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Crystal Violet Dye Adsorption by Biochar Produced from Sugarcane Bagasse under Different Temperatures

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ABSTRACT

Biochar has been successfully used to treat wastewater. The adsorption capacity of biochar and their properties depended on the temperature used at their production as well as on each type of feedstock. In this study biochar was produced from sugarcane bagasse at 500 ºC and 650 ºC, to investigate the adsorption behavior of crystal violet dye (CV). The batch technique was used to investigate the effects of physiochemical parameters (contact time and initial dye concentration). The data was submitted to first and second pseudo-order kinetic models. These equations were used to characterize the dye kinetics adsorption process. The study's findings demonstrated that the pseudo-second-order equation was the best fit for the kinetic studies (R^2 = 1 and R^2 = 0.9998) for both biochar 500 ºC and biochar 650 ºC, respectively. Furthermore, the quantity equilibrium (q values) calculated (qe_{cal}) from the pseudo-second-order were highly consistent with experimental q values (qe_{exp}) compared to those calculated from the pseudo-first-order. Freundlich and Langmuir's adsorption isotherm models were used to calculate the adsorption constants. Freundlich adsorption isotherm correlation coefficient (R^2) values for biochar at 500 °C and biochar at 650 ºC were 0.9944 and 0.9751, respectively. This finding indicates that crystal violet adsorption data can be best suited by the Freundlich adsorption isotherm.

Keywords: Adsorption, Crystal violet, Biochar, Isotherm, Kinetics.

1. Introduction

Despite water's status as the most critical commodity for sustaining lifestyles, one in nine people worldwide lacks access to it for various reasons. Water pollution is a significant problem, and solving it requires innovative methods for purifying water and other aqueous solutions free of harmful organic and inorganic compounds[1]. An estimated 80% of all ailments can be traced back to contaminated water, according to the World Health Organization. Numerous businesses, such as those working with textiles, leather, paper, printing, dyestuff, plastics, etc., produce large amounts of wastewater containing color. Natural or manufactured, dye imparts its color to a substance through absorption and is often applied as a fine dispersion solution. Dyes, a significant contributor to water pollution, can be seen by the naked eye even at low concentrations and, by blocking out sunlight, can have a significant impact on the photosynthetic activity of aquatic life. They have several applications in the manufacturing of textiles, papers, leathers, prints, plastics, cosmetics, drugs, foods, and minerals[2, 3].

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Dye exposure can lead to serious health problems, including kidney, reproductive system, liver, brain, and CNS dysfunction[2]. The charge, functional group, and application of a dye are three criteria that might be used to categorize it. They can be categorized as cationic dyes, anionic dyes, and nonionic dyes based on their chemical structures, and as triarylmethane dyes, indigoid dyes, azo dyes, nitro dyes, and anthraquinone dyes, depending on their uses. The charge of these dyes is the most important property since it has a profound impact on the performance of the adsorption process[4]. The basic cationic dye Crystal Violet (CV) Gentian violet is commonly used in manufacturing. It is a tri-phenylmethane dye that produces a blue hue in water solutions with maximum absorption at around 590 nm. It finds extensive use as a staining agent in dermatological agents, microbial activities, and in a wide range of practical textile applications. It is an essential dye with the chemical formula $C_{25}H_{30}N_3Cl$ and is also known as hexa methyl pararosaniline chloride. The mitotic stage poisoning and carcinogenicity of the dye led to its classification as a threat to human health. This makes its removal from wastewater before disposal necessary to ensure environmental safety[5,6]. The increasing expansion of industry has made wastewater treatment a significant issue on a global scale[7]. Separation processes, flocculation or coagulation combined with precipitation and flotation, electroflotation, electrodialysis (ion exchange, sedimentation, filtration, electrocoagulation, and chemical oxidation), membrane filtration (ultrafiltration, nanofiltration, reverse osmosis), and biological degradation oxidation processes (free radicals and membranes processes). Adsorption is the most flexible and frequently adopted technique because of its low cost, ease of operation, and accessible nature[4, 8]. Biochar is the byproduct of low-oxygen pyrolysis of biomass such as food scraps, animal manure, and tree leaves. Biochar is mainly composed of carbon, but it also has smaller amounts of other elements, such as oxygen, hydrogen, sulfur, and nitrogen. Biochar can be used as an adsorbent for the adsorb of pollutants in wastewater due to its high specific surface area, consistent pore size, and abundance of functional groups. Adsorption with biochar is rising[9, 10, 11]. Carbonaceous biochar is created through hydrothermal carbonization or inert-atmosphere pyrolysis of biomass. Biochar's characteristics change depending on the biomass it was made from, how it was made, and the environmental circumstances. Biochar's use as an adsorbent and as a soil supplement, both of which help reduce greenhouse gas emissions, has garnered much attention[12, 13]. Biochar produced at different temperatures gave different properties as well as different adsorption behaviors to different pollutants[14]. For instance, researchers who produced biochar from a mushroom at different temperatures (300, 500 and 700 ºC) found that the adsorption capacity was highest with biochar producing at 700 C for Pb removal[15]. Therefore, the aim of this study will focus on producing biochar from sugarcane bagasse at different temperatures (500 ºC and 650 ºC) to study their efficiency for removal of CV from aqueous solution.

2. Materials and Methods

A UV-visible spectrophotometer (721, China) was used to calculate the dye's exact percentage. The pH meter BP 3001, Singapore, was used to measure the acidity or alkalinity of every liquid sample. An isothermal water bath shaker (model BS-11, Korea) maintained a constant temperature.

2.1 Adsorbents preparation

Sugarcane Bagasse samples were collected from the College of Agriculture at the University of Diyala. Samples were over-dried, crushed, and sieved < 2mm. Then, the samples were pyrolysis at different temperature (500 or 650 ºC) using a furnace (type-Nabenthem, Max Temperatures 1300 ºC, 400V, IS.OA, 50160 HZ, (Germany) with heating rate 12 ºC min^{-1} for 2 hours. All biochars were crushed and sieved with a sieve < 50 µm[16]. The yield was calculated as: -

Biochar yield (%)= (biochar (g) / dry mass of sugarcane (g))×100 ------- (2.1)

Some chemical properties are shown in Table 1.

Table 1: Some chemical properties of produced biochars.

Properties	Biochar 500 °C	Biochar 650 °C
pH	8.70	8.95
EC ms cm^{-3}	2.75	2.18
Ash content %	15.1	14.26
Yield%	31.97	24.99

2.2 Preparation of Crystal violet dye

Stock solutions that are the norm Dissolving crystal violet dye in distill water yielded a final concentration of 100 mg L^{-1}. Crystal violet dye was diluted from a standard stock solution to create different concentrations (0, 5, 10, 15, 20, 25, and 30 mg L^{-1}). The concentration of these solutions was calculated by measuring their absorbance at a wavelength of λ_{max} = 590 nm.

2.3 Batch adsorption method studies

Percentage metal removal (R%) was examined as a function of contact time and initial adsorbate concentration.

2.3.1 Contact time

The contact time influence was studied by varying time (5, 10, 20, 30, 40, 50 and 60) minute. The working solution concentration (5 mg L^{-1}) was prepared and each (20 mL) of Crystal violet dye solution was put in volumetric flasks with a volume of (50 mL) containing (0.2 g) of biochar (500 C˚ or 650 C˚). Then the glass stoppers were used to cover the flasks were placed in a shaker at room temperature of 25 °C with a speed of 150 rpm.

2.3.2 Initial concentration

Evaluation of the initial concentration influence was studied (5, 10, 15, 20, 25 and 30) mg L^{-1} at a pH of 7, adsorbent dose of 0.2 gm, and 25 °C with a speed of 150 rpm and at contact time 20 minute for biochar 500 °C and biochar 650 °C. After that the samples were filtered off and measured by UV - visible spectrophotometer.

2.3.3 Calculation of dye removal

The dye removal percentage, was determined by:

$$\text{Removal\%} = \frac{Co - Ct}{Co} \times 100 \qquad (2.2)$$

C_o: The concentration of dye before adsorption (mg L^{-1}).

C_t: The dye concentration after adsorption at any time t (mg L^{-1}).

2.4 Adsorption isotherms

At 25 degrees Celsius, with a constant shaking speed of 150 revolutions per minute, and a contact time of 20 minutes for biochar 500 ºC and biochar 650 ºC, the adsorption isotherms for crystal violet dye solutions were determined by adding 20 milliliters of a solution whose concentration ranged from 5 to 30 milligrams per milliliter to volumetric flasks containing 0.2 grams of biochar at each temperature. The following equation was used to determine the adsorption capacity of the adsorbent:

$$Q_e = \frac{(Co - Ce)V}{m} \qquad (2.3)$$

Q_e : the amount of dye adsorbed at equilibrium (mg g^{-1}).

C_o : Initial concentrations of dye (mg L^{-1}).

C_e : Equilibrium concentrations of dye after adsorption (mg L^{-1}).

V : Volume of solution (L).

m : Weight of biochar (g).

Langmuir isotherm model

$$\frac{Ce}{qe} = \frac{1}{b\,Qmax} + \frac{Ce}{Qmax}$$

Q_{max} is the maximum adsorption capacity (mg g^{-1}) of the metal ion per unit weight of sorbent. b (L mg^{-1}) indicates the affinity of the metal for binding on the sorption sites.

$$R_L = \frac{1}{1 + bC_e}$$

where C_e (mg L^{-1}) is the equilibrium concentration of CV and b (mL mg^{-1}) are the affinity constant of the Langmuir isotherm model.

Freundlich isotherm model

$\log q_e = \log K + 1/n \log C_e$

where q_e is adsorbed weight of metal ion per unit weight of adsorbent, K_F and n are Freundlich empirical constants (L g^{-1}) and C_e is the ion equilibrium concentration

2.5 Kinetic study for adsorption of crystal violet dye

At 25 C° and pH of 7, volumetric flasks containing (0.2 g) of biochar 500 °C and biochar 650 °C were treated with crystal violet dye (20 mL) at a known concentration of (5 mg L^{-1}). After 20 minutes of contact time at 500 and 650 °C, respectively. The mixture was filtered and quantified using a UV. visible spectrophotometer. The flasks were then placed in a shaker at a constant speed shaking (150 rpm). Several models of kinetic were used to examine the adsorbate-adsorbent interaction order, and the resulting equations may be found below:

$$\ln (q_e - q_t) = \ln q_e - k1\,t \quad (2.4)$$

$$\frac{t}{q_t} = 1/k2{q_e}^2 + \left(\frac{1}{q_e}\right) t \quad (2.5)$$

q_e (mg g^{-1}): the equilibrium sorption capacity

q_t (mg g^{-1}): the quantity of dye adsorbed at time t (min)

k_1 (min $^{-1}$): the rate constant pseudo first order

k_2 (min $^{-1}$): the rate constant pseudo second order

Values of k_1 and k_2 were obtained from the slope of the plot of ln(qe-qt) vs time and t/qt versus time respectively.

3. Results and Discussion

3.1 Adsorption study

3.1.1 Determine the equilibrium time

Crystal violet adsorption at 25 °C is shown to be affected by contact time (Figure 1). The results showed that the equilibrium period for removals greater than 96% using biochar 500 °C and greater than 98% using biochar 650 °C was 20 minutes. Increases in the initial availability of free sites may account for the quick increase in the first amount of adsorbed dye[17].

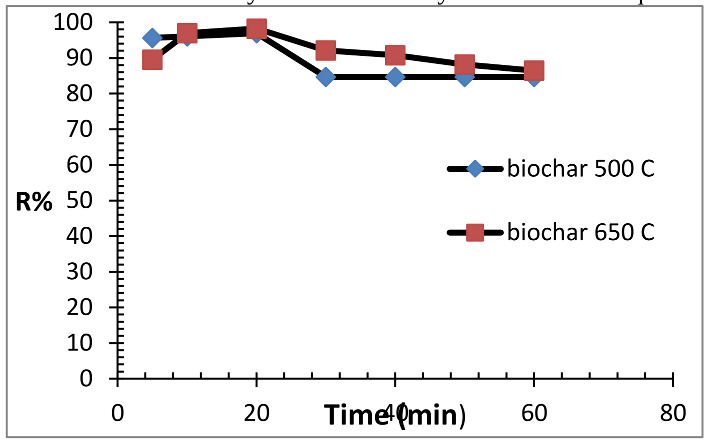


Figure 1: The effect of equilibrium time on adsorption of crystal violet dye on the biochar surfaces (500 ˚C and 650 ˚C).

3.1.2 Effect of Initial Concentration of Crystal Violet Dye.

(Figure 2) lists the results of measuring adsorption at various concentrations. It was discovered that a concentration of 5 mg L^{-1} resulted in the best percentage of dye removal for both surfaces (500 and 650 °C). This may be because all of the dye molecules in the solution can interact with the biochar at low concentrations due to high surface-active sites. The initial concentration affected the dynamic equilibrium[18].

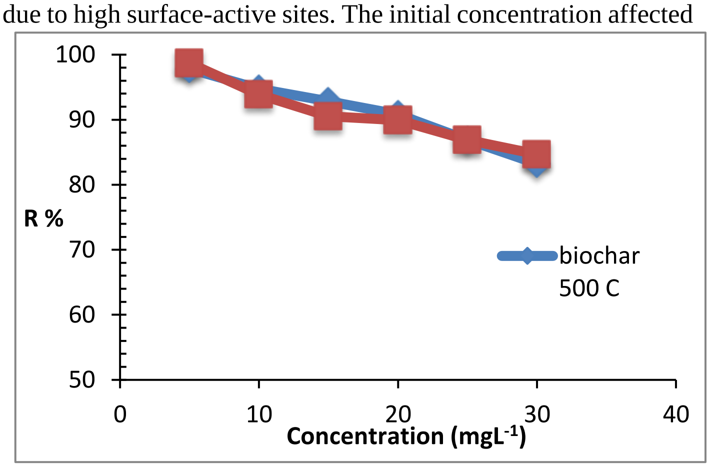


Figure 2: Effect of initial concentration on adsorption of crystal violet dye on the biochar surfaces (500 ˚C and 650 ˚C).

3.2 Adsorption Isotherm:

Isotherm adsorption provides valuable data. It illustrates the movement of molecules from the liquid to the solid phase during the adsorption process. The crystal violet dye adsorption isotherms to four different isotherms, including the Langmuir and Freundlich isotherms, on the biochar surfaces (500 °C and 650 °C). Based on the data in Table 2 and Figure 3, biochar at 500 °C and 650 °C are both amenable to crystal violet adsorption on their surfaces. The constant Freundlich value "n" shows the degree of nonlinearity between solution concentration and adsorption, if n equals one, adsorption is linear; if n is less than one, the process is a chemisorption type; and if n exceeds one, the process is physisorption type. According to Table 2, the n value, was 2.2904 for biochar at 500 °C and 2.5726 for biochar at 650 °C, which indicates that C.V. dye was physically and favorably adsorbed onto biochar at 500 °C and 650 °C. The equilibrium data had an R2 value of 0.9944 for biochar at 500 °C and 0.9751 for biochar at 650 °C, which fit the Freundlich expression[19]. The Langmuir constant R_L was in the favorable range of (0.15850.1772). In addition, the Freundlich adsorption isotherm correlation coefficient (R^2) was 0.9944 for biochar at 500 °C and 0.9751 for biochar at 650 °C. Adsorption data for crystal violet were experimentally analyzed, and the data were fitted to the Freundlich adsorption isotherm[4]. Table 2 shows the results of q max where 2.8768 and 2.9420 for biochar at 500 °C and 650 °C, respectively. Compared to previous studies published in[20], our results it close to that q max value obtained by using different adsorbents (Sugarcane dust, Coir path, Calotropis procera leaf, Avocado pear seed) were (3.8, 2.56, 4.14 and 3.3254), respectively.

Table2 : The calculated adsorption parameters of the four equations used (Langmuir, Freundlich) isotherms.

	Langmuir				Freundlich		
	K_L	R_L	q_{max}	R^2	K_F	n	R^2
Biochar 500 ˚C	1.0617	0.1585	2.8768	0.9839	1.3004	2.2904	0.9944
Biochar 650 ˚C	0.9284	0.1772	2.9420	0.9272	1.3091	2.5726	0.9751

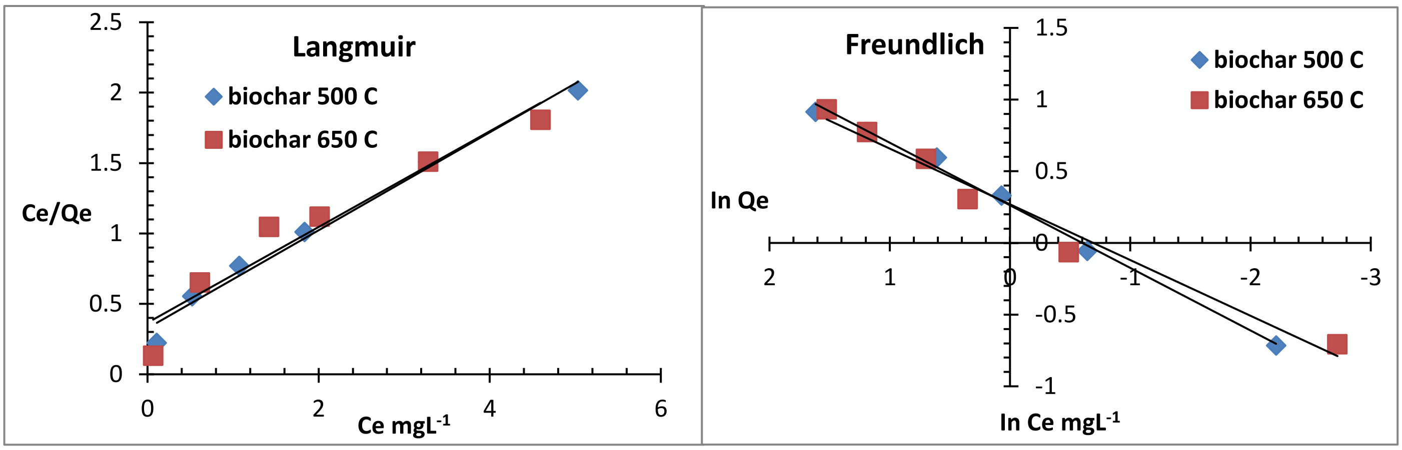


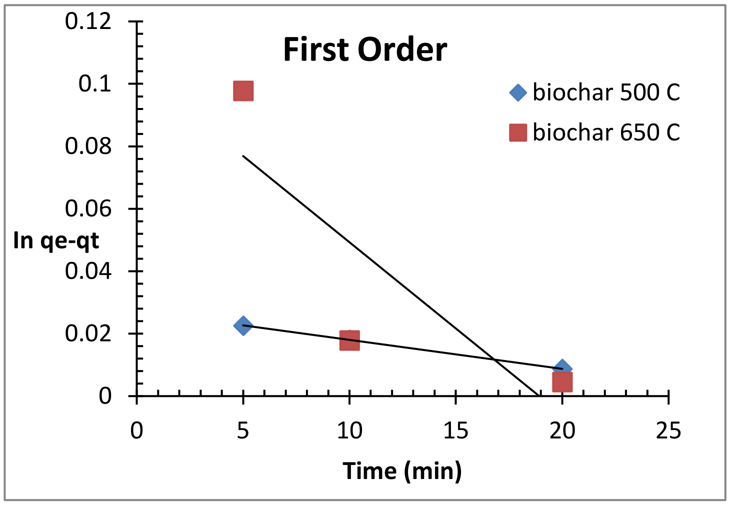
Figure 3: Langmuir and Freundlich adsorption isotherms for the adsorption of CV on biochar surfaces (500 ˚C and 650 ˚C).

3.3 Adsorption kinetics studies

Both the pseudo-first and second-order model was used to analyze the kinetics of crystal violet dye's adsorption from an aqueous solution onto a solid surface. Parameter values (k1, k2, and qe (cal.)) are offered in Table 3 and Figure 4. The results show that the pseudo second-order equation has higher values of the correlation coefficient (R^2) than the pseudo first-order equation does. Both biochar at 500 °C and 650 °C have ideal fits to the pseudo-second-order equation (R2 = 1 and R2 = 0.9998, respectively). Also, compared to the q values estimated from the pseudo first-order model, the q values computed from the pseudo second-order model were more in line with the experimental q values (qe_{exp}). The pseudo second-order equation is more suited to the problem than the pseudo first-order equation. This points to a pseudo-second-order adsorption[21].

Table3 : Kinetics parameters for pseudo-first and second order.

C_o = 5 (mg L^{-1})		Q_e (exp.)	Pseudo first order			Pseudo second order		
			q_e (calculated)	k_1 min^{-1}	R^2	q_e (calculated)	k_2 g mg^{-1} min^{-1}	R^2
	Biochar 500 ˚C	0.489059	1.0276	- 0.0009	0.9999	0.4872	17.8792	1
	Biochar 650 ˚C	0.493435	1.1101	- 0.0055	0.6992	0.5063	3.4411	0.9998



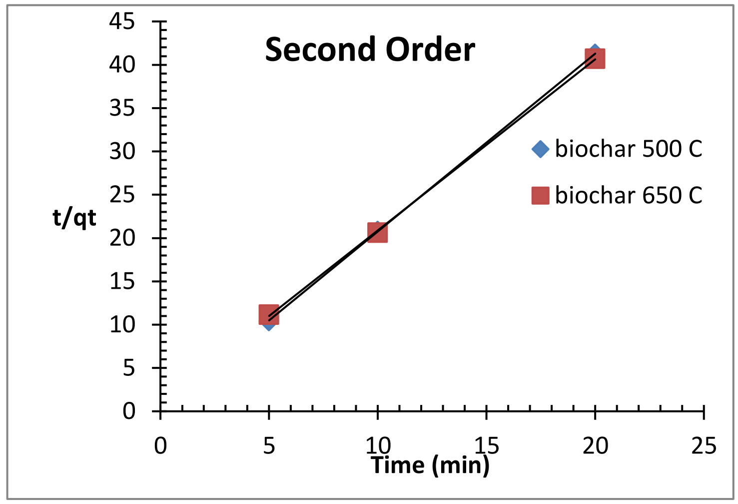


Figure 4: Kinetics parameters for pseudo-1st order and pseudo-2nd order.

Conclusions

The results of this research show that both biochars are pretty effective at removing crystal violet color from water. The equilibrium period for biochar at 500 °C and 650 °C is 20 minutes, and which rises with contact time. The highest percentage of dye removal was seen at a concentration of (5 mg L^{-1}) of dye when the initial concentration of adsorbate was increased. Applying the Langmuir and Freundlich models indicated that the Freundlich isotherm provided the best fit to the data. The results suggest that the adsorption is pseudo second-order since the pseudo second-order equation better describes the data compared to the pseudo first-order equation. Biochar made at either temperature (500 °C or 650 °C) was equally effective at removing the violet color from water.

Conflict of interests

The authors have confirmed that they have no personal stakes in the outcome of this work.

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