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Optimization of Methylene Blue Dye Adsorption in Fixed Bed Column Packed with Tea Waste via Response Surface Methodology

Novi Sylvia [1,*], Rozanna Dewi [1], Zulnazri [1], Hendi Setiawan [1], Dinda Humaira [1], Mutia Reza [2]

[1] Department of Chemical Engineering, Malikussaleh University, Lhokseumawe 24351, Aceh, Indonesia
[2] Department of Chemical Engineering, Institut Teknologi Kalimantan, Balikpapan 76127, East Kalimantan, Indonesia

* Corresponding author: novi.sylvia@unimal.ac.id

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Abstract

Tea waste is a low-cost alternative material for making adsorbent to remove methylene blue from synthetic dye wastewater perpetually. Optimization of the adsorbent process utilized Response Surface Methodology (RSM) and a continuously operating system in a fixed bed column. The independent variables in the research are X_1 (bed height), X_2 (contact time), and X_3 (flow rate). The dependent variable is Y_1 (removal efficiency) with a matrix design by Box-Behnken. The optimum condition of methylene blue (MB) B removal was found at X_1=16 cm, X_2=90 min, and X_3=4 L/min with an adsorption efficiency of 90.45%. After the activation and adsorption of MB dye, the complete FTIR spectrum shows a distinct peak at 2933.7 cm^{-1}. The results of the EDX analysis performed on tea waste reveal the presence of nitrogen (element N) following the adsorption process. This observation strongly suggests that the tea waste has effectively absorbed MB, as nitrogen is a constituent element found in the molecular structure of MB.

1. Introduction

The chemical industry is proliferating along with the increase in the world's population. Industries that use synthetic dyes in manufacturing their products are also increasing, including the textile, paper, medicine, food, cosmetics, printing, and rubber industries [1]. Synthetic dyes contain compounds with complex aromatic molecular structures, making them challenging to decompose when discharged naturally into the environment [2].

The presence of dyes in waste can contribute to environmental issues. Waste exhibiting vibrant colors and increased levels of Chemical Oxygen Demand (COD) poses a threat to aquatic life due to compound molecules in the waste that bind to metal ions [3]. Certain synthetic dyes employed in industrial processes exhibit stability. Methylene blue (MB) is a notable example of a compound that remains unaffected by oxidation and light exposure and is resistant to aerobic decomposition. It finds extensive application in the textile, leather, and printing industries [4, 5, 6]. The textile industry is the leading contributor to industrial waste, accounting for around 54 percent of the total dye waste [7, 8, 9]. While these dyes are not highly toxic to humans, they can irritate the eyes, skin, and circulatory system.

Furthermore, exposure to these compounds at specific concentrations may lead to symptoms such as vomiting, nausea, diarrhea, vertigo, excessive perspiration, and inflammation of the gastrointestinal tract [10]. Methylene blue is a toxic aromatic hydrocarbon compound, a highly absorbent cationic dye with the formula $C_{16}H_{18}ClN_4S$. Approximately 5% of MB is employed in the textile dyeing process, with the remaining 95% being discharged into the environment [7, 8, 9]. As a result, proper management of liquid waste containing MB is imperative.

Diverse biological, physical, and chemical methodologies are employed to remediate MB waste. These methods include adsorption, biosorption, coagulation or flocculation, advanced oxidation, ozonation, membrane filtration, and liquid extraction. The benefits of each approach have been extensively discussed [11]. Among these physical methods, adsorption is one of the most commonly utilized techniques for treating dye-containing waste. Its popularity is attributed to its simplicity, efficiency, low energy requirements, and the capability to utilize various cost-effective adsorbent materials, such as biomass waste [12]. Biodegradable waste is commonly used as an absorbent to remove synthetic pigments from waste. The widespread use of biomass as an absorber for methylene blue dye is attributed to its enhanced selectivity, effectiveness, and cost-effectiveness. Examples of such materials include bagasse [9], activated lignin-chitosan [6], rice husk [13], *Balanites Aegyptiaca* [14], and other cellulose-containing substances.

The investigated biomass waste comprises tea leaves. Tea waste is a newly generated organic byproduct from the brewing process. Despite being a fundamental material for compost and board production, using tea waste as a resource remains limited. According to the Badan Pusat Statistik [15], in 2021, Indonesia's national tea production reached 145.1 thousand tons, reflecting a notable increase of 13.45% compared to the previous year's total of 127.9 thousand tons. It can be asserted that the residues generated align with the scale of Indonesian tea production. Undoubtedly, the substantial amount of discarded tea waste poses significant environmental issues. As a potential solution, tea sludge is being considered for use as an adsorbent. This consideration is supported by the presence of cellulose compounds (37%), hemicellulose and lignin (14%), and polyphenols (25%) in tea residue. Cellulose contains functional groups such as hydroxyl, methyl, and carbonyl that can incorporate dyes in waste [13]. According to previous research, tea waste can adsorb heavy metal waste and dyes found in liquid waste [15, 16, 17, 18, 19]. However, it is essential to note that these studies were conducted in separate segments.

This research employed a continuous system and the process optimization method on a fixed bed column. In the historical context of utilizing tea waste, previous studies [20, 21, 22] focused on batch systems to optimize operating conditions, including adsorbent dose, pH, and MB concentration. This research aims to enhance the efficiency of the adsorption process within a fixed bed column. To accomplish this goal, the study employs the Box-Behnken design under the framework of Response Surface Methodology to optimize the flow rate, adsorbent bed height, and contact time. Additionally, analyses of the physical and chemical properties of the adsorbent were conducted.

2. Experimental

2.1. Materials

The raw materials used in this study were tea waste collected from nearby cafes in Lhokseumawe city, distilled water, methylene blue ($C_{16}H_{18}ClN_4S$, 99% Merck), and HCl (37% Merck).

2.2. Equipment

The tools used in the study included an adsorption column made of acrylic pipe with a diameter of 6.4 cm and a height of 30 cm. The set of tools used is shown in Figure 1. Other additional tools used were a spatula, 500 mL beaker glass, 100 mL measuring cup, 1000 mL beaker glass, sample bottles, stirred, aluminum foil, pH meter (AS218), measuring flask 500 mL, funnel, analytical balance, stopwatch, container 5 L, Fourier Transform Infra-Red (FT-IR, IR Prestige 21), UV-Vis spectrophotometer (UV-1800), and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX, CARL ZEISS type EVO MA 10), oven (Memmert UN 30), and valve (VG 16 DD).

2.3. Chemical Activation of Adsorbent

The activation was started by putting 250 grams of tea waste into a 1000 mL beaker glass beaker. Subsequently, 1000 mL of 0.1 N HCl solution was added until the tea waste was submerged entirely, and this mixture was left for approximately 24 hours. After that, the tea waste was filtered and washed with distilled water until a neutral pH was reached. Then, the tea waste was dried using an oven at 105°C until the mass of the tea waste was constant. The activated tea waste was ready to be used as an adsorbent and inserted into the adsorption column.

2.4. Preparation of Methylene Blue Adsorbate

This adsorbate preparation process used methylene blue with a concentration of 30 ppm. Methylene blue solution was made by dissolving 30 mg of methylene blue powder in distilled water to a limit of 1000 mL using a 1000 mL measuring flask.

2.5. Fixed-bed Column Adsorption Process

As shown in Figure 1, the adsorbent from the material that had undergone the manufacturing process was inserted into the column. This research used the Box- Behnken matrix, with the independent and dependent variables detailed in Table 1. Each experiment was conducted by downflowing MB at a concentration of 30 ppm. Samples of the adsorption column's output solution were collected according to the contact duration. The absorbance of the adsorbate was measured using a spectrophotometer with a wavelength of 663 nm. FTIR and SEM/EDX instruments were employed to analyze the adsorbent characteristics of tea residue at various stages, including before, during, and after the activation and adsorption processes. The efficiency and adsorption capacity were subsequently calculated using Equations (1) and (2) [14, 15].

Table 1. Factors and levels in the independent

Independent variable	Level code and range		
	-1	0	+1
Bed height, cm (X_1)	8	12	16
Contact time, min (X_2)	60	90	120
Flow rate, L/min (X_3)	4	6	8

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{flowrate\ (C_0 - C_e)}{m} \quad (2)$$

where, C_o is the initial concentration of MB solution ($mg.L^{-1}$), C_e is the final concentration of MB solution ($mg.L^{-1}$), q_e is the adsorption capacity ($mg.L^{-1}$), m is the adsorbent mass (gr), flowrate is the flow rate of MB solution ($L.min^{-1}$).

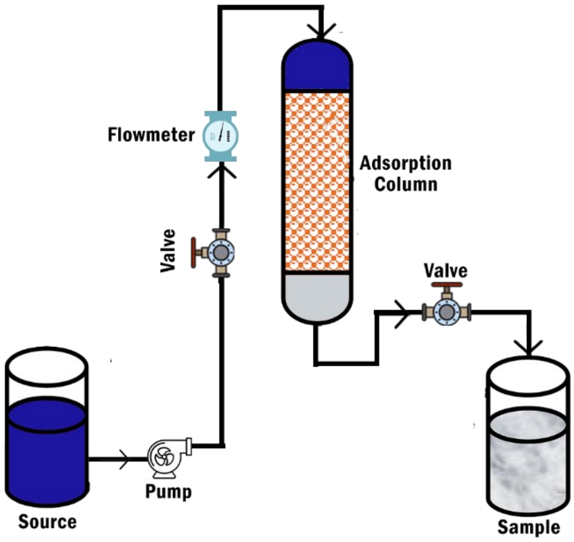

Figure 1. Continuous model adsorption column

2.6. Fixed-bed Column Data Analysis

The research conducted was to determine the optimum value in the methylene blue adsorption process using adsorbents from tea waste by optimizing the bed height, contact time, and flow rate on removal efficiency. Considering multiple response variables, the study employed Response Surface Methodology (RSM) with the Desirability Function (DF) approach. A Box-Behnken design was used with three independent variables, namely bed height (X_1), contact time (X_2), and flow rate (X_3), comprising 17 treatments conducted randomly, as outlined in Table 1. The equation model is expressed in Equation 3.

$$Y_i = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum \sum_{i \to j} \beta_{ij} X_i X_j + \varepsilon_j \quad (3)$$

This research used process optimization analysis, carried out by processing data using Design Expert 13 software to obtain response surface shapes and contour plots and diversity analysis of the research response. The coding (+1, 0, and -1) and the original value for each factor. The relationship between these values is addressed in Equation 4.

$$Z = \frac{X - X^0}{\Delta X} \quad (4)$$

3. Results and Discussion

3.1. Removal Efficiency of MB

Tables 2 and 3 detail the design matrix, its relationship to the experimental data results, the predicted values of the model's response variable, and removal efficiency. The predicted response values were calculated from the quadratic model using Design Expert software. The efficiency equation for tea residue adsorption was converted into a statistical model based on experimental data using multiple regression analysis. Equation 5 illustrates the relationship between the response variable of sorption efficiency and the independent variables of bed height, contact time, and flow rate.

Table 2. Box-Behnken-based experimental design matrix for adsorption efficiency (%)

No	X_1 (cm)	X_2 (min)	X_3 (L/ min)	Removal Efficiency (%)
1	8	60	6	46.14
2	12	90	6	81.36
3	8	120	6	47.27
4	12	120	4	83.64
5	16	120	6	88.18
6	12	60	8	56.36
7	12	90	6	81.36
8	16	90	4	90.45
9	12	60	4	79.09
10	12	120	8	58.64
11	12	90	6	81.36
12	12	90	6	81.36
13	8	90	4	58.64
14	16	90	8	63.18
15	12	90	6	81.36
16	16	60	6	79.09
17	8	90	8	48.41

The observations in Table 2 show that the highest adsorption efficiency (%) (Y) obtained is 90.45%, followed by the lowest adsorption efficiency of 46.14%. The percentage error of the RSM presented in Table 2 shows that the highest error for response Y is -2.4441%. The correlation equation of the adsorption independent variable is shown in Equation 5.

$$Y = 81.36 + 15.055X_1 - 2.1313X_2 - 10.654X_3 + 1.99X_1X_2 - 4.26X_1X_3 - 0.568X_2X_3 - 10.226{X_1}^2 - 5.963{X_2}^2 - 5.963{X_3}^2 \quad (5)$$

where, Y is the adsorption efficiency, X_1 is the bed height (cm), X_2 is the contact time (minute), and X_3 is the flow rate (L/min).

Table 3 shows that the R^2 value is close to 1 in the quadratic model, indicating a strong predictability for the removal efficiency response variable. Additionally, the standard deviation among all models is comparatively smaller. If the R^2 value is close to 1, the standard deviation is smaller, and the model is better for predicting the response [23, 24]. Table 3 shows that the quadratic model exhibits a modest standard deviation of 3.96, a substantial R^2 value of 0.97, a predictive R^2 value of 0.544, and an adjusted R^2 value of 0.93. Based on Table 2, it can also be seen that the quadratic model for response Y is not aliased. This implies that the quadratic model can describe the relationship between the Y response and interaction variables.

Table 4 shows the results of the analysis of variance (ANOVA) quadratic model of methylene blue adsorption efficiency. ANOVA for the quadratic model in Table 4 shows that probability values (Prob > F) for variables X_1 and X_3 are smaller than 0.05. This indicates the quadratic model (order 2), where variable A2 significantly affects methylene blue adsorption efficiency. In contrast, X_2 = contact time, and the interaction variables X_1X_2, X_1X_3, and X_2X_3 and the squared variables X_2^2 and X_3^2 appeared insignificant. This indicates that statistically, these variables have little effect on the methylene blue sorption efficiency. Nevertheless, they are retained in the model, given the possibility that these variables have a significant impact on adsorption.

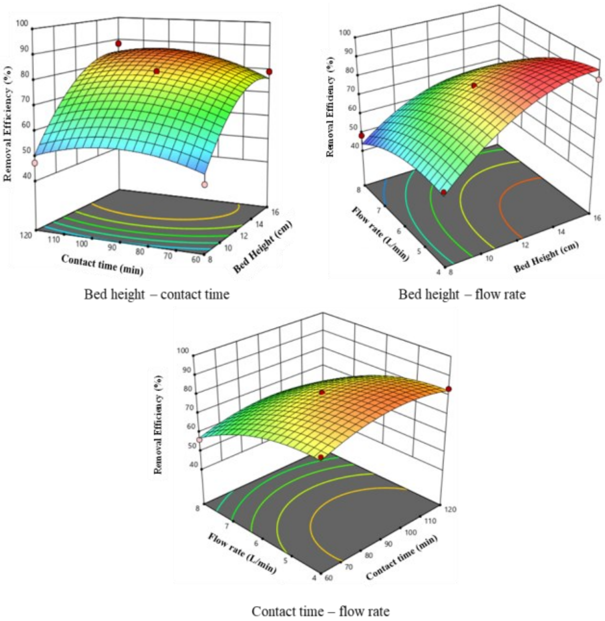

Figure 2. Response surface plots showing influences of contact time, bed height, and flow rate

Table 3. Regression optimization statistics for adsorption efficiency (%) model summary statistics

Source	Std. Dev.	R^2	Adj. R^2	Pred. R^2	
Linear	8.84	0.7308	0.6687	0.5755	
2FI	9.62	0.7546	0.6074	0.3167	
Quadratic	3.92	0.9715	0.9349	0.5440	Suggested
Cubic	0.0000	1.0000	1.0000	-	Aliased

Table 4. Analysis of variance (ANOVA) data sorption efficiency (%)

Source	Sum of squares	df	mean square	F-value	p-value	
Model	3665.62	9	407.29	26.51	0.0001	significant
X_1-Bed height	1813.22	1	1813.22	118.02	< 0.0001	
X_2-Contact time	36.34	1	36.34	2.37	0.1680	
X_3-Flow rate	908.02	1	908.02	59.10	0.0001	
X_1X_2	15.84	1	15.84	1.03	0.3437	
X_1X_3	72.59	1	72.59	4.72	0.0663	
X_2X_3	1.29	1	1.29	0.0839	0.7805	
X_1^2	440.32	1	440.32	28.66	0.0011	
X_2^2	149.75	1	149.75	9.75	0.0168	
X_3^2	149.75	1	149.75	9.75	0.0168	
Residual	107.54	7	15.36			
Lack of fit	107.54	3	35.85			
Pure error	0.0000	4	0.0000			
Cor total	3773.16	16				

Table 5. Analysis of optimization with constraints on adsorption using tea waste adsorbent

Alternative	X_1	X_2	X_3	Removal Efficiency Prediction (%)	Removal Efficiency Experiment (%)	Desirability
1	16	90	4.00	95.139	90.45	1.00
2	15	106	4.40	94.706	90.20	1.00

Figure 2 shows the contour plot graph and three-dimensional response surface graph describing the methylene blue adsorption efficiency with variations in bed height, contact time, and flow rate. The three figures show that the surface response graph and contour plot have a maximum shape. Based on Figure 2, it can be seen that the response optimization of methylene blue adsorption efficiency of 90.45% is at a bed height of 16 cm, contact time of 90 minutes, and flow rate of 4 L/min.

The relationship observed indicates that as the bed height increases, the absorbed concentration of methylene blue also increases and conversely decreases with a lower bed height. This phenomenon is attributed to the larger contact surface area between the tea content and methylene blue at greater bed heights, leading to an enhanced adsorption process [18]. Tea waste require adequate contact time to adsorb methylene blue optimally. Hence, a longer contact duration provides the adsorbent, tea waste, with increased opportunities to interact with the methylene blue contained within the pores of the tea waste. Based on the presented research, the Desirability Function (DF) is employed to ascertain the optimal operating conditions for independent variables to achieve maximal methylene blue adsorption efficiency. A DF closer to one signifies that the targeted response is optimal.

The optimization results show that the combination of independent variable levels that can provide the optimal response value is at a bed height of 16 cm, a contact time of 90 minutes, and a flow rate of 4 L/min. Based on the DF value, the design expert software produces two solutions, as shown in Table 5. Considering the DF value and methylene blue adsorption efficiency, solution number 1 was chosen to represent the optimal response variable.

3.2. Characteristics of Tea Waste Using FTIR

Tea waste adsorbent samples were analyzed using FTIR before and after activation using HCl and after adsorption. FTIR analysis aims to determine the functional groups contained in the adsorbent [14]. Qualitative testing of functional groups was carried out by interacting with the adsorption peaks of the infrared spectrum, and the resulting range can be seen in Figure 3. Figure 3 shows the difference between the adsorbent before and after the adsorption process. The tea waste adsorbent undergoes activation, modifying its functional groups [20].

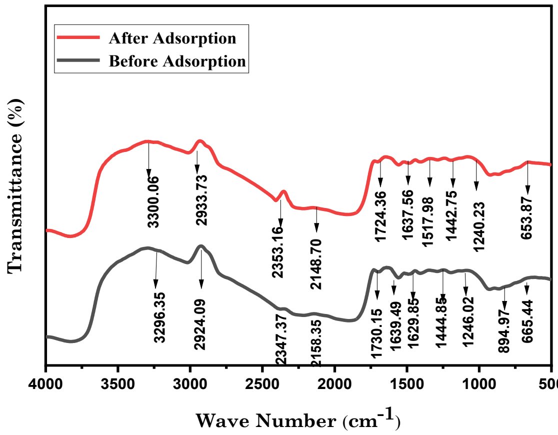

Figure 3. FTIR spectrum on tea waste adsorbent

Several wavenumbers are absorbed from the entire FTIR spectrum of the activated sample. The absorption band at 3296 cm^{-1} corresponds to the primary vibration of a hydroxyl group (-OH). The peak at 2924 cm^{-1} is attributed to symmetric groups. Peaks at 1730 and 1629.8 cm^{-1} are associated with asymmetric C=O stretching, aromatic C=C, and C=O/C=C stretching of amide groups. Notably, the cluster functions shifted after the adsorption of MB on tea waste.

The main subdistricts at the peak of the spectrum are shown for functional groups, such as –OH (3296→3300.6), C–H (2924→2933.7), C=C, C=N (2347→2353), C=O (1730→1724), C=C (1629.8→1637). Thus, it can be concluded that MB interacts with functional groups in tea waste and involves complex formation. Adsorption of MB dye is shown at 2933.7 cm^{-1}. This result aligns with the adsorption peak reported by other researchers who performed the MB adsorption band in the 2500-3000 cm^{-1} [23].

3.3. SEM /EDX Analysis

The adsorbent was characterized to determine its physical and chemical properties, and the tea waste adsorbent was characterized using Scanning Electron Microscopy (SEM). SEM analysis was employed to ascertain the morphological structure of the substance [24]. The results of SEM analysis reveal a more detailed scaly surface structure and shape. Additionally, the analysis was enhanced with EDX, enabling the detection of elements present in the sample, and the surface was observed through electron conductors [25]. The SEM analysis was conducted at a magnification of 1,000 times, and the results showcasing the three types of adsorbent morphological structures are depicted in Figure 4.

The morphological structures of the three adsorbent samples, as determined by SEM analysis, exhibit distinct characteristics. In Figure 4a, the activated tea waste displays significantly larger and cleaner pore sizes, ranging from 14 to 20 µm, making it suitable for use as an adsorbent. Figure 4b shows the pores of tea waste after adsorption process, where the pores are covered with methylene blue. In contrast, Figure 4a depicts the pores of tea waste before the adsorption process, as evidenced by the finer adsorbent particles ranging from 2 to 4 µm. It can be concluded that the increased surface area of the adsorbent correlates with a higher adsorption capacity [17, 26, 27].

The chemical activation of the tea waste adsorbent led to the development of larger absorbent pores compared to physical activation alone. Additionally, the adsorbent exhibited larger functional groups after adsorption, indicating the effective adsorption of numerous methylene blue particles. This underscores that chemical activation plays a crucial role in enlarging the pores on the adsorbent, contributing to the effectiveness of the adsorption process. The components or atomic compositions of the samples (before and after activation and after adsorption) were determined by EDX analysis. The outcomes of the EDX analysis are displayed in Table 6 [26].

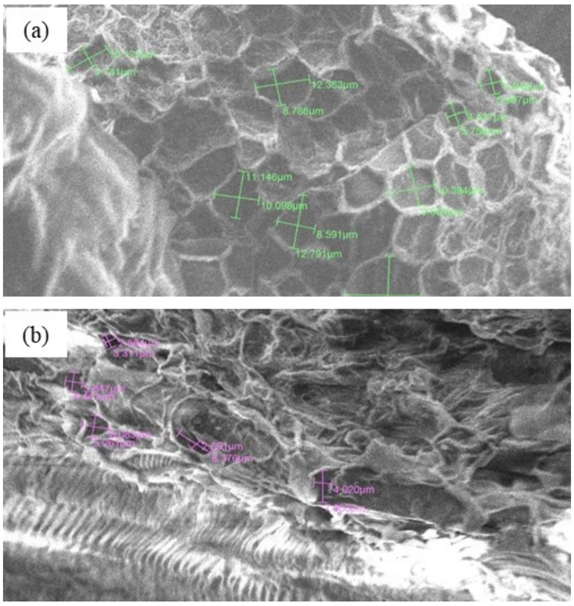

Figure 4. SEM images of tea waste (a) before adsorption and (b) after adsorption

Table 6. SEM-EDX adsorbent analysis results before and after activation and after adsorption

Element	Atom (%)		
	Before activation	After activation	After adsorption
Carbon	75.62	76.04	59.21
Oxygen	23.41	23.23	38.08
Aluminum	0.26	-	0.5
Calcium	0.71	0.5	1.72
Copper	-	-	0.46
Chlorine	-	0.23	-
Nitrogen			7.6

The results from the EDX analysis of tea waste are outlined in Table 6. The composition of tea waste includes elements C, O, Al, Ca, Cu, and Cl, with carbon and oxygen being the predominant constituents. After activation, chlorine is observed due to the activation process involving HCl, and suboptimal washing of the adsorbent after activation contributes to the remaining chlorine. Notably, after the adsorption process, the appearance of nitrogen indicates the adsorption of methylene blue in the tea waste, as nitrogen is a constituent of methylene blue.

4. Conclusion

The Design of Experiments (DF) approach was employed to optimize several process variables: bed height (8, 12, and 16 cm), contact time (60, 90, and 120 minutes), and flow rate (4, 6, and 8 L/min). The goal was to achieve the highest removal efficiency of methylene blue (MB), which resulted in an impressive 90.45% in the fixed bed column configuration. This optimal MB removal efficiency was attained using a 16 cm bed height, a 90- minute contact time, and a 4 L/min flow rate. Following the activation and adsorption of MB dye, a comprehensive FTIR spectrum emerged, featuring a distinctive peak at 2933.7 cm^{-1}. The results of the EDX analysis conducted on the tea waste displayed the presence of nitrogen (element N) after the adsorption process. This observation provides strong evidence that the tea waste has efficiently adsorbed MB, as nitrogen is a constituent element inherent in the molecular structure of MB.

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