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 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 trees, are grown for their delicious, edible fruit. The species can be found in many tropical and subtropical areas across the world. Date trees can grow to be up to 30 meters tall, and if properly cared for, they can live for over 100 years. Dates are sweet fruits that are eaten 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

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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 $CaCO_3$ of 1 cm thickness and subjected to pyrolysis at 600 ^oC for 1h. The char was maintained at 900 ^oC for 30 min for activation by CO_2. The activated material soaked in 10 % HCl, washed with distilled water, dried at 105 ± 5 ^oC. 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. 100 mL 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

3.1Effect 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. In highly acidic media, anionic form $HCrO_4^-$ will be adsorbed on the adsorbent surface as it may be more protonated.

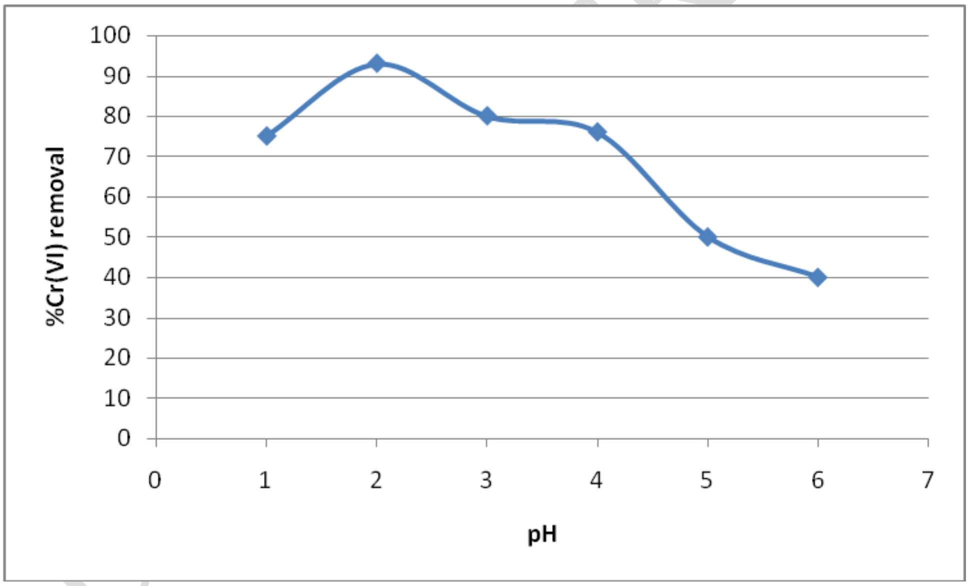

Figure 1. Effect of pH on Cr(VI) removal

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 as the quantity of metal ion is constant.

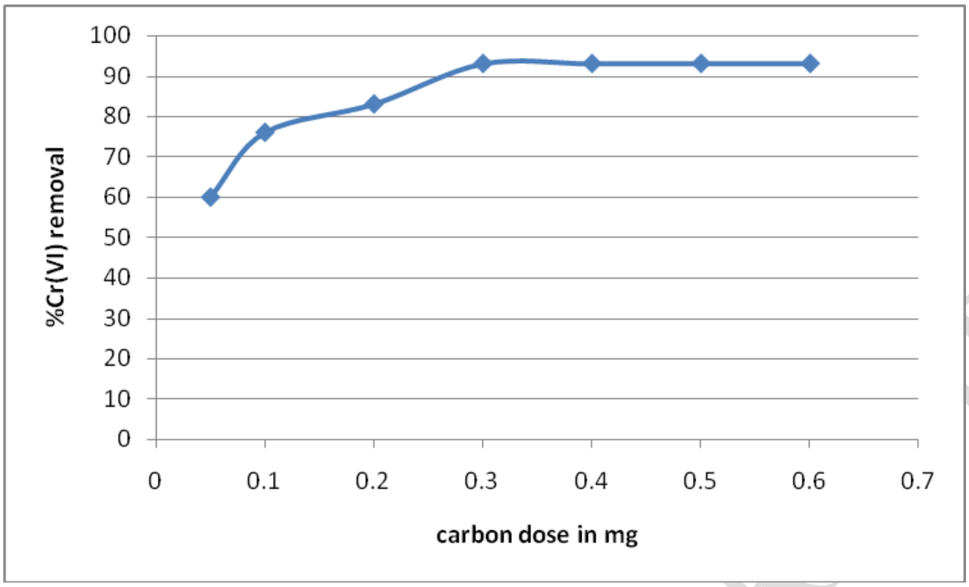

Figure 2. Effect of carbon dose on Cr(VI) removal

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). The quantity of active sites on the adsorbent's external surface, which are available for interaction with Cr(VI), accounts for the rapid kinetics of adsorption rate.

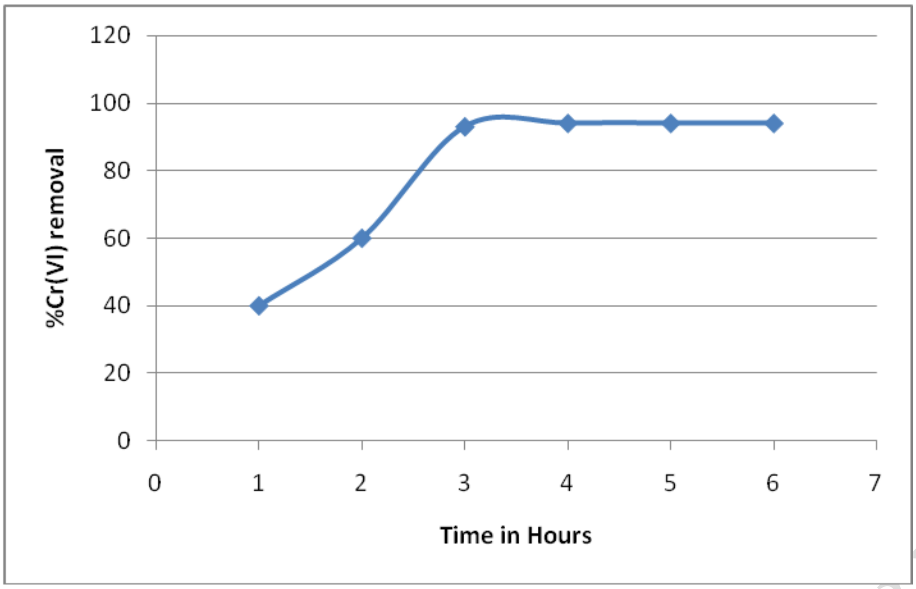

Figure 3. Effect of equilibration time on Cr(VI) removal

Kinetic studies

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

$$\ln(1 - U_t) = -kt \tag{1}$$

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

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

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.

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

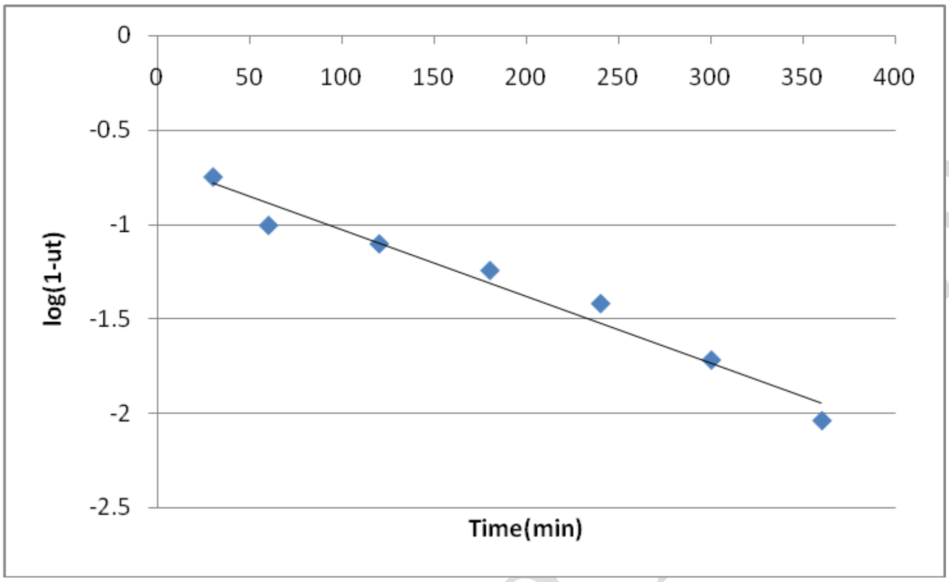

Figure 4 Reversible first order kinetics for Cr(VI) removal

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 slope values, which represent the overall rate constants (k) of the process, were calculated using the straight line portions of the curves. Equation 3 was used to get the forward k_1 and backward k_2 rate constants. Table 1 includes these statistics as well as R2 values.

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

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

The forward rate constant was substantially larger than the backward rate constant in Table 1, indicating that the rate of adsorption was dominant. The regression co-efficient R2 values were close to unity, confirming the application of the reversible first order rate equation.

CONCLUSION

Date nut has been explored to remove Cr(VI) as date fruits are available locally in the market and the nuts are thrown as wastes and it could be used as a potential sorbent for removal of Cr(VI) from wastewater. 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.

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