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Adsorption of Chromium (VI) on Activated Carbon Prepared by Acid Activation of Date Stones

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Abstract: ***Date stones (DS) were used as precursor for the preparation of activated carbon (DSAC) by chemical activation with sulphuric acid. The batch adsorption of Cr(VI) on DSAC were carried out at room temperature (25±2°C) and effects of various parameters such as pH solution, initial metal ion concentration, adsorbent dose and contact time were studied. It was observed that the adsorption decreased with increasing solution pH from 2 to 8. The maximum adsorption was observed at pH 2. The time required to reach equilibrium was found dependent of both solute and adsorbent initial concentrations. The experimental data were analysed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The Langmuir model gave better correlation for Cr (VI) adsorption onto the DSAC with R^2 value of 0.992 and a maximum adsorption capacity of 58.82 mg/g at pH of 2. The experimental kinetic data were also fitted to pseudo-first order and pseudo-second order models. The first model was more suitable to describe the kinetics data. The results obtained indicated that DSAC is effective in the removal of Cr (VI) from aqueous solutions and can be used as alternative of high cost commercial adsorbents.***

Keywords: Chromium (VI), Date Stones, Activated Carbon, Isotherms, Kinetics.

1. Introduction

The discharge of toxic heavy metals into aquatic environment has been known to cause serious pollution problems [1]. Among these pollutants, chromium posses the most sever environmental concern due to its high toxicity [2]. Chromium is usually found in industrial effluents like electroplating, leather tanning and textile industries [3]. In waste water chromium can exist in hexavalent Cr (IV) and trivalent Cr (III) forms, of which Cr (IV) is more toxic than Cr (III) and is known to be human carcinogen [4]. Many methods are employed for decontamination of water polluted with Cr (IV) such as chemical precipitation [5], coagulation [6], ions exchange [7], membrane filtration [8] and adsorption [9]. Among these methods, adsorption appears to be an attractive technique since it is simple, effective and economical in the removal of heavy metals from waste water [10]. Among various adsorbents available, activated carbon (AC) is the most widely used for waste water treatment since it owns a great adsorption capacity, due to its highly developed porosity, large surface area and variable surface chemistry [11]. However, high cost of commercially activated carbon limits its use as an adsorbent in developing countries [12-13]. Recently, immense research have been developed to produce the activated carbon from cheap and renewable precursors, such as coir pith [14], banana pith [15], orange peel [16], bagasse pith [17], apricot shell [18], oil palm fiber [19] and date stones [20]. This technology not only solves the problems of waste disposal but also converts it into available product that can be employed as an adsorbent for wastewater treatment. Date stones are a potential precursor for the production of AC as they are rich in carbon. They represent about 10% of the date weight; therefore, considerable quantity of waste is generated annually. Any attempt to reuse this waste will be useful. So the objective of this work was to evaluate the adsorption potential of date stones based activated carbon for Cr (VI) removal from aqueous solution. The batch adsorption of Cr(VI) on activated carbon prepared were carried out and effects of several operating parameters such as pH solution, contact time, initial metal ion concentration and adsorbent dose on the adsorption of Cr(IV) were studied. The experimental data were also analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and again fitted to pseudo-first order and pseudo-second order models.

2. Experimental

2.1. Preparation of date stones activated carbon DSAC

The date stones were first washed with water to remove impurities, dried at 105 °C for 24 h, crushed and sieved. Fraction with average particle size of 5 mm was selected for this study. 10 g of dried stones were well mixed with sulphuric acid solution at impregnation ratio (weight of H_2SO_4: weight of dried stones) of 4.85 and heated at activation time of 20h at 200°C (21). At the end of activation time the sample was withdrawn from furnace and allowed to cool. For the removal of residual H_2SO_4, the sample was repeatedly washed with distilled water until the pH of washing solution reached 6.5-7. After that, the sample was dried at 105 °C for 24 h, crushed, sieved and stored in tightly closed bottles. Particles with size between 0.5 to 0.60 µm were used for adsorption experiments.

2.2. Adsorption procedure

Simulated wastewaters with different Cr (VI) concentration (10-30 mg/L) were prepared by dilution of the stock $K_2Cr_2O_7$solution. The influence of experimental parameters, contact time (0-900 min), solution pH (2-8) and DSAC dose (0.05-0.35 g/L) on the removal of Cr (VI) from aqueous solution were studied in a batch mode operation under constant conditions (stirring rate 150 rpm at 298° K). The pH of solution was adjusted by adding few drops of diluted 0.1N NaOH or 0.1N HCl. At after predetermined intervals time, the samples were filtrated through 0.45 μm membrane, and the filtrates were immediately analyzed. The residual Cr (VI) concentration was determined by the diphenylcarbazide colorimetric method on a visible spectrophotometer HACH DR-2000 at 540 nm.

The adsorption capacity q (mg/g) and removal efficiency were calculated according to the equations (1) and (2) respectively:

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad (Eq. 1)$$

$$\% = \frac{(C_0 - C_t)}{C_0} x\,100 \qquad (Eq. 2)$$

Where C_0 and C_t were the concentrations of chromium (VI) (mg/l) initially and at a given time t in the solution, V is the volume of solution (L) and m is the used amount of adsorbent (g).

3. Results and Discussion

3.1. Effect of pH solution on Cr (IV) adsorption

The pH of the aqueous solution is an important water chemistry parameter that affects both the surface charge of an adsorbent and speciation of chromium. The effect of solution pH on metal ion adsorption was studied using 10 mg/L of initial concentration, 0.2 g/L of DSAC, pH 2-8 at 25 °C. The equilibrium adsorption (q_e) was found to decrease with increasing pH as shown in Figure 1.

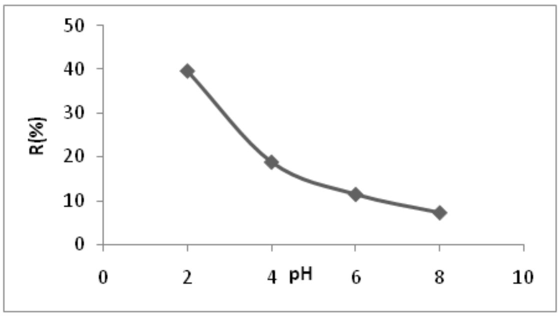


Figure 1: Effect of pH value on adsorption capacity of Cr (VI): DSAC dosage, 0.20 g/L; contact time, 600min.

The removal efficiency decreases from 39 to 7 % for increase in pH from 2 to 8. The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution [22]. More adsorption at acidic medium indicates that the lower pH results in an increase in H^+ ions on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and anionic species of chromium (VI) in the solution $HCrO_4^-$, CrO_4^-, $Cr_2O_7^{2-}$[23]. The decrease of the adsorption of Cr (VI) at higher pH values could be due to the decrease of electrostatic attraction. The surface of the carbon was negatively charged, which tended to repel the negatively charged Cr ions via electrostatic repulsion and decrease the adsorption capacity. Meanwhile, the competition between the Cr ions and OH^- ions in aqueous solution for the adsorption sites was also causes the reduction of Cr removal in the alkaline medium [25]. A similar results were reported for the adsorption of Cr (VI) by others adsorbents [25-26].

3.1 Effect of contact time and initial Cr(VI)concentration on Cr(VI) adsorption

The adsorption of Cr (VI) by DSAC was investigated at 3 different initial metal ion concentrations (10, 20 and 30 mg/L). Figure 2 shows the obtained results.

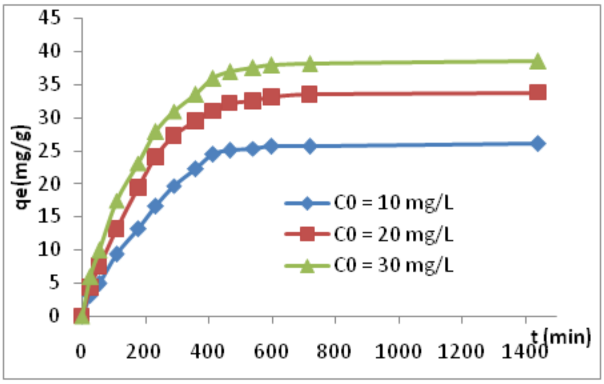


Figure 1: Effect of initial concentration and contact time on adsorption capacity of Cr (VI), DSAC, 0.20 g/l; pH, 2.

As can been seen from Figure 2, in all cases, the amount of the adsorbed Cr (VI) increased sharply in the initial stage and then gradually become slower until the equilibrium was reached. The initial fast adsorption may be attributed to large uncovered surface area of the DSAC. With further increasing time, the availability of the uncovered surface area gradually decreased, and adsorption equilibrium was established. Also Figure 2 indicated that the amount of adsorbed Cr (VI) at lower initial concentration reached adsorption equilibrium in approximately 500 min, while at high initial concentration, the time required to achieve equilibrium was 700 min. On the other hand it can be observed that increase in initial concentration conducts to increase in the adsorption of Cr(VI) on DSAC. The equilibrium adsorption increases from 25 to 39 mg/g with the increase initial concentration from 10 to 30 mg/L. It can be due to the fact that adsorption of ions metal on the DASC is diffusion based process. At higher initial concentration, the mass transfer driving force is larger, and hence, this results more adsorption of Cr (VI).

3.3 Effect of the DSAC dose

For effective metal sorption, adsorbent dose is a significant factor to be considered. The effect of adsorbent dose in the range of 0.05-0.36 g/L was studied at adsorption temperature 25°C and Cr (VI) initial concentration of 10 mg/L. The results of the amount adsorbed at equilibrium (mg/g) versus the adsorbent dose (g/L) have been illustrated in Figure 3 which shows that the significant increase in adsorption was observed when the dose was increased from 0.05 to 0.36 g/L. This may be due to the greater availability of the exchangeable sites on surface area at higher concentration of the adsorbent. These results are in agreement with previous studies on many other adsorbents [25-26]. After 0.32 g/L as adsorbent dose the amount adsorbed is not increase significantly.

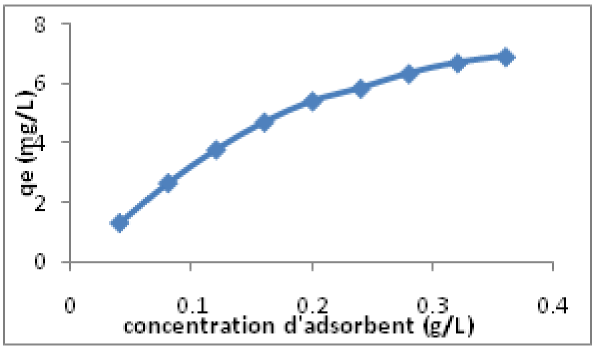


Figure 3: Effect of adsorbent dose on adsorption capacity of Cr (VI), Cr (VI) initial concentration of 10 mg/L; pH, 2.

3.2 Adsorption isotherms

The adsorption isotherms are important in the study and design of adsorption systems. Four commonly used isotherm models, Langmuir (Eq. 3) [27], Freundlich (Eq. 4) [28], Temkin (Eq. 5) [29] and Dubunin-Radushkevich (Eq. 6) [30] given below, have been applied to describe the adsorption of Cr (VI) onto the (DSAC).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad \text{(Eq. 3)}$$

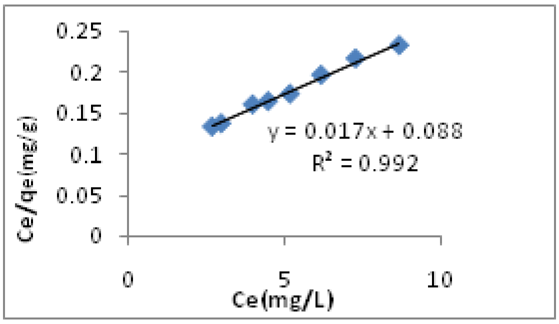
$$Lnq_e = \frac{1}{n} LnC_e + LnK_F \qquad \text{(Eq. 4)}$$

$$q_e = BLnCe + BLnA \qquad \text{(Eq. 5)}$$

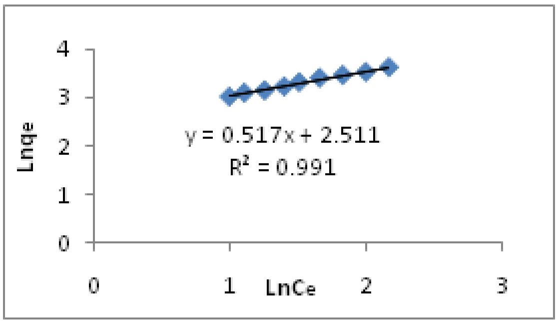
$$\mathrm{Lnq_e} = \mathrm{Lnq_m} - 2B_D \mathrm{Ln}\left(1 + \frac{1}{C_e}\right) \qquad \text{(Eq.6)}$$

Where q_e and C_e are the amount of Cr(VI) adsorbed per unit weight of adsorbent and equilibrium concentration of Cr(VI) remained in solution, respectively. In Eq. 3., q_{max} gives the theoretical monolayer adsorption capacity (mg/g) and K_L is the equilibrium constant (L/mg). In Eq. 4, K_F (mg/g) is related to the adsorption capacity and 1/nindicatesthe adsorption intensity. In Eq. 5, A (L/mg) is the equilibrium binding constant that corresponds to the maximum bindingenergy and B is related to the heat of adsorption:B = RT/b, T (K) is the absolute temperature; R is the universal gas constant (8.31 J/Kmol) and b is the Temkin isotherm constant.. In Eq. 6, q_m is the theoretical saturation capacity (mg/g), B_D is a constant related to the mean free energy of adsorption per mole of the adsorbate ($mol^2\ J^{-2}$).

The adsorption isotherms for Cr (VI) were studied using initial concentration of an adsorbent between 0.05 g/L and 0.35 g/L at Cr (VI) initial concentration of 10 m g/L. The experimental data were fitted to the isotherm models and graphical representations of these models are presented in Figure 4



(a)



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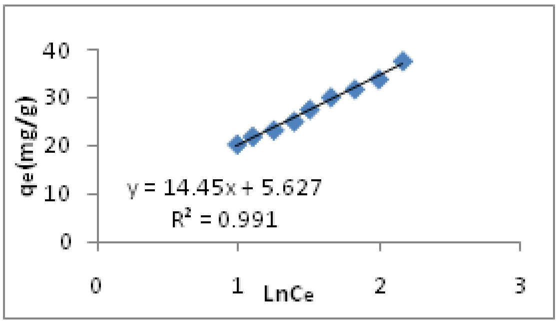

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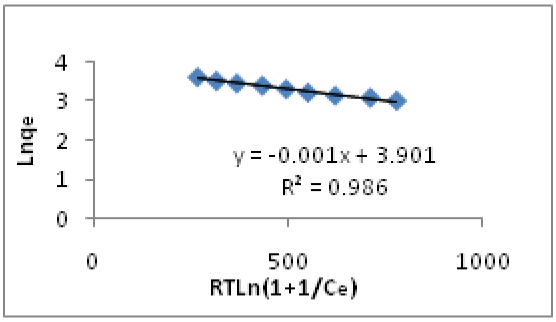


(d)

Figure 4: Adsorption isotherm plots for Cr (VI) onto the DSAC (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubunin-Radushkevich

The applicability of the isotherm models to fit the adsorption data was compared by judging the correlation coefficients, R^2 and the sum of squared error (SSE) values.The closer the R^2 value to unit, the better the fit. The SSE values were calculated by the equation:

$$SSE = \sum_{i=1}^{N} (q_{e,cal} - q_{e,exp})_i^2 \qquad \text{(Eq. 7)}$$

N is the number of data points, $q_{e,\ exp}$ and $q_{e,cal}$ (mg /g) are the experimental and the calculated values of the amount adsorbed at equilibrium, respectively. The lower the value of SSE indicates the better a fit is. The fit is accepted to be good when SSE is below 5 [31].

The slope and the intercept of each linear plot are used to calculate Langmuir, Freundlich, Temkin and Dubinin–Radushkevich parameters which are listed in Table1 together with associated correlation coefficients and the sum of error squares values.

The results listed in table 1 indicated that Langmuir, freundlich, and temkin isotherm models fit the experimental data for the adsorption of Cr (VI) onto the DSAC, better than the Dubinin–Radushkevich isotherm based on the very high values of R^2 ($R^2 > 0.99$) and the lower values of SSE compared to the Dubinin–Radushkevich model ($R^2 = 0.956$, SSE=10).

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter RL which is defined by Hall et al. [32]:

$$R_L = \frac{1}{1+K_L C_0} \qquad \text{(Eq. 8)}$$

Where C_0 is the initial concentration of metal ion (mg/L) and K_L is the Langmuir adsorption constant (L/g). The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L>1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The adsorption process was favorable as Langmuir separation factor, R_L was $0 < R_L < 1$ and supported by 1/n value of Freundlich which was less than one [33-34]. The q_m value using Langmuir isotherm was 58.82 mg/g which demonstrated that the DSAC has high adsorption ability toward Cr (VI).

Table 1: Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm constants, correlation coefficients and sum of error squares values for adsorption of Cr (VI) onto the DSAC.

Isotherm	Parameters	R^2 value	SSE %
Langmuir	q_{max}= 58.82mg/g K_L = 0.193 L/g $R_L = 0.341$	*0.992*	*1.7*
Freundlich	$K_F = 12.32$ $1/n = 0.517$	*0.991*	*1.94*
Temkin	*A = 1.476 L/mg* *B = 14.45J/mol*	*0.991*	*1.79*
Dubinin–Radushkevich	q_m *= 49.48 mg/g* *E = 28.86 J/mol*	*0.986*	*10*

The Temkin constants A and B were found to be 1.476 L/mg and 14.45 J/mol, respectively. The positive values(Table 1) of adsorption energy (B) obtained indicate that the process is exothermic. The D-R constants q_m and B_D found to be 49.48 mg/g and 6.10^{-4} mol^2/J^2, respectively. The values of the sorption energy E (kJ/mol) can be correlated to B_D by using the following equation:

$$E = \frac{1}{\sqrt{2B_D}} \qquad \text{(Eq. 9)}$$

If the magnitude of E is between 8 and 16 kJ·mol^{-1}, the adsorption process proceeds by ion exchange, while for values of E < 8 kJ·mol-1, the adsorption process is of a physical nature [35]. In this study, the value of E is (0.028 kJ mol^{-1}) which shows that the adsorption process can be considered as the physical adsorption.

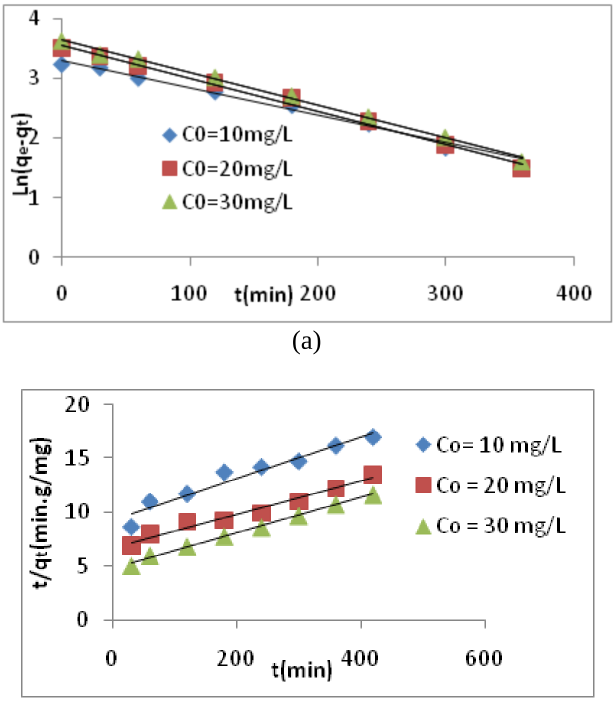
3.3 Adsorption Kinetics

Kinetics of the adsorption of Cr (VI) onto DSAC was investigated using two models, namely, the Lagergren pseudo-first- order (Eq. 11) [36], and the Ho pseudo-second-order models (Eq. 12) [37].

$$ln(q_e - q_t) = lnq_e - k_1 t. \qquad \text{(Eq.10)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad \text{(Eq. 11)}$$

Where q_e and q_t are the amount of Cr (VI) adsorbed in mg/g at equilibrium, and at time t, respectively, k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and k_2 (g/mg min) is the pseudo-second-order rate constant. Figure 5 shows plots of linearized form of pseudo-first-order and pseudo second-order at all concentrations studied.



(a)

(b)

Figure 4: Kinetics for adsorption of Cr (VI) onto DSAC: (a) pseudo-first-order; (b) pseudo second-order model.

The slopes and intercepts of plots were used to determine the parameters of both kinetic models and equilibrium adsorption q_e. The parameters of kinetic models and thecorrelation coefficient (R^2) values are listed in Table 2. As can be seen, the R^2 values obtained from the pseudo firs-order were consistently higher than those from the second pseudo-order. In addition the theoretical qe values found from the pseudo-second-order kinetic model did not give reasonable values. This suggests that this adsorption system is not a second-order reaction. Therefore, the adsorption kinetics can well be described more favorably by first order kinetic model for Cr (VI).

Table 2: Kinetic model parameters and correlation coefficients for adsorption of Cr (VI): (a) pseudo-first-order; (b) pseudo second-order model.

(a)

C_0(mg/L)	$q_{e,exp}$ (mg/g)	K_1(min^{-1})	q_e (mg/g)	R^2
10	26.00	*0.004*	*26.10*	*0.992*
20	*33.75*	*0.005*	*33.18*	*0.991*
30	*38.43*	*0.005*	*36.67*	*0.991*

(b)

C_0(mg/L)	$q_{e,exp}$ (mg/g)	K_1(min^{-1})	q_e (mg/g)	R^2
10	26.00	*0.019*	*52.63*	*0.942*
20	*33.75*	*0.015*	*62.50*	*0.996*
30	*38.43*	*0.016*	*66.67*	*0.969*

Similar results has been observed in the adsorption of Cr (VI) by coconut shell carbon, treated sawdust and H_2SO_4–activated carbons produced from hazelnut shell [11].

4. Conclusion

The present study shows that activated carbon prepared from date stones can be used as an adsorbent for the removal of Cr (IV) from aqueous solutions. The equilibrium data were fitted to the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The equilibrium data were best described by the Langmuir isotherm model (R^2=0.992, SSE=1.7%) with a maximum adsorption capacity of 58.82 mg/g. The suitability of the kinetic models for the adsorption of Cr (IV) on the activated carbon was also discussed. It was found that the adsorption kinetics of Cr (IV) obeyed pseudo-first-order adsorption kinetics.

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