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Biochar made fromcoffee ground for adsorption of crystal violet dye

ABSTRACT

Biochar was prepared by anaerobic heating coffee ground at 800 °C for 3 hours. The prepared sample was used to adsorb crystal violet dye in an aqueous environment. The result showed that the biochar sample had good adsorption capacity for crystal violet dye, with the maximum adsorption capacity of 128.87 (mg/g). Thus, low-cost biochar prepared from coffee grounds has great potential to be used as an adsorbent material to remove crystal violet dye in an aqueous environment.
Keywords:*Biochar, crystal violet, coffee ground, isothermmodels, adsorption kinetics, wastewater treatment.*

1. INTRODUCTION

Persistent organic dyes are often found in wastewater from the textile industry. A typical example is crystal violet dye (Cristal Violet – CV) ($C_{25}H_{30}N_3Cl$), a strong color pollutant that hinders light penetration through water, causing harm to organisms. In addition, some reports have shown that CV can be dangerous to humans such as respiratory and kidney failure, skin and gastrointestinal irritation, cytotoxicity, and CV is even reported to be a carcinogen [1]. Therefore, removing CV in the aquatic environment is an urgent issue to create a safe living environment for humans and organisms. Recently, biochar has been used as a friendly, inexpensive adsorbent material to remove organic dyes in the aquatic environment [2].Although the adsorption efficiency of biochar is lower than that of activated carbon, biochar is much cheaper due to the simple fabrication process from diverse biomass sources.Several studies have reported on the fabrication of biochar to remove organic dyes from agricultural biomass sources such as meliaazedarach seeds [3], peanut shells [4], straw [5], walnut shells [6], date palm kernels [7], and cashew shells [8]. In this study, we fabricated biochar from coffee grounds using a simple thermal decomposition method, then the biochar samples were used to adsorbCVin an aqueous medium. Different parameters of the adsorption experiment such as adsorption time and initial concentration of CV were investigated. The mechanism of CV adsorption by biochar was also evaluated based on the Langmuir and Freundlich isotherm adsorption models.

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2. EXPERIMENT AND METHODS

2.1. Process of making biochar from coffee ground

The coffee ground was thoroughly washed to remove impurities and dried at 80 °C in a drying oven for 24 hours to obtain dried coffee ground. Then, the coffee ground was anaerobically calcined at 800 °C for 3 hours. At the end of the calcination process, the biochar obtained was ground in a porcelain mortar and passed through a 60 μm sieve. The manufactured biochar sample was denoted as biochar-800 °C.

2.2. Crystal violet adsorption experiment

The biochar samples were placed in Erlen flasks (250 mL capacity) containing 60 mL of crystal violet solution. The reaction flasks were sealed with ground glass stoppers and placed in a thermostatic shaking system (GFL 1083).

At the end of the reaction, centrifugation was performed to separate the solid fractions, and the solutions were used to measure the remaining CV concentration using a UV-VIS spectrophotometer. The adsorption efficiency of CV was calculated using the formula: $R = \frac{C_o - C}{C_o} . 100\%$

Where:

C_o - initial concentration; C - remaining concentration after adsorption; R - removal (%).

2.2.1. Adsorption equilibrium time

Adsorption equilibrium time was determined by the experiments at the adsorption time of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 minutes. The remaining parameters such as the mass of adsorbent material is 0.06 g; CV concentration is 20 mg/L; stirring speed is 150 rpm.

2.2.2. Effect of CV concentration

The experiment on the effect of CV concentration on the adsorption process of biochar material was carried out by changing the initial concentration of CV to 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L, respectively. The remaining parameters such as the mass of adsorbent material is 0.06 g; stirring speed is 150 rpm; and reaction time is determined as the time to reach adsorption equilibrium in the above experiment.

2.2.3. Adsorption isotherm equation

The adsorption isotherm equation was constructed based on the experimental results of using biochar to adsorb CV at different concentrations. The experimental data were calculated and fitted with the Langmuir and Freundlich isotherm adsorption models as shown in equations (1) and (2).

Langmuir isotherm model:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L.Q_m} \quad (1)$$

Freundlich isotherm adsorption model:

$$LnQ_e = LnK_F + \frac{1}{n}.LnC_e \quad (2)$$

The Q_e value is calculated as follows:

$$Q_e = \frac{(C_o - C_e).V}{m} \quad (3)$$

Here, C_e (mg/L) and Q_e (mg/g) represent the concentration and adsorption capacity at equilibrium, respectively; Q_m (mg/g) is the maximum adsorption capacity; K_L is the Langmuir constant, K_F is the Freundlich constant, n is the Freundlich coefficient.

3. RESULTS AND DISCUSSION

3.1. CV adsorption standard curve

The standard curve shows the relationshipbetween CV concentration and the maximum adsorption intensity constant Abs. The standard curvewasdetermined by measuring the UV-Vis spectrum of CV solutions atdifferent concentrations from 1 mg/L to 15 mg/L. The UV-Vis spectrum of CV solutions and the standard curve are shown in Fig. 1. The constructed standard curvewasused to determine the concentration of CV solutions afterbeingadsorbed by biochar.

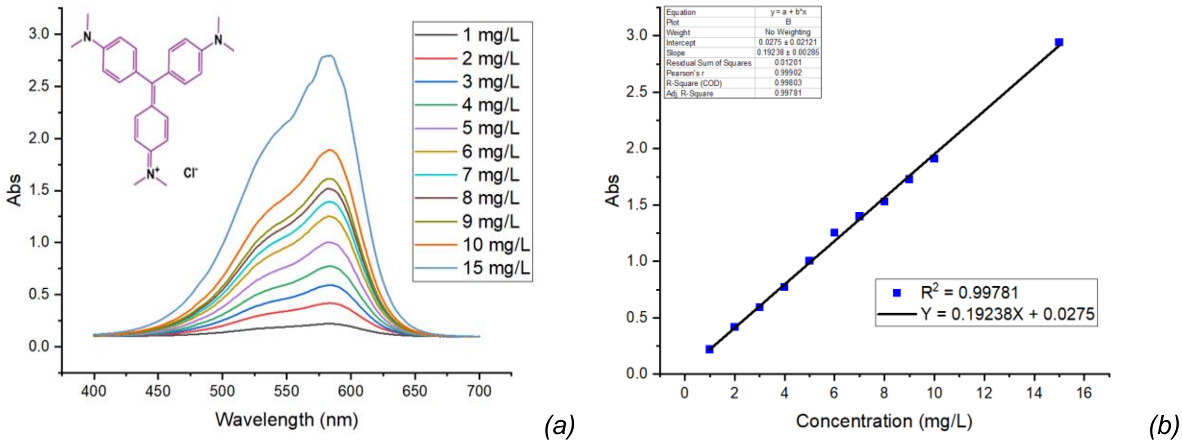

Figure 1. UV-Vis spectra of CV solutions atdifferent concentrations (a) and adsorption standard curve (b)

3.2. Adsorption equilibrium time

Figure 2 shows the results of the investigation of the adsorption capacity of CV solution according to the reaction time of biochar. It wasobservedthat the adsorption capacity of CV dyeincreasedrapidly in the first 10 minutes, with an adsorption efficiency of 89.3%.Subsequently, the adsorption efficiency increased gradually, reaching 96.5% at 60 minutes, beyond which no significant increase was observed. Thus, itcanbeseenthat the adsorption equilibrium occurred within 60 minutes. Afterthis time, the content of adsorbed CV remained almost unchanged because the active centers of the biochar adsorbent were complete lyoccupied [9]. Thus, the CV adsorption capacity of biochar was quite fast in a short time of only 10 minutes, after which the adsorption rate gradually slowed down and reached equilibrium.

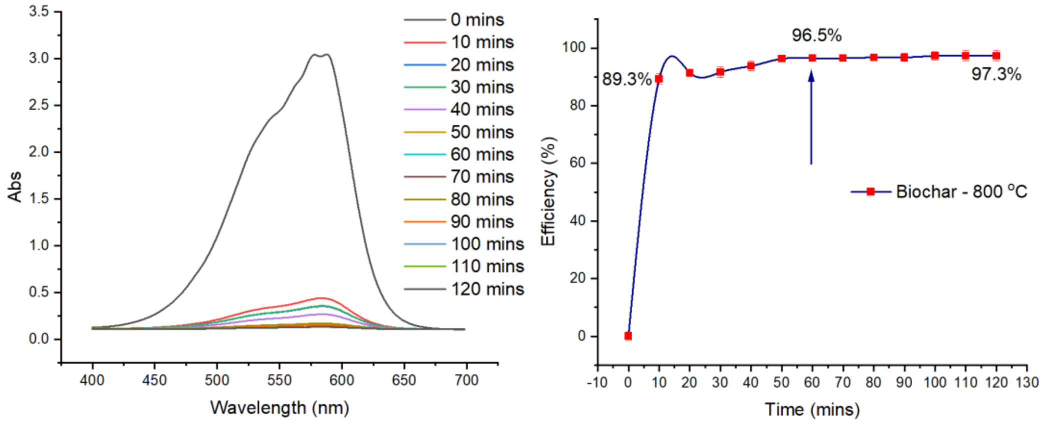

Figure 2. UV-Vis spectra of CV solution after adsorption by biocharatdifferent times and the dependence of adsorption efficiency on time

3.3. Adsorption capacity of biochar with CV solution at different concentrations

Figure 3 presents the results of the investigation of the effect of the initial concentration of CV dye on the adsorption efficiency of biochar. The results show that as the initial concentration of CV dyeincreases, the adsorption capacity of the coalsampledecreases. This isbecause the biochar adsorbent has enough active sites atlowdye concentrations. After all, the vacant active sites on the adsorbent surface are filledwith CV dye[9,10].Surface saturation of the adsorbent mayoccurwhen the concentration of the dyeincreases. Saturation occurs due to the limited surface area of the adsorbent, leading to a decrease in the removalefficiency of CV dye in the aqueousenvironment. Although the adsorption efficiencydecreases as the initial concentration of CV increases, the adsorption efficiency of the biocharsampleisquite high (over 90%) for all initial concentrations of the CV solution examined, demonstrating the adsorption efficiency of CV dye by biochar in thisstudy.

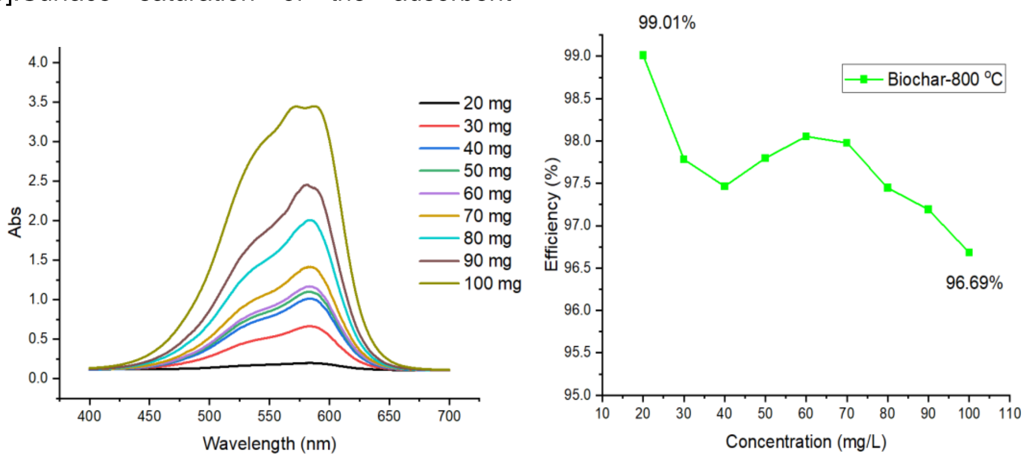

Figure 3. CV adsorption efficiency of biocharinvestigatedatdifferent concentrations

3.4. Isotherm adsorption mechanism

To determine the adsorption isotherm equa-tions, experiments using TSH to adsorb CV crystal violet solution at different concentrations were performed as shown above. Table 1 presents the experimental and calculated data to construct the Langmuir and Frendlich isotherm adsorption models. From the calculated values, the adsorption isotherms were constructed using Origin software as shown in Figure 4.Figure4a shows the Langmuir isotherm adsorption model of the biochar sample. The results show that the biochar sample shows a relative agreement with the Langmuir isotherm adsorption model with a correlation coefficient value of R^2 = 0.75509.

The linear equation Y = AX + B according to the Langmuir isotherm adsorption model is Y = 0.00776X + 0.07342. From this equation, the maximum adsorption capacity value Q_m (mg/g) of the biochar sample can be calculated according to the formula $1/Q_m = A$ (A is the coefficient in the equation Y = AX + B). The calculation results show that Q_m = 128.87 (mg/g). The maximum adsorption capacity of the biochar sample in this study is relatively high, similar to the biochar samples reported in previous studies [7,8].Figure 4b shows the Freundlich isotherm adsorption model of the biochar sample. The results show that the correlation coefficient R_2 is relatively high (R_2 = 0.89289), indicating that the CV adsorption law of the biochar sample is more consistent with the Freundlich isotherm adsorption model [8,9]. The calculated parameters such as K_F = 17.782 and n = 1.81 are quite similar to previous studies [8,9].

Table 1. Data for building Langmuir and Frendlich adsorption isotherm models

C_o	20	30	40	50	60	70	80	90	100
C_e	0.886	3.314	5.128	5.580	5.928	7.218	10.471	12.998	17.094
Q_e	19.114	26.686	34.872	44.420	54.071	62.783	69.529	77.002	82.906
C_e/Q_e	0.046	0.124	0.147	0.126	0.110	0.115	0.151	0.169	0.206
LnC_e	-0.121	1.198	1.635	1.719	1.780	1.977	2.349	2.565	2.839
LnQ_e	2.950	3.284	3.552	3.794	3.990	4.140	4.242	4.344	4.418

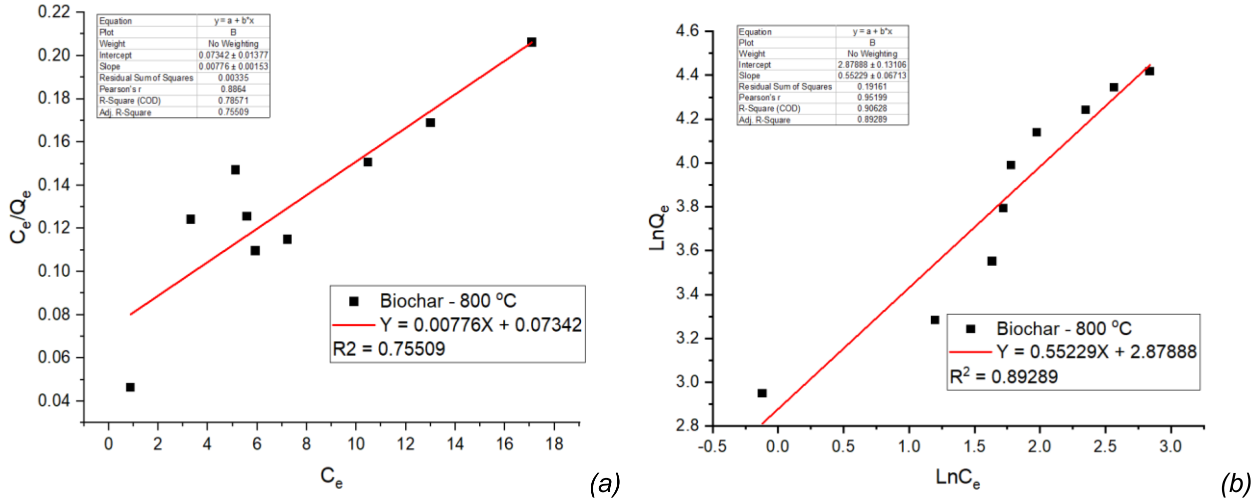

Figure 4. Langmuir and Freundlich adsorption isothermmodels of biochar

4. CONCLUSION

This study successfully synthesized biochar material by a simple one-stage calcination method of coffee grounds in anaerobic conditions at 800 °C. Experiments were conducted to evaluate the CV adsorption capacity of biochar in the solution environment. The results showed that the biochar sample could remove the CV crystal violet dye well with high adsorption capacity. CV adsorption kinetics were studied according to the Langmuir and Freundlich isotherm adsorption models. The results showed that the biochar sample was more suitable for the Freundlich isotherm adsorption model than the Langmuir model because the correlation coefficient R^2 value was higher.Therefore, biochar made from coffee grounds is a cheap adsorbent material capable of treating crystal violet dyes, especially colored dyes in textile wastewater.

5. REFERENCES

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IZVOD

BIOUGALJ NAPRAVLJEN OD MLEVENE KAFE ZA ADSORPCIJU KRISTALNO LJUBIČASTE BOJE

Biougalj je pripremljen anaerobnim zagrevanjem mlevene kafe na 800 °C tokom 3 sata. Pripremljeni uzorak je korišćen za adsorbovanje kristalno ljubičaste boje u vodenom okruženju. Rezultat je pokazao da uzorak biouglja ima dobar kapacitet adsorpcije kristalno ljubičaste boje, sa maksimalnim kapacitetom adsorpcije od 128,87 (mg/g). Stoga, jeftin biougljen pripremljen od taloga kafe ima veliki potencijal da se koristi kao adsorbujući materijal za uklanjanje kristalno ljubičaste boje u vodenom okruženju.

Ključne reči: *biougalj, kristalno ljubičasta boja, mlevena kafa, izotermni modeli, kinetika adsorpcije, tretman otpadnih voda*

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