

Optimization of malachite green adsorption from aqueous solution onto Anchote peel based activated carbon using Box Behnken design

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Abstract. Malachite green-contaminated wastewater discharged without proper treatment poses serious risks to human health and the environment. Therefore, this study evaluated the adsorptive removal of malachite green from aqueous solution using activated carbon derived from anchote peel. The adsorbent was prepared via chemical activation with phosphoric acid followed by thermal activation in the absence of oxidizing agents. Adsorption optimization was performed using the Box–Behnken design of response surface methodology with four variables: pH (3, 6, 9), initial dye concentration (50, 100, 150 mg/L), adsorbent dosage (0.5, 1.0, 1.5 g/100 mL), and contact time (30, 60, 90 min), resulting in 30 experimental runs. The maximum dye removal efficiency of 99.07% was achieved at pH 9, 50 mg/L initial concentration, 1.5 g/100 mL dosage, and 90 min contact time. ANOVA confirmed strong agreement between adjusted and predicted values ($R^2 = 0.9935$ and 0.9917) based on the quadratic regression model. These findings demonstrate that anchote peel-based activated carbon is an efficient adsorbent for malachite green removal, and its optimization using the Box–Behnken design provides a promising approach for large-scale treatment of dye-laden industrial wastewater

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1 Introduction

Malachite green is an N-methylated diaminotriphenylmethane dye widely used for its brilliant coloration and antimicrobial properties in textile, leather, paper, and aquaculture industries [1]–[3]. Chemically, the dye is pH dependent and exists in equilibrium among several forms: the cationic chromatic form (MG⁺) that predominates at neutral to acidic pH, the carbinol base at alkaline pH, and the reduced metabolite leucomalachite green (LMG), which is more lipophilic and shows longer persistence in tissues [3], [4]. Mechanistically, malachite green can intercalate into DNA, preferentially binding to A:T-rich regions, and it is readily reduced to LMG in biological systems, which complicates both toxicological risk assessment and treatment performance [3], [4].

The environmental and toxicological profile of malachite green raises serious concerns. The dye and its metabolite LMG are persistent and bioaccumulative, concentrating in fish tissues including liver, kidney, muscle, eggs, and fry, and producing multi-organ toxicity and histopathological damage in aquatic organisms [4], [5]. Malachite green and LMG are associated with genotoxic effects, including DNA damage through reactive oxygen species generation and covalent adduct formation, as well as mutagenic and tumor-promoting activities observed in laboratory studies [3], [4], [6]. At the ecosystem level, residual malachite green dye in surface waters and sediments reduces light penetration and primary productivity, may alter microbial communities, and creates pathways for human exposure through contaminated seafood and water [4], [5].

Accordingly, research has focused on developing robust and scalable remediation approaches. Adsorption is widely studied and often demonstrates high removal efficiency, using conventional activated carbon as well as low-cost adsorbents derived from agricultural wastes, seed kernels, and biomass-based materials [7]–[9]. Advanced oxidation processes and photocatalysis provide complementary routes for degradation, with TiO₂-based systems, visible-light composites, and H₂O₂-mediated catalytic systems showing promising results under optimized condition [10]–[12]; however, these methods often suffer from high operational costs, require specialized equipment, and may produce secondary pollutants or incomplete mineralization of the dye. Electrochemical methods and hybrid adsorption-photocatalysis systems offer additional options for difficult effluents [6], [10], but their application can be limited by high energy consumption, electrode fouling, and complex maintenance requirements. Biological and nature-based systems, including bacterial-augmented floating treatment wetlands and constructed wetland approaches, present sustainable, low-cost alternatives for large-scale or decentralized treatment [12], yet these approaches generally require long treatment times, are sensitive to environmental conditions, and may show lower removal efficiency for highly concentrated or persistent dyes. However, the

adsorptive removal of malachite green from water systems has recently emerged as a low-cost, efficient and promising technique. Optimization tools such as response surface methodology, particularly the Box–Behnken design, are commonly used to tune pH, initial concentration, adsorbent dosage, and contact time to achieve maximal removal and to support scale-up studies [9]. Taken together, these trends highlight the need for developing efficient, reusable, and economically viable adsorbents [4], [8], [10]. Therefore, this study focuses on optimizing the adsorptive removal of malachite green from aqueous solution using activated carbon derived from anchote peel, employing the Box–Behnken design of response surface methodology.

2 Materials and Methods

2.1 Adsorbent preparation

Fresh anchote tubers were peeled, and the peels were carefully washed with distilled water to remove soil, residual starch, and other soluble impurities. The cleaned peels were then oven-dried at 105 °C until a constant weight was achieved. Once dried, the material was ground using a laboratory mill and sieved to obtain a uniform particle size below 250 µm. The resulting powder was impregnated with phosphoric acid (H₃PO₄) at a 1:1 mass ratio (biomass to acid). The mixture was thoroughly mixed and allowed to stand at room temperature for 24 h to ensure proper penetration of the activating agent. The acid-treated biomass was then carbonized in a muffle furnace at 500 °C for 2 h under limited oxygen, with a heating rate of 10 °C/min. After cooling to ambient temperature, the carbonized material was repeatedly rinsed with distilled water until the wash water reached neutral pH. Finally, the activated carbon was oven-dried again at 105 °C, stored in airtight containers, and subsequently used for characterization and adsorption experiments.

2.2 Experimental design

The optimization of malachite green adsorption was carried out using the Box–Behnken design of response surface methodology (RSM). Four independent variables were selected for the study: solution pH, initial dye concentration, adsorbent dosage, and contact time. Each variable was studied at three levels, and the design generated a total of 30 experimental runs to evaluate the combined effects of these factors on dye removal efficiency as shown in Table 1. The ranges of the parameters were determined from preliminary experimental findings.

Table 1. Independent variables and their corresponding levels used in the Box–Behnken experimental design for malachite green adsorption.

Factor	Low (-)	Middle (0)	High (+)
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pH	3	6	9
Initial MG concentration (mg/L)	50	100	150
Adsorbent dosage (g/100mL)	0.5	1	1.5
Contact time (min)	30	60	90

2.3 Batch adsorption experiments

Batch adsorption experiments were performed to investigate the removal of malachite green from aqueous solutions using anchote peel-derived activated carbon. In each run, a predetermined amount of adsorbent was added to 100 mL of dye solution in Erlenmeyer flasks. The mixtures were agitated at 250 rpm on a mechanical shaker to ensure uniform contact between the adsorbent and the dye molecules. The experimental conditions, including pH, initial dye concentration, adsorbent dosage, and contact time, were selected according to the Box-Behnken design matrix. At the end of the specified contact time, the suspensions were filtered, and the residual dye concentration in the filtrate was determined using a UV-Vis spectrophotometer at the maximum absorption wavelength of 620 nm. The percentage of dye removal and adsorption capacity were calculated using equations 1 and 2 respectively.

$$\text{Adsorption capacity } (Qt) = (Co - Ct) \times V/M \quad (1)$$

$$\text{Removal Efficiency } (RE) = \frac{(Co - Ct)}{Co} \times 100 \quad (2)$$

Where C_0 and C_t (mg/L) are the initial and final dye concentrations, V (L) is the solution volume, and M (g) is the mass of the adsorbent. All experiments were performed in triplicate, and the mean values were reported [13], [14].

3 Result and discussion

3.1 Experimental design results

The batch adsorption performance of malachite green (MG) from aqueous solution using anchote peel-based activated carbon shows clear trends influenced by pH, MG concentration, adsorbent dosage, and contact time as shown in Table 2. One of the most significant findings is the effect of pH on removal efficiency. Higher pH values, particularly pH 9, lead to a substantial improvement in removal efficiency, with a maximum of 99.07% observed at pH 9, MG concentration 50 mg/L, adsorbent dosage 1 g/100 mL, and contact time 90 minutes. This trend suggests that alkaline conditions enhance the activated carbon's performance by increasing the negative charge on its surface, thereby facilitating electrostatic attraction

between the activated carbon and the positively charged MG molecules. In contrast, lower pH levels, such as pH 3 with MG concentration 150 mg/L, adsorbent dosage 0.5 g/100 mL, and contact time 30 minutes, result in reduced removal efficiency of 56.98%. MG concentration also plays a pivotal role in adsorption performance. Lower dye concentrations, such as 50 mg/L, consistently yield higher removal efficiencies, particularly at higher pH levels, compared to higher concentrations like 150 mg/L. For example, at pH 3, adsorbent dosage 0.5 g/100 mL, and contact time 30 minutes, decreasing the concentration from 150 mg/L to 50 mg/L increases removal efficiency from 56.98% to 67.58%. Higher MG concentrations saturate the activated carbon more quickly, leading to lower efficiencies.

Adsorbent dosage is another important factor, with higher dosages improving removal performance. Increasing the activated carbon dosage from 1 g/100 mL to 1.5 g/100 mL at pH 6, MG concentration 50 mg/L, and contact time 60 minutes results in an increase in removal efficiency from 80.62% to 81.03%. This indicates that a greater adsorbent dosage provides more active sites for MG molecules, enhancing overall efficiency. Finally, contact time critically affects adsorption, as longer durations allow more interaction between the activated carbon and MG molecules. At pH 9, MG concentration 50 mg/L, and adsorbent dosage 1.5 g/100 mL, increasing the contact time from 60 minutes to 90 minutes improves removal efficiency from 94.49% to 99.07%. This time dependency demonstrates that the system requires sufficient duration to reach adsorption equilibrium. Overall, the anchote peel-based activated carbon performs optimally under alkaline conditions, with lower MG concentrations, higher adsorbent dosages, and extended contact times. These specific parameters collectively maximize removal efficiency, making this activated carbon a promising candidate for treating malachite green-contaminated water.

Table 2. Batch adsorption performance of malachite green from aqueous solution using anchote peel based biosorbent

Run	pH	MG concentration(mg/L)	Adsorbent dosage(g/100mL)	Time (min)	RE (%)
1.	3	150	0.5	30	56.98
2.	3	50	1.5	30	67.58
3.	6	50	1	30	78.29
4.	3	150	1.5	30	57.81
5.	9	150	0.5	30	79.22
6.	6	50	0.5	30	77.87
7.	3	100	0.5	30	61.87

8.	6	150	1.5	30	68.93
9.	3	100	0.5	30	61.87
10.	6	50	1	30	78.29
11.	3	100	1.5	60	65.02
12.	9	50	1.5	60	92.15
13.	6	50	1	60	80.62
14.	3	100	1	60	64.61
15.	6	150	1.5	60	71.26
16.	6	100	0.5	60	75.32
17.	3	50	0.5	60	69.08
18.	9	50	1	60	91.74
19.	6	50	1.5	60	81.03
20.	9	100	0.5	60	86.44
21.	9	50	1.5	90	94.49
22.	3	100	0.5	90	66.53
23.	9	150	1.5	90	84.72
24.	9	50	1	90	99.07
25.	9	150	0.5	90	83.89
26.	9	50	0.5	60	91.33
27.	9	150	1.5	60	82.38
28.	6	150	1.5	60	71.26
29.	3	50	0.5	60	69.08
30.	6	150	1.5	60	71.26

The activated carbon prepared from anchote peel achieved 99.07% removal of Malachite Green (MG) at pH 9, 50 mg/L initial dye concentration, 1.5 g/100 mL adsorbent dose and 90 min contact time, with a

corresponding maximum adsorption capacity of 3.33 mg/g. This is comparable to the 98.33% MG removal reported for untreated anchote peel (AP) and 98.11% for coffee husk under their respective optimal conditions [15] and slightly exceeds those values. More advanced biochars, such as functionalized Banana Peel Biochar (BPB) prepared via microwave-assisted pyrolysis, have demonstrated extremely high MG adsorption capacities (up to 2297.8 mg/g) within 120 min, indicating that banana peel-derived sorbents can achieve very high uptake per unit mass [16]. Similarly, Rumex abyssinicus derived activated carbon achieved a maximum MG removal of 99.9% at pH 6, 100 mg/L initial concentration, 0.10 g/100 mL adsorbent dose and 40 min contact time [17]. These comparisons show that your activated anchote-peel carbon performs at the high end of removal efficiencies reported for agro-waste based adsorbents; at the same time, biochars from banana peel and other biomass offer potential for high adsorption capacities and lower mass requirements, which might be advantageous for scale-up or cost-sensitive applications.

3.2 ANOVA and Fit summary

The statistical analysis of the removal efficiency model indicates a highly significant model with an F- value of 1111.85 and a p-value of less than 0.0001. This result demonstrates that the factors included in the model, namely pH, Malachite Green concentration, biosorbent dosage, and contact time, are all statistically significant and contribute meaningfully to explaining the variation in removal efficiency. Among the individual factors, pH (A) and Malachite Green concentration (B) have the most pronounced effects, with p-values less than 0.0001, indicating their high significance. The biosorbent dosage (C) also significantly impacts removal efficiency, though to a lesser extent, with a p-value of 0.0461. Contact time (D) is another crucial factor with a p-value less than 0.0001. The residual sum of squares and lack of fit analysis suggest that the model fits the data well, with no significant additional errors beyond those accounted for by the model.

The fit statistics further confirm the robustness of the model. The high R² value of 0.9944 indicates that the model explains 99.44% of the variability in removal efficiency. The Adjusted R² of 0.9935 supports this finding, taking into account the number of predictors. The Predicted R² of 0.9917 aligns closely with the Adjusted R², indicating strong predictive performance. Additionally, the Adeq Precision value of 104.5943, well above the desired threshold of 4, confirms an adequate signal-to-noise ratio and suggests that the model can effectively navigate the design space. The final equation in terms of coded factors is shown in Equation 3.

$$\text{Removal Efficiency (\%)} = 75.94 + 11.25A - 5.07B + 0.3998C + 2.67D \quad (3)$$

Equation 3 shows a linear regression model that allows for predictions of removal efficiency based on the coded levels of each factor. Positive coefficients for pH (A) and contact time (D) suggest that these factors enhance removal efficiency, while the negative

coefficient for Malachite Green concentration (B) indicates a reduction in efficiency. The coefficient for biosorbent dosage (C) is also positive, but with a smaller impact. Overall, the model is robust and reliable, providing valuable insights into the factors affecting removal efficiency and their relative impacts, as shown in Table 3.

Table 3. ANOVA for malachite green removal from aqueous solution

Source	Sum of Squares	df	Mean Square	F- value	p-value
Model	3672.47	4	918.12	1111.85	< 0.0001
A-pH	2073.46	1	2073.46	2510.98	< 0.0001
B-MG concentration	565.91	1	565.91	685.32	< 0.0001
C-Bio sorbent dosage	3.64	1	3.64	4.40	0.0461
D- contact time	83.32	1	83.32	100.90	< 0.0001
Residual	20.64	25	0.8258		
Lack of fit	20.64	20	1.03		
Pure Error	0.0000	5	0.0000		
Cor Total	3693.11	29			

4 Conclusion

In this study, batch adsorption of malachite green dye from aqueous solutions onto anchote peel-derived activated carbon was optimized using the Box–Behnken design of response surface methodology. The results showed that the maximum experimental malachite green dye removal efficiency of 99.07% was achieved at pH 9, contact time of 90 min, initial dye concentration of 90 mg/L, and adsorbent dosage of 1.5 g/100 mL. Furthermore, ANOVA and regression analysis confirmed this agreement, with R² values of 0.9917 (predicted) and 0.9935 (adjusted). Overall, this study demonstrates that anchote peel, an agricultural waste, can be effectively utilized for the development of adsorbents for the efficient removal of malachite green dye from aqueous solutions. Moreover, the optimization using the Box–Behnken design provides a reliable foundation for scaling up the prepared activated carbon for industrial applications. Future studies will focus on detailed adsorbent characterization followed by kinetic and isotherm modeling, as well as regeneration and cost analysis to evaluate its industrial feasibility.

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