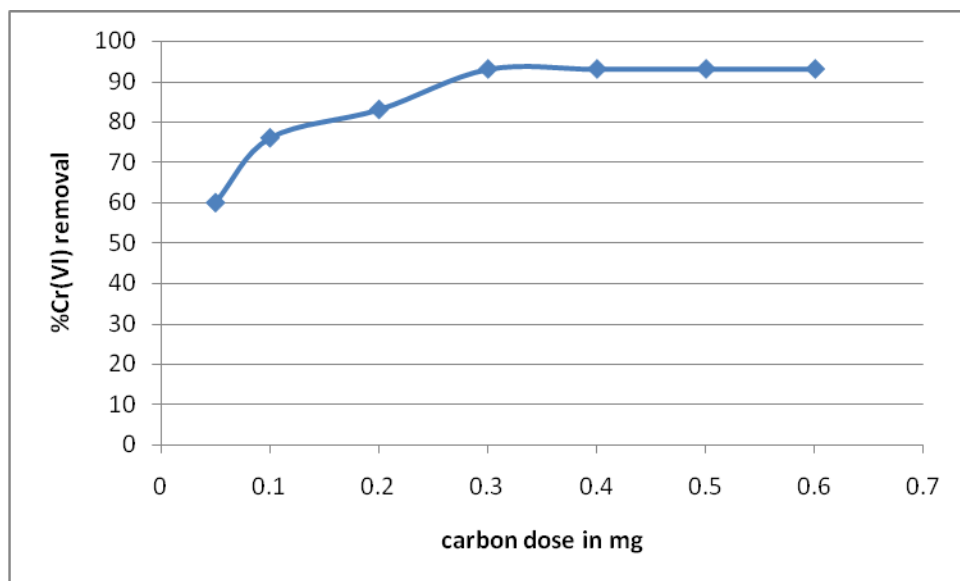


**Figure 1. Effect of pH on Cr(VI) removal**

#### 3.2 Effect of Carbon Dose

For 93 % removal of Cr(VI) a minimum dose of 0.3 g of DNC was required (pH=2, equilibration time=24h) (Figure 2). The increase in the removal efficiency with a simultaneous

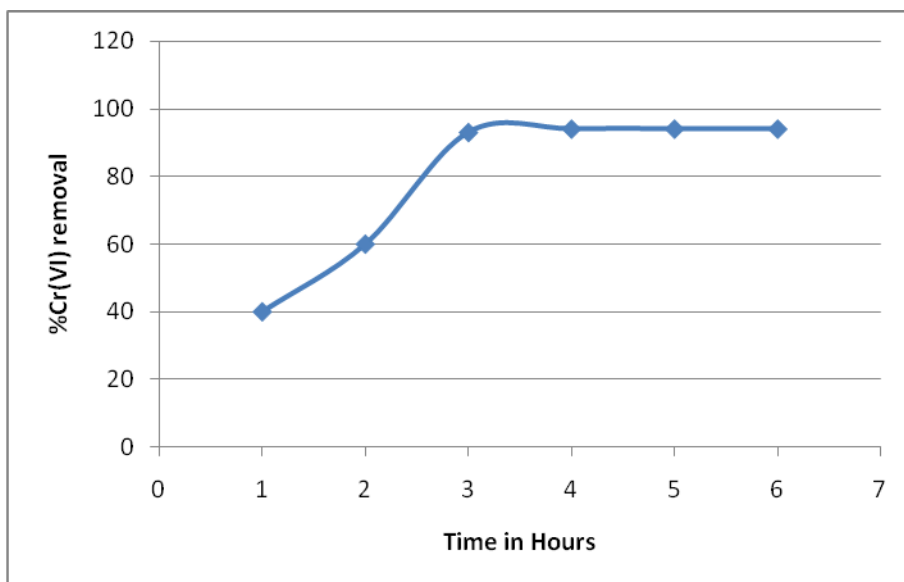
increase in adsorbent dose is due to the increase in surface area and hence more active sites are available for the adsorption of chromium Cr (VI). After 0.3 g, amount of Cr(VI) bounded to adsorbent remains nearly constant.



**Figure 2. Effect of carbon dose on Cr(VI) removal**

### 3.3 Effect of equilibration time

For DNC, an optimum time of 3 hours was needed for 93 % removal of Cr(VI) at pH 2 and 0.3g of DNC (Figure 3). Rapid kinetics of adsorption rate, is due to the abundance of active sites on the adsorbent's external surface, which are available for interaction with Cr(VI).



**Figure 3. Effect of equilibration time on Cr(VI) removal**

### Kinetic studies

The reversible first order rate equation is written in the form [22]

$$\ln(1 - u_t) = -kt \quad (1)$$

where  $u_t = x/X_e$  and  $k$  is the overall rate constant  $u_t$  can be calculated using the expression

$$\frac{C_{A(o)} - C_{A(t)}}{C_{A(o)} - C_{A(e)}} = \frac{x}{X_e} \quad (2)$$

where  $u_t$  is called fractional attainment of equilibrium

$C_{A(o)}$  = initial concentration of metal ion

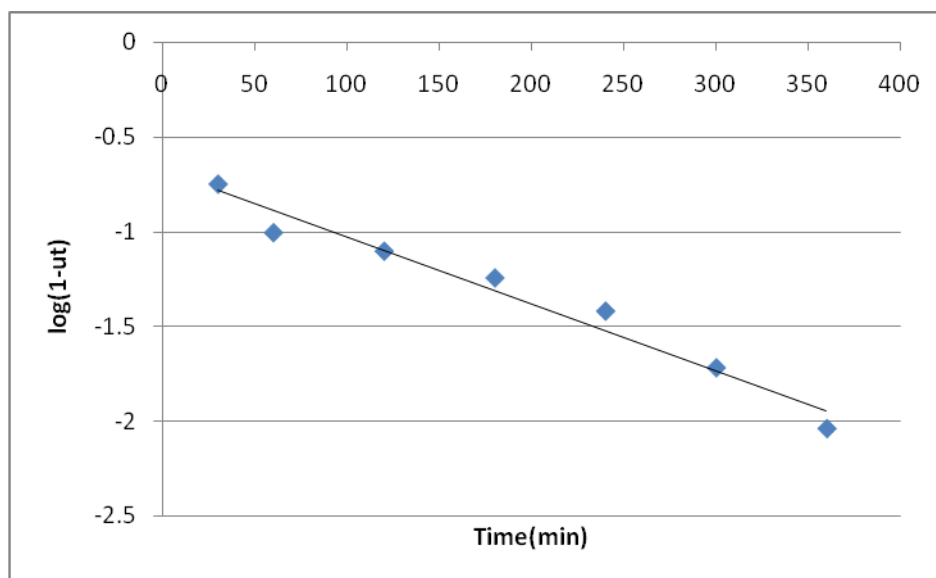
$C_{A(t)}$  = the concentration of metal ion present at any time (t)

$C_{A(e)}$  = the concentration of metal ion present at equilibrium condition

By plotting  $\ln(1 - u_t)$  Vs time, the overall rate constant ( $k$ ) of the reaction can be obtained from the slope values of the curves.

By knowing the values of ' $k$ ' and ' $k_c$ ', it is possible to calculate  $k_1$  and  $k_2$  using the expression.

$$k = k_1 + k_2 = k_1 + \frac{k_1}{k_c} = k_1 \left( 1 + \frac{1}{k_c} \right) \quad (3)$$



**Figure 4 Reversible first order kinetics for Cr(VI) removal**

The  $\log[1-u_t]$  values were plotted against the corresponding time (Figure 4). If the plots were linear then adsorption followed reversible first order kinetics[23]. The straight line plot of  $\log(1-u_t)$  vs  $t$  as shown in Figure 4 indicated that the adsorption of Cr(VI) on DNC followed reversible first order kinetics. The straight line portions of the curves were used for obtaining the slope values, which give the overall rate constants ( $k$ ) of the process. The forward  $k_1$  and backward  $k_2$  rate constants were calculated using equation 3. These data are furnished alongwith  $R^2$  values in Table 1

**Table 1. Rate constant for the adsorption of Cr(VI)**

Sorbent	$k = k_1 + k_2 \text{ (min}^{-1}\text{)}$	$k_1 \text{ (min}^{-1}\text{)}$	$k_2 \text{ (min}^{-1}\text{)}$	$R^2$
HDNC	0.0036	0.00359	0.0000037	0.9660

From Table 1 it is evident that the forward rate constant was much higher than the backward rate constant suggesting that the rate of adsorption was dominant. The applicability of

reversible first order rate equation was also confirmed by the regression co-efficient  $R^2$  values which were near to unity.

## CONCLUSION

Owing to its easy preparation and removal efficiency of 93%, High Temperature Date nut can be used as a productive adsorbent for the removal of Cr(VI) from wastewater. Batch assessment revealed that removal was effective at pH 2. An optimum dose of 0.3 g of DNC was enough for the removal of 93 % removal of Cr(VI) for 3 hrs of equilibration time.

## REFERENCE

1. Mojdeh Owlad, Mohamed Kheireddine Aroua, Wan Ashri Wan Daud, Saeid Baroutian(2008) Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review *Water, air and soil pollution*, **200**:59-77.
2. Ai, Tian , Jiang, Xiaojun, Liu, Qingyu (2018) Chromium removal from industrial wastewater using Phyllostachys pubescens biomass loaded Cu-S nanospheres, *Open Chemistry*, **16**: 842-852.
3. Khalil, Usman , Shakoor, Muhammad , Ali, Shafaqat , Rizwan, Muhammad (2018) Tea waste as a potential biowaste for removal of hexavalent chromium from wastewater: Equilibrium and kinetic studies, *Arabian Journal of Geosciences*, **11**.
4. Chandra Mouli R, Madhuranthakam, Archana Thomas, Zhainab Akhter, Shannon Q. Fernandes, Ali Elkamel(2021) Removal of Chromium(VI) from Contaminated Water Using Untreated Moringa Leaves as Biosorbent, *Pollutants*, 51-64.
5. Utkarsh Maheshwari, Suresh Gupta (2016) Removal of Cr(VI) from wastewater using activated neem bark in a fixed-bed column: interference of other ions and kinetic modelling studies, *Desalination and Water Treatment*, **57(18)**:8514-8525.
6. E Suganya, N Saranya, Chandi Patra, N Lity Alen Varghese, Selvaraju (2019) Biosorption potential of Gliricidia sepium leaf powder to sequester hexavalent chromium from synthetic aqueous solution, *Journal of Environmental Chemical Engineering*, **7(3)**:103112
7. Rifaqat Ali Khan Rao, Shaista Ikram, Mohammad Kashif Uddin. (2015) Removal of Cr(VI) from aqueous solution on seeds of *Artimisia absinthium* (novel plant material), *Desalination and Water Treatment*, **54(12)**: 3358-3371.
8. Naba Kumar Mondal, Sambrita Basu, Kamalesh Sen, Priyanka Debnath. (2019) Potentiality of mosambi (Citrus limetta) peel dust toward removal of Cr(VI) from aqueous solution: an optimization study, *Applied Water Science*, **9(4)**.
9. Yunhong Yi, Junliang Lv, Yi Liu, Gongqing Wu (2017) Synthesis and application of modified Litchi peel for removal of hexavalent chromium from aqueous solutions, *Journal of Molecular Liquids*, **225**: 28-33.

10. Razavi Mehr, Maryam & Fekri, mohammad hossein & Omidali, Faezeh & Eftekhari, Noushin & Akbari-Adergani, Behrouz (2019) Removal of Chromium (VI) from Wastewater by Palm Kernel Shell-based on a Green Method, *Journal of chemical health risks*, **9(1)**:75-86.
11. J Yang , Yu M, Chen, W (2015) Adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from Longan seed: Kinetics, equilibrium and thermodynamics, *Journal of Industrial and Engineering Chemistry*, **21**:414–422.
12. I Enniya, A Jourani, L Rghioui,(2018) Adsorption of hexavalent chromium in aqueous solution on activated carbon prepared from apple peels, *Sustainable Chemistry and Pharmacy*, **7**:9-16.
13. M K Rai, G Shahi, V Meena, R Meena, S Chakraborty, R S Singh, B N Rai(2016) Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H<sub>3</sub>PO<sub>4</sub>, *Resource Efficient Technologies*, **2**: S63–S70.
14. G C Ghosh, S Zaman, T K Chakraborty(2018) Adsorptive removal of Cr(VI) from aqueous solution using rice husk and rice husk ash, *Desalination and Water Treatment*, **130**.
15. A Shakya, T Agarwal(2019)Removal of Cr(VI) from water using pineapple peel derived biochars: adsorption potential and re-usability assessment, *Journal of Molecular Liquids*, **293**.
16. T Kokab, H S Ashraf, M B Shakoore et al., (2021)Effective removal of Cr(Vi) from wastewater using biochar derived from walnut shell, *International Journal of Environmental Research and Public Health*, **18**.
17. F Mutongo, O Kuipa, P K Kuipa(2014) Removal of Cr (VI) from aqueous solutions using powder of potato peelings as a low cost sorbent, *Bioinorganic Chemistry and Applications*, **7**: 973153.
18. Yigezu Mekonnen Bayisa, Tafere Aga Bullo, Desalegn Abdissa Akuma(2021) Chromium removal from tannery effluents by adsorption process via activated carbon cat stems (Catha edulis) using response surface methodology, *BMC Research Notes*, **14**:431
19. Santosh kumar singh(2017)Removal of hexavalent chromium Cr(VI) by using sugarcane bagasse as an low cost adsorbent , *Indian Journal of Scientific Research*, **13(1)**: 73-76.
20. AWWA, APHA (1992) *Standard Methods for the Examination of Water and Wastewater*, Washington DC.
21. K Srinivasan K, N Balasubramanian,T V Ramakrishna(1988) Studies on chromium removal by rice husk, *Indian Journal of Environmental Health*, **30**: 376-387.
22. L D Michelson, P G Gideon,E G Pace,L H Kutal (1975) US Department of Industry, Office of Water Research and Technology, Bulletin No.74.



23. K Srinivasan, Suganthi N(2009b) Nickel(II) removal by phosphorylated tamarind nut carbon, *Asian Journal of Chemistry*, **21(6)**:4515-4532

UNDER PEER REVIEW