Equilibrium and Modelling Studies for the Removal of Crystal Violet Dye from aqueous solution using eco-friendly activated carbon prepared from *Sargassm wightii* seaweeds

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Abstract

This research article describes the preparation of an eco-friendly activated carbon from *sargassm wightii* seaweeds for the efficient removal of crystal violet dye in an aqueous solution. The presence of hydroxyl and carboxyl and other functional groups in the adsorbent material was detected using FTIR spectroscopy. The morphological studies of the adsorbent materials were done using SEM and EDX analysis. The physical nature of the materials was analyzed with XRD pattern studies. The batch mode dye adsorption behavior of the activated carbon was investigated as a function of dosage, solution pH, initial dye concentration, temperature and contact time. The equilibrium modeling studies were analyzed with Freundlich and Langmuir adsorption isotherms and the adsorption dynamics was predicted with Lagergren's pseudo-first order, pseudo-second order equations and intra particle diffusion model. The thermodynamic parameters, like standard Gibbs energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), were determined for the considering the feasibility of the adsorption process. The results from the experimental and correlation data revealed that the activated carbon prepared from *sargassm wightii* seaweeds proved to be an excellent adsorbent material for the removal of dye.

1. Introduction

Currently the dyes and pigments are extensively used in textile, leather dyeing, paper, printing, pharmaceutical and cosmetic industries for the coloration of their products. During the process, nearly 20% of the dye is released into the aquatic environment [1]. The effluent released from these industries often contains large quantities of dyes and even a very trivial quantity of the dye in the aquatic environment is clearly visible and toxic to living organisms present in water [2]. Industrial effluent water containing dyes is very difficult to treat, as the dyes are unmanageable organic molecules, are resistant to aerobic digestion and are stable to light, heat and oxidizing agents. Further their degradation products are toxic and carcinogenic and some cannot be destroyed at all [3]. The extremely toxic unprocessed effluent can seriously affect plants and animals and a large number of biological activities related to living things and also can cause severe damage to entire organisms [4]. Environmentally, the dye containing wastewater can absorb and reflect sunlight entering the water body and hinders the growth of microorganisms and making them insufficient for biological activities thus resulting in the imbalance of environmental ecology. This makes the removal of dye from wastewater an environmentally important activity. Conventional treatment technologies for the removal dyes from wastewater have been investigated extensively, like biological treatment, adsorption, coagulation, membrane separation, chemical oxidation, and reverse osmosis. However, the above methods suffer from one or more limitations and none are successful in entirely removing the colour from wastewater [5]. On comparison the adsorption process was found to be superior to other techniques for water treatment in terms of cost, design, operation and insensitivity to toxic sludge formed [6,7]. The adsorption process using activated carbon is an efficient process, but is expensive and is not used for the commercial wastewater treatment applications [8].Hence, it is has become

imperative to find out a low-cost, easily available and renewable of activated carbon that can be prepared from locally available agricultural and other solid waste products [9,10,11].The development of low cost activated carbon has minimized the cost of the adsorbent and the advantages of these materials are not only purely economic in value, but many of them are renewable and plentiful natural resources, which are currently industrial or agricultural wastes. In addition, these materials can be used as adsorbents with little or no pre-treatments and can be prepared with low cost methodologies [12]. In this view the marine seaweeds that are abundantly available in the seashore are taken for the present study. The cell wall of seaweeds have some organic functional groups, which are accompanying along with starch, alginic acid and proteins which can be help them to remove the organic pollutants from waste water[13]. The survey of literature showed that *sargassm wightii* seaweed activated carbon has not been studied for the removal of crystal violet dye and hence it has been chosen for the preparation of the low cost activated carbon.

Crystal violet (CV) is a tri-phenylmethane dye, which is extensively used as a dermatological agent in various commercial textile processes [14]. The dye has been found to be a poisoning agent in aquatic ecosystem that creates many problems to living things [15]. Therefore, the removal of Crystal violet dye from waste effluents becomes environmentally important, making the removal of CV dye with SWAC adsorbent material as the focus of the present study.

2. Materials and Methods

2.1 *Adsorbate*

The stock solution of the crystal violet dye [Tris(4-(dimethyl amino) phenyl) methylium chloride] having a molecular formula $C_{25}H_{30}N_3Cl$ and formula weight of 407.979 was prepared by dissolving a calculated quantity of the dye in distilled water with further dilutions made to get particular concentrations of dye for batch experiments. The commercially available reagents (Merck, India and SD-fine, India) were also used in the present study.
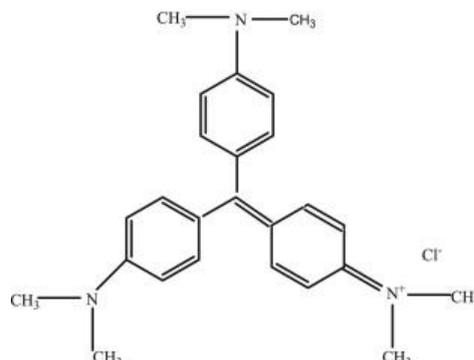
Figure 1. Structure of Crystal Violet dye.

2.2. *Preparation of Sargassum weightii Activated Carbon (SWAC).*

The *Sargassum wightii* seaweed was collected in the seashore region of Rameswarm, Tamilnadu, India. It was washed with ordinary water followed by distilled water for the removal of impurities present on the surface of the material. It was dried in sunlight for seven days and then soaked in sulfuric acid for 12 hours. The carbonized material was washed with distilled water, till the washings become neutral (pH = 7 ± 0.5). It was then dried at 110 ℃ in an hot air oven for 12 hours followed by heat treatment in a muffle furnace at 450 ℃ for about 8 hours for the extensive carbonization of carbon. The *Sargassum weightii* activated carbon(SWAC) was then ground into 180 to 300 μm standard sieves using a mechanical sieve.

2.3 *Experimental Methods*

Sorption studies were performed by the batch mode technique by varying the parameters like pH (2 to 10), concentration of the CV(20 to 100 mg/L), and adsorbent dose (0.1 to o.5g) to acquire the rate and equilibrium data. 25 mL of crystal violet dye solution and 100 mg of the adsorbent containing the mixture was stirred for 50 min at 30 ± 0.5 ℃ in an orbital shaker. The absorbance of the residual dye concentration was measured before and after adsorption with double beam spectrophotometer. All the experiments were carried out twice for accuracy. The effect of pH was observed for the pH ranges from 2 to 10 by adding NaOH or HCl solution. The

sorption studies were carried out by varying the temperatures from 30-70 °C with 10 °C variation. The amount of sorption at time t, q_t (mg/g) were calculated using the following equation,

$$q_t = (C_i - C_t)V/M \qquad (1)$$

where, C_i is the initial concentration of dye, C_t is the concentration at specified time t, V is the volume of the dye solution in L and M are the weight of activated carbon in g. The percentage of dye removal in solution was calculated using the following equation,

$$\text{Dye removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

Where, C_i = initial concentration of dye and C_f = final concentration of dye, before and after the adsorption process.

3. Results and Discussion

3.1. *Characterization of the Adsorbent*
The FTIR spectrum is a best tool for the identification of different type of functional groups present in the adsorbent and that are liable for the adsorption of dyes during the adsorption process. The FTIR spectrum of SWAC and SWAC-CV are presented in Figure 2a. The line spectrum shows various peaks at 3409.47 cm^{-1}, 2924.65 cm^{-1}, 2290.08 cm^{-1}, 1720.05 cm^{-1}, 1619.91 cm^{-1}, 1404.27 cm^{-1}, 1329.09 cm^{-1} and 1152.77 cm^{-1} position. These peak positions shows the presence of -OH, C-H, C=O, N-H groups in the adsorbent material. The FTIR also reveals the presence of intermolecular hydrogen bonding in the adsorbent material. The adsorption spectrum in dotted line shows shifted peak positions and reduction in the peak intensities. These functional groups are responsible for the physical or chemical adsorption that takes place between the adsorbent and dye molecules and the functional groups in the SWAC strongly adsorb the dye molecule. This peak reduction reveals that there is a strong characteristic adsorption of dye onto the surface of the activated carbon [16].

The XRD studies are helpful for analyzing the physical nature of the adsorbent materials. Fig.2b shows the XRD spectrum of SWAC where the characteristic intensity peaks obtained before adsorption indicating the crystalline nature of the material. The absence of intensity in XRD peaks in the sample after adsorption indicates that the crystalline nature of the SWAC -dye to have a distorted or physical adsorption between activated carbon and dye.

The scanning electron microscopy (SEM) is a primary tool for characterizing the surface morphology of the adsorbent. SEM images of adsorbent material taken before and after dye adsorption. Fig. 2c and 2d showed a definite variation in the images with the before sorption image showing a very bright and porous nature while the images of the adsorbed samples show notable dark spots which may be occupied by a the dye indicating its effective adsorption in the cavities and pores of SWAC. Thus the after adsorption studies clearly show a good possibility for dyes to be strongly adsorbed onto these pores.

3.2. *Effect of pH*
The solution pH is very important in an adsorption process, since the solution pH massively affect the nature as well as progression of the adsorption process. Solutions with different pH were prepared ranging from 2 to 10, by adding 0.1 N HCl and NaOH solutions. The effect of pH was presented in Fig. 3a. From the investigation of various pH values, the pH value of 7 shows a higher percentage removal when compared to other pH values (Fig.3a). The lower adsorption of CV on SWAC at acidic pH implies that the adsorbent surface may attain positive charge due to the presence of excess H$^+$ ions in acidic medium resulting in the competition between H$^+$ ions and cationic groups on the dye for adsorption process, while at neutral solution pH, the adsorbent surface attains negative charge, which may attract the positively charged dye ions through electrostatic forces of attraction, thus showing a maximum percentage of removal at neutral solution. At pH higher than 7, the dye removal was decreased due to hydrolysis of adsorbents surfaces, that creates positively charged sites, which is responsible for the electrostatic repulsion between dye and adsorbent.

3.3. *Effect of dose of the adsorbent*
The effect of dose of the adsorbent is a major factor that gives the information about the efficiency of an adsorption process. If the dose of the adsorbent increases, the effectiveness of the adsorbent also gradually increases, due to the rise of number of available sites on the adsorbent surface [17].
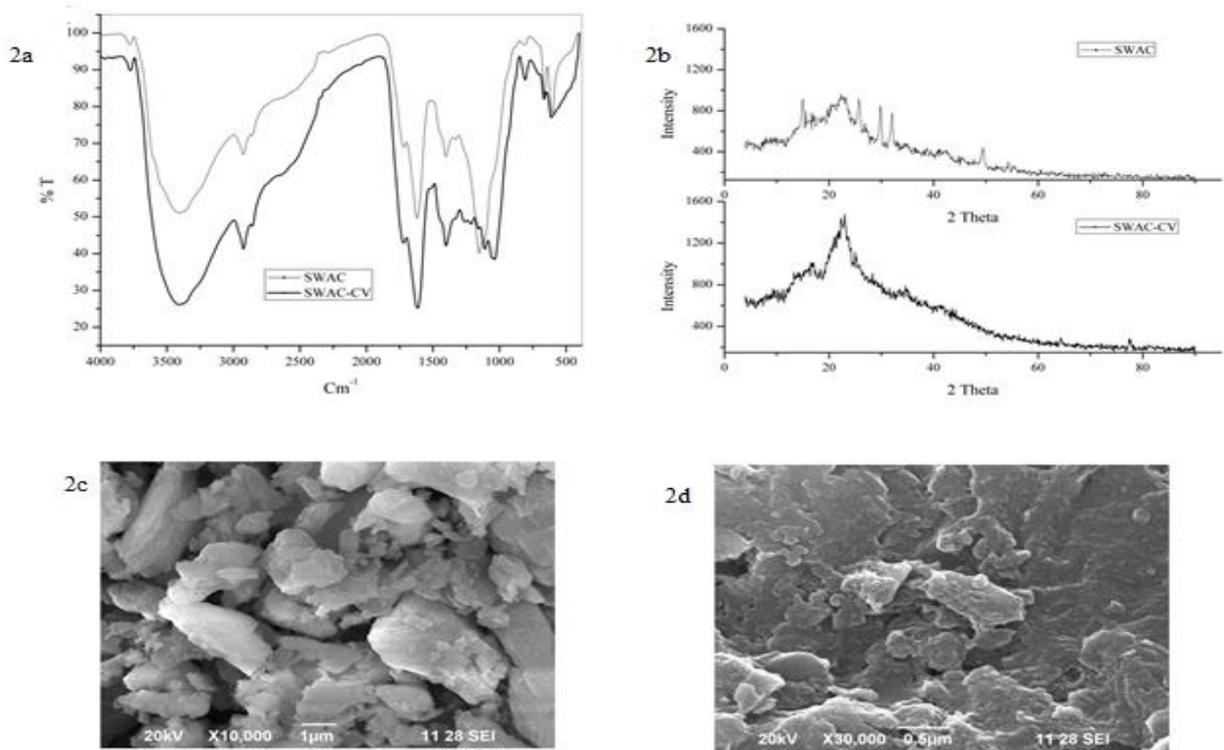
Figure.2 a)FTIR of SWAC and SWAC-CV dye, **Figure.2** b) XRD of SWAC and SWAC-CV dye
Figure.2 c) SEM image of SWAC,   **Figure.2** d) SEM image of SWAC-CV dye
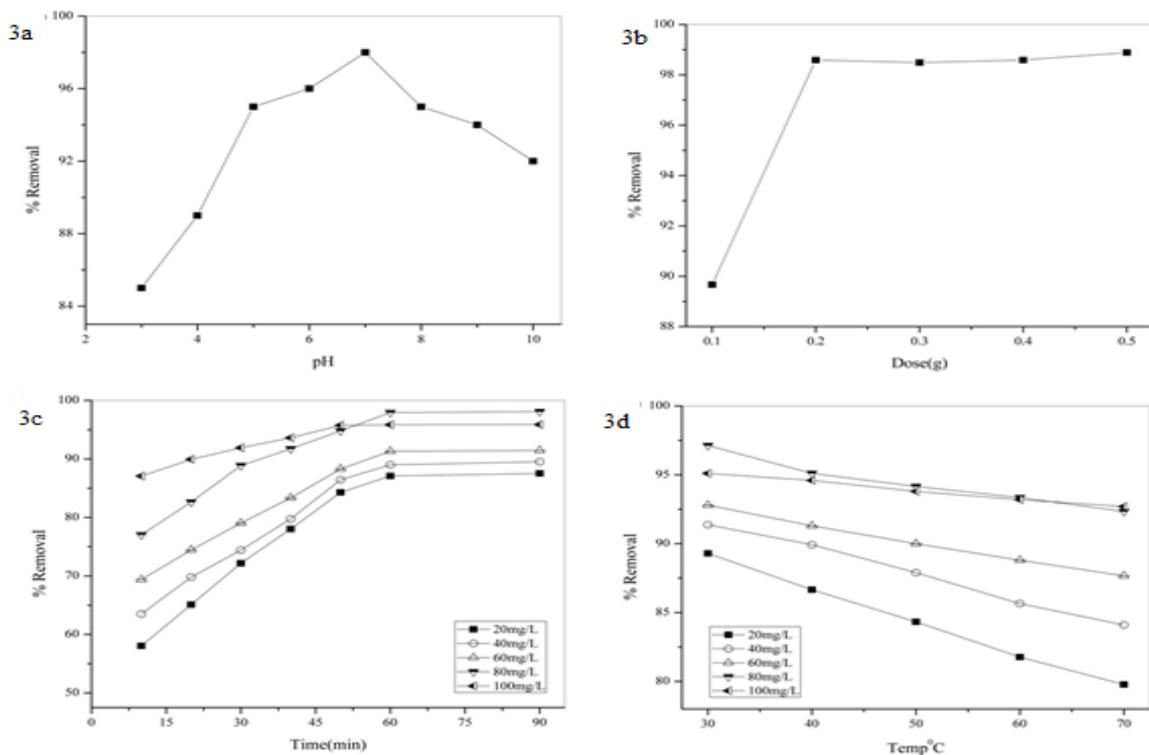
Figure 3. a)Effect of pH for the adsorption of CV dye, b) Effect of adsorbent dose for the adsorption of CV dye, c) Effect of time for the adsorption of CV dye, d) Effect of temperature for the adsorption of CV dye

The effect of dose of the adsorbent was evaluated using various quantities of adsorbents ranging from 0.1 to 0.5 g in increments of 0.1 g. From the various adsorbent dosage values studied, 0.2 g of adsorbent dosage gives 98.3% removal of crystal violet dye (Fig. 3b) as compared with the other adsorbent dosages .The CV dye removal was significantly enhanced with the increasing dosage of adsorbent up to the attainment of equilibrium

dosage of adsorption. After that, the adsorbent dosage increases in the adsorption system, while the percentage of removal remains constant due to the unavailability of the adsorbent sites on the adsorbent surface.

3.4. *Effect of dye concentration and contact time*
The concentration of dye and agitation time of the adsorption process was determined by varying the concentration of dye in the range of 20–100 mg/L with 20 mg/L variation and the time was varied from 15–90 min with 15 min variation. Fig. 3c shows the various quantities of dye used, the 80 mg/L of dye concentration showing excellent dye removal as compared to other concentrations and 60 min of contact time showing highest dye removal as compared with other time intervals. This was an optimum dye concentration and contact time for the adsorption process.

3.5. *Effect of temperature*
The effect of temperature was investigated with different temperature ranges from 30 ℃ to 70 ℃ with the increment of 10 ℃. Fig. 3d shows that the optimum temperature for the effective removal of crystal violet dye was at 30 ℃. Though the increasing temperature did not significantly altered the adsorption process, the decrease in adsorption with increasing the temperature was found to be mainly due to the enhancement of the desorption step in the process. The temperature is thought to weaken the physical forces of attraction between the active sites on the activated carbon and the dye species and also between adjacent dye molecules on the adsorbed phase.

3.6. *Equilibrium modelling studies*
The equilibrium of the adsorption process was evaluated with the help of Freundlich [18]and Langmuir[19] adsorption isotherm equations. The Freundlich isotherm is an assumption of the ratio of amount of solute molecules adsorbed on a mass of adsorbent molecules to the concentration of solute in the solution and it varies with different concentrations. The non-linear form of Freundlich equation is given by

$$q_e = K_F C_e^{1/nF} \qquad (3)$$

The linearized form Freundlich equation is

$$\log q_e = \log\left(K_F\right) + \frac{1}{nF}\log\left(C_e\right) \qquad (4)$$

where q_e is the amount of adsorbate adsorbed at equilibrium condition (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_F is the Freundlich adsorption isotherm constant which related to adsorption capacity of the adsorbent ((mg/g)(L/mg)$^{1/n}$) and 1/n is the adsorption intensity. The values of K_F and 1/n were calculated from the intercept and slope of the plot of C_e/q_e *vs*. C_e(Fig. 3b)

The Langmuir isotherm is an assumption of uniform distribution energies of the sorption on the surface and there is no transmigration of sorbate particles in the plane of the surface of the adsorbent. The non-linear form of Langmuir equation is

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad (5)$$

The linearized form of Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_a q_m} \qquad (6)$$

Where q_e(mg/g) and C_e(mg/L) are the amounts of dye adsorbed per unit mass of adsorbent and unabsorbed dye concentration in the solution, q_m is the maximum amount of dye adsorbed per unit mass of adsorbent on the entire monolayer surface, and K_a is a constant related to the affinity of the binding sites. Linear regression is the most common method to evaluate the adsorption process and so the adsorption constants were obtained by using linear least square method (Fig. 4a).

The experimentally calculated values of Freundlich and Langmuir isotherm parameters are presented in Table 1. From the table it could be seen that the Freundlich isotherm shows a correlation coefficient value (r^2) of 0.9593

and the Langmuir isotherm shows the correlation coefficient value (r^2) of 0.9990. These values conclude that the Langmuir isotherm was the most suited isotherm rather than the Freundlich isotherm for the removal of CV dye. As Langmuir-1 is the best suited model when compared with other form of Langmuir and Freundlich isotherms it could be said that there is a specific monolayer adsorption along with slight multilayer adsorption was found in this adsorption process.
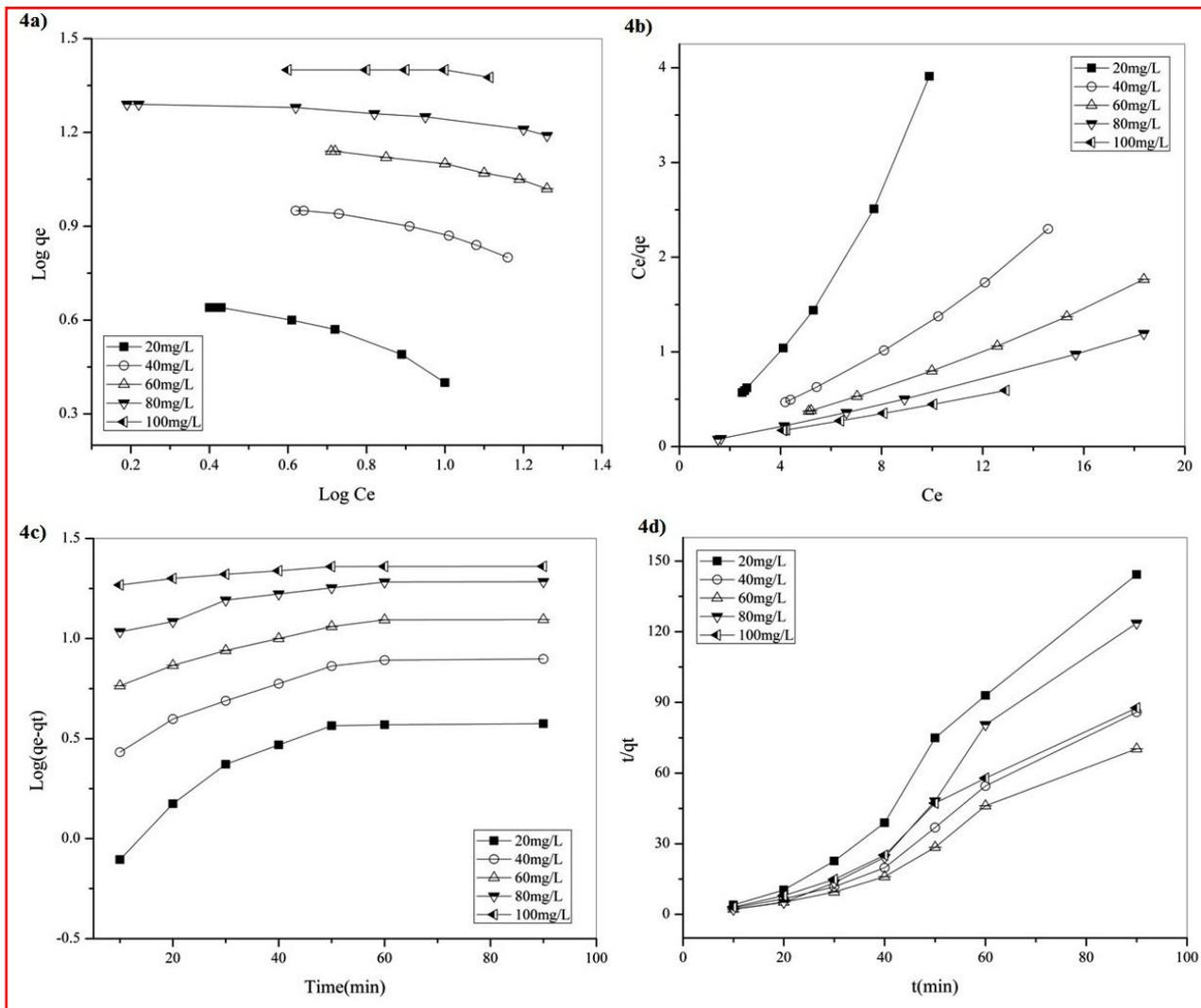
Figure 4. a) Freundlich isotherm for the adsorption of CVdye,
Figure 4. b) Langmuir isotherm for the adsorption of CV dye,
Figure 4. c) Pseudo-first order plot for the adsorption of CV dye,
Figure 4. d)Pseudo-second order plot for the adsorption of CV dye

3.7. *Kinetic studies*
Adsorption kinetic profiles were correlated in order to determine the rate limiting steps involved in the sorption process of CV dye onto SWAC. Lagergren's pseudo first order (Eq. (7)) and pseudo second order (Eq. (8)) kinetic models were used for the kinetic modeling studies [20].

$$\log\left(q_e - q\right) = \log\left(q_e\right) - \frac{K_1 t}{2.303} \tag{7}$$

Where, K_1 is the pseudo first order adsorption rate constant, q_e is the amount of dye adsorbed on the SWAC at equilibrium (mgg^{-1}), qt is the amount of CV dye adsorbed on the SWAC at any time t (mg/g):

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

Where, K_2 is the pseudo-second order adsorption rate constant, q_e amount of dye adsorbed on the SWAC at equilibrium (mg/g), q^2_e is the pseudo second order adsorption rate constant (g/mg/min).

Table 1. Isotherm Parameters for the adsorption of SWAC-CV dye

Isotherms	Parameters	Concentrations (mg/g)				
		20	**40**	**60**	**80**	**100**
Langmuir 1	q_m (mg/g)	2.3101	5.8465	9.7200	15.2235	21.0482
	K_a (L/mg)	0.6952	0.5737	0.5568	1.4024	1.7820
	r^2	0.9746	0.9888	0.9928	0.9954	0.9990
Langmuir 2	q_m (mg/g)	2.5367	6.1908	9.9532	16.4771	21.4638
	K_a (L/mg)	0.8755	0.7123	0.6257	3.5868	2.3734
	r^2	0.7252	0.8203	0.7514	0.5532	0.8567
Langmuir 3	q_m (mg/g)	2.0633	3.9929	6.4990	9.6614	13.3113
	K_a (L/mg)	1.2056	1.5167	1.5416	0.4011	0.4914
	r^2	0.8623	0.8927	0.8773	0.6003	0.8990
Langmuir 4	q_m (mg/g)	2.4675	4.5040	7.4127	9.0314	12.6572
	K_a (L/mg)	1.0672	1.3810	1.3840	0.2675	0.4500
	r^2	0.8623	0.8927	0.8773	0.6003	0.8990
Freundlich	1/n	0.3665	0.2640	0.2055	0.0852	0.0278
	K_F(mg/g)(L/g)	0.2205	0.1176	0.2561	0.2753	0.3499
	r^2	0.9213	0.9454	0.9593	0.8453	0.3074

The values of pseudo-first order rate constant (K_1), pseudo-second order rate constant (K_2), equilibrium uptake capacity (q_e) and their corresponding regression coefficient (r^2) values were calculated and presented in Table 2. From the table it is seen that the coefficient values of pseudo-first order rate constant and the q_e values (Fig. 4c) are comparatively very low (0.7632). But in the case of pseudo-second order kinetics (Fig. 4d) the resultant correlation coefficient values are 0.9713, confirming that the sorption process follows second order rate reaction. This result concludes that the rate of the process depends on the concentration factor (Pseudo-first order) and as well as concentration and time (Pseudo-second order), while the rate-controlling step indicates the adsorption of dyes was chemisorption rather than physisorption.

The calculated values of intra-particle parameters were presented in table 3. and are used to plotting q_t *vs.* $t^{1/2}$ provides a line, if intraparticle diffusion lines pass through the origin then intra-particle diffusion is the rate-controlling step[21]. The mechanism of diffusion process was predicted using the widely used Weber and Morris intra-particle diffusion kinetics model [22].The mathematical expression for the intra-particle diffusion equation is:

$$q_t = K_{id}\, t^{1/2} + C \qquad\qquad (7)$$

Where, k_{id} is the intra-particle diffusion rate constant (mg/g/min$^{1/2}$) and C is boundary layer thickness of the intercept segments (Fig. 5a). There are two linear segments of a line was obtained. The first segment indicates boundary layer diffusion of the dye solution to the outer surface of the SWAC and the second portion show that the adsorption happens throughout the porous surface of the SWAC. It further reveals that the adsorption of dye

on SWAC may involve several modes of sorption rather than a single mode. Hence, these results confirm that the multi-mode diffusion process of adsorption was involved rather than the single mode of diffusion process.

Table 2. Kinetic parameters for the adsorption of CV dye onto SWAC

C_0	Pseudo-First Order			Pseudo Second Order			
	K_1	q_e	r^2	$q_e.exp$	K_2	$q_e.cal$	r^2
20	0.0181	1.4424	0.6235	0.85	0.1408	0.5322	0.9713
40	0.0131	0.3102	0.7389	1.75	0.0753	0.9052	0.9585
60	0.0095	0.0993	0.7632	2.82	0.0609	1.0997	0.9516
80	0.0073	0.0237	0.7218	3.74	0.0967	0.6096	0.9430
100	0.0026	0.1074	0.7010	4.67	0.0935	0.8837	0.9711
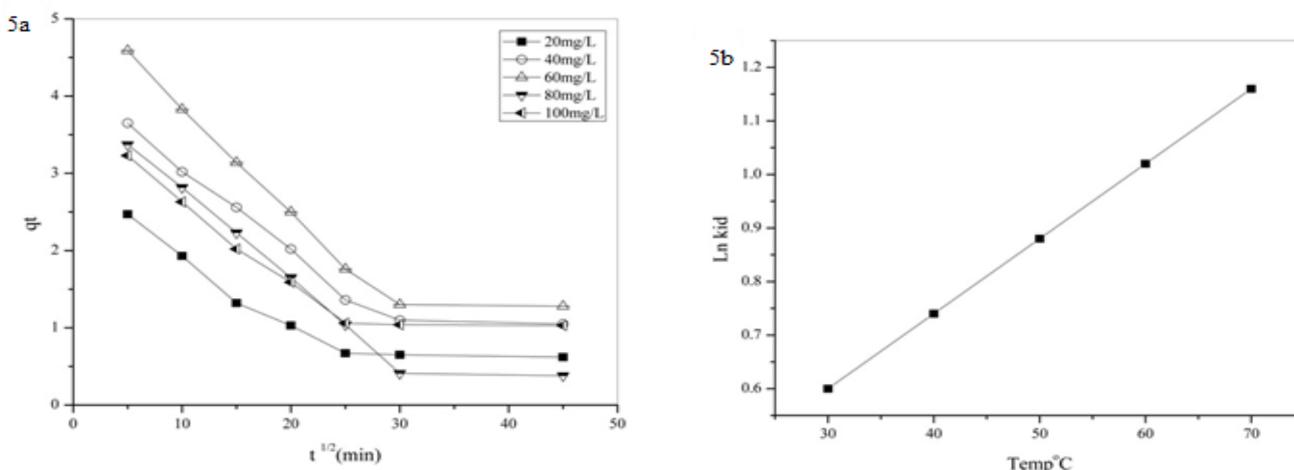
Figure 5. a) Intra-particle diffusion model plot for the adsorption of CV dye,
Figure 5. b) Van't Hoff plot for the adsorption of CV dye.

Table 3. Intra-particle diffusion parameters for the adsorption CV dye using SWAC.

$C_0 (mgg^{-1})$	$k_{id} (mgg^{-1}s^{1/2})$	$C (mgg^{-1})$	r^2
20	0.046	2.2285	0.6927
40	0.0688	3.5846	0.8106
60	0.0878	4.5102	0.8145
80	0.0811	3.4373	0.8502
100	0.0566	3.0118	0.7169

3.8. Thermodynamic parameters

The effect of heat on adsorption of the CV dye onto the SWAC material was determined using the thermodynamic parameters such as standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) by the following equations [23]:

$$K_{id} = \frac{q_e}{C_e} \qquad (9)$$

$$\Delta G^0 = - RT \ln K_{id} \qquad (10)$$

$$\ln K_{id} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (11)$$

A plot of $\ln K_{id}$ *vs.* 1/T (Fig. 5b) yields a straight line with the slope and the intercept gives the values of ΔG^0, ΔS^0 and ΔH^0[24].The calculated values of the thermodynamic parameters are presented in Table 4. The ΔG^0 values for the various temperature ranges from 30 to 70 ℃ shows a negative value which indicates that the adsorption process of CV dye onto the SWAC was spontaneous in nature[25-26] and that the adsorption process does not gain energy from any source. Also when the temperature is increased from 30 to 70 ℃ the degree of free energy shifts to a higher negative value indicating that the adsorption is more spontaneous at high temperatures [27]. The ΔH^0 value was found to be positive in the temperature range of 30 to 70 ℃ (Table. 4). This indicates that the endothermic nature of adsorption process was feasible. The positive value of entropy (ΔS^0) shown that the disorder of the molecule increases in the interface between the dye and SWAC with an affinity of dye molecule towards the SW activated carbon. These experimental results conclude that the adsorption of CV dye onto SWAC was favorable.

Table 4. Thermodynamic parameters for the adsorption of CV dye using SWAC.

T (℃)	ΔG^0 (KJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0 (KJ mol^{-1})
30	-0.15	2.03	32.5
40	-0.25		
50	-0.37		
60	-0.51		
70	-0.68		

Conclusion

Batch mode adsorption studies shows the parameters and their optimum values for dye removal to be; a pH value of 7, dose of adsorbent as 0.2 g, agitation time of 60 min, temperature 30 ℃ and concentration to be 80mg/L. The calculation of isotherm parameter studies of Freundlich isotherm and Langmuir isotherm equations shows that the Langmuir isotherm process was a more suitable mechanism compared to the Freundlich mechanism which implies that the monolayer process is predominant than the multi-layer process. From the correlated experimental values of pseudo-first order and pseudo-second order kinetic equations, the pseudo-second order model was seen to have higher correlation coefficient (r^2) values as compared to the pseudo-first order equation. This relates that the adsorption process follows pseudo second order kinetic equation reasonably well compared to pseudo-first order equation. The thermodynamic parameter value ΔG^0 shows a negative value indicating that the adsorption process of CV dye onto the SWAC was spontaneous in nature. The degree of free energy shifts to a higher negative value indicating that the adsorption was more spontaneous at higher temperatures. The positive ΔH^0 value indicates that the endothermic nature of adsorption process was feasible. The positive value of entropy (ΔS^0) shows that the randomness of molecule increases in the interface between the dye and SWAC with noted affinity of the dye molecule towards the SW activated carbon.

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