Research Article

Adsorption Equilibrium and Kinetics of Crystal Violet Dye from Aqueous Media onto Waste Material

Arun Kant, Panmei Gaijon and Uzma Nadeem*

Department of Chemistry, University of Delhi, Delhi-110007, India.

Abstract

In the present work adsorption studies of Crystal Violet (CV) dye onto cardboard (CB) was studied. The experiments were carried out as a function of pH, contact time and concentration of dye solution. The percentage removal of CV dye onto CB showed that pH plays an important role in the adsorption of CV dye from aqueous solutions. The maximum 92 % adsorption of dye was obtained for 20 mg L^{-1} with 25 mg of cardboard. Langmuir and Freundlich, models were applied to describe the equilibrium isotherms. The kinetic data were fitted well to pseudo-second-order model and intraparticle diffusion model was also investigated.

Keywords: Crystal violet, adsorption, wastewater, Isotherms, Kinetics
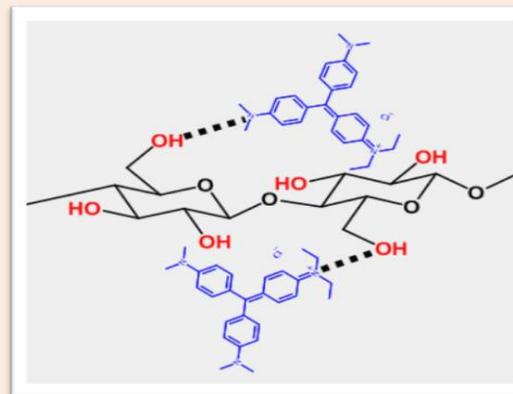
*Correspondence
Dr. Uzma Nadeem
Email: uzmanadeem3@gmail.com

Introduction

Different type of dyes are used in textiles, printing inks, plastics, leather, pharmaceutical industries, tannery, Kraft bleaching industries, and food, which has been discharge into the water bodies from the effluents of industries [1]. The removal of dyes is of great concern because most of them and their degradation products cause serious environmental problems like toxic, mutagenic and carcinogenic [2-8] due to their high stability and complex aromatic structures [9]. Their presence in water could directly affect the photosynthesis phenomenon of aquatic and disturb the aquatic life, ecosystem and food chain because of their color and toxicity respectively[10, 11]. Before discharging colored effluents into the water bodies, the effluents should to be properly treated. Research in the past few years was focused on utilizing waste materials from agricultural products because they are inexpensive, ecofriendly, and renewable [12]. In recent years, more than 100,000 dyes are available in market. Worldwide, nearly 1 million tones of synthetic dyes are produced annually [13]. A wide range of methods have been developed for the removal of synthetic toxic dyes from waters and wastewaters to reduce their impact on environment. Among these physico-chemical methods like adsorption [14] and electrochemical coagulation [15] are the most popular methods in recent days. Adsorption is a useful and simple technique, which allows kinetic and equilibrium measurements without any highly sophisticated instruments [16, 17]. This limitation has encouraged the search for inexpensive and readily available adsorbents for the removal of dyes, such as natural materials, biosorbents, and waste materials from industrial and agricultural process [18-20].

In present work the cardboard, a waste material has been applied as an adsorbent for the adsorption of crystal violet dye from aqueous solutions. The main objective of the research is therefore to investigate the kinetics and equilibrium of crystal violet dye onto cardboard (a cellulose material), which is a low cost, easily available and biodegradable material.

Experimental
Materials

Cardboard (CB) is easily available in market. After cutting into small pieces the cardboard was soaked into water for 5 days. The water absorbed CB was further washed with distilled water and dried in oven at 40- 45°C for 2 hours. The CB was crushed into a mixer and a fibrous material (**Figure 1A**) was obtained. Molecular structure of cellulose which is the major constituent of CB [21] is shown in **Figure 1B.**
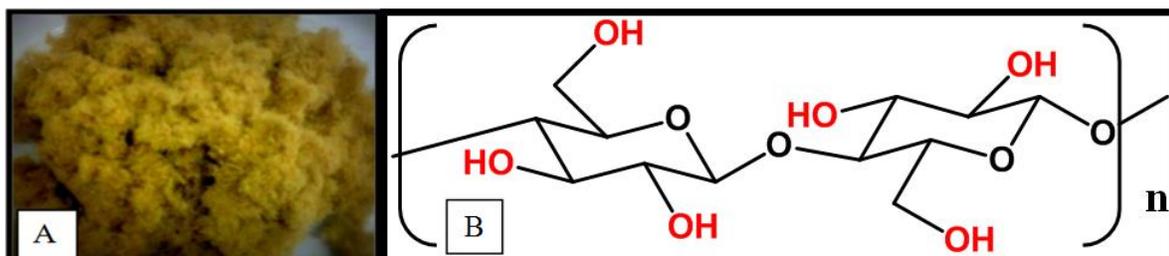

Figure 1 (A), Fibrous structure of cardboard; (B) Molecular structure of cellulose

Organic dye crystal violet (Other names of this dye Aniline violet, Basic violet 3 and Methyl Violet 10B) is a cationic dye. C.I. number 42555, molecular weight 407.99 and molecular formula $C_{25}H_{30}ClN_3$ was procured from Thomas Baker Chemical Limited Mumbai. All the chemicals and reagents used in the study were of analytical-grade. The chemical structure of crystal violet is shown in **Figure 2**.
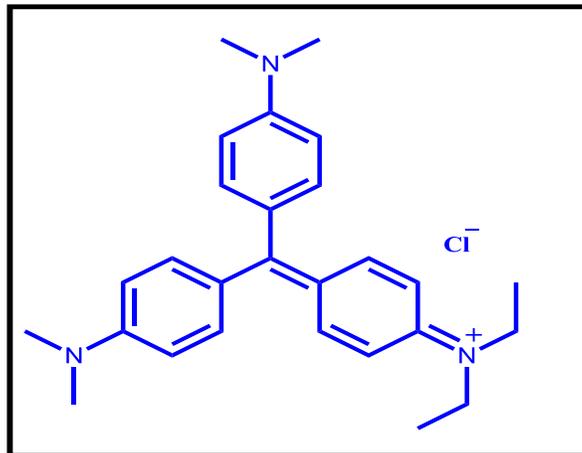

Figure 2 Molecular structure of crystal violet dye

Instruments

In the adsorption experiments, the concentration of (CV) dye was calculated by the absorbance values, recorded by UV-VIS spectrophotometer (Systronics 2201), Powder X-ray diffraction (PXRD) measurements of samples were performed on a powder X-ray diffractometer (D8 DISCOVER BRUKER AXS, Germany) the measurement conditions were Cu α radiation generated at 40 kV and 40 mA as X-ray source 2-40° (2θ) and step angle 0.02° s⁻¹, FT-IR spectra was recorded with an FTIR spectrophotometer (Perkin Elmer, Spectrum BXFTIR Spectrometer) using the KBr (Merck, Germany) disc method.

pH stability study of the aqueous Crystal Violet Dye solution

In the pH stability study it was observed that the aqueous crystal violet dye was stable in the pH range 3–9 with constant λ_{max} 586nm but the observed absorbance values were different. At pH 1 and pH 2 the recorded λmax is 620nm and 608 nm respectively. Absorption spectra of crystal violet (CV) dye as a function of pH is shown in **Figure 3.**
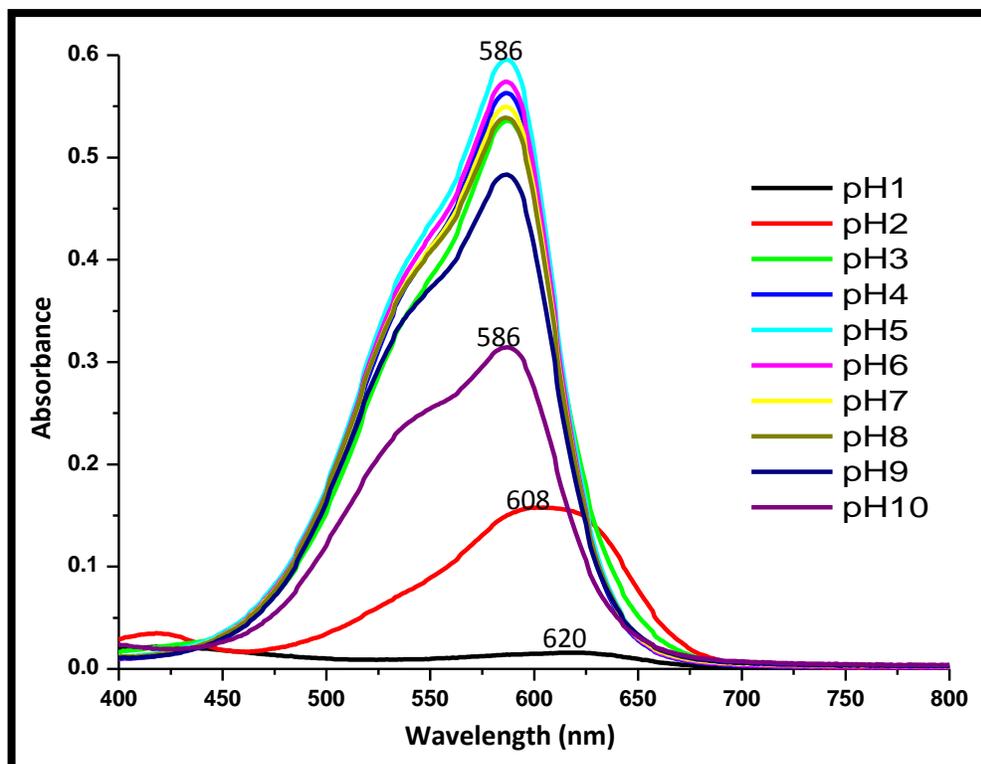

Figure 3 Absorption spectra of crystal violet (CV) dye as a function of pH

Batch Adsorption Studies

The absorption behavior of CV dye was performed by taking known concentration of dye. The pH range used for the study was from 1 to 10. The pH of the dye solution was adjusted by using 0.01M, 0.1M, and1M NaOH and 0.01M, 0.1M, and1M HCl solutions by using a pH meter (Systronics 335) with a combined pH electrode. pH meter was standardized with buffers (CH_3COONa & CH_3COOH for acidic buffer, $NaHCO_3$ & Na_2CO_3 for basic buffer [22] before every measurement. At lower pH (less than 2), color of dye solution was changed from violet to light green color. Batch experiments were conducted to evaluate the adsorption behaviors of CV dye on CB was investigated as a function of the pH of the aqueous dye solution, contact time for batch adsorption and concentration of the dye solution.

All the Batch experiment was performed at room temperature (28 ^{o}C). The pH value of most industrial effluents containing the dye solution is generally 6 to 7, but CV dye showed higher absorption value at 5 pH, and on the basis of this all the experiment were performed at pH 5. To study the effect of pH on the uptake of CV dye on the CB, separate batches of the aqueous CV dye solution (20 mg L^{-1}) at pH (1-10), with the adsorbents dose 25 mg was treated for a period of 15 minutes.

The effect of contact time on the adsorption process was studied by allowing the aqueous dye solution (20 mg L^{-1}) to remain in contact with the adsorbent for the period of 2 to 60 minutes. The effect of initial dye concentration experiments were performed in the range of 10-100 mg L^{-1} of 25 mL dye solution, with 25 mg of CB dose.

After each batch experiment, the adsorbent was centrifuged and the supernatant was used for the spectrophotometric estimation of the absorbance of dye remained in the solution at a wavelength of 586nm by UV-

visible spectrophotometer (Analytik Jena Specord 250). The concentration of the dye was determined from the calibration plot of the corresponding Beer–Lambert plot. The percentage removal of dye from the solution was calculated by the following equation (1).

$$\varphi = 100 \, \frac{C_i - C_e}{C_i} \tag{1}$$

Where C_i is the initial concentration of dye solution and C_e is the concentration of dye in the supernatant at the equilibrium stage.

The amount of adsorbed dye q_e (mg/g), was calculated by the mass-balance relationship shown as equation (2)

$$q_e = \frac{(C_i - C_e)V}{m} \tag{2}$$

Where C_i and C_e are the initial and equilibrium concentrations of the dye (mg L^{-1}) respectively, V is the volume of the solution (L), and m is the mass of the adsorbent (g).

Results and discussion
Adsorption studies
Adsorption as a function of the pH of the aqueous dye solution

The pH value of the dye solution has been recognized as an important factor in adsorption process, which influences not only the surface charge, the dissociation of functional groups on the active sites, the degree of ionization of the adsorbents, but also the dye chemistry [23].The adsorption amount of dye on CB surface was found less in acidic media as compare to basic media but remained almost constant in basic conditions.

The uptake efficiency of CV dye by CB was found 19% and 74.5% at pH 1 and 4 respectively. At pH 5, 90.5% uptake (**Figure 4**) was observed. The low adsorption rate of CV dye on the cardboard at pH < 5 may be because of electron pair containing cellulose ssaturate by protons and it becomes positively charged, thus making (H^{+}) ions compete effectively with dye cations causing a decrease in the amount of dye uptake on the surface of the CB.
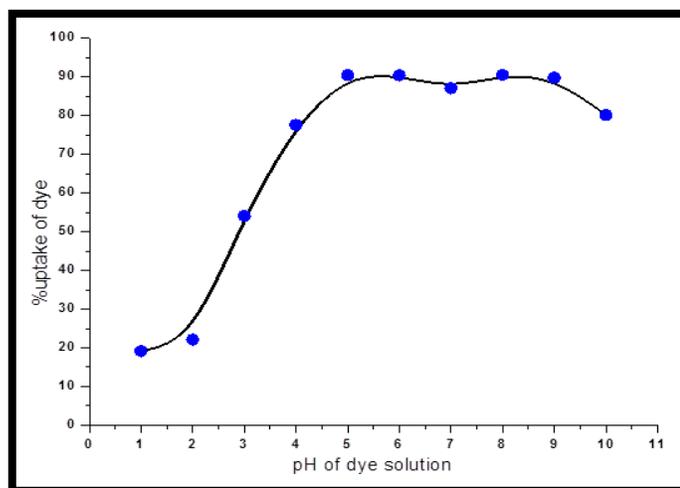

Figure 4 Effect of pH on the percentage uptake of CV dye on CB

Adsorption as a function of contact time

The effect of the contact time on the adsorption behaviour of CV by CB was investigated by varying the contact time from 2 to 60 minute at 28 °C. The uptake of crystal violet dye by CB was rapid at room temperature, with adsorption efficiency of 60% within 6 minutes and 91.6 % within 25 minute (**Figure 5**).The maximum uptake was only 92% which was attained within 40 minutes and after that reaches equilibrium up to 60 minutes.
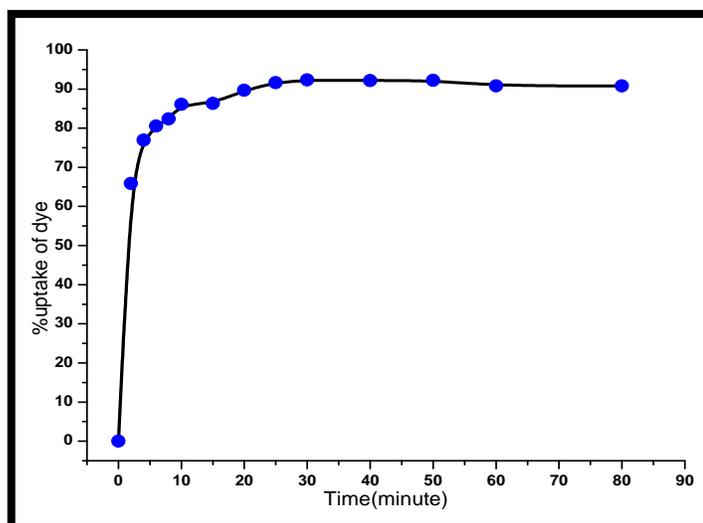
Figure 5 Effect of contact time on the percentage uptake of CV dye by CB

Adsorption as a function of initial dye concentration

To study the effect of initial dye concentration on the adsorption behaviour of CV dye on CB, experiments were conducted in the concentration range of 10-100 mg L^{-1} of 25 mL solution, with the fixed adsorbent dose (25 mg) at room temperature (28 ^{o}C). It was observed that on increase of dye concentration there is a decrease in % uptake of CV dye by CB. It is evident from the **Figure 6** that percentage uptake of crystal violet dye first increases at lower concentration of dye and on increase of dye concentration percentage uptake of dye decreases gradually. The decrease in the dye uptake with increase in the concentration of dye might be due to the lack of available adsorption sites on CB surfaces. Maximum uptake of dye observed was 92% and constantly decreases up to 100 mg L^{-1}.
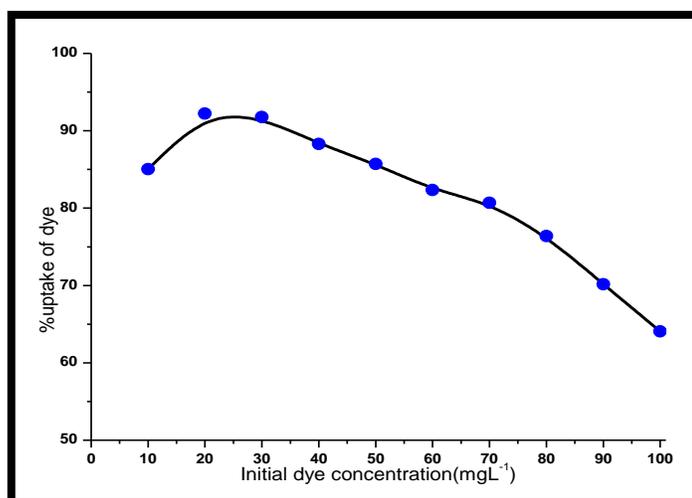

Figure 6 Effect of the initial dye concentration on the percentage uptake of CV dye by CB.

Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate dye uptake per unit mass of adsorbent (cardboard), q_e, to the equilibrium adsorbate concentration in the bulk aqueous phase C_e.

Freundlich Isotherm

This is commonly used to describe the adsorption characteristics of the heterogeneous surface [24]. These data often fit the empirical equation (3) proposed by Freundlich:

$$q_e = K_f C_e^{1/n} \tag{3}$$

Where K_f = Freundlich isotherm constant (mg/g), n = adsorption intensity, C_e = the equilibrium concentration of adsorbate (mg/L), q_e = the amount of dye adsorbed per gram of the adsorbent (cardboard) at equilibrium (mg/g). Linearize of the equation 3, is given as equation (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

The plot of log q_e versus log C_e was linear (**Figure 7**), with a slope equal to 1/n and an intercept equal to log K_f. The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process [25].
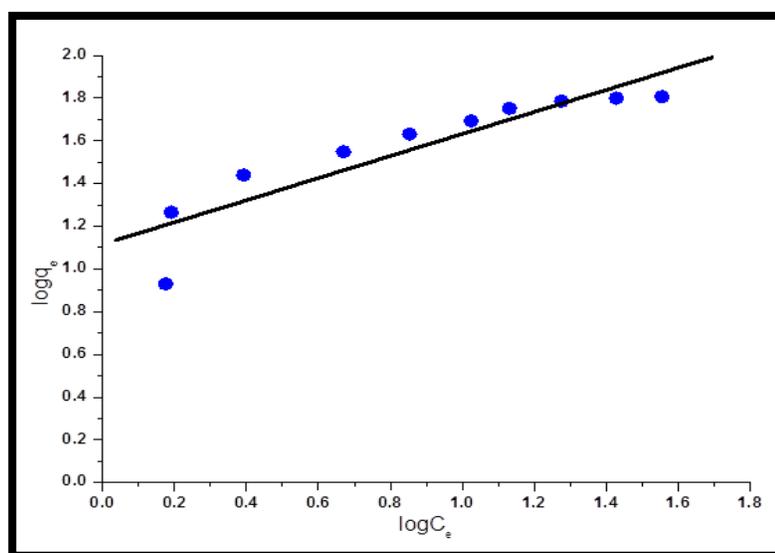

Figure 7 Linearized plot for Freundlich adsorption isotherm

If n = 1 then the partition between the two phases are independent of the concentration. If a value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption [26].

Langmuir Isotherm

This isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of crystal violet dye ions between the solid and liquid phases [27]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. Based upon these assumptions, the Langmuir isotherm equation can be expressed in a linearized form is shown in equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{5}$$

Where q_{max} is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant (dm³/mg). The plot of C_e/q_e versus C_e is linear (**Figure 8**), with a slope equal to $1/q_{max}$ and an intercept equal to $1/(q_{max}K_L)$.
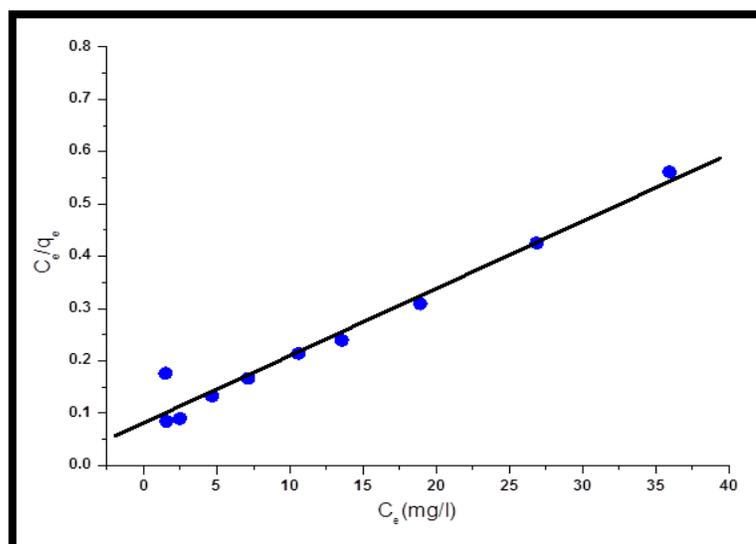
Figure 8 Linearized plot for Langmuir adsorption isotherm

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless constant (R_L) which is called equilibrium parameter defined as:

$$R_L = \frac{1}{1 + K_L C_i}$$

(6)

Where K_L is the Langmuir constant, which is used to determine the enthalpy of adsorption, and C_i is the highest initial dye concentration employed. The value of R_L indicates whether the type of isotherm observed is unfavorable ($R_L>1$), linear ($R_L=1$) or favorable ($R_L<1$) [28]. For all the adsorption studies of crystal violet dye onto cardboard, the R_L values were in the range $0<R_L<1$, indicating that the adsorption process was favorable. The magnitude of K_L also quantifies the relative affinity between an adsorbent and the adsorbent surface. All the Freundlich and Langmuir constants/parameters calculated by the isotherm plots are given in **Table 1**. The R^2 value suggests that Langmuir adsorption isotherm fitted well for the adsorption of CV dye on CB. The R_L values calculated for all the concentrations are less than 1 and indicate the favorable adsorption (**Figure 9).**
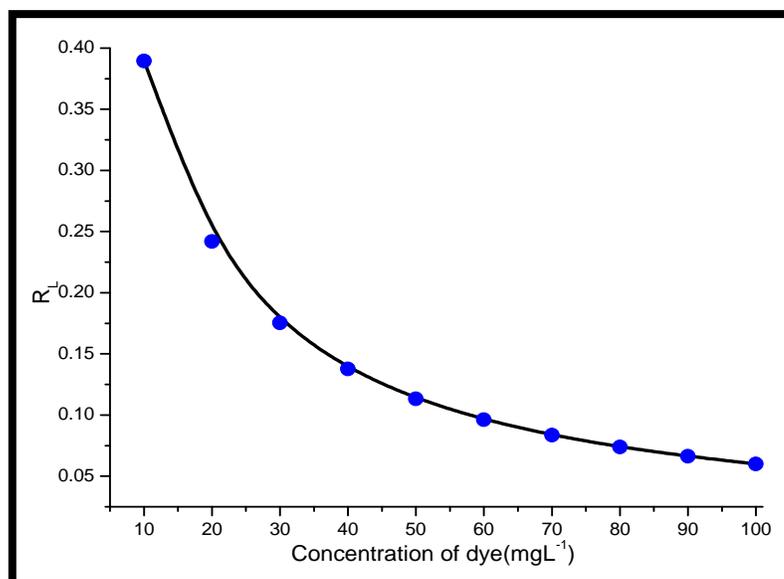

Figure 9 R_L vs Concentration

Table 1 Isotherm Model constants

Equilibrium Parameters	
Freundlich	
$1/n$	0.5163
K_f (mg/g)	13.0677
R^2	0.8246
Langmuir	
q_{max} (mg/g)	78.125
K_L (dm^3/mg)	0.15667
R^2	0.9646

Adsorption kinetics

Various kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism of the adsorption process and to test the experimental data. In the present investigation, the adsorption data were analyzed using three kinetic models, the pseudo-first-order, pseudo-second-order kinetic and the intra particle diffusion model.

The pseudo-first-order model was presented by Lagergren [29]. The Lagergren's first-order reaction model is expressed in linear form as equation (7):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (7)$$

Where q_e and q_t are the amounts of CV dye (mg/g) adsorbed on the cardboard at equilibrium, and at time t, respectively and K_1 is the rate constant (min^{-1}) of the pseudo-first-order adsorption process. The plot of log ($q_e - q_t$) versus t for CB with a slope of $-K_1/2.303$ and an intercept of log q_e is shown in **Figure 10**).
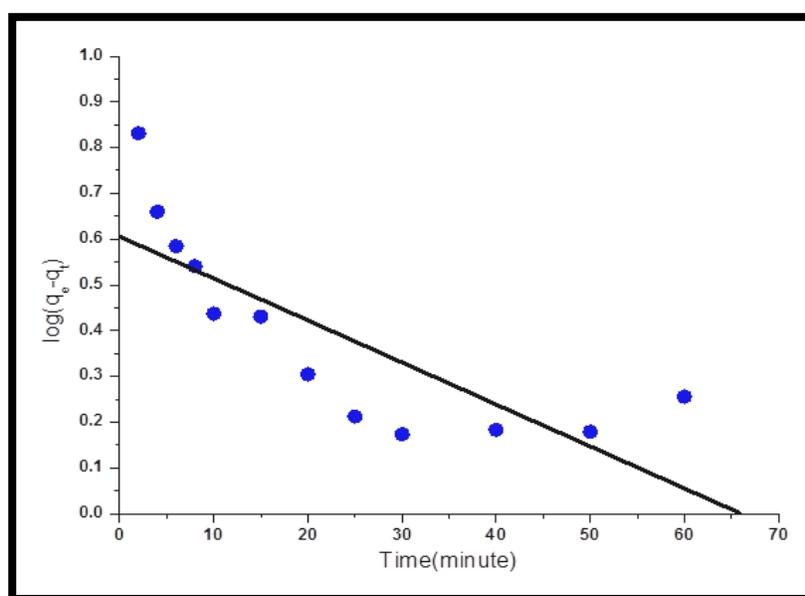

Figure 10 Plot of pseudo-first-order kinetic model for the adsorption of CV by CB.

The adsorption data was also analyzed in terms of pseudo-second-order mechanism, described by Y. S. Ho and McKay [30] the linear form of the equation (8):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

Where K_2 is the rate constant of pseudo-second-order adsorption (g/mg min), $K_2 q_e^2$ is the initial rate of adsorption (mg/g min). The plot of t/q_t against t of equation 13 shows a linear relationship for cardboard with a slope of $1/q_e$ and an intercept of $1/K_2 q_e^2$ (**Figure 11**).
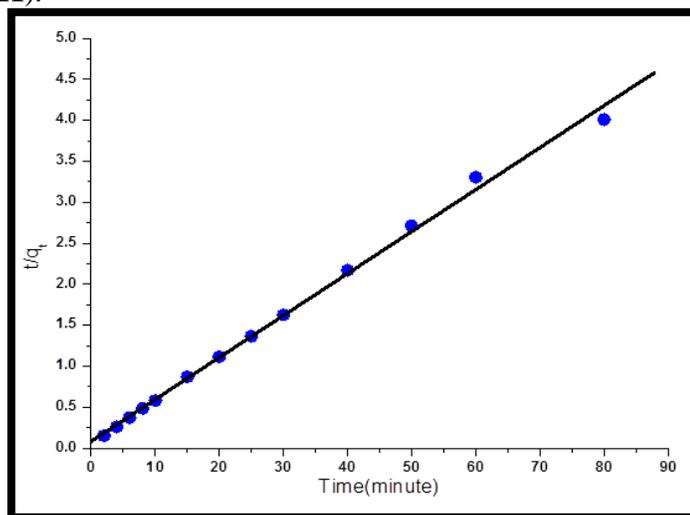

Figure 11 Plot of pseudo-second-order kinetic model for the adsorption of CV onto CB.

The Intraparticle Diffusion model has been applied to determine the effect of temperature on the adsorption of CV dye by cardboard. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach was described by Weber and Morris [31] and the linear form can be represented as equation (9):

$$q_t = K_d t^{1/2} + C \tag{9}$$

The plot of q_t against $t^{1/2}$ of equation (9) gives a linear relationship for cardboard with a slope of K_d and an intercept of C (**Figure 12**). Where q_t is the amount of dye adsorbed (mg/g) at time t, K_d (mg/gmin$^{1/2}$) is the rate constant for intraparticle diffusion.
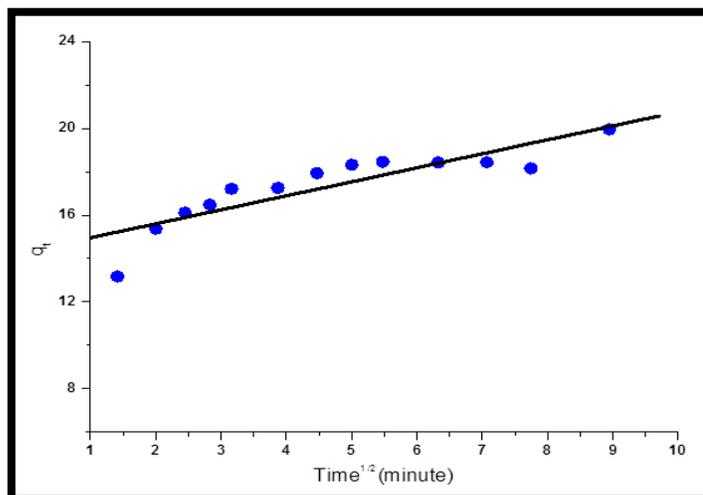

Figure 12 Plot for the intraparticle Diffusion model

**Table 2** Parameters for kinetic of Pseudo-first-order, Pseudo-second-order and intraparticle diffusion model

Kinetic Parameters	
Pseudo-first-order model	
K_1 (min^{-1})	0.02112
q_e(mg/g)	4.03367
R^2	0.6443
Pseudo-second-order model	
K_2 [g/(mg min)]	0.03102
q_e (mg/g)	19.53125
R^2	0.9967
Intraparticle diffusion model	
K_d	0.6453
C	14.314
R^2	0.7647

Table 2 shows the equilibrium sorption capacity (q_e), the correlation coefficient, R^2, and the rate constants for the pseudo-first-order (K_1) and pseudo-second-order (K_2) models. The data demonstrate good compliance with pseudo-second-order rate law rather than the pseudo-first-order rate law. This can be probably true in the present case CB is electronegative in nature which attracts the positively charged dye. This can allow the electrostatic interaction between the positively charged crystal violet dye and the cardboard surface. The calculated R^2 value (0.7647), the slope of K_d for cardboard is 0.6453 with an intercept C is 14.314 were calculated by using equation 9 and indicates that intra-particle diffusion is a rate limiting step.

Characterizations
XRD analysis
The physical status of CB and dye adsorbed CB has been compared with the help of XRD. The XRD studies indicate that the cellulose fibres are crystalline and amorphous in nature [32]. XRD pattern of CB shows a hump at $2\theta =11.63$ and a peak of low intensity at $2\theta = 22.54$ (**Figure 13**), indicating amorphorous nature of CB. After the adsorption of crystal violet dye on CB, the hump shifted towards higher $2\theta = 15.01$ value with lower intensity hump.
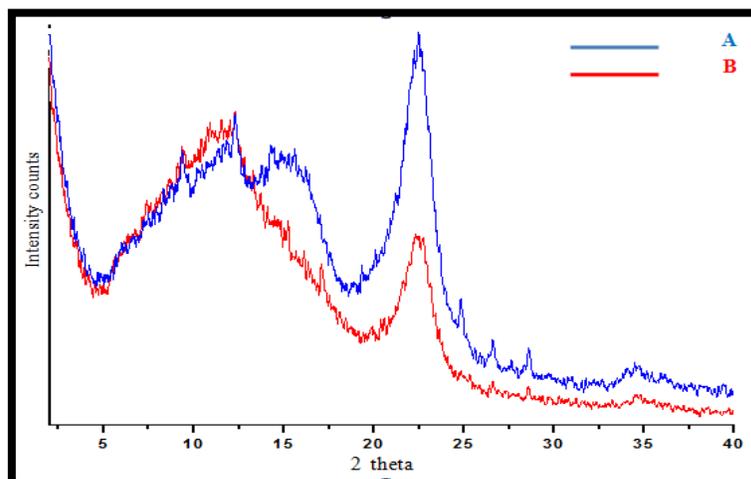
Figure 13 XRD patterns for (A) dye adsorbed cardboard (B) cardboard

After the adsorption of dye on CB, the peak intensity as well as the number of XRD peaks increased and suggested that crystal violet dye gets adsorbed on the active sites of CB by ion-ion interaction, ion- dipole interaction and dipole- dipole interaction or through hydrogen bonding. The increase in the intensity of the CB (cellulose) indicates that the plane at that particular 2θ values increases and it may be because of the adsorption of CV dye on CB.

FT-IR analysis

FT-IR spectra of cardboard, crystal violet and crystal violet adsorbed cardboard were recorded in the wave number range of 4000-400 cm^{-1}. The spectrum (**Figure 14**), displays the adsorption peaks at 3423.39 cm^{-1}(O-H)1715cm^{-1} (C=O) 1647 cm^{-1} (H$_2$O) and 1059cm^{-1} (C-O) of cardboard [33]. Quite similar spectra were observed for cellulose. The FTIR of pure crystal violet shows characteristic adsorption bands at 1582, 1358 and 1164 cm^{-1}[34]. New peaks were observed after the adsorption of crystal violet on the cardboard at 2067, 1589 and 1369 cm^{-1}which indicates C=C in the aromatic ring and C-N stretching in aromatic tertiary amine.

The broad band in the wavenumber 3600-3100 cm^{-1} region, is due to the OH-stretching vibration, gives considerable information concerning the hydrogen bonds and the band 2900 cm^{-1}, corresponding to the C–H stretching vibration. FTIR absorption band at 1430 cm^{-1}, assigned to a symmetric CH$_2$ bending vibration. The FTIR absorption band at 898 cm^{-1}, assigned to C– O–C stretching at β-(1-4) glycosidic linkages, is designed as an "amorphous" absorption band, an increase in its intensity occurring in the amorphous samples [22].
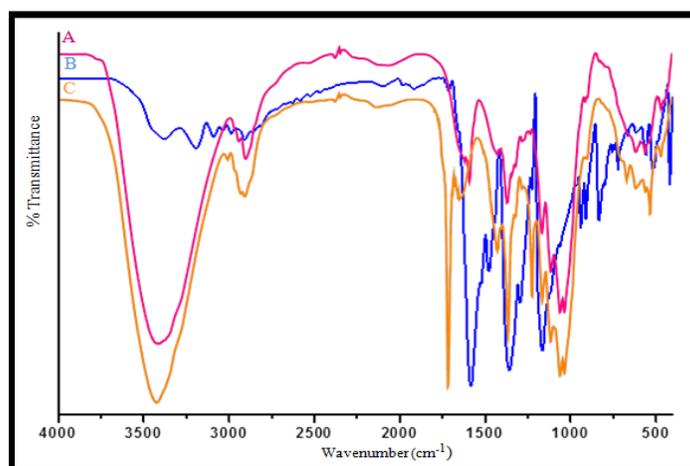

Figure 14 FT-IR spectra of (A) Cardboard + Crystal violet dye, (B) crystal violet dye, (C) Cardboard
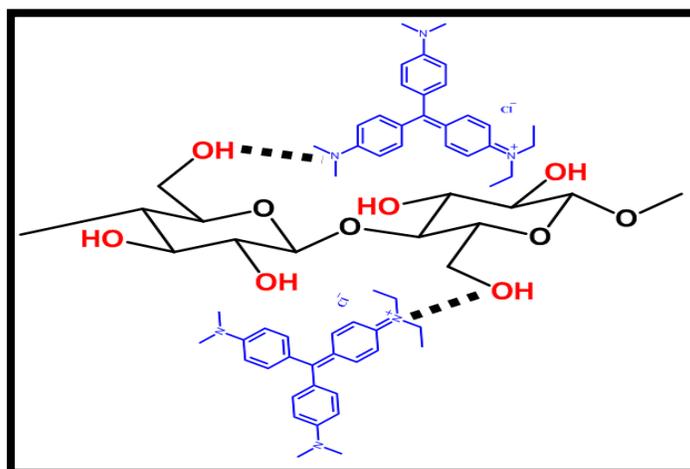
Adsorption mechanism

Figure 15 Adsorption mechanism interactions between Crystal Violet dye and CB molecule

Dyes are organic compounds that can be used to impart bright, permanent colors to fabrics. The affinity of a dye for a fabric depends on the chemical structure of the dye and fabric molecules and on the interactions between them. Chemical bonding thus plays an important role in how and why dyes work. Crystal violet dye have positive charge on nitrogen atom which attract the electron pair containing oxygen atom through electrostatic interaction and second process hydrogen bonding between hydrogen atom of hydroxyl of adsorbent with nitrogen atom of crystal violet, which have unshared pair of electrons of CV dye as shown in **Figure 15**. The formation of dye fiber hydrogen bonds is controlled by the presence of hydrogen bonding functional groups in the fiber and the dye and also by the macromolecular fiber structure [35].

Conclusions

The present study suggests that cardboard is a good adsorbent and can be used for the removal of CV dye from aqueous solutions. The major constituent of cardboard is cellulose, which contains electron pair containing oxygen atom and attracts the positive charge containing nitrogen atom of crystal violet dye by electrostatic interaction. Maximum 92% of crystal violet dye adsorption was observed on 25mg of cardboard from 20 mg L^{-1} of 25 mL dye solution. The adsorption isotherm data for CV dye fitted well to Langmuir adsorption isotherm thus, indicating the applicability of monolayer and multilayer coverage of CV on the CB and the adsorption mechanism was found to be physio-chemisorption. In the kinetic studies pseudo-second-order kinetic model fitted well over pseudo first order kinetics and intraparticle diffusion model is a rate limiting step. Finally suggests the application of low cost cardboard as an effective adsorbent for the removal of crystal violet dye from the waste effluents.

Acknowledgements

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