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Batch Adsorption System of Hazardous Crystal Violet onto Treated Walnut Shell: Kinetic and Thermodynamic Studies

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Abstract: This research concern with removal of (CV) by adsorption system onto base-activated walnut shell, adsorption studies were achieved using batch experiments. The parameter studied includes contact time, initial dye concentration, pH, adsorbent dose, particle size of adsorbent, agitation speed and temperature. Experimental results showed the application of both Langmuir and Freundlich equations. The equilibrium of CV was achieved within 60 min for the different initial dye concentration (10 – 50 mg.l^{-1}). pH was found to be an important factor in controlling the adsorption of cationic dye. Removal of CV from aqueous solution was found to increase with increase in pH, increasing temperature and decrease of particle size of the adsorbent. The thermodynamic functions including (ΔG, ΔH and ΔS) for the adsorption process have been also evaluated using which it was concluded that the process of adsorption was spontaneous and endothermic.

Keywords: Adsorption modeling, Crystal violet, Isotherms, Kinetics, Natural adsorbent.

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1. INTRODUCTION

At present, population growth increases the need for coloration purposes such as, calico, leather, textile, food processing, dying, paper, cosmetics and dye manufacturing industries. This increased production lead to the release of hazardous and toxic wastes into the environment in liquid, solids or gaseous form. This causes enormous atmospheric change occurs. This can be defined as an unfavorable change in our surrounding partly or completely due to humans activities directly or indirectly through radiation, chemical addition, physical addition or addition of micro organism. Crystal violet belongs to the class of triphenylmethane dyes and is used largely as histological stain in veterinary medicine, as bacteriostatic agent and skin disinfectant in the medical community [21]. Crystal violet is harmful when ingested or inhaled and can cause life-threatening injury to the conjunctiva, skin irritation and permanent blindness[2,15,17]. The harmful effects of CV^+ warrant it removal from industrial wastes prior to discharge into water bodies and this has motivated us to take up research for its removal from wastewater. Any substance which causes pollution is termed as pollutant. They are discharged from industries, agriculture, automobiles and household activities into the environment.

Lately, the word pollution was used with reference to contaminating of water, soil and air. Pollution means addition of any foreign material or any physical changes in the natural water or air which may affect the living life. Several methods such as, precipitation, oxidation, ozonation, coagulation, ion exchange, membrane filtration, reverse osmosis, and adsorption have been proposed for the treatment of wastewater contaminated with dyes [18]. In addition, many of these technologies are cost prohibitive, especially when applied for treating large waste streams. Thus, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment, because of their proven efficiency in removal of organic and mineral pollutants and for economic consideration. Many adsorbents have been used previously such as, activated carbon and showed high adsorption capacity and good surface reactivity. However its regeneration results in 9–14% loss and decreased uptake capacity [16]. Other low cost adsorbents have been exploited for dye removal such as, orange peel, saw dust, , banana peel and papaya seeds [1,5,11,17,21], but there is a need for more efficient, abundantly available and low cost eco-friendly adsorbents with high adsorption capacity to be used for this purpose, and this is a prominent concern for the researcher and environmental technologists. In the present study base modified walnut shell that was prepared from walnut shell (BMWS) was used as an adsorbent for the removal of crystal violet

2. MATERIALS AND METHODS

2.1 Adsorbate :

Crystal violet (CV), a monovalent cationic basic dye (CI = 42,555, molecular formula $C_{25}H_{30}N_3Cl$, MW 407.98 g/mol and λmax= 585 nm) was supplied by Merck and used without further purification. Double-distilled water was used for preparation of all experimental solutions. A stock solution of CV 1000 mg/l was prepared in double-distilled water. Further, desired concentrations for the actual experiments were obtained by successive dilutions.

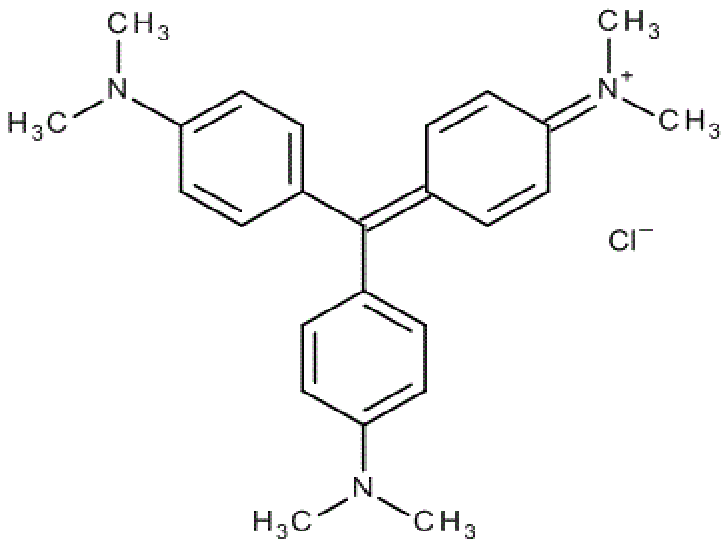

Fig.1: (Chemical structure of crystal violet)

2.2 Preparation of Adsorbent:

The walnut shell used in this study. was obtained from peeling the walnut fruits which was obtained from the local market. The hard external peel was milled and then sieved into different particle sizes the fraction 250 µm < d < 500 µm was selected. The sieved pulverized walnut shell was washed with double distilled water for dust and fine removals. The prepared walnut shell was dried at105°C over night, cooled and stored in a desiccators until required for use. Base modification walnut shell adsorbent was prepared by mixing 1g material/10 ml solution ratio by treating with NaOH (3% w/w) at room temperature for period 1h. After the treatments, the material was filtered and washed with double distilled water to remove an

2.3 Determination of CV

The concentrations of CV in aqueous solutions were determined by measuring the absorbance of the solution at 585 nm using a UV-visible spectrophotometer type (Agilent Technology cary series model UV/VIS spectrophotometer). Aqueous solutions of the dye within the concentration range (0-20) mg/l were used for calibration. Plot of absorbance versus concentration were linear as shown in figure2.

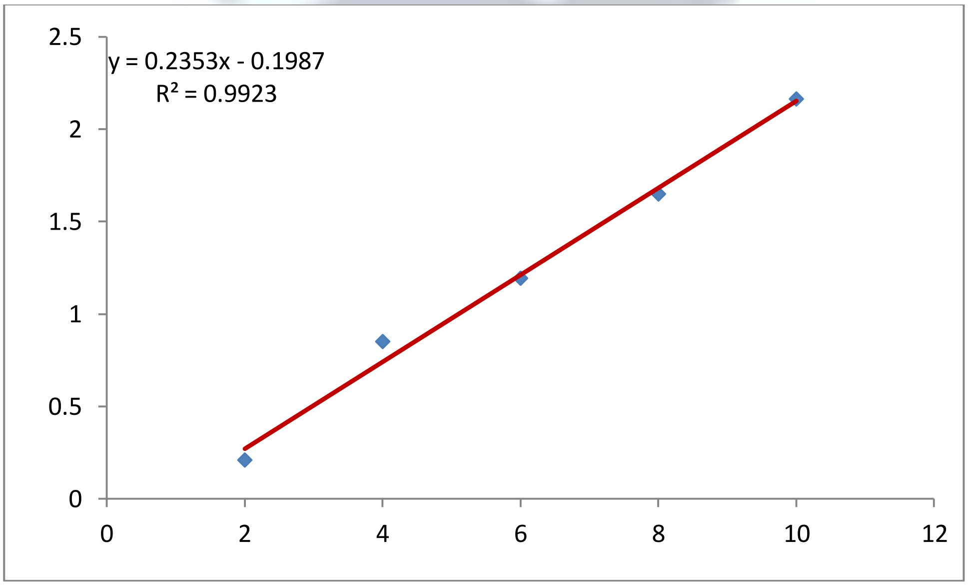

Fig. 2: Calibration curve of CV

2.4 Batch studies

The efficiency of adsorbent is evaluated by conducting laboratory batch mode studies. Batch adsorption experiments were carried out aliquots of 25 mg of adsorbent by shaking in 25 ml aqueous solution of dye of varying concentration for different time periods at natural pH (≈7) and temperature (≈ 298 K). In addition adsorbent dose, variation in pH, particle size, agitation speed and temperature were examined. The uptake of dye adsorbed onto pine cone powder at time t is qt (mg g-1) and was calculated using the following mass balance relationship:

$$q_t = \frac{(C_0 - C_t)}{m} V \quad (1)$$

and the percentage (%) of removal was calculated as

$$\% \text{ Removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Where C_0 is the initial dye concentration (mg L^{-1}), C_t is the concentration of dye at any time t, V is the volume of solution (L) and m is the mass of walnut shell powder in (g). All measurements are, in general, reproducible within ±10 %.

Adsorption isotherm

The adsorption isotherm experimental data were fitted with two well-known isotherms, the Freundlich (1906) and the Langmuir (1918) adsorption isotherm models, to explain CV dye–walnut shell adsorption mechanism.

Freundlich adsorption isotherm

This model assumed a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption. The linearized form of Freundlich can be written as

$$Inq_e = InK_F + \frac{1}{n} InC_e \quad (3)$$

Where q_e is the amount of dye adsorbed at equilibrium time (mg g^{-1}), C_e is equilibrium concentration dye in solution (mg L-1), n is the intensity of adsorption constant and K_F is the capacity of the adsorbents [4, 15, 20]. Freundlich isotherm parameters can be obtained from the slope and intercept of plot between In q_e vs. In C_e.

Langmuir adsorption isotherm

This model considers that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The linearized form of Langmuir isotherm model can be expressed as

$$\frac{1}{q_e} = \frac{1}{K_a q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad (4)$$

Where q_e is the amount of dye adsorbed at equilibrium time (mg g^{-1}), C_e is equilibrium concentration of dye in solution (mg L^{-1}), q_m is maximum adsorption capacity (mg $g\text{-}^1$) of adsorbent and Ka is Langmuir isotherm constants (L mg^{-1}). Ka and q_m can be determined from slope and intercept of plot between C_e/q_e and C_e [1,7,12].

Adsorption kinetics

The applicability of the pseudo-first-order model, pseudo second-order model and intraparticle diffusion model was investigated to identity the mechanism of CV adsorption on treated walnut shell as follows:

Pseudo-first-order model

The Lagergren pseudo-first-order model illustrated the adsorption kinetic data, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The integral form of the pseudo-first-order model is generally expressed as [7, 12].

$$\text{Log}\ (q_e - q_t) = \text{Log}\ qe - \frac{k_1}{2.303}t \tag{5}$$

Where k_1(L min^{-1}) and predicted q_e can be determined from the slope and intercept of the liner plot between log (q_e-q_t) and t, respectively.

Pseudo-second-order model

The adsorption kinetic may be described by the pseudo second-order model. The differential equation is generally known and described as [7, 12].

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \tag{6}$$

Where k_2(g mg^{-1}min^{-1}) is the second-order rate constant of adsorption. Integrating Eq. (6) for the boundary conditions q_t =0-q_t at t =0-t is simplified and linearized to obtain

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

The second-order rate constants were used to calculate the initial adsorption rate given by the following equation:

$$h = k_2 q_e^2 \tag{8}$$

The plot of t/q_t versus t shows a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plot of t/q_t versus t according to Eq. (7).

Adsorption mechanism

Intraparticle diffusion model

The adsorption proceeds in several steps involving transport of solute molecules from the aqueous phase to the surface of the solid particles and then interior of the solid. According to Weber and Morris (1963), for most adsorption processes the amount of adsorption varies almost proportional with $t^{1/2}$, which can be expressed as

$$q_t = K_{id}t^{1/2} \tag{9}$$

Where q_t is the adsorption capacity at time t, $t^{1/2}$ is the half life time in second and K_{id} (mg g^{-1}min $^{-1/2}$) is the rate constant of the intraparticle diffusion model.

Liquid film diffusion model

In the transport of the adsorbate molecules from the liquid phase to the solid phase, the boundary layer plays an important role in adsorption and the equation of the liquid film diffusion model can be written as

$$\ln(1 - q_t/q_e) = -K_{fd}t \tag{10}$$

Where q_t/q_e is the fractional attainment of equilibrium, and K_{fd} is the film diffusion rate constant.

Thermodynamic study

Thermodynamic consideration of an adsorption process is needed to conclude whether the exothermic or endothermic process is natural. The thermodynamic parameters, namely Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have an important role to determine heat change during the adsorption process. Assuming that the activity coefficients are unity at low concentrations, the relationship of these thermodynamic parameters with adsorption equilibrium constant K_e is given by the following classical Van't Hoff equation [5,10,13].

$$K_e = 1000\frac{q_e}{C_e} \qquad (11)$$

$$\log q_e = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \qquad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (13)$$

Where K_e is the distribution coefficient of the adsorbate, and q_e and C_e are the equilibrium concentration of CV on the treated walnut shell (mg g^{-1}) and in the solution (mg L^{-1}), respectively. R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the temperature in (K). ΔH°and ΔS° parameters can be calculated from the slope and intercept of the plot Log K_e vs. 1/T, respectively.

2.4.1 Effect of contact time

Adsorbent amount 25 mg with dye solution(25 ml) was kept constant for batch experiments with an initial dye concentration of 50 ppm were performed at nearly 303K on a oscillator at 230 rpm for 10, 20, 30, 40, 50, 60 and 70 minutes at pH = 7. Then optimum contact time was identified for further batch experimental study.

2.4.2 Effect of adsorbent dosage

200 mg/l of initial dye concentration were used in conjunction with adsorbent dose of 0.5, 1, 1.5, 2, 2.5 and 3 g/l. Contact time (60 min), pH (7), agitation speed (230rpm), temperature (303K) and particle (≥ 5o mesh) were kept constant.

2.4.3 Effect of initial dye concentration

Variable concentration such as 50, 75, 100, 125, 150, 175 and 200 mg/l of initial dye concentration were used in conjunction with adsorbent dose of 1 g/l. Contact time (60 min), pH (7), agitation speed (230rpm), temperature (303K) and particle (≥ 5o mesh) were kept constant.

2.4.4 Effect of pH

Initial pH of dye solutions were adjusted to 4, 6, 8 and 10 for 100 mg/l concentration. Contact time (60 min), adsorbent dose (1g/L), agitation speed (230rpm), temperature (303K) and particle (≥ 5o mesh) were kept constant.

2.4.5 Effect of particle size

Different sized particles of ≥ 300, 300 ≤ 250 and 250 ≤ 200 µm (300 µm equal to 50 mesh) were used in conjunction with150 mg/l dye concentration. Contact time (60 min), adsorbent dose (1g/L), pH (7), agitation speed (230rpm), temperature (303K) and particle (≥ 5o mesh) were kept constant.

2.4.6 Effect of temperature

303K, 313K and 323K temperatures were used in conjunction with 150 mg/l dye concentration. Contact time (60 min), adsorbent dose (1g/L), pH (7), agitation speed (230rpm) and particle (≥ 5o mesh) were kept constant.

Results and Discussions

2.5 Effect of contact time

Uptake of CV was rapid in first 10 minutes and after 60 minutes amount of dye adsorbed was almost constant. Effect of contact time on adsorption of CV is presented in Figures 3. The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage. Later on the process becomes relatively slower and equilibrium conditions are reached within 50 to 60 minutes. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the treated walnut shell. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. Therefore, further batch experiments were carried out at 60 minutes optimum contact time.

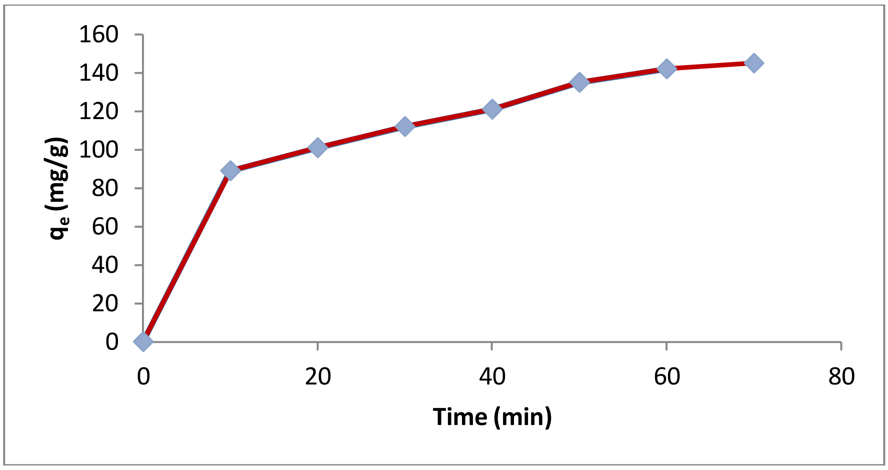

Fig. 3: Effect of contact time on adsorption of CV

2.6 Effect of adsorbent dosage

Removal of CV was studied by varying the adsorbent dosage. The percentage of adsorption increased with increase in dosage of adsorbent. However, amount of dye adsorbed per unit mass of adsorbent decreased with increased in adsorbent dose from 0.5 to3g/l. Figures 4 and 5. As amount of adsorbent increases, number of active sides available for adsorption also increases therefore % removal also increases. Since all active sides may not be available during adsorption due to overlapping between the active sides themselves and thus amount adsorbed mg/g of adsorbent decreases. Therefore, the adsorption of dye increased with the sorbent dosage and reached an equilibrium value after certain sorbent dosage (1.5 to 2 g/l) for the adsorbent.

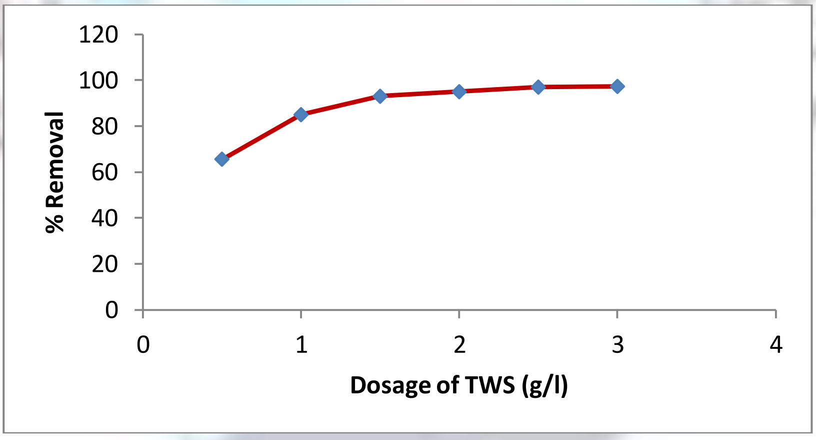

Fig.4: Effect of TWS dose on % removal of CV

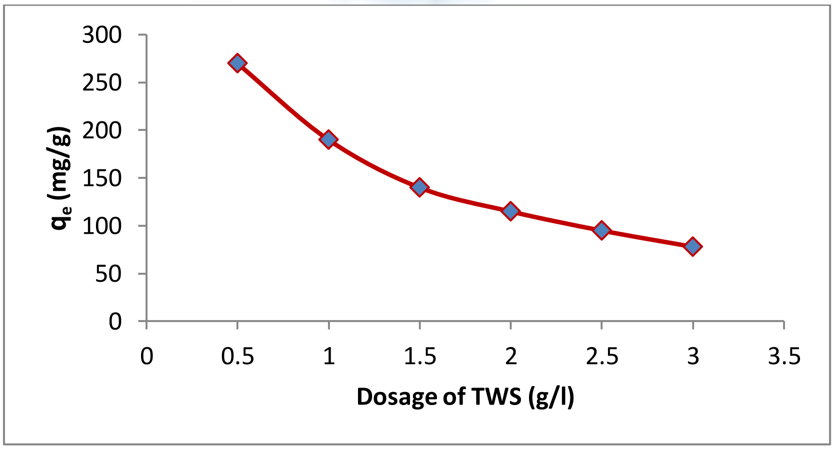

Fig. 5: Effect of TWS dose on amount adsorbed (mg/g) of CV

2.7 Effect of initial dye concentration

The amount of CV adsorbed per unit mass of adsorbent (mg/g) increased with increase in CV concentration from 50 to 200 mg/l but the adsorption percentage decreased, figures 6 and 7. The Initial concentration provides an important driving force to overcome all mass transfer resistances of the CV between the aqueous and surface of solid phases. Thus, a higher initial concentration of dye will enhance the adsorption process.

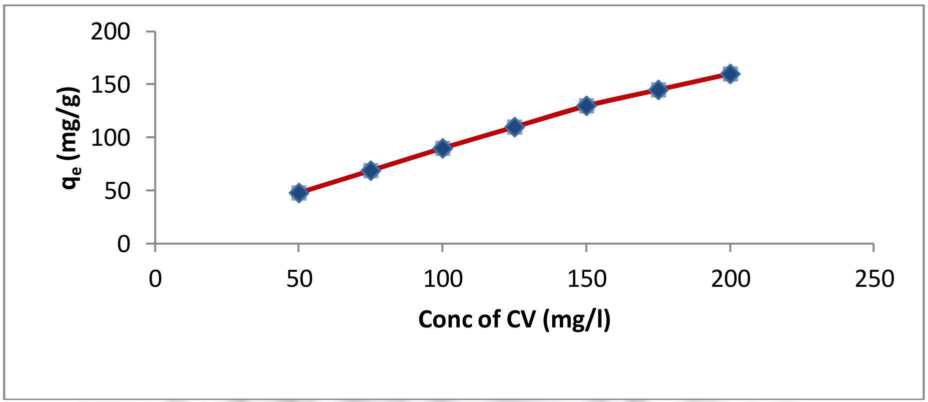

Fig.6: Effect of initial dye concentration on adsorption of CV

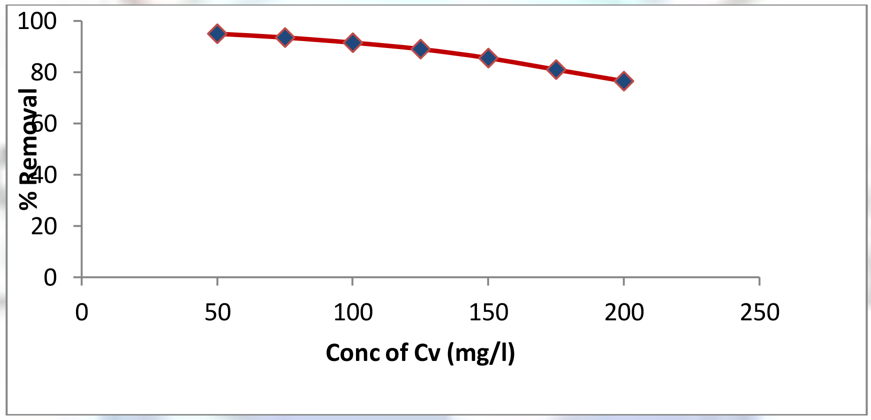

Fig.7: Percentage removal of CV

2.8 Effect of pH

pH is a key and one of the important factors in controlling the adsorption process, which is function of hydrogen and hydroxyl ions concentrations. The effects of solution pH on CV adsorption within TWS were investigated and the results are illustrated in figure 8, which shows that the elevation of pH leads to increase in the adsorbed mass of pollutant (q_e) onto TWS.

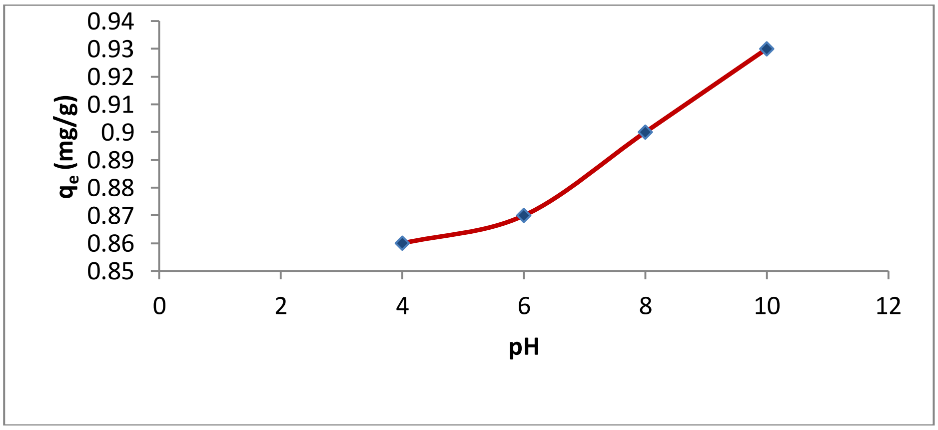

Fig.8: Effect of pH on adsorption of CV

When the pH of aqueous solution increased from (4 to 10), q_e increased from (0.86 to 0.93) mg/g. The result can be attributed to the effect of the solution pH on the charge of reactive group within TWS which, in turn makes it more effective to adsorb dye in alkaline pH and increase the ionized able sites. In other word, the presence of H^+ ions compete with the cationic dye molecules in the solution and preferably occupy the binding sites available in the sorbent particles. As the pH of the adsorbate solution increases number of H+ ions decreases thus making the adsorption process more favorable. In the vicinity of pH value of 10, optimum dye uptake is obtained. Similar results have also been reported elsewhere.

2.9 Effect of particle size

The effect of particle size of adsorbent on the adsorption process was studied by varying the particle size of the adsorbent and keeping other factors as constant. Generally, the amount of adsorption increases with decrease in the particle size of the adsorbent. Adsorption of CV on three sized particles of ≥ 300, $300 \leq 250$ and $250 \leq 200$ µm of adsorbent was studied. The results of variation of these particle sizes on dye adsorption are shown in figure 7. In general the decrease in particle size will show an increase in the available surface area. Therefore, the percentage removal of dye was maximum in lower particle size of an adsorbent.

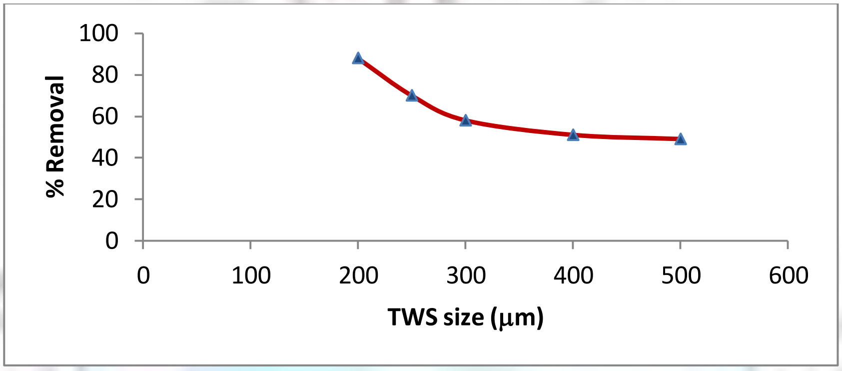

Fig.9: Effect of particle size on % removal of CV dye

2.10 Effect of temperature

The temperature has a significant effect on the process of adsorption. Adsorption of CV onto TWS was studied at three different temperatures (303 K, 313 K and 323 K) for 200 mg/l initial concentration of CV. The results, From the figure 8, clearly indicate that dye uptake increases with temperature. This may be due to the fact that increase in temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent owing to decrease in the viscosity of the solution [21]. Further, the mobility of adsorbate molecules also increases with temperature, thereby facilitating the formation of surface mono layers. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate.

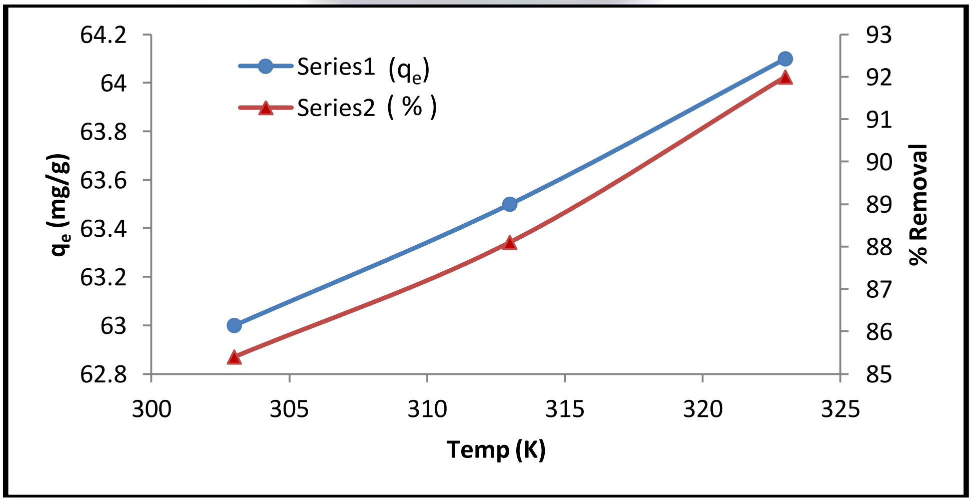

Fig.10: Effect of temperature

Evaluation of Thermodynamic Parameters:

Thermodynamic parameters such as change in free energy change (ΔG) (J/mol), enthalpy change (ΔH) (J/mol) and entropy change (ΔS) (J/K/mol), were determined using the following equations:

$$K_{\circ} = \frac{C_{solid}}{C_{liquid}} \tag{14}$$

Where K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg.l^{-1}), C_{liquid} is liquid phase concentration at equilibrium (mg.l^{-1}).

$$\Delta G = -RT \ln K_{\circ} \tag{15}$$

$$\ln K_{\circ} = \frac{-\Delta G}{RT} \tag{16}$$

$$\ln K_{\circ} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{17}$$

A plot of ln K_o vs. 1/T gives a straight line with slope is equal to ΔH/ R and intercept is equal to ΔS/R. Knowing the value of R, ΔH and ΔS can be calculated from the value of ΔH, ΔS and ΔG can be determined using the equation (13). The results are presented in table 1.

The positive values of ΔH indicate endothermic nature of adsorption. The negative values of ΔG indicated that the adsorption of CV onto TWS is favorable and a spontaneous process. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of CV with the adsorbent. The increase in the capacity of the adsorbent to remove CV at higher temperatures was due to activation of the adsorbent surface thereby enlargement of the pore size [16,21].

Kinetic models

Adsorption mechanism and the potential rate controlling steps involved in the process of adsorption has been studied using kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion model[19]. The linear forms of these models are obtained by equation (5), (7) and (9).

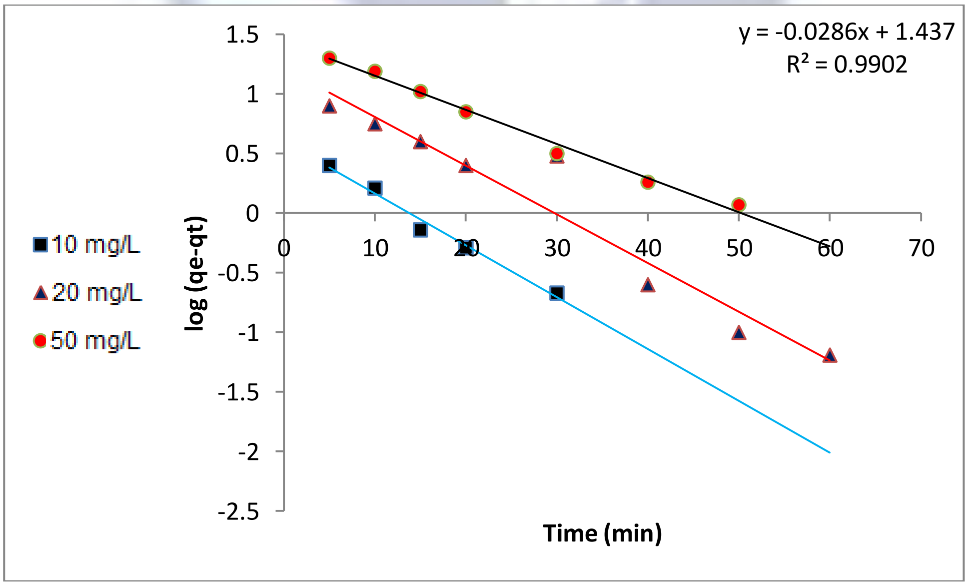

Fig.11: Plot of pseudo-first order kinetic model for adsorption of CV onto TWS at different initial concentration

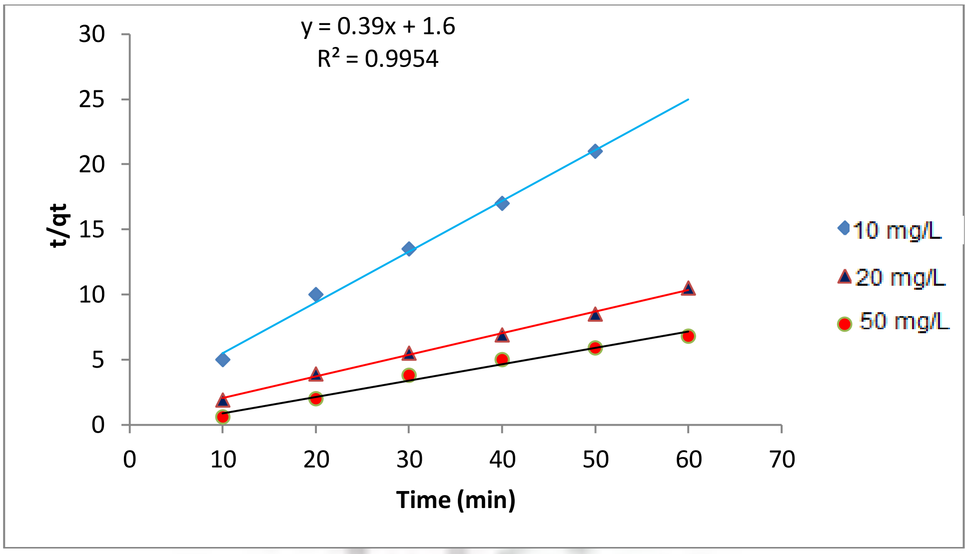

Fig.12: plot of pseudo-second order kinetic model for adsorption of CV onto TWS at different initial concentration

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively k_1 (min^{-1}) and k_2 (mg. g/min) are pseudo-first and pseudo-second order rate constant. Pseudo –second order model was developed based on the assumption that the rate controlling step is chemisorption involving valance force due to sharing or exchange of electrons between adsorbent and adsorbate molecules[5]. Fig. 9 presents the plot of pseudo-first order kinetic for adsorption of CV onto TWS at different initial concentrations. The higher ($R^2 > 0.99$) for the pseudo-second order kinetics (Fig.10) indicate the fitness of this model and it was suggested that chemisorption might be a rate controlling step [5]. Furthermore, the q_e values calculated using pseudo-second equation agreed well with the experimental q_e indicating that the adsorption of CV onto TWS could be well represented using the pseudo-second order kinetic model.

The Freundlich equation was employed for the adsorption of CV onto the adsorbents. The isotherm was rep resented by

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{18}$$

Where q_e is amount of CV adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of CV in solution (mg/l), K_f and n are constant incorporating factors affecting the adsorption capacity and intensity of adsorption respectively . The plots of log q_e vs log C_e showed good linearity (R^2= 0.99) indicating the adsorption of CV obeys the Freundlich adsorption isotherm, Fig.13.

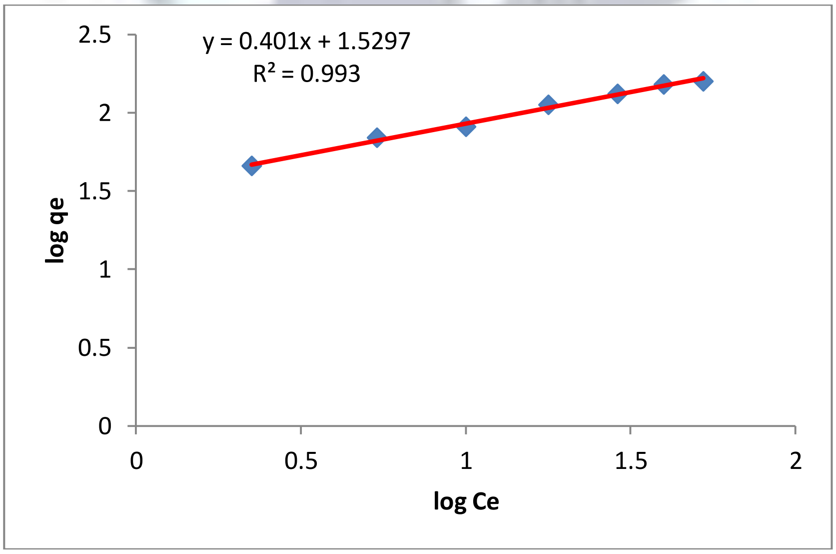

Fig.13: Freundlich isotherm plot of effect of initial d y e concentration on adsorption of CV

The values of K_f and n given in the Table (3). Values of n between 1 to 10 indicates an effective adsorption [19], while higher values of K_f represents an easy uptake of adsorbate from the solution [20]. The Langmuir isotherm was rep resented by the following equation

$$\frac{C_e}{q_e}=\frac{1}{(q_m b)}+\frac{C_e}{q_m} \qquad (19)$$

Where q_m is monolayer adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption (1/mg). A linear plots of Ce / qe vs Ce suggest the applicability of the Langmuir isotherm Figure 12 (R^2 = 0.996). The values of q_m and b were determined from slop and intercepts of the plots, Table (3)

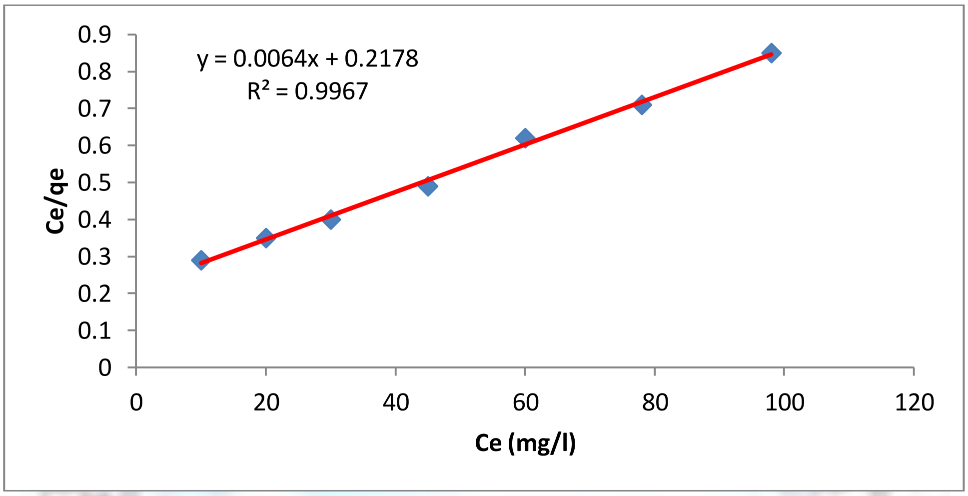

Fig.14: Langmuir isotherm plot of effect of initial dye concentration on adsorption of CV

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L, which is defined by the following relation given by [21]

$$R_L=\frac{1}{(1+bC_\circ)} \qquad (20)$$

Where C_o is initial CV concentration (mg/ l). R_L values indicates favorable adsorption (Table 5).

Table 1: Thermodynamic parameters for the adsorption of CV

ΔG (KJ.mol^{-1})			ΔH (KJ.mol^{-1})	ΔS (KJ. K^{-1}mol^{-1})
303K	313K	323K	165	0.7428
-31.7381	-38.1761	-44.6822		

Table 2: adsorption kinetic model parameters obtained using spectral study

Pseudo-first order kinetic model					**Pseudo-second order kinetic model**				
Initial CV Conc. (mg/l)	K_1	$q_{e(exp)}$ (mg/g)	$q_{e(the)}$ (mg/g)	R2	K_2	$q_{e(exp)}$ (mg/g)	$q_{e(the)}$ (mg/g)	h (mg/g.min)	R2
200	0.0374	156	53.372	0.990	0.0012	156	166.766	34.33	0.995
100	0.0529	78	48.753	0.989	0.0013	78	91.909	11.75	0.995
50	0.0529	92	33.735	0.989	0.0025	92	101	25.64	0.996

Table 3: Adsorption isotherm model parameters

Langmuir isotherm parameter			Freundlich isotherm parameter		
q_m	b	R^2	K_f	n	R^2
198	0.09197	0.993	29.379	2.0786	0.996

Conclusion

The treated walnut shell biomass can be used as an effective alternative eco-friendly and low cost adsorbent for removal of crystal violet from its aqueous solutions. The parameters such as contact time, pH, initial dye concentration, particle size and temperature have shown significant effect on the removal of CV. The maximum uptake of CV dye by TWS occurred at pH 10. Langmuir and Freundlich were found to be best fitting models with respect to R^2 values. Lagergren pseudo-second order model best fit the kinetics adsorption. The correlation coefficient $R^2 = 0.995$ for second order kinetic adsorption and $q_{e(exp)}$ values are consistent with $q_{e(the)}$ showed that pseudo second order kinetic equation of Lagergren fit well with whole range of contact time. Evaluation of thermodynamic parameters indicated that the adsorption process favorable, spontaneous, endothermic and there occurs increased disorder at the solid-solution interface. The various results obtained preferable that the adsorbent chosen for the study was efficient and could be used for the removal of industrial dye effluents.

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