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Adsorptive Removal of Crystal Violet Dye Using Agricultural Waste Cocoa *(theobroma cacao)* Shell

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Abstract

In this study, the ability of Cocoa (Theobroma cacao) Shell Activated Carbon (CSAC) to adsorb Crystal Violet (CV) dye from aqueous solution was investigated. Activated carbon was prepared from cocoa shell, an agricultural waste and batch mode adsorption experiments were conducted. The influence of various factors such as initial concentration (20, 40, 60,80mg/lt), contact time, pH (1.0-10.0) and carbon dosage on the adsorption capacity were investigated and optimal experimental conditions was ascertained. Adsorption data were modeled using Langmuir, Freundlich, Temkin and Dubinin-Raduskevich (DR) adsorption isotherms. Adsorption kinetics was verified by pseudo-first order, pseudo-second order and intraparticle diffusion models. The kinetic adsorption data fitted the pseudo-second order kinetic model well and also followed the intra-particle diffusion model. The results indicated that CSAC could be employed as low cost adsorbent in waste water treatment for the removal of CV.

Key words: Adsorption, activated carbon, cocoa shell, crystal violet.

Introduction

Effluents from industries such as food, paper, plastics and textiles generate considerable amount of colour due to dyes and cause serious water pollution, which affects the nature and sunlight penetration into the stream and reduces the photosynthetic action[1]. Therefore the removal of colour from effluent prior to discharge into water sources is necessary. There are several methods used for treatment of dye containing wastewater. Some of them involve reverse osmosis[2], chemical oxidation[3], photodegradation[4], electocoagulation-electroflotation[5] and adsorption[6]. Among these methods, adsorption had become superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design and ease of operation. Adsorption using activated carbon has been successfully used as an adsorbent for the removal of dyes from wastewater[7]. However, regeneration and reuse of activated carbon make it more costly. Consequently, many investigators have studied the feasibility of using low cost substances as adsorbents[8]. Utilization of agricultural solid waste is of great significance for the adsorbents[9]. Many agricultural waste materials for activated carbon preparation includes maize cobs, tamarind fruit shell, coir pith, cashewnut shell, palmkernel fibre, bannana pith, saw dust, sunflower seed hull, etc[10-17]. In the present study removal of CV from aqueous solution using carbon prepared from an agricultural waste, cocoa shell as an adsorbent was investigated.

Materials and Methods

Adsorbent preparation: Cocoa shell collected from local agricultural field was air–dried and allowed to chemical activation, by the addition of 50% sulfuric acid with constant stirring (w/v). The resulting product obtained was kept in muffle furnace maintained at 550°C for 7 hours. The carbon obtained was washed with double distilled water and soaked in 10% sodium bicarbonate solution and allowed to stand overnight to remove the residual acid from pores of the carbon. The material was washed with distilled water, until the pH of the adsorbent reached 7.0. Then it was dried in a hot air oven at 100±5 ºC for 12 hours. The dried material was grounded and sieved to get the particle size of 150µm and stored in an airtight container. The physico-chemical characteristics of CSAC were studied as per the standard testing methods and the physico-chemical properties were reported in our earlier paper[18].

Adsorbate preparation: Crystal violet (Molecular formula: $C_{25}H_{30}N_3Cl$, M.W.: 407.979, C.I. no. 42555, CAS: 548-62-9, mp=205°C) was purchased from Sd-fine chemicals Ltd., Mumbai and used without purification. Stock solution of dye was prepared by dissolving 1gm of dye in 1000ml of double distilled water to give the concentration of 1000mg/L. The stock solutions were diluted with known initial concentrations say 20, 40, 60 and 80mg/L in accurate proportions.

Adsorption experiment: Adsorption experiments were carried out in temperature controlled orbital shaker at a constant speed of 125rpm using 250mL conical flasks containing 100mg of CSAC with 50mL of dye solution at 35°C. All the experiments (except the study of pH effect) were carried out at pH of 8±0.5. After agitating the flasks for predetermined time intervals, samples were withdrawn from the flasks and the adsorbents were separated from the solution by centrifugation (REMI make) at 2000rpm for 10 minutes. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, measured at λ_{max} = 590nm spectrophotometrically using Elico make UV-Visible spectrophotometer. The amount of adsorbate adsorbed at equilibrium condition, q_e (mg/g) was calculated using the following equation:

$$q_e = (C_o - C_e)\frac{V}{W} \qquad (1)$$

where, C_o and C_e are the initial and equilibrium adsorbate concentrations (mg/ L), respectively, V is the volume of solution (L) and W is the mass of adsorbent (g).
The dye removal percentage can be calculated as follows:

$$\%\,removal = \frac{C_0 - C_e}{C_0}100 \qquad (2)$$

where, C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of isotherm and kinetic equations, respectively.

Results and Discussion

Effect of agitation time and initial concentration: For this study, CV solution with initial concentrations 20, 40, 60 and 80 mg/L were agitated with 100mg of CSAC at 35°C. As shown in figure1, the adsorption at different dye concentrations was rapid at the initial stages and then gradually decreases with the progress of adsorption until the equilibrium was reached. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of activated carbon and the contact time needed for CV solution to reach equilibrium was 90 minutes. The results indicated that there was no change in the sorption capacity after 90 minutes, therefore 120 minutes was fixed as the agitation time for isotherm studies.

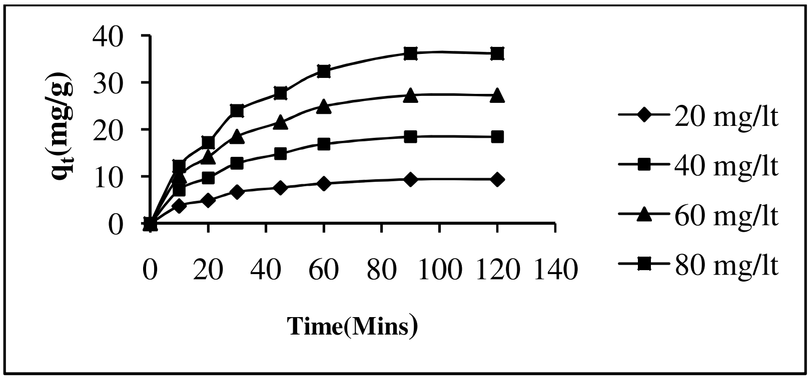

Figure-1
Effect of agitation time on adsorption: Initial concentration variation

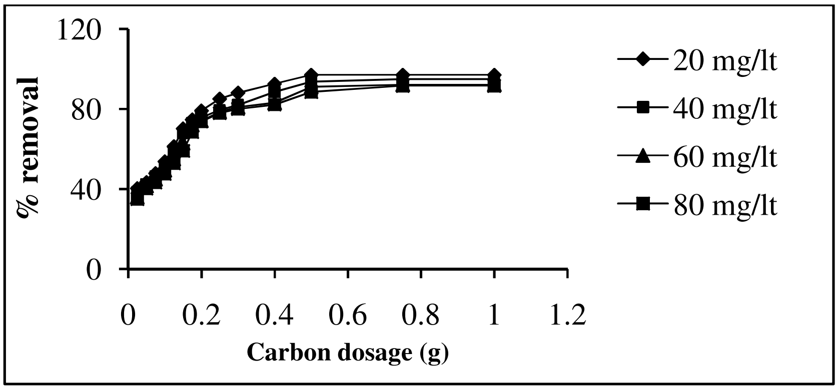

Figure-2
Effect of adsorbent dose on the removal on CV onto CSAC

Effect of adsorbent dosage: In order to investigate the effect of adsorbent mass on the adsorption, a series of adsorption experiments was carried out with different adsorbent dosages at initial concentration of 40mg/L without changing the volume of dye solution (50ml) with constant speed of 125rpm for 2 hours. Similarly the pH (8±0.5) and temperature (35^0C) was kept constant. The results follow the expected pattern, in which the percentage sorption increased with increased adsorbent dosage (figure- 2). The increase in carbon dosage is due to the increase in surface area or due to conglomeration of carbons at higher doses[19].

Effect of initial solution pH: pH is one of the most important factors controlling the adsorption of dye onto adsorbent particles, which affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants[20]. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. As the pH increases, it is usually expected that the cationic dye adsorption also increases due to increasing of the negative surface charge of adsorbents[21]. The effect of solution pH was studied between 1 to 10, initial pH controlled by the addition of 0.1M HCl or 0.1M NaOH and agitated with 100mg of adsorbent for 2 hours at 35°C. The effect of initial pH of dye solution on the adsorption of CV for initial dye concentration of 40 mg/L was illustrated in figure-3. For cationic dye CV, lower adsorption at acidic pH was probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption. In view of the above results, higher percentage removal was occurred at pH 8.0 and remaining tests were conducted at pH 8±0.5.

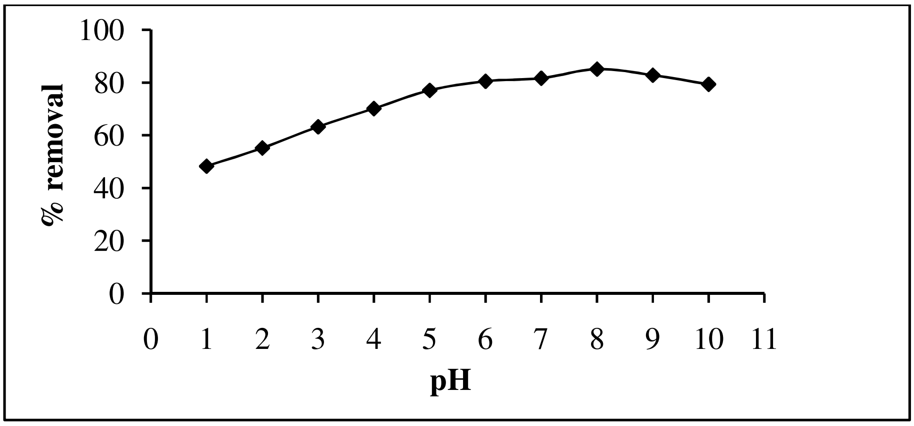

Figure-3
Effect of pH on the removal of CV by CSAC

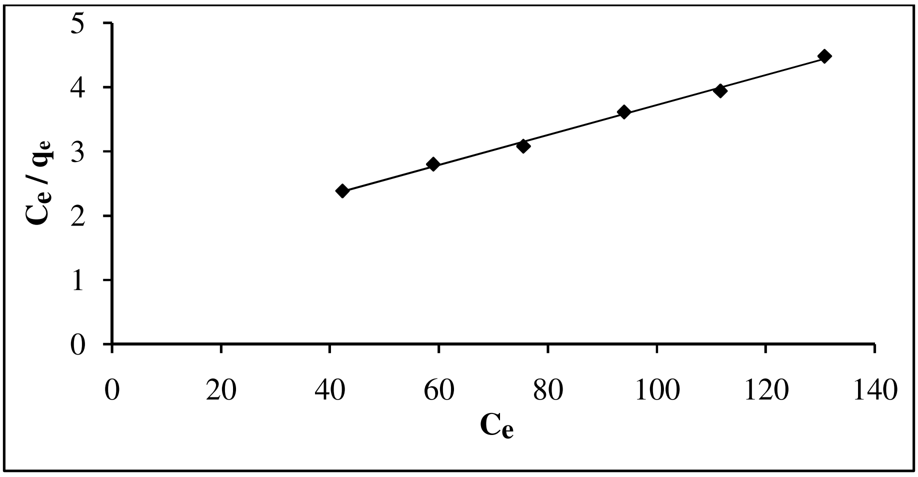

Figure-4
Langmuir plot for the removal of CV onto CSAC

Adsorption Isotherms: Adsorption isotherms parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and the important isotherms, Langmuir, Freundlich, Temkin and Dubinin - Radushkevich (DR) isotherms are applied in this study.

Langmuir isotherm: Langmuir adsorption isotherm model was usually adopted for homogenous adsorption and it is used successfully in monomolecular adsorption processes[22]. Linear form of Langmuir model was expressed as

$$\frac{C_e}{q_e} = \frac{1}{b}Q_0 + \frac{C_e}{Q_o} \qquad (3)$$

where, C_e is equilibrium constant of dye (mg/L), q_e is amount of dye adsorbed at equilibrium (mg/g), Q_0 is Langmuir constant related to adsorption capacity (mg/g), b is Langmuir constant related to energy of adsorption capacity (L/mg). The linear plot of C_e/q_e versus C_e was shown in figure 4. The constants Q_0 and b can be calculated from slope and intercept of the plot and the values are tabulated in table1. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption[23]. R_L was calculated as follows

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

where, C_o is the initial dye concentration(mg/L). R_L indicates the type of isotherm to be irreversible (R_L= 0), favorable ($0 < R_L < 1$), linear (R_L = 1) (or) unfavorable ($R_L > 1$). In the present investigation, the R_L values were less than one, showing favorable adsorption for CV onto CSAC.

Freundlich isotherm: Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface[24]. Linear form of Freundlich model was expressed by

$$\log C_e = \log k_f + \frac{1}{n}\log C_e \qquad (5)$$

where, q_e is dye concentration in solid at equilibrium (mg/g), C_e is dye concentration in solution at equilibrium (mg/L), K_f is the Freundlich isotherm constant related to adsorption capacity(L/mg) and n is the Freundlich isotherm constant related to adsorption intensity. The linear plot of $\log q_e$ versus $\log C_e$ was shown in figure 5 and the values of n and k_f calculated from the slope and intercept are given in table 1. The value of n was greater than one indicating the favorable adsorption of CV onto CSAC.

Temkin isotherm: Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption[25]. Linear form of Temkin equation was expressed by

$$q_e = \beta \ln \alpha + \beta \ln C_e \qquad (6)$$

where,

$$\beta = \frac{RT}{b}, \qquad (7)$$

T is the absolute temperature in Kelvin, R is the universal gas constant, 8.314 J/mol K and b is the Temkin constant related to heat of sorption (J/mg). A plot of q_e versus $\ln C_e$ (figure not shown) enables the determination of the isotherm constants α and b and the parameters are given in table 1.

Table- 1
Results of isotherm plots for the adsorption of CV onto CSAC

Models	**Isotherm constants**			
Langmuir	**Q_m (mg/g)**	**b x 10^{-3} (L/ mg)**	**R_L**	**r^2**
	43.50	16.6	0.27-0.50	0.996
Freundlich	**k_f (mg/g)**	**n**		**r^2**
	3.4	2.2		0.982
Temkin	**α (L/ mol)**	**β**	**b**	**r^2**
	0.4	24.04	106.4	0.992
Dubinin-Radushkevich	**q_m (mg/g)**	**K_{DR} (10^{-7} mol^2/J)**	**E (kJ/mol)**	**r^2**
	1	3.4	0.4	0.954

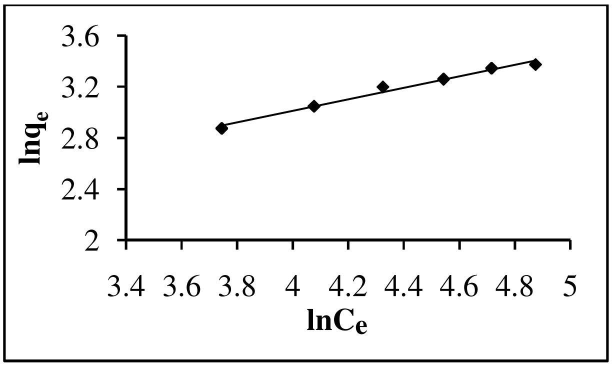

Figure-5
Freundlich plot for the removal of CV onto CSAC

Dubinin-Raduskevich (DR) isotherm: Dubinin-Raduskevich (DR) isotherm was used to determine the characteristic porosity and the apparent free energy of adsorption[26]. Linear form can be expressed as

$$\log q_e = \log q_m - K_{DR}\varepsilon^2 \qquad (8)$$

where, K_{DR} is a constant related to the mean free energy of adsorption (mol^2/J^2), q_m is the theoretical saturation capacity (mol/g), ε is the polyani potential (J/mol), which is related to the equilibrium concentration C_e, (mg/L) as follows:

$$\varepsilon = RT \ \ln(1 + \frac{1}{C_e}) \qquad (9)$$

The slope of the plot of $\ln q_e$ versus ε^2 (figure not shown) gives K_{DR} and the intercept yields the adsorption capacity q_m and the results are given in table-1. The mean free energy of adsorption (E) (KJ/mol) was calculated from the equation

$$E = \frac{1}{\sqrt{2K_{DR}}} \qquad (10)$$

Based on the correlation coefficients (r^2 values) of all the isotherms studied, it was found that Langmuir isotherm was the most-suitable isotherm for the experimental data followed by Temkin, Freundlich and Dubinin-Raduskevich (DR) isotherm.

Adsorption kinetics: Kinetic studies are necessary to optimize different operation condition for the sorption of dyes. The kinetics of CV onto CSAC was analyzed using pseudo-first order, pseudo-second order and Intraparticle diffusion kinetic models.

Pseudo – first order kinetic model: This model was suggested for the adsorption of solid/liquid systems[27]. The integrated linear form of the model is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (11)$$

A plot of log (q_e-q_t) versus t gives a linear line figure 6 from which the values of k_1 and q_e were determined from the slope and intercept respectively and presented in table 2.

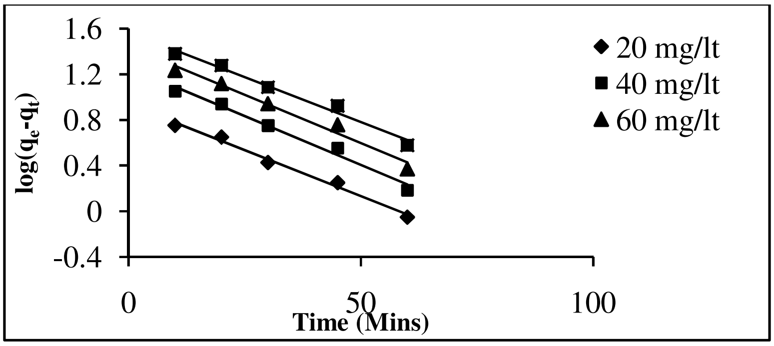

Figure-6
Pseudo–first order plot- Initial CV concentration variation

Table -2
Results of kinetic plots for the adsorption of CV onto CSAC

Concentration (mg/L)	**20**	**40**	**60**	**80**
Pseudo-first order kinetics				
k_1 x 10^{-2}(1/min)	3.68	3.91	3.68	3.45
$q_e$exp(mg/g)	9.4	18.5	27.3	36.2
$q_e$cal(mg/g)	11.4	22.7	34.5	47.6
r^2	0.989	0.982	0.976	0.980
Pseudo-second order kinetics				
k_2 x10^{-3}(g/mg min)	4.04	1.9	1.17	0.71
$q_e$cal (mg/g)	8.7	18.2	27.6	37.0
h	0.3	0.6	0.9	1.0
r^2	0.995	0.995	0.995	0.992
Intraparticle				
K_d(mg/ g min)	0.93	1.9	2.81	3.92
C (mg/g)	1.1	1.9	2.1	2.8
r^2	0.963	0.968	0.972	0.975

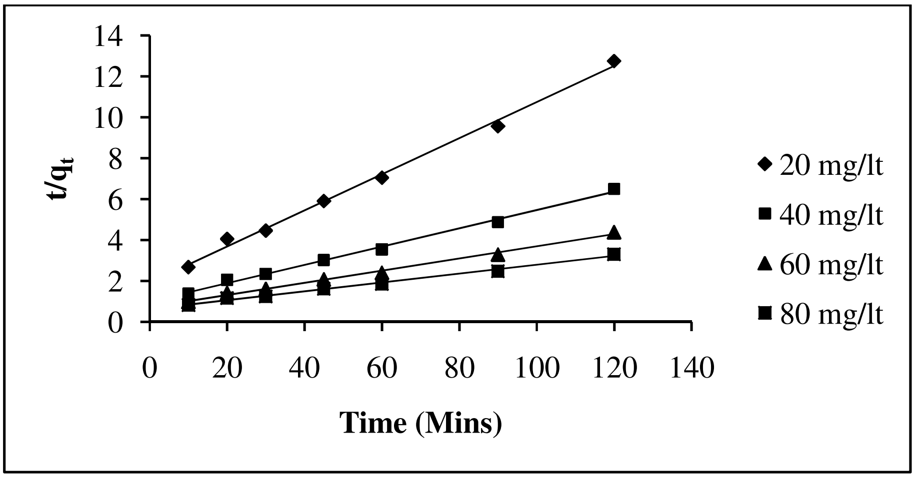

Figure-7
Pseudo–second order plot- Initial CV concentration variation

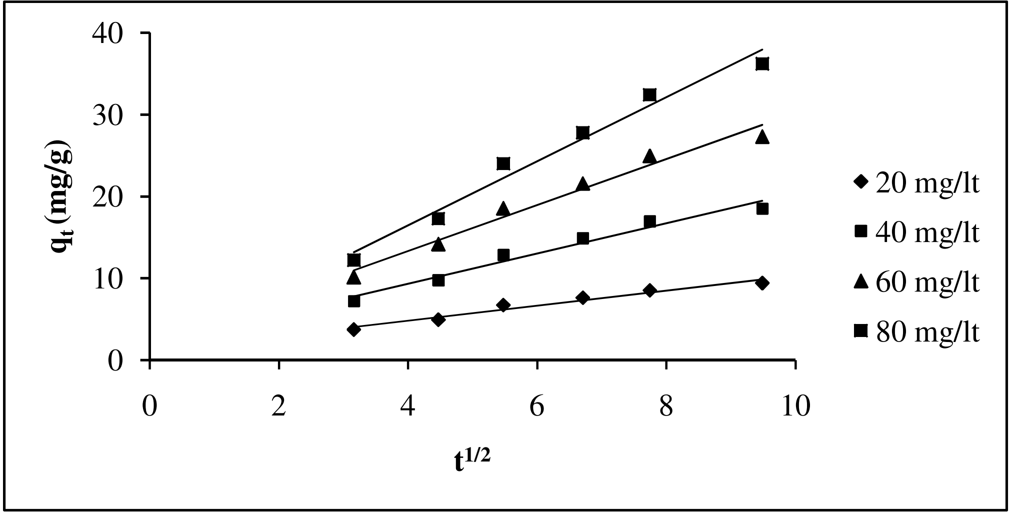

Figure-8
Intraparticle diffusion plot for the removal of CV onto CSAC

Pseudo – second order kinetic model: The adsorption mechanism over a complete range of the contact time is explained by the pseudo – second order kinetic model[28]. The integrated linear form of the model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{2}} + \frac{t}{q_e} \qquad (12)$$

The initial adsorption rate, h (mg/g min), as t → 0 can be defined as

$$h = k_2 q_e^{2} \qquad (13)$$

A plot of t/q_t versus t gives a linear relationship figure7, from which q_e and k_2 were determined from the slope and intercept of the plot respectively and presented in table 2. For all the systems studied, good correlation coefficients were obtained ($r^2 \approx 1$) by fitting the experimental data to pseudo-second order kinetics than that for the pseudo-first order kinetic model. Therefore, the sorption was more favorably by pseudo-second order kinetic model, which was based on the assumption that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate[29].

Intraparticle diffusion model: The possibility of intraparticular diffusion was expressed by the following equation[30]

$$q_t = k_d t^{1/2} + C \qquad (14)$$

A plot of q_t versus $t^{1/2}$ gives a linear relationship figure 8, from which k_d values determined from the slope was presented in table 2. The intercept of the plot reflects the thickness of the boundary layer[31]. If the regression of the plot is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, in this study the linear plots at each concentration did not pass through the origin. The deviation of straight lines from the origin may be due to the difference in rate of mass transfer in the initial and final stages of adsorption[32]. Such a deviation from the origin indicates that the pore diffusion is only the controlling step and not the film diffusion. The high correlation coefficient (r^2 values) proves the pore diffusion plays a significant role for the adsorption of CV onto CSAC.

Conclusion

The present study focuses on the adsorption of CV dye from aqueous solution using activated carbon derived from cocoa shell. The adsorption characteristics have been examined by initial concentration and contact time, initial pH and adsorbent dose. The maximum removal of CV was observed at pH 8.0. The adsorption of CV onto CSAC was found to increase with increase in adsorbent dose. Based on correlation coefficient (r^2 value), the experimental data was best fitted for Langmuir model than Freundlich, Temkin and Dubinin-Raduskevich isotherm models. The suitability of pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models for the sorption of CV onto CSAC was also discussed. Kinetic data follows the pseudo-second order kinetic model. Intraparticle diffusion model proves that pore diffusion plays major in the dye adsorption. The results showed the possibility of CSAC for dye removal from aqueous solution as an alternative for most costly used adsorbents.

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