

Studies on adsorption of crystal violet dye from aqueous solution onto *calligonum comosum* leaf powder (CCLP)

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Abstract: The adsorption of Crystal Violet (CV) by *Calligonum Comosum* Leaf Powder (CCLP) was studied. Experiments were conducted using initial dye concentration, CCLP adsorbent dose, stirring speed, and temperature as variables. Equilibrium was attained in 4 h. The extent of dye uptake (mg/g) was found to increase with an increase in initial dye concentration. The %adsorption was found to decrease with an increase in the amount of adsorbent. The stirring speed had effect on the adsorption rate. The adsorption of CV on CCLP decreased as the solution temperature increased. The thermodynamic parameters were also calculated and a negative value of ΔH° indicated the exothermic nature of adsorption. The applicability of the two isotherm models for the present data followed the order: Langmuir > Freundlich.

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1. Introduction

As a result of rapid industrialization and population growth, environmental pollution has become the most challenging threat to human beings. Many industries, such as dyestuffs, textiles, paper, and plastics, use dyes to color their products. As a result, they generate a considerable amount of colored wastewater. Color is the first contaminant to be recognized in wastewater [1]. The presence of small amounts of dyes in water (less than 1ppm for some dyes) is highly visible and undesirable [2]. Because of increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged.

The various treatment methods for the adsorption of color and dye include coagulation using alum, lime, ferric sulphate or ferric chloride, chemical oxidation using chlorine and ozone, membrane separation processes, and adsorption. Among these, adsorption appears to show the greatest potential for treatment.

Various agricultural products and byproducts for removing dyes from aqueous solutions have been investigated. These include cotton waste-rice husk-bark-sugar industry mud-palm fruit bunch-jack fruit peel-wood-orange peel-sugar cane dust and peat [3], teak leaves [4], sewage sludge [5], waste apricot [6], hardwood sawdust [7], rice husk [8], pine wood saw dust [9], waste tyres [10], coir pith and orange peel [11], waste materials [12–15], TiO₂ catalyst [16], hen feathers [17–20], coniferous pinus bark powder [21], grapefruit peel [22] and male flowers of the coconut tree [23]. Activated carbon adsorption has been found to be an

effective and widely employed method of water and wastewater treatment. The adsorption capacities of activated carbons are usually related to their specific surface area and porosity. The adsorption properties of activated carbons depend strongly on the activation process.

Crystal violet (CV) dye, a member of the triphenylmethane group, is extensively used in animal and veterinary medicine as a biological stain, for identifying bloody fingerprints (being a protein dye), and in various commercial textile operations [23]. It is carcinogenic and has been classified as a recalcitrant molecule because it is poorly metabolized by microbes, is non-biodegradable, and can persist in a variety of environments [24]. Its adsorption from wastewaters before their discharge is, therefore, essential for environmental safety. Adsorption has been reported to be an efficient and economical method for the treatment of wastewaters containing dyes, pigments and other colorants [25].

Calligonum comosum leaf powder (CCLP) is produced in the Mediterranean, Asia, and North America, and regions of the Kingdom of Saudi Arabia, namely northern Hijaz and northeastern Najd, as well as the eastern and southern regions. Therefore, substantial amount of CCLP is available worldwide. The purpose of this study is to evaluate the adsorption of CV dye from aqueous solution onto CCLP as an inexpensive and environmentally friendly method of treating wastewaters containing the cationic CV dye.

The study is unique because no previous report has investigated the adsorption of any dye by using CCLP. The adsorption capacity of the adsorbent was investigated using batch experiments.

The influence of dye concentration, adsorbent concentrations, stirring speed, and temperature were investigated and the obtained experimental data were evaluated and fitted using adsorbent equilibrium isotherms, and thermodynamic parameters.

2. Material and Methods

2.1. Adsorbent material

Calligonum comosum was purchased from a local shop. It was washed under running water and peeled, and the leaves were then air-dried and grinded using a blender. The sieved fiber was kept dry in a closed container until required. No chemical or physical treatments were performed prior to the adsorption experiments.

2.2. Crystal violet stock solution

The adsorbate, *CV*, (C₂₅H₃₀N₃Cl, basic dye, C.I. 42555, λ_{max}. abs. = 584 nm), obtained from Dystar, Mumbai, India, was used as received (Fig. 1). Double distilled water was used. Concentrations of dye solutions were measured by monitoring the maximal absorbance using a Jenway model 6800 UV/VIS spectrophotometer.

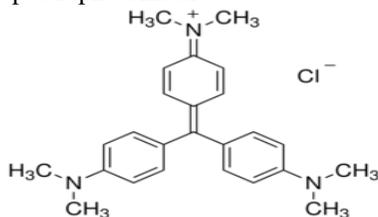


Figure 1. Crystal violet-dye structure.

2.3. Equilibrium studies

Batch adsorption studies were performed at room temperature. Fifty milliliters of various initial concentrations (10, 20, 40, 80 and 100 mg/l) of the dye solution were measured into 25 ml conical flasks containing 500 mg of *CCLP*.

The flasks were agitated at room temperature at 100 rpm for a pre-determined time intervals using a thermostated water-bath rotary orbital shaker at the initial solutions pH. The dye concentrations were measured using a UV/V is spectrophotometer at time t=0 and at equilibrium. The maximum absorbance of color was read at 584 nm. A known amount of adsorbent was then added to the solutions, and the mixture was agitated until equilibrium. The adsorption capacity q_e (mg/g) after equilibrium was calculated using a mass-balance relationship equation as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \times 100 \quad [1]$$

where V is the volume of the solution (l) and m is the mass of the adsorbent (g).

The effect of the *CCLP* concentration was studied at various concentrations (100 to 500 mg) with 25 ml of an 80 mg/l dye solution agitated for 4 h at room temperature. Twenty-five milliliters of an 80mg/l dye solution mixed with 500 mg of *CCLP* at solutions pH was agitated at various temperatures (25°C to 100°C).

Samples were filtered and analyzed for the remaining dye concentration. The percent adsorption of dye from the solution was calculated using the following equation:

$$\% \text{adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad [2]$$

where C_0 is the initial concentration of dye and C_e is the equilibrium concentration of dye. Isotherm studies were recorded by varying the initial concentration of dye solution from 10 to 100 mg/l.

3. Results and discussion

3.1. Effect of initial dye concentration

To study the effect of the initial concentration of *CV* in the solution on the rate of the adsorption onto *CCLP*, as shown in Fig. 2, the adsorption experiments were performed in the concentration range of (10 to 100 mg/l), with 500 mg of adsorbent, at room temperature. As the initial *CV* concentration increased from 10 to 100 mg/l the percent adsorption of *CV* increased from 81.7% to 97.7%, and the adsorption capacity increased from 0.42 to 4.98 mg/g. This was because the increase in the driving force of the concentration gradient, increased the initial dye concentration. As shown in Fig. 2, the maximal amount of dye adsorbed onto the *CCLP* was 100 mg/g. The value is much higher than that of other biowaste materials previously reported as adsorbents of dyes, such as; 85.47 mg/g for skin almond waste [26]; 60.42mg/g for activated carbon from male flowers of coconut tree [23]; and 64.87 mg/g for activated carbon prepared from rice husks [8].

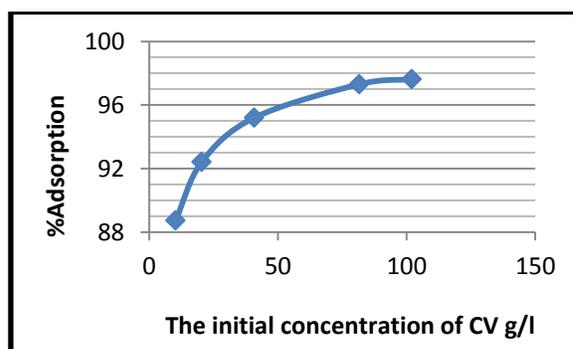


Figure 2. Effect of initial dye concentration

3.2. Effect of adsorbent doses

For *CCLP*, it was observed that the uptake of the dye increased when the amount of the adsorbent increased Fig. 3, at various adsorbent concentrations (10 to 500 mg/ 25 ml), a fixed equilibrium time of 4 h, and a *CV* concentration of 80 mg/l. This can be attributed to an increase in the adsorbent concentration which resulted in an increase in the available *CCLP* surface area and the availability of additional adsorption sites.

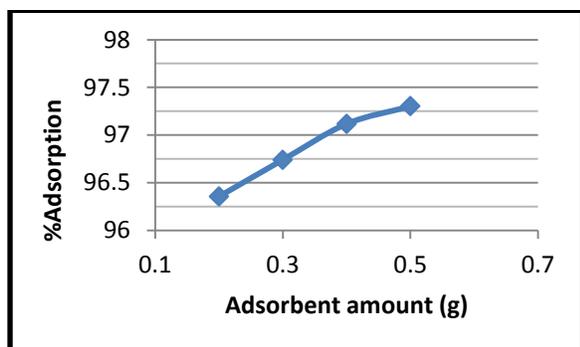


Figure 3. Effect of adsorbent dosages

3.3. Effect of stirring speed

A series of experiments were performed, using various stirring speeds in the range of 50 to 150 rpm at an initial *CV* concentration of 80 mg/L, and 25°C with 0.5 g of adsorbent. The stirring speed affected adsorption rate. When the stirring speed was increased from 50 to 150 rpm the adsorption percentage increased from 95.95% to 98.96% Fig. 4. Therefore, the stirring speed was set at 100 rpm in following experiments.

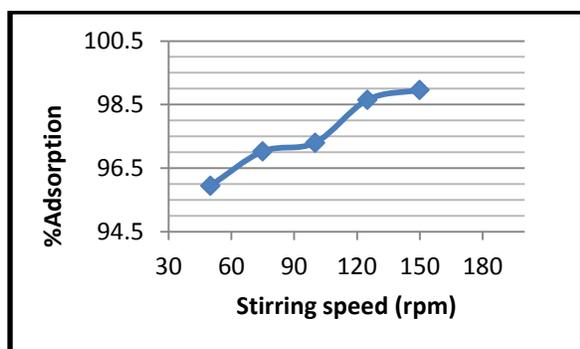


Figure 4. Effect of stirring speed

3.4. Effect of temperature on dye adsorption

The effect of temperature on the adsorption of *CV* by *CCLP* at equilibrium was investigated at five temperatures: 25°C; 40°C; 60°C; 80°C; and 100°C, at the initial *CV* concentration of 80 mg/L, with 500mg of adsorbent Fig. 5. The adsorption of *CV* on *CCLP* decreased as the solution temperature

increased. This can be explained by the exothermic spontaneity of the adsorption process and by the weakening of bonds between the dye molecules and the active sites of the adsorbent at high temperatures.

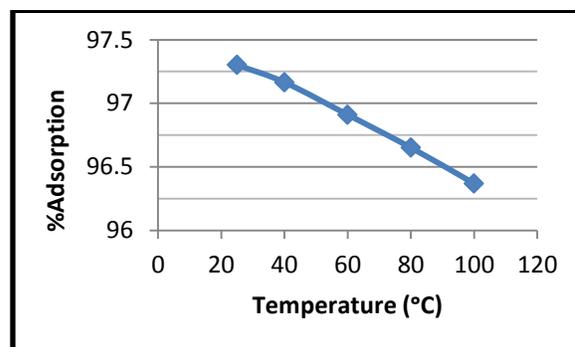


Figure 5. Effect of temperature on dye adsorption

3.5. Thermodynamic parameters

Thermodynamic parameter, change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations [27]:

$$K_c = \frac{C_{ac}}{C_e} \quad [3]$$

$$\Delta G^\circ = -RT \ln K_c \quad [4]$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad [5]$$

where K_c is the equilibrium constant, C_{ac} and C_e are the equilibrium concentrations (mg/l) of the dyes on the adsorbent and in the solution, respectively, T is the temperature in Kelvin and R is the gas constant.

ΔH° and ΔS° were obtained from the slope and intercept of a Van't Hoff plot of $\ln K_c$ versus $1/T$, Fig. 6, and values are presented in Table 1.

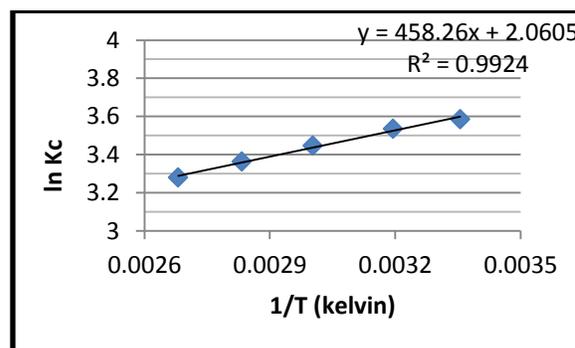


Figure 6. $\ln K_c$ versus $1/T$ according to Vant Hoff equation

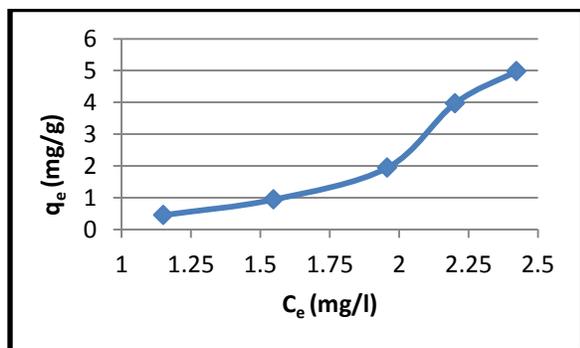
Table 1. Thermodynamic parameters

25°C (298K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
	-8.914	-3.810	17.131

Negative values of ΔH° confirm the exothermic nature of the adsorption of CV on CCLP. The negative values of ΔG° in Table 1 indicate the feasibility of dye adsorption, and the spontaneity of the process. The positive value of ΔS° reflects the affinity of CCLP for CV and also shows the increased randomness at the solid-solution interface.

3.6. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches a state of equilibrium. The adsorption isotherm of CV onto CCLP is illustrated in Fig. 7. This isotherm belongs to type S of the Giles et al. classification [27], which indicates that adsorption becomes easier as the concentration rises. In practice, the S curve of the adsorption isotherm means that strong competition exists between the molecules of the solvent and the adsorbed species to occupy the adsorbent surface sites. From Fig. 7, the experimental maximal adsorption capacity for the dye onto CCLP was approximately 5 mg/g.

**Figure 7.** Adsorption isotherm of CV onto CCLP

To successfully represent the equilibrium adsorption behavior, a satisfactory description of the equation state between the two phases composing the adsorption system is necessary.

Two types of isotherms equations were tested to fit the experimental data [28]:

Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}K_L C_e} + \frac{1}{q_{max}} \quad [6]$$

Freundlich equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad [7]$$

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of dye in the solution (mg/l).

The other parameters are various isotherms constants, which can be determined by regression of the experimental data. In the Langmuir equation, q_{max} mg/g is the measure of adsorption capacity under the experimental conditions and K_L is a constant related to the energy of adsorption. The Freundlich treatment uses the parameters n , which is indicative of adsorption intensity, and K_F , which is related to adsorption capacity. The linearized Langmuir and Freundlich isotherms of the dye are shown in Figs. 8 and 9. The estimated model parameters with correlation coefficient R^2 for the models are shown in Table 2. The values of R^2 are considered a measure of the goodness of-fit of the experimental data to the isotherm models. The applicability of the two isotherm models for the present data approximately follows the order: *Langmuir* > *Freundlich*.

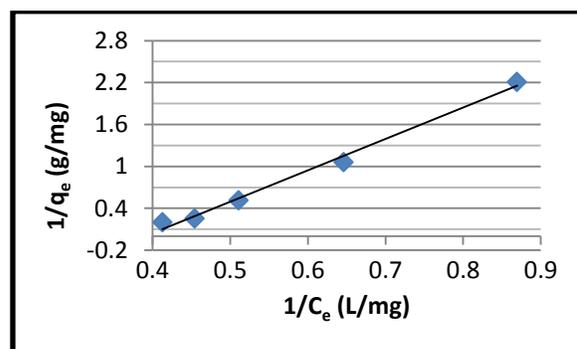
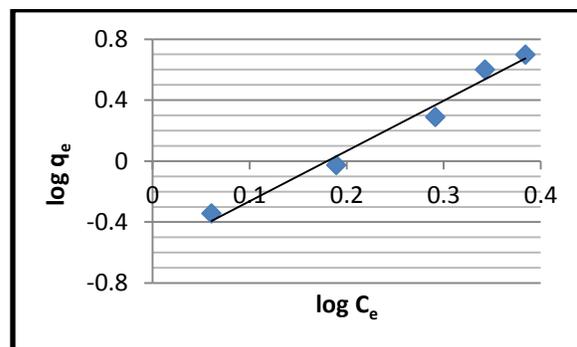
**Figure 8.** Langmuir isotherm**Figure 9.** Freundlich Isotherm

Table 2. The constants values of different adsorption models

<i>Langmuir</i>		
R^2	q_{max} (mg/g)	K_L (L/mg)
0.992	- 0.571	- 0.390
<i>Frindulish</i>		
R^2	K_F	n
0.978	0.255	0.304

For the Langmuir model, the maximal value of adsorption q_{max} was negative, which reflects the inadequacy of this model for explaining the adsorption process, although it shows a good linearity compared with other models [27].

For the Freundlich model, the value of exponent n indicates the favorability of adsorption. In general, values of n in the range 2 to 10 represent favorable adsorption, 1 to 2 represent moderately difficult adsorption, and >1 indicates poor adsorption characteristics [29]. In this study, the calculated value of n was less than one, indicating poor adsorption.

4. Conclusions

The present study shows that *CCLP* is a potential adsorbent for the adsorption of *CV* dye from aqueous solutions. Equilibrium was attained in 4 h. The amount of dye uptake (mg/g) was found to increase from 0.45 to 5 mg/g in the concentration range of 10 to 100 mg/l. The adsorption percentage decreased from 96.3% to 97.3% when the amount of adsorbent was increased from 0.1 to 0.5 g. The stirring speed affected the adsorption rate. When the stirring speed was increased from 50 to 150 rpm the adsorption percentage increased from 95.95% to 98.96%. The adsorption of *CV* on *CCLP* decreased as the solution temperature increased. The thermodynamic parameters were also calculated and a negative value of ΔH° indicates the exothermic nature of the adsorption. The applicability of the two isotherm models for the present data follows the order: *Langmuir* > *Freundlich*.

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