OPTIMIZATION OF CRYSTAL VIOLET ADSORPTION BY BIOCHAR USING RESPONSE SURFACE METHODOLOGY (RSM)

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TÓM TẮT

TỐI ƯU HÓA HẤP PHỤ TÍM TINH THỂ BẰNG THAN SINH HỌC SỬ DỤNG PHƯƠNG PHÁP BỀ MẶT ĐÁP ỨNG

Than sinh học được chế tạo bằng phương pháp nhiệt phân kỵ khí bã cà phê ở 800 °C trong 3 giờ và được đánh giá bằng các phương pháp như XRD, BET và SEM. Vật liệu được sử dụng để loại bỏ tím tinh thể trong môi trường nước. Phương pháp bề mặt đáp ứng với thiết kế BBD được sử dụng để xây dựng mô hình thực nghiệm để loại bỏ CV. Các yếu tố ảnh hưởng đến sự hấp phụ CV được chọn làm biến đầu vào bao gồm pH, nồng độ ban đầu của dung dịch CV và liều lượng than sinh học; biến đáp ứng là hiệu suất loại bỏ CV (%). Kết quả cho thấy mô hình bậc hai biểu diễn mối quan hệ giữa hiệu suất loại bỏ CV và các biến đầu vào. Phân tích ANOVA cho thấy mô hình có ý nghĩa thống kê vì giá trị R^2 cao (R^2 = 0,9927) và P < 0,0001. Điểm tối ưu cho quá trình hấp phụ CV bằng than sinh học được xác định ở pH là 11,95, nồng độ CV ban đầu là 62,87 mg/L và liều lượng than sinh học là 36,52 mg. Hiệu suất loại bỏ CV tại điểm thực nghiệm tối ưu là 99,11%, rất gần với giá trị dự đoán, khẳng định tính hiệu quả trong việc dự đoán điều kiện tối ưu để xử lí CV than sinh học.

Từ khóa: *Tím tinh thể, than sinh học, hấp phụ, phương pháp bề mặt đáp ứng, phổ UV-Vis.*

1. INTRODUCTION

Crystal violet (CV) dye has the chemical formula $C_{25}H_{30}N_3Cl$. It was a cationic dye commonly used in various applications, including veterinary medicine, fungus inhibitors, antiparasitic drugs, especially in the textile dyeing and paper manufacturing industries [1]. However, this compound, released into the aquatic environment, was classified as persistently biodegradable and possibly carcinogenic [2]. Therefore, the removal of CV dye was an urgent issue that needed to be addressed. Different methods were employed to eliminate CV dye from aquatic environments, including adsorption, oxidation, and biological techniques [3-4]. Among them, adsorption methods were popular due to their simplicity and cost-effectiveness. Various adsorbent materials were commonly used, including activated carbon, ash, slag, sawdust, clay, silica gel, and aluminum gluconate. Recently, biochar materials produced by burning biomass under oxygen-deficient conditions were widely exploited as potential adsorbents to remove pollutants in aquatic environments [5-6]. The use of biochar for the adsorption of crystal violet dye in particular, and colored dyes in general, was extensively studied. S. Sudan's research group used the pyrolysis method to synthesize biochar from rice husks. The resulting biochar exhibited superior adsorption capacity for Eriochrome dye in an aqueous environment [7]. Y. Song's research group used biochar made from corn cobs to effectively adsorb crystal violet dye in aqueous environments [8]. The study showed the influence of adsorption parameters such as pH, temperature, contact time, and initial CV concentration on the adsorption capacity of biochar. Biochar prepared from corn cob was a promising adsorbent for removing CV in wastewater, with a maximum adsorption capacity Q_{max} of 71.43 mg/g. The research group of A. Saeed used grapefruit peel to prepare biochar as an adsorbent for CV dye [9]. The CV adsorption by biochar quickly reached adsorption equilibrium within 60 min, with adsorption efficiency reaching 96% and a maximum adsorption capacity of 254.16 mg/g. References to published works showed that many studies have applied biochar from agricultural by-products to treat wastewater, including crystal violet (CV) dye. However, the adsorption processes seemed to survey experimental parameters manually over a wide range of pH, initial CV concentration, adsorbent dosage, and contact time to develop the adsorption process with the most suitable parameters. Few works used computational tools to derive the optimal adsorption process for crystal violet adsorption. In experimental planning, response surface methodology (RSM) was an experimental model that used mathematical and statistical techniques to relate input variables (experimental parameters) and responsed variables (outcome variables). The RSM method could be used to optimize the production of a substance or an experimental process by optimizing operating factors [10]. The RSM method was built when considering independent input variables x_1, x_2,...and the output variable y would depend on the variables (x_1, x_2,...) according to the equation y = f (x_1, x_2,...) + ε, with ε being the residual in the equation describing the model. Then, the response surface was the surface represented by the equation η = f (x_1, x_2,...), with η being the response surface area. In this study, we used the RSM method to design experiments on the adsorption of crystal violet dye using biochar prepared from coffee grounds. The efficiency of crystal violet adsorption was evaluated through input variables including pH, initial concentration of CV solution, and biochar adsorbent dosage, thereby determining the optimal condition for the adsorption process. This unique research method clearly explained the influencing factors, as well as the CV adsorption mechanism of biochar.

2. EXPERIMENT

2.1. Synthesis of biochar from coffee grounds

Collected coffee grounds were washed to remove impurities and dried under the sunlight. The dried coffee grounds were anaerobically heated at 800 ^oC for 3 hours to produce biochar [11]. The obtained biochar was ground in a mortar and then sieved through a 150-350 µm sieve. The sieved biochar samples were sealed in jars with lids and stored for use in subsequent experiments.

2.2. Batch adsorption study and pH_{pzc} determination

Experimental adsorption of CV by biochar was performed by adding biochar samples to flasks containing 60 mL of CV solutions. The flasks were stirred at 150 rpm for 60 minutes at room temperature. After completing the reaction, the solid residue was filtered out, and the remaining liquid was analyzed using UV-Vis spectroscopy at the maximum absorption wavelength of 590 nm to determine the concentration of the remaining CV solution after adsorption [9]. The concentrations of the remaining CV solutions were determined through a calibration curve showing the relationship between the concentrations of CV solutions and the maximum absorbances (Abs). The calibration curve was established by measuring the UV-Vis spectrum of the CV solution at different concentrations from 1 mg/L to 15 mg/L, as shown in Fig. 1. The removal (%) of CV was calculated using the following formula.

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} . 100 \qquad (1)$$

Here, C_0 and C_e were the initial and equilibrium concentrations of CV in the solution.

To clearly explain the effect of pH on the adsorption capacity of biochar. The pH point zero charge (pH_{pzc}) was identified by preparing solutions of 50 mL NaCl 0.01 M with initial pH (pH_i) values ranging from 2.0 to 11.0, adjusting by HCl or NaOH solutions [5, 6, 9, 11]. To each experiment, 30 g of biochar was added, and shaken at 200 rpm for 6 hours at ambient temperature. The final pH (pH_f) was recorded to calculate the pH change ($\Delta pH = pH_f - pH_i$). The pH_{pzc} was identified as the point at which $\Delta pH = 0$. In this work, the pH_{pzc} was determined as 7.3 for the synthetic biochar.

2.3. Experiment design

Adsorption experiments were set up using Box-Behnken Design (BBD) under RSM on Design Expert software. Three factors affecting the removal of crystal violet in aqueous medium by biochar were considered input variables: pH (from 2 to 12), initial concentration of CV (from 20 to 100), and dosage of adsorbent biochar (from 20 to 100). To adjust different pH values, NaOH and HCl solutions were added to the solution connected to the pH meter. The response variable is the removal (%) of CV in solution by the biochar material. The BBD generated seventeen experimental run, as shown in Table 1. The variables were denoted as A – pH, B – initial concentration of CV, and C – Dosage of adsorbent biochar.

Table 1. Generated experimental runs and diagnostic case studies for the removal (%) of CV from designed experiments

Runs	**Input variables**			**Removal (%)**		
	A	**B**	**C**	**Actual value**	**Predicted value**	**Residual**
1	2	20	60	78.0772	78.03	0.0424
2	2	80	60	65.7611	66.38	-0.6171
3	12	80	60	99.2690	99.31	-0.0424
4	2	50	20	65.3134	64.84	0.4711
5	12	50	100	98.9968	99.47	-0.4711
6	7	20	100	93.1776	93.32	-0.1460
7	7	50	60	81.2922	80.17	1.12
8	7	20	20	76.2319	76.75	-0.5135
9	7	50	60	81.0219	80.17	0.8504
10	7	50	60	81.7393	80.17	1.57
11	12	20	60	97.5179	96.90	0.6171
12	12	50	20	98.9344	99.04	-0.1036
13	2	50	100	81.968	81.86	0.1036
14	7	50	60	79.0675	80.17	-1.10
15	7	80	100	81.3618	80.85	0.5135
16	7	50	60	77.7368	80.17	-2.43
17	7	80	20	80.1207	79.97	0.1460

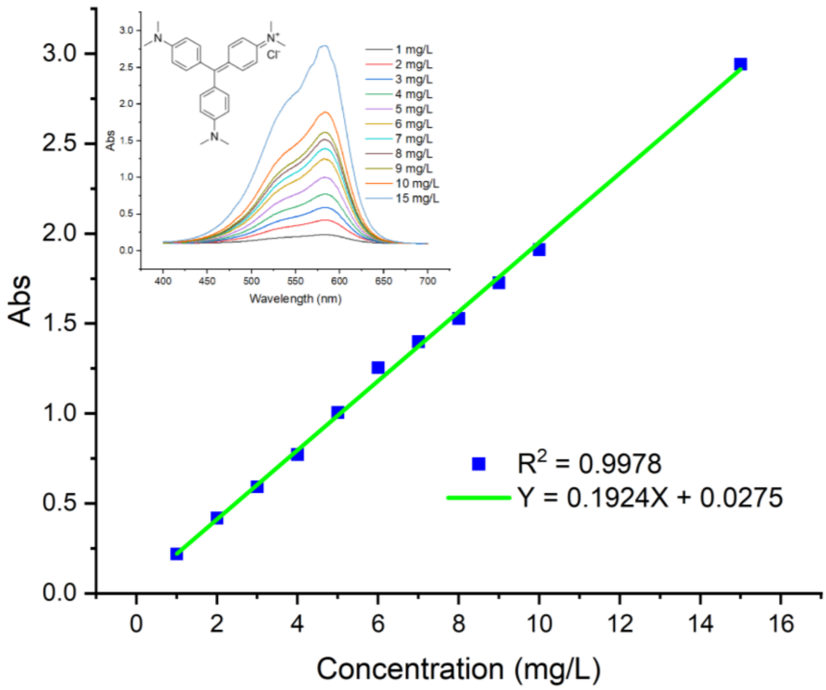

Figure 1. Calibration curve between CV concentration and maximum absorbance (Abs)

2.4. Evaluation methods

The structural composition of the synthesized biochar was analyzed using the X-ray diffraction (XRD) method. The porous characteristics of the biochar were determined through the Brunauer-Emmett-Teller (BET) method, which was based on nitrogen (N_2) adsorption and desorption. The structural morphology of the biochar sample was observed using Scanning Electron Microscopy (SEM). The concentrations of the crystal violet solution were determined through maximum absorbances (Abs) using Ultraviolet-Visible (UV-Vis) spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Material characterization

The XRD diagram of the biochar sample presented a broad diffraction pattern characteristic of amorphous material (Fig. 2a). The XRD pattern also showed slight peaks characteristic of the SiO_2 phase [12]. Fig. 2b showed the adsorption/desorption isotherm of biochar samples prepared from coffee grounds. The adsorption/desorption isotherm shape indicated that the synthesized biochar belonged to type IV of the IUPAC classification. This biochar was a mesoporous material with an average pore diameter from 2 to 50 nm [13]. Pore distribution analysis showed that the pore size ranged from 3 to 120 nm, with a strong distribution from about 5 to 30 nm as shown in the inset image in Fig. 2.b. The adsorption/desorption hysteresis loop was classified as type H1, indicating the presence of numerous pores within the mesoporous structure of biochar material. The multi-point BET curve of biochar samples was presented in Fig. 2c. The obtained values for pore volume and specific surface area are 2.47 cm^3/g and 642.3 m^2/g, respectively. Fig. 2d showed the SEM image of the biochar sample at a magnification of 5000. The biochar sample exhibited a 3D structure with a rough surface and wide pores that created a porous structure of the synthetic material.

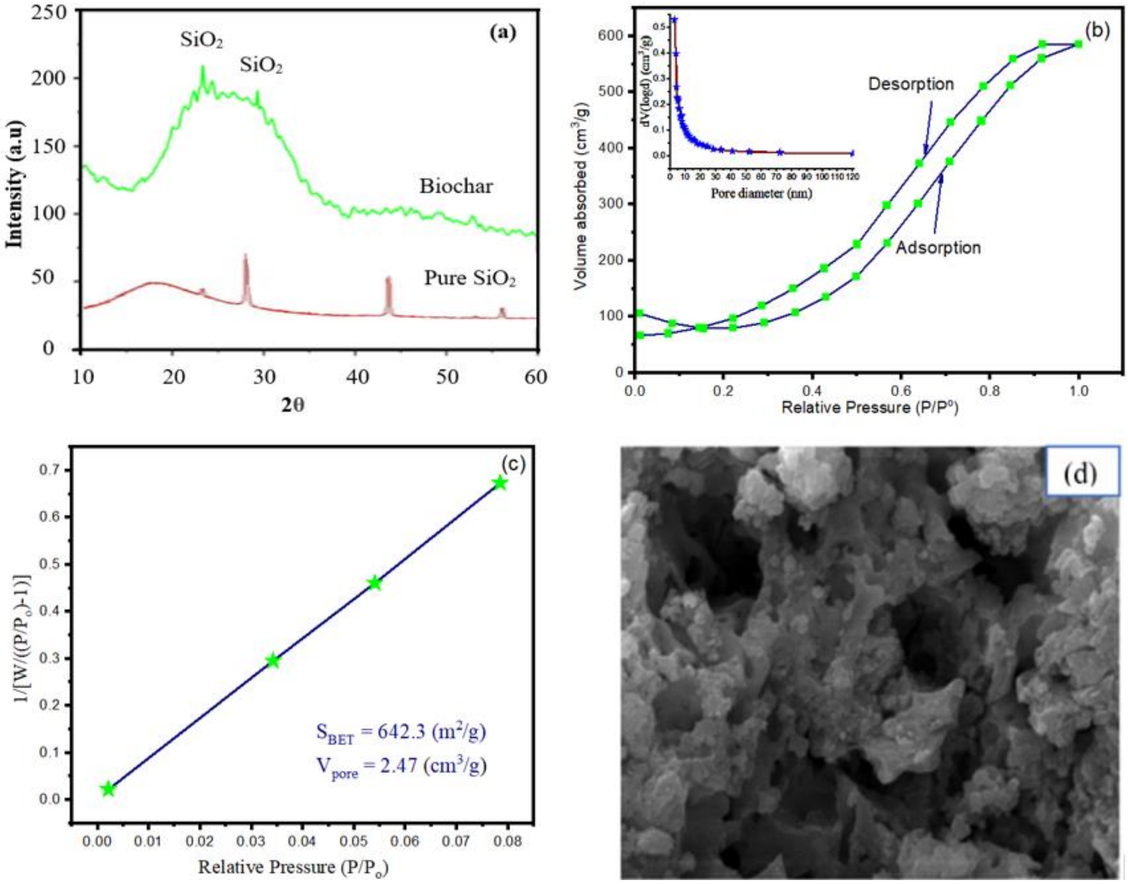

Figure 2. Characterization of biochar: (a) XRD diagram; (b) N_2 adsorption and desorption isotherm; (c): multi-point BET curve; (d) SEM image

3.2. Diagnostic case studies for designed experiments

The removal (%) of CV in the designed experiments of the diagnostic case studies was presented in Table 1. The actual values indicated the removal (%) of CV in the designed experiments, while the predicted values represented the software's standards. The residuals were calculated as the differences between actual and predicted values. The residual value was positive when the predicted similarity exceeded the actual similarity, and vice versa. The data showed that the residual values fluctuate from -2.43 to 0.8504, indicating a close match between actual and predicted values, confirming the suitability of the designed model [14].

3.3. Variance analysis for the removal of CV

The compatibility of the developed model was assessed using analysis of variance (ANOVA), as shown in Table 2. A model was considered statistically significant under the following conditions [15]: (1) the P value of the model < 0.0001; (2) the adequate precision (AP) was more than 4.0, which helped guide the design space; (3) the lack of fit (LOF) value, which indicated discrepancies in the data, had to not be statistically significant; and (4) the R^2 value should be high, more than 0.8. The data confirmed that the quadratic model satisfied all four criteria above with $P < 0.0001$; AP = 32.6489; LOF = 0.8866; $R^2 = 0.9927$. The relationship between the removal (%) of CV and the independent variables A – pH, B – Initial Concentration, and C – Dosage was expressed as follows:

Removal (%) = 63.53463 + 0.263918*A – 0.122896*B + 0.279159*C + 0.023445*AB –0.020740*AC – 0.003272*BC + 0.171299*A² + 0.000780*B² + 0.001156*C² (2)

$$\text{Removal (\%)} = 63.53463 + 0.263918A - 0.122896B + 0.279159C + 0.023445AB - 0.020740AC - 0.003272BC + 0.171299A^2 + 0.000780B^2 + 0.001156C^2 \quad (2)$$

In this equation, terms A, B, C, AB, AC, BC, A^2, and C^2 were all significant terms contributing to the model because their P values were less than 0.0500.

Table 2. ANOVA for the Quadratic model of the removal (%)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1816.56	9	201.84	105.56	< 0.0001	significant
A-pH	1341.58	1	1341.58	701.64	< 0.0001	
B-Initial Concentration	42.74	1	42.74	22.36	0.0021	
C-Dosage	152.28	1	152.28	79.64	< 0.0001	
AB	49.47	1	49.47	25.87	0.0014	
AC	68.82	1	68.82	36.00	0.0005	
BC	61.66	1	61.66	32.25	0.0008	
A^2	77.22	1	77.22	40.39	0.0004	
B^2	2.08	1	2.08	1.09	0.3320	
C^2	14.40	1	14.40	7.53	0.0288	
Residual	13.38	7	1.91			
Lack of Fit	1.80	3	0.6002	0.2072	0.8866	not significant
Pure Error	11.58	4	2.90			
Corrected Total	1829.94	16				
R^2 = 0.9927, Predicted R^2 = 0.9744, adjusted R^2 = 0.9833, adequate precision = 32.6489						

3.4. The effect of reaction parameters on the response of removal (%)

Figure 3 presented the 3D response surfaces, showing that the removal (%) of CV by biochar depending on two of three independent variables A – pH, B – Initial concentration of CV, and C – Biochar dosage. The results mentioned that pH strongly affected the removal of CV in solution by biochar, as shown in Fig. 3a and Fig. 3b. Biochar exhibited more suitable crystal violet dye removal at high pH environments. At low pH, the high concentration of H^+ resulted in competitive adsorption between H^+ ions and crystal violet cations on the adsorption sites of the biochar surface, which led to a reduced capacity for crystal violet adsorption by biochar. At high pH, the high concentration of OH^- led to an increase in the negative charge of the biochar surface, resulting in better adsorption of crystal violet cationic dye by the biochar [16]. Additionally, the initial concentration of CV solution also affected the adsorption capacity of biochar. Biochar showed better crystal violet adsorption at low concentrations than at high concentrations. At high concentrations of crystal violet, the number of adsorption sites on the biochar surface became inadequate to adsorb the cations effectively, leading to a decrease in CV removal. The adsorbent content also relatively affected the crystal violet removal as shown in Fig. 3b and Fig. 3c. As the biochar content increased, the number of adsorption sites increased, leading to better crystal violet adsorption capacity [16-17].

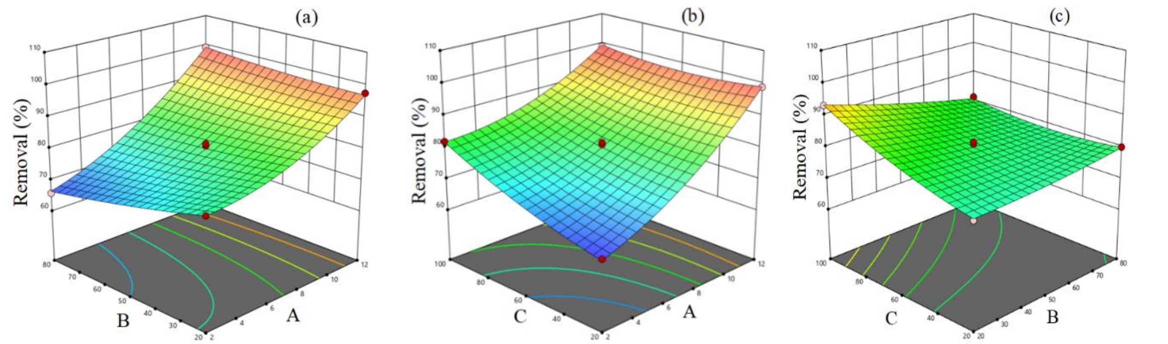

Figure 3. 3D surface plots for the effects of reaction parameters on the removal (%) of CV

3.5. Adsorption of CV by biochar at the optimal point

The optimization software determined the optimal parameters for CV adsorption using biochar. Specifically, biochar optimally adsorbed crystal violet at the pH value of 11.95, CV initial concentration of 62.87 mg/L, biochar dosage of 36.52 mg, predicted CV removal of 99.30 %, with the highest desired level set at 1. To confirm, experiments of CV adsorption using biochar were performed at the above-optimized parameters. The result showed that the CV removal reached 99.11 % with an error of only 0.19 % compared to the predicted value, confirming the suitability of the optimal point indicated by the model. In addition, this adsorption efficiency was quite high compared with previous studies [8, 14, 16].

4. CONCLUSION

Biochar was successfully synthesized from coffee grounds by anaerobic pyrolysis at 800 ^oC for 3 hours. The physical-chemical properties showed that biochar is an amorphous material exhibiting a mesoporous structure with the pore volume V_{pore} = 2.47 cm^3/g and the specific surface area S_{BET} = 642.3 m^2/g. The Response Surface Methodology (RSM) with Box-Behnken Design (BBD) determined a statistically significant quadratic model representing the CV removal according to the experimental variables pH, initial concentration of CV solution, and biochar dosage. The optimal parameters of CV adsorption by biochar were determined as pH of 11.95, initial CV concentration of 62.87 mg/L, and biochar dosage of 36.52 mg. The CV removal at the optimal point reached 99.11%, closely aligning with the predicted value. Thus, the RSM model was effectively used to enhance the efficiency of CV removal in aqueous environments.

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