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Optimization of Carbonization Conditions for Pig Dung-Derived Activated Carbon in the Removal of Methylene Blue Dye

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ABSTRACT

The conversion of agro-waste into value-added products offers a sustainable solution for environmental remediation. This study optimized the carbonization and activation conditions for Activated Carbon derived from dried pig dung to enhance its adsorption efficiency for Methylene Blue Dye (MBD) removal. Box-Behnken Design (BBD) in Design Expert 13 was employed to investigate the effects of temperature (500–700°C), activation time (60–120 min), and mass of potassium hydroxide (KOH) (5–7 g) on carbonization yield and MB removal efficiency. Quadratic regression models developed for yield and removal efficiency demonstrated strong predictive capabilities, with R^2 values of 0.9643 and 0.9836, respectively. Optimization using the desirability function identified the optimum conditions as 535.39°C, 117.32 minutes, and 7 g of KOH, resulting in a predicted carbonization yield of 75.11% and MB removal efficiency of 82.44%. The validation of these conditions achieved an experimental removal efficiency of 83.21%, with a deviation of only 0.93%, confirming the model's accuracy. The research proved that pig dung-derived activated carbon, as a cost-effective adsorbent, is highly effective for removing dye from wastewater.

INTRODUCTION

Managing agricultural waste poses a major global challenge, with various types of waste contributing to environmental pollution (Koul *et al.,* 2022). Various residues, including plant seeds, shells, and animal manure, can be repurposed for industrial applications, thereby enhancing waste management. Pig waste is a type of biomass that can be reused as manure or converted into value-added products. The odour from pig dung can deteriorate air quality, leading to tensions and complaints between pig farmers, which may result in litigation and potential farm closures (Amola *et al.,* 2020; Iregbu *et al.,* 2014; Enahoro *et al.,* 2024).

Pig dung can be converted into activated carbon, a valuable material with various industrial applications. Activated carbon is a carbon-based material typically produced through pyrolysis. It is also known as activated charcoal or biochar and is produced from renewable agricultural waste, making it a more cost-effective alternative to industrial and petroleum-based precursors such as wood, coal, and lignite (Mohammed *et al.,* 2018). Activated carbon is a solid, porous, tasteless, and black carbonaceous material prepared from a variety of carbon-containing materials, including agricultural residues (AAFCO, 2012). Emerging reports revealed that activated charcoal adsorbs more toxins than any natural substance known to mankind (Maklad *et al.,* 2012). It is a carbonaceous material resembling granular or powdered charcoal with highly developed porosity, a large internal surface area, and high mechanical strength (Bansal and Goyal, 2005). They are widely used as adsorbents in wastewater and gas treatments as well as in catalysis (Amola *et al.,* 2020; Esther *et al.,* 2019; Lee and Valla, 2019). Among other applications, activated carbon is used in air filtration systems, water purification, deodorization, dechlorination, and gold mining operations (Marsh and Rodríguez-Reinoso, 2006).

The global expansion of pig farming, driven by rising demand for pork and associated by-products, has led to significant waste generation, with each pig producing approximately 2–4 kg of waste daily (FAO, 2021). This waste, primarily composed of organic residues, poses environmental challenges such as water contamination, methane and CO_2 emissions if not managed sustainably (Smith *et al.*, 2020). Green-activated carbon derived from agricultural waste, such as pig dung, has emerged as a sustainable solution due to its high adsorption efficiency and cost-effectiveness (Zhang *et al.*, 2019). For instance, studies demonstrate that chemically activated pig dung–derived carbon achieves >95% removal efficiency for pollutants like methylene blue (MB) dye, rivaling commercial adsorbents (Lee and Park, 2022). This study aimed to optimize the carbonization process of pig dung by evaluating key parameters—including carbonization temperature (539°C), activation agent concentration (using either KOH or $ZnCl_2$), and residence time—to maximize carbon yield and adsorption capacity. Preliminary trials assessed the material's performance in a single-pass Methylene Blue (MB) dye treatment system, focusing on critical variables such as pH (6–9), initial dye concentration (50–200 mg/L), and contact time (30–120 minutes) (Gupta *et al*., 2020). The findings contribute to circular economy frameworks by transforming agro-waste into value-added products and addressing industrial wastewater challenges (European Commission, 2023).

MATERIALS AND METHODS

The materials used in this research include pig dung and garlic (*Allium sativum*) peel extract. The pig dung (PD) was collected from the Piggery Unit of the Ladoke Akintola University of Technology (LAUTECH) Research Farm, Ogbomoso, Oyo State. The reagents used in this study include potassium hydroxide (KOH), hydrochloric acid (HCl), sodium hydroxide (NaOH), and MBD. All reagents were of analytical grade and used without further purification.

Material Pre-treatment

The steps for preparing adsorbents from Pig Dung (PD) are illustrated in Figure 1. First, dirt and other solid residues were manually removed from the PD. The cleaned PD was then dried until no further weight change was observed, ensuring complete moisture removal. After drying, the PD was milled to reduce its particle size and subsequently stored in an air-tight polyethylene bag. At this stage, the material is referred to as Dried Pig Dung (DPD).

Pig Dung Carbonization and Activation

The modified method of Tsai *et al*. (2019) was used for the activation and carbonization of dried pig dung (DPD). Twenty (20) g of DPD was weighed into a 100 mL beaker, and the values of the three selected parameters (time, mass of KOH and carbonization temperature) are varied within the tabulated range of values in Table 1. Table 1 was used for the generation of **Table 2**. For each of the experimental runs in **Table 2** RE and yield were obtained.

Batch Adsorption Study

Fifteen experimental runs were generated using the Box-Behnken Design (BBD) in Design Expert 13, with three independent variables: temperature, time, and KOH mass, as presented in Table 1. The adsorptive properties of the Carbonized Pig Dung (CPD) samples were evaluated based on their ability to adsorb MBD from the solution.

The activation yield and the removal efficiency of MBD (from a 100 mg/L MBD solution) were recorded as response variables for the 15 experimental runs. For each adsorption test, 20 mL of the MBD solution and 0.1 g of ACDPD were added to a 50 mL beaker. The mixture was maintained at 25°C with a fixed agitation rate of 400 rpm for 1 hour (Wirnkor *et al.,* 2019). After treatment, the concentration of MBD was determined using a UV-visible spectrophotometer at an absorbance wavelength of 665 nm.

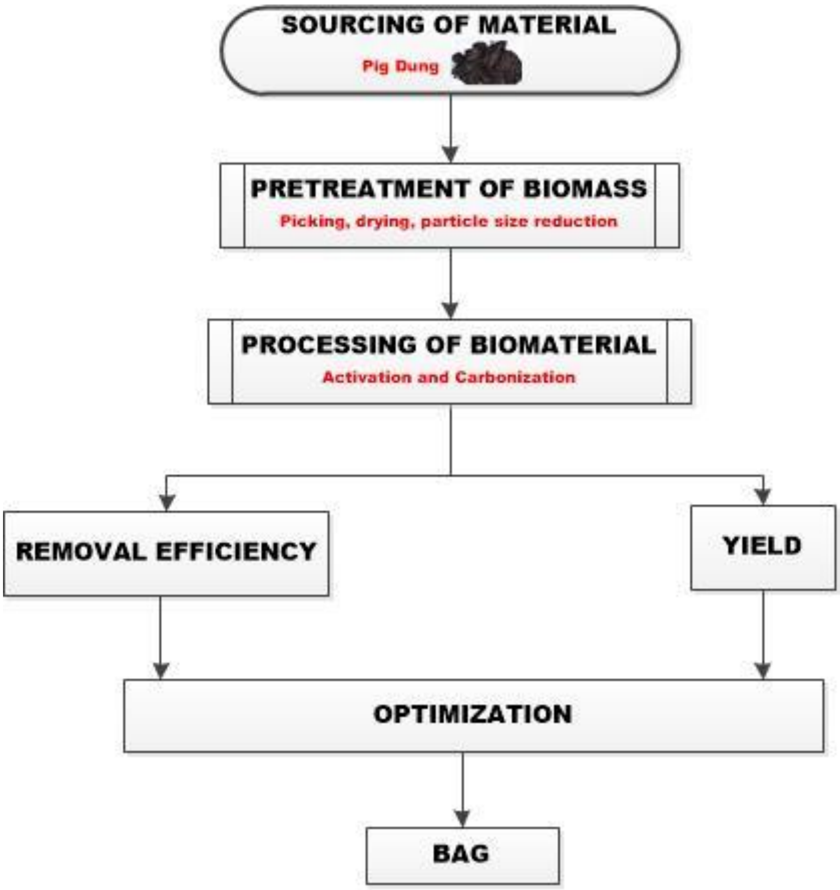

Figure 1: Flow diagram for the carbonization of PD

Table 1: Activation and Carbonization Conditions

Parameters	Unit	Minimum	Mid-point	Maximum
Temperature	℃	500	600	700
Mass of activant	G	3	5	7
Time	Minutes	60	90	120

The removal efficiency and activation yield are calculated using Equations 1 and 2, and the results were subsequently optimized to determine the optimal KOH mass required for maximum removal efficiency and yield.

$$\text{Removal Efficiency} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$Yield = \frac{W_c}{W_o} \times 100 \quad (2)$$

Where:

C_0 is the initial concentration of MB solution at starting time in mg/L

C_e is the equilibrium concentration of MB at time t in mg/L;

W_c is the dry weight of carbonized carbon;

W_o is the dry weight of precursor

RESULTS AND DISCUSSION

Regression Analysis

The results of the 15 experimental runs under different test conditions for the activation and carbonization of pig dung are presented in Table 2. The carbonization yield of activated pig dung (ACDPD**)** ranged from 31.4 % to 75.10 %, with the maximum yield observed in run 1 and the minimum yield in run 4**.** The adsorption efficiency of ACDPD for the removal of methylene blue from the solution ranged from 81.98% to 83.34%**,** with the minimum adsorption recorded in experimental run 7 and the maximum in experimental run 13**.c**

Table 2: Results of Activation and Carbonization of Pig Dung

Std	Run	A: Temp (°C)	B: Mass (g)	C: Time (min)	Yield (%)	Removal (%)
5	1	500	5	60	75.1	82.3091
4	2	700	7	90	39.45	82.3266
11	3	600	3	120	33.2	82.3317
2	4	700	3	90	31.4	82.3204
1	5	500	3	90	60.8	82.2978
14	6	600	5	90	49.9	82.303
8	7	700	5	120	41.2	81.9809
13	8	600	5	90	49.4	82.3378
10	9	600	7	60	62.5	82.3696
15	10	600	5	90	66.2	82.344
3	11	500	7	90	74.4	82.3625
7	12	500	5	120	74.98	82.3563
12	13	600	7	120	62.6	82.4394
9	14	600	3	60	65.9	82.3204
6	15	700	5	60	48.7	82.3378

Developed Models

The experimental results obtained by systematically varying the operational parameters: temperature (°C), time (min), and mass (g), were used to evaluate their effects on yield and removal efficiency, as shown in **Table 2**, respectively. The quadratic regression models, developed using the Box–Behnken design (BBD), are presented as follows:

$$Yield = 384.78 - 0.529 * Temp - 9.32188 * \text{Mass} - 2.38082 * \text{Time} + 0.136667 * \text{Mass} * \text{Time} + 0.000311 * Temp^2 + 0.008499 * Time^2 \quad (3)$$

$$Removal\ efficiency = +81.03329 + 0.000391 * \text{Temp} + 0.053883 * \text{Mass} + 0.028376 * \text{Time} - 0.000073 * \text{Temp} * \text{Mass} - 0.000191 * Time^2 \quad (4)$$

These models incorporate main effects (A: temperature, B: time, C: mass), interaction terms (BC), and quadratic terms (A^2, C^2), all of which demonstrate statistical significance for both responses. The interpretation of these models was supported by correlation coefficient values (R^2) of 0.9643 for yield and 0.9836 for removal efficiency, indicating a strong model fit. Validation was further supported by predicted R^2 values of 0.7764 for yield and 0.9700 for removal efficiency, along with an adjusted R^2 of 0.9336 for yield. These results emphasize the robustness of the models in capturing the nonlinear relationships between parameters and responses, thus enabling reliable process optimization. The predicted R^2 of 0.7764 presented in Table 3 is in reasonable agreement with the Adjusted R^2 of 0.9336, indicating that the difference between the two values is less than 0.2, which suggests a good model fit. Adequate Precision measures the signal-to-noise ratio, and a ratio greater than 4 is considered desirable. The observed ratio of 17.964 and 29.970 for yield and removal efficiency, respectively, indicates an adequate signal, meaning the model has a reliable predictive capability and this suggests that the model can be used effectively to navigate the design space.

Table 3: Statistical Interpretation of the Developed Models

Statistical parameter	Yield	Removal Efficiency
Std deviation	3.92	0.0179
Mean	54.97	82.30
CV%	7.13	0.0218
R^2	0.9643	0.9836
Adjusted R^2	0.9336	0.9700
Predicted R^2	0.7764	NA[(1)]
Adequate R^2	17.9635	29.9696

Analysis of Variance (ANOVA)

Table 4 presents the Analysis of Variance (ANOVA) for the yield of carbonization and the Model F-value for the yield of carbonization was 31.49, indicating that the model is statistically significant for this response. The probability of obtaining an F-value this large due to noise is only 0.01%**.** P-values less than 0.0500 suggest that the corresponding model terms are significant. In this case, the terms A (temperature), B (time), C (mass), BC (interaction between mass and time), and C^2 (quadratic term for mass) are significant. Terms with P-values greater than 0.1000 indicate non-significance. If many insignificant terms are present (excluding those needed for hierarchy), model reduction may improve the model's performance.

Table 4: ANOVA of the Yield of Carbonization

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2900.07	6	483.34	31.49	0.0001	Significant
A-Temp	1938.47	1	1938.47	126.28	< 0.0001	
B-Mass	283.82	1	283.82	18.49	0.0036	
C-Time	202.21	1	202.21	13.17	0.0084	
BC	268.96	1	268.96	17.52	0.0041	
A^2.	32.28	1	32.28	2.10	0.1903	
C^2	195.05	1	195.05	12.71	0.0092	
Lack of Fit	107.33	6	17.89	143.10	0.0639	not significant

Perturbation and **3-D Surface Plots of the Developed Models**

Figure 3 (a) illustrates the relationship between key process parameters, time (minutes), temperature (°C), and mass (grams) and their impact on product yield. The analysis reveals that maximum yield is achieved under specific conditions: a minimum temperature of 600°C (Parameter A), a maximum mass of 5 g (Parameter B), and a minimum processing time of 90 minutes (Parameter C). These optimal conditions are derived from perturbation analysis, which shows that any deviations from these values, whether for temperature, mass, or time, result in reduced yield. The results emphasize the importance of maintaining Parameter A at its lower threshold, Parameter B at its upper limit, and Parameter C at its minimum duration to maximize system performance, as demonstrated by the sensitivity trends in the Figure.

Table 5 present the Analysis of Variance (ANOVA) for the removal efficiency of MBD**.** The Model F-value of 72.12 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, B, C, and C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The Lack of Fit F-value of 0.49 implies the Lack of Fit is not significant relative to the pure error. There is a 75.76% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit. The cross plots of GNSAC and (Figure 2) show that the data points of yield and removal efficiency are close to the 45-degree line plotted. Diagonally, which implies that the predicted values are close to the measured values (Olowonyo *et al.*, 2023).

Perturbation and 3-D Surface Plots of the Developed Models

Figure 3 (a) illustrates the relationship between key process parameters, time (minutes), temperature (°C), and mass (grams) and their impact on product yield. The analysis reveals that maximum yield is achieved under specific conditions: a minimum temperature of 600°C (Parameter A), a maximum mass of 5 g (Parameter B), and a minimum processing time of 90 minutes (Parameter C). These optimal conditions are derived from perturbation analysis, which shows that any deviations from these values, whether for temperature, mass, or time, result in reduced yield. The results emphasize the importance of maintaining Parameter A at its lower threshold, Parameter B at its upper limit, and Parameter C at its minimum duration to maximize system performance, as demonstrated by the sensitivity trends in the Figure.

Table 5: ANOVA of Removal Efficiency of Methylene Blue

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.1156	5	0.0231	72.12	< 0.0001	significant
A-Temp	0.0000	1	0.0000	0.1232	0.7375	
B-Mass	0.0024	1	0.0024	7.50	0.0338	
C-Time	0.0899	1	0.0899	280.17	< 0.0001	
AB	0.0009	1	0.0009	2.67	0.1535	
C^2	0.0593	1	0.0593	184.75	< 0.0001	
Lack of Fit	0.0009	4	0.0002	0.4850	0.7576	not significant

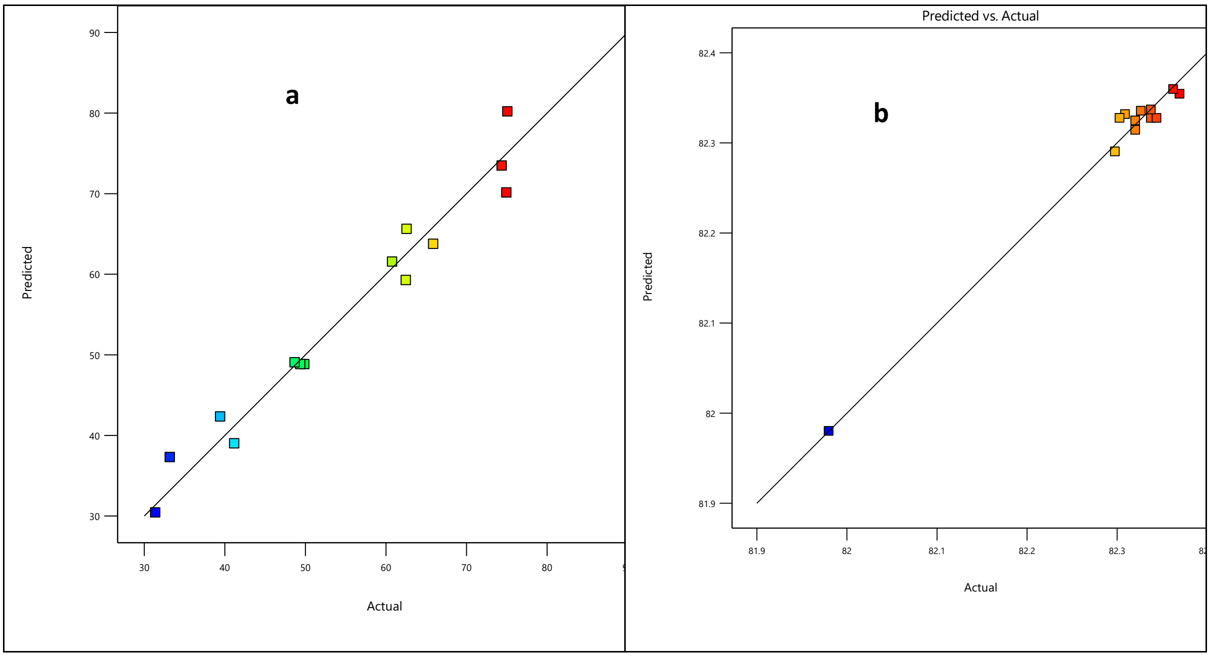

Figure 2: Cross plot of predicted against actual values for (a) yield of carbonization, (b) removal efficiency of MB

Figure 3(b) highlights the influence of time (minutes), temperature (°C), and mass (grams) on the removal efficiency (MBD RE**)** of the system. The analysis suggests that peak removal efficiency is achieved under the following optimal conditions: a fixed temperature of 600°C (Parameter A), a mass of 5 g (Parameter B), and a processing time of at least 90 minutes (Parameter C). These conclusions, derived from perturbation analysis, show that any deviation from these optimal conditions for temperature, mass, or time leads to a decline in removal efficiency. The findings underscore the critical role of maintaining Parameter A at a constant level, Parameter B at its maximum value, and Parameter C at its minimum duration to achieve optimal performance, as supported by the sensitivity trends shown in the figure. **Figure 4** illustrates the interactive effects of process parameters on both carbonization yield and methylene blue removal efficiency, using three-dimensional surface plots. In **Figure 4**(a) The carbonization yield is analyzed under varying levels of parameters B and C, with parameter A fixed at its midpoint. At a shorter reaction time (C = 60 minutes), increasing parameter B from 3 to 7 g led to a decline in yield, from 63.74% to 59.25%.

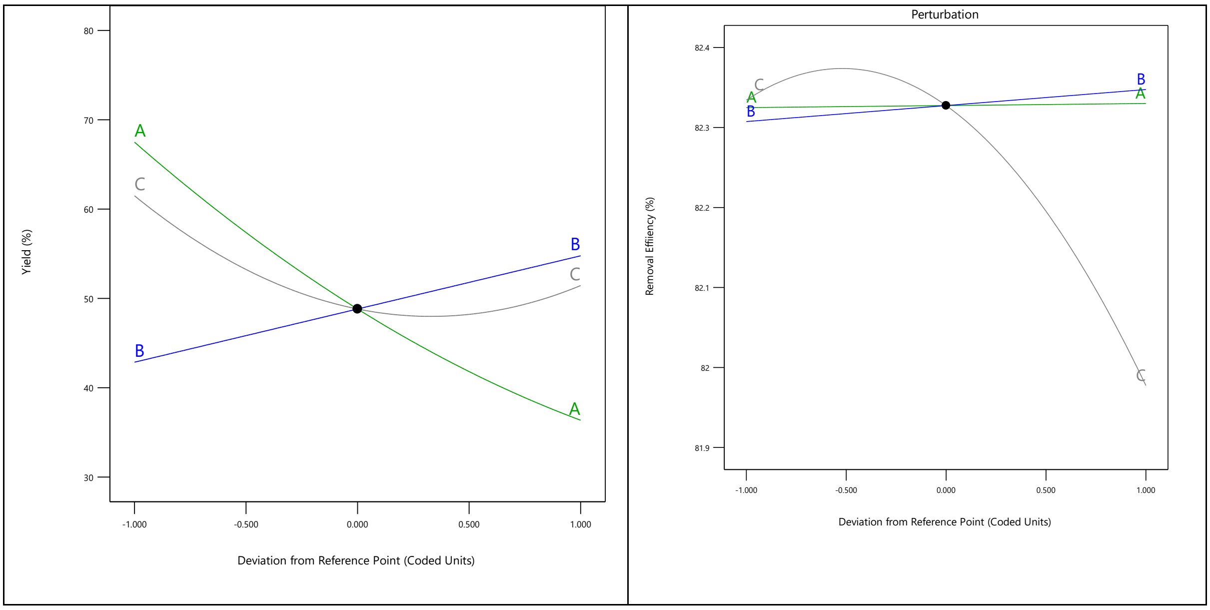

Figure 3: Perturbation plot of the yield of carbonization and RE of MBD

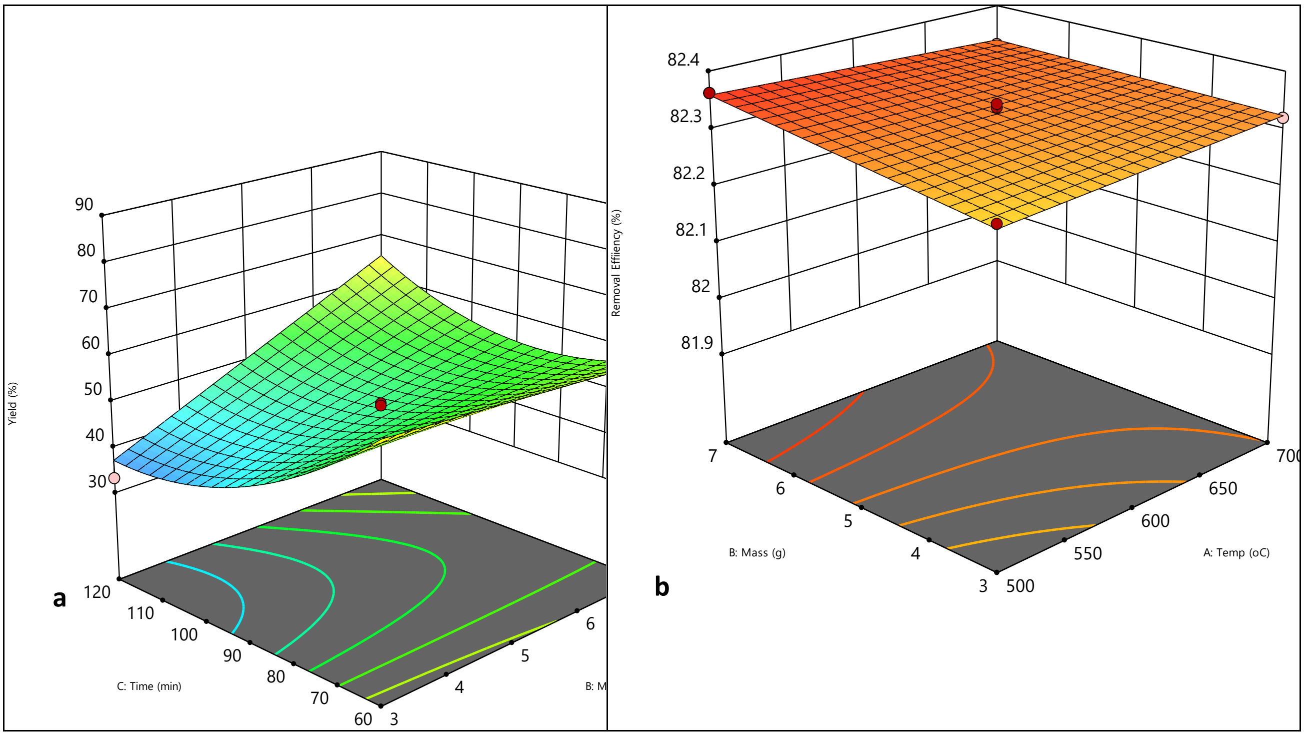

Figure 4: Surface plot of interactions between parameters for (a) yield of carbonization and (b) RE of MBD

In contrast, at a longer reaction time (C = 120 minutes), increasing parameter B within the same range significantly enhanced the yield, from 37.28% to 65.59%. **Figure 4**(b) examines the removal efficiency of MBD under the combined influence of parameters A (temperature) and B, with parameter C held at its midpoint. When parameter B was kept at a lower value (3 g), the removal efficiency showed a slight increase, from 82.29% to 82.32%, as temperature (A) increased from 500°C to 700°C. However, at a higher parameter B (7 g), the removal efficiency exhibited a slight decrease, from 82.35% to 82.33%, under the same temperature increase. These results underscore the complex interdependencies among the parameters, highlighting how interactions between the variables critically influence the process outcomes.

Optimization of Carbonized Process Conditions

Optimization using the desirability function criteria was performed to maximize methylene blue (MB) removal efficiency and carbonization yield**.** This optimization was carried out using Equations 3 and 4**,** subjected to the experimental constraints outlined in Table 1**.** The optimization ramps, presented in Figure 5, indicate that the optimal conditions for time (117.32 minutes), temperature (535.39°C), and KOH mass (7 g) resulted in a predicted MB removal efficiency of 82.44% and a carbonization yield of 75.11%**.** To validate these findings, an experimental trial was conducted in the laboratory under the optimized conditions. The removal efficiency (RE) of MB achieved during validation was 83.21%**,** exhibiting a deviation of 0.93% from the predicted value, confirming the reliability of the optimization model. The Activated Carbon from Pig Dung (ACDPD**)** produced under these validated conditions was subsequently synthesized in bulk for further investigations.

This study compared its findings with the findings previously published where PD was carbonized and used for the removal of pollutants. Literature considered (**Table 6**) indicated that carbonized PD from other sources achieved removal efficiencies of 86–95% for pollutants such as diethyl phthalate, hydrogen sulfide (H_2S), and methylene blue. In contrast, the removal efficiency of the digestate-derived pig dung (DPD) in this work was 82.3%, slightly lower than reported values. This discrepancy arises because the current study measured a single-point adsorption value rather than conducting exhaustive adsorption or desulfurization experiments. Concerning carbonization yield, the DPD in this work demonstrated a higher yield (75%) compared to previous studies, which typically reported yields below this threshold. Additionally, the carbonization process in this study required shorter exposure times than conventional methods, enhancing its practicality and energy efficiency for scalable applications.

Table 6. Comparison of RE and Yield of ACDPD with Previous Studies

Author	Pollutant	Removal Efficiency	Yield	Condition	dosage
Min *et al.,* 2024	Diethyl phthalate	90%	26%	500°C, 4hrs	1g/L
Gupta *et al.,* 2020	H2S	88%	28%	550°C, 2hrs	0.5g/L
Li *et al.,* 2019	Methylene Blue	85%	35%	500°C, 1.5hrs	1g/L
Wang *et al.,* 2022	SO2	92%	24%	500°C, 2hrs	1g/L
This study	Methylene blue	82.3%	75%	500°C, 1.12hrs,	1g/L

CONCLUSION

This study successfully optimized the activation and carbonization conditions for ACDPD using the BBD in Design Expert 13. The quadratic regression models developed exhibited strong predictive accuracy, with R^2 values of 0.9643 (yield) and 0.9836 (removal efficiency), demonstrating their robustness. Optimization using the desirability function identified the optimal conditions as 117.32 minutes, 535.39°C, and 7 g of KOH, achieving a predicted methylene blue (MB) removal efficiency of 82.34%.

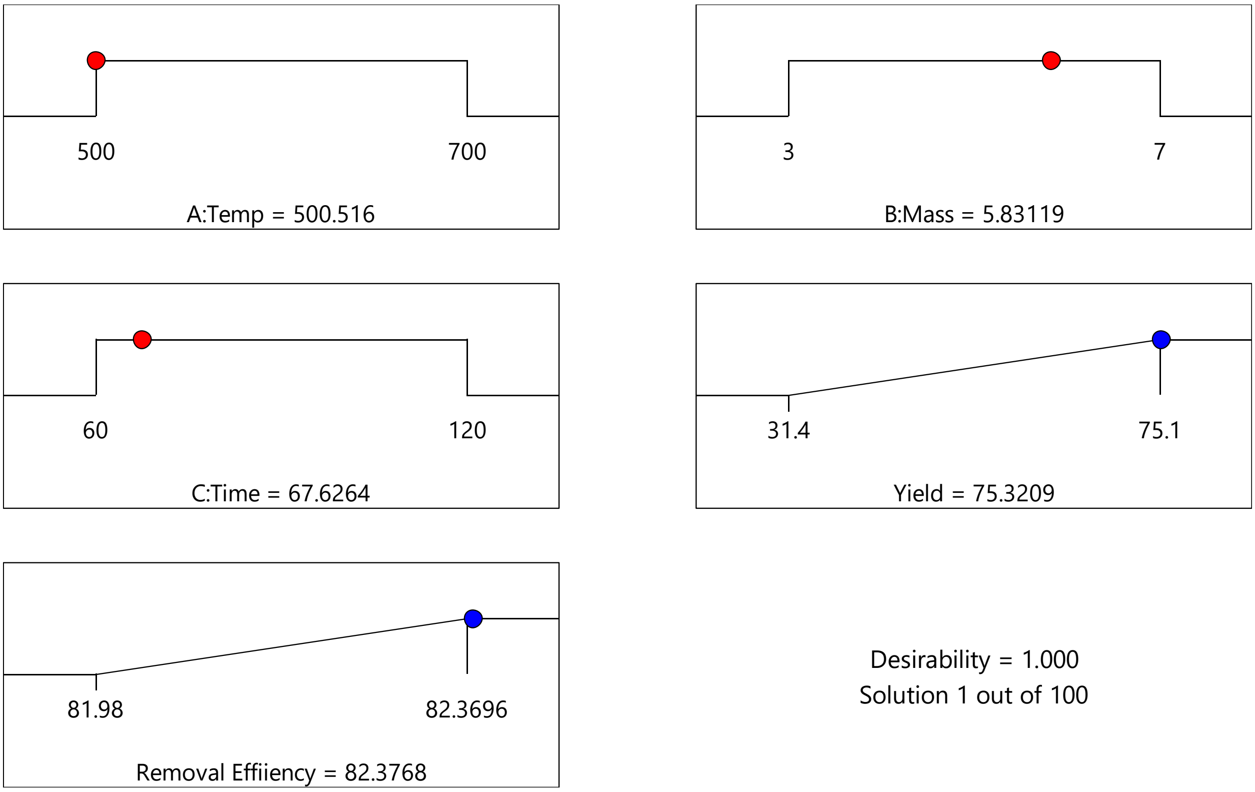

Figure 5: Ramp of Optimization

Laboratory validation under these conditions resulted in an experimental MB removal efficiency of 83.21%, with a deviation of just 0.93%, further confirming the model's accuracy. These findings highlight the potential of pig dung-derived activated carbon as an efficient, low-cost, and sustainable adsorbent for the desulphurization process. Future research is focused on the scaling up of the production of ACDPD and evaluating its adsorption kinetics for diverse contaminants.

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