



Utilization of Fly Ash Palm Oil Mill Waste as an Adsorbent of Methylene Blue in a Fixed Bed Column System by Using Response Surface Methodology

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Abstract

Palm kernel shell combustion waste in boiler units called fly ash (FA) is a low-cost alternative material as an adsorbent. FA contains high levels of silica (SiO_2) and aluminium oxide (Al_2O_3). The content of both compounds is an important component as an adsorbent. FA was used to absorb methylene blue (MB) continuously from synthetic dye wastewater. The study was conducted by continuous system process optimization using Response Surface Methodology (RSM) Box-Behnken design. MB was flowed on a set of fixed-bed adsorption columns with independent variables in this study are X_1 (bed height; 8, 12, 16 cm), X_2 (contact time; 90, 120, 150 min) and X_3 (flow rate; 2, 4, 6L/min). The dependent variables were Y_1 (removal efficiency) and Y_2 (adsorption capacity) with matrix design by Box-Behnken. Optimisation of MB removal in this study was obtained at $X_1 = 16$ cm, $X_2 = 150$ min and $X_3 = 2$ L/min with removal efficiency of 98.45% and adsorption capacity of 0.115 mg/g. FA pores according to SEM analysis were obtained at 1-2 μm . Likewise, the results of EDX analysis showed that there were N and Cl atoms in FA after the adsorption process. This shows that FA is able to adsorb MB.

INTRODUCTION

Methylene Blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}$), as a cationic dye, has been widely used in chemical indicators and dyes in industry. A significant increase in wastewater containing the organic dye methylene blue (MB) occurs in industrial processes such as printing and dyeing. This wastewater has characteristics such as high flow rate, intense colour saturation, high organic matter concentration, and low biodegradation sustainability. The presence of this dye effluent has a very negative impact on aquatic ecosystems and the photosynthetic activity of microorganisms in the aquatic environment (Meili et al., 2019; Sivakumar et al., 2022)

As time has passed, many researchers have considered diverse methods to address the wastewater problems caused by MB dyes. Among the various treatment methods that have been used,

including flocculation (Khan et al., 2022), membrane filtration (Wakhid et al., 2022), advanced oxidation (Sivakumar et al., 2022) and photocatalytic degradation (Xia et al., 2015). Adsorption method has received special attention. It is considered superior compared to other treatment methods due to its high efficiency, low operational cost, simple process, and immunity to toxic materials (Meili et al., 2019)

Various low-cost alternative adsorbents from agricultural solid waste, industrial solid waste, agricultural by-products, and biomass are used in wastewater treatment. For example, clay (Auta et al., 2012), sludge (Hu et al., 2018), rice husk biochar (Ahmad et al., 2020; Samad et al., 2019) and bagasse (Al-Mokhalelati et al., 2021), as adsorbents have been used for dye wastewater adsorption treatment. Apart from that there is solid waste from palm oil processing plants called fly ash (FA). This

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waste is the residue of burning palm kernel shells in the boiler unit and is generated up to ± 136 kg per month (Chong et al., 2022; Hamzah et al., 2019). When the plant is operating normally, it will continue to accumulate if there is no good waste handling. Waste accumulation can be reduced by utilising FA waste as an adsorbent so as to provide added value. Several studies have reported that palm oil mill FA has good absorption ability as an adsorbent in absorbing dye pollutants (Pelita et al., 2023; Pinem et al., 2020; Rafatullah et al., 2010; Triawan et al., 2017) metals (Yusof et al., 2018) and carbon dioxide (CO₂) (Alhamed et al., 2015). FA contains high levels of silica (SiO₂) and aluminium oxide (Al₂O₃). The content of both compounds is an important component as an adsorbent (Pinem et al., 2020). Palm oil mill FA waste can be a low cost adsorbent because of its abundant availability, easy to obtain and low price (Chong et al., 2022; Khanday et al., 2017; Pinem et al., 2020; Rafatullah et al., 2010). The use of FA in dye absorption has been carried out by previous researchers using a batch system (Chong et al., 2022; Triawan et al., 2017) with an optimisation process (Ghaedi et al., 2015).

Based on the content of FA, this study was conducted to utilise FA as a biosorbent applied to a fixed bed column system for MB absorption. This research was carried out by varying the adsorbent bed height, flow rate and contact time in the column system optimised using Design Expert software. FA characterisation tests were also conducted prior to the use of FA as an adsorbent. Adsorption capacity and sorption efficiency are important parameters to evaluate the effectiveness of adsorbents in addressing water pollution by MB.

MATERIAL AND METHODS

Material

FA used in the study was obtained from PT Syaukath Seejahtera Palm Oil Mill, North Aceh. Methylene blue (C₁₆H₁₈N₃ClS) with a molecular weight of 373.91 g/mol used was P.A chemical (Merck). Supporting raw materials used were tapioca flour (SMS Genigel 48 Modified) and distilled water as a mixture for making tapioca glue.

Equipment

The adsorbent was applied to an acrylic pipe as an adsorption column with a diameter of 6.4 cm and a length of 30 cm, as shown in Figure 1,

which was carried out on one column. Additional equipment used were oven (Mettler UN 30), hot plate (Heidolph C-MAG MS 4), mesh sieve 100 (Standard ASTM E 11, 150 microns), adsorbent mould (stainless steel cylinder mould 1.5 × 1 cm), desiccator, spatula, 500 mL beaker, 100 mL measuring cup, porcelain cup, scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX, CARL ZEISS type EVO MA 10), UV-VIS spectrophotometer (UV Shimadzu 1800), furnace (FNC-2 B-One Furnace).

Adsorbent Preparation Procedures

Fly ash was dried in an oven at 105°C. The preparation process begins with sieving 100 g of fly ash using a 100 mesh sieve. Then, 15 g of tapioca starch and 45 mL of distilled water were heated until it became glue. Next, 100 g of fly ash and glue were mixed and stirred until evenly distributed. Next, the mixture was moulded using a 1.5 cm diameter mould with a thickness of 1 cm and then dried in an oven for 2 hours at 105°C. After that, the mixture was calcined in a furnace at 600°C for 120 minutes. The adsorbent was then cooled using a desiccator to room temperature and ready for the MB adsorption process.

The adsorption process was started by flowing 20 ppm MB (C₀) into the adsorption column. First, the bottom ash adsorbent used was placed in a column with a diameter of 30 cm and 6.4 cm, while the adsorbent height (Z) in the column was varied by 4 cm (25 g), 8 cm (50), and 12 cm (75 g). Next, MB was flowed into the column with flow rates of 2, 4, and 6 L/min and varied contact times of 90, 120 and 150 min, as shown in Figure 1. After that, the efficiency and capacity of MB adsorption were calculated with Eq. (1) and (2) (Kutluay et al., 2020)

$$\text{Efficiency} = \frac{MB_{\text{initial}} - MB_{\text{final}}}{MB_{\text{initial}}} \times 100\% \quad (1)$$

$$q_t = \frac{\text{flowrate} (MB_{\text{initial}} - MB_{\text{final}})}{m} \quad (2)$$

Fixed-bed column data analysis

The research conducted was to determine the optimum value in the methylene blue adsorption process using adsorbents from FA by optimizing the bed height, contact time and flow rate on removal efficiency. This study has more than one response variable, so it uses the Response

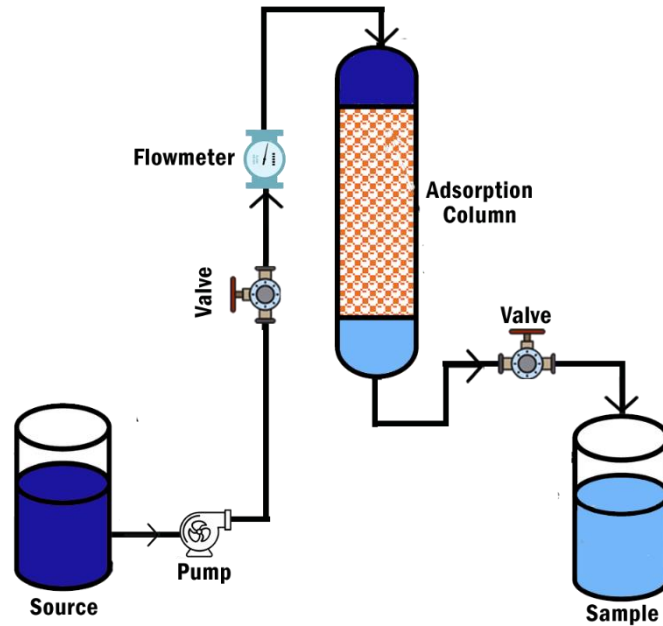


Figure 1. Methylene blue adsorption process on fixed bed column.

$$Y_i = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i \rightarrow j} \beta_{ij} X_i X_j + \varepsilon_j \tag{3}$$

Surface Methodology (RSM) which uses the Desirability Function (DF) approach with Box-Behnken design of 3 independent variables, and consist of 17 treatments and is run randomly. The independent variables are: bed height (X_1), contact time (X_2), and flow rate (X_3). The design is presented in Table 1. The equation model is shown in Eq. (3) (Dbik et al., 2022).

$$Z = \frac{X - X^0}{\Delta X} \tag{4}$$

RESULTS AND DISCUSSION

Removal Efficiency and Capacity Adsorption MB

Tables 2 outline the design matrix, its correlation with the experimental data outcomes, and the anticipated values for the model's response variable, removal efficiency. Utilizing Design Expert software, the forecasted response values were computed using a quadratic model. Through multiple regression analysis, the equation for MB removal efficiency was transformed into a statistical model based on experimental data, as depicted in Equation 5. This equation demonstrates the resultant relationship between the removal efficiency response variable and the independent variables of bed height, contact time, and flow rate. The optimization stages for the independent variables concerning the dependent variable are subsequently executed following Table 3.

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)	90	120	150
Flow rate, L/min (X_3)	2	4	6

This research uses process optimization analysis which is carried out by processing data using Design Expert 13 software to obtain response surface shapes and contour plots as well as 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 Eq. (4) (Elmoubarki et al., 2017).

Table 2. Box-Behnken based experimental design matrix for removal efficiency (%) and adsorption capacity (mg/g).

No	X ₁ (cm)	X ₂ (min)	X ₃ (L/ min)	Removal Efficiency %	Adsorption Capacity (mg/g)
1	12	90	6	90.422	0.132
2	16	90	4	90.367	0.097
3	12	90	2	74.583	0.109
4	16	120	2	98.658	0.106
5	8	150	4	95.535	0.215
6	12	120	4	64.193	0.093
7	16	120	6	77.245	0.083
8	12	120	4	64.193	0.093
9	8	90	4	50.035	0.112
10	12	120	4	64.193	0.093
11	16	150	4	94.877	0.102
12	8	120	2	93.332	0.210
13	12	120	4	64.193	0.093
14	8	120	6	98.161	0.221
15	12	150	2	93.571	0.136
16	12	150	6	86.409	0.126
17	12	120	4	64.193	0.093

Table 3. Parameters and boundary conditions.

Name	Goal	Lower Limit	Upper Limit
X ₁ :Bed Height	is equal	8	16
X ₂ :Contact time	is in range	90	150
X ₃ :Flowrate	is in range	2	6
Removal Efficiency	maximize	50.0355	98.6581
Adsorption Capacity	minimize	0.083659	0.221416

From the data presented in Table 2, it is evident that the highest achieved removal efficiency (%) (Y₁) stands at 98.658%, while the lowest absorption efficiency recorded is 50.035%. The maximum recorded adsorption capacity was 0.221 mg/g, while the minimum was 0.083 mg/g. The percentage error observed in the RSM, as detailed in Table 2, shows the highest error for response Y at 0.05%. The correlation equation of the adsorption independent variable are shown in Eqs (5) and (6).

$$Y_1 = 90.482 - 3.804X_1 - 0.042X_2 - 10.351X_3 - 0.085X_1X_2 - 0.820X_1X_3 - 0.095X_2X_3 + 0.7538X_1^2 + 0.007X_2^2 + 3.89980X_3^2 \quad (5)$$

$$Y_2 = 0.024 - 0.033X_1 + 0.002X_2 - 0.026X_3 - 0.0002X_1X_2 - 0.001X_1X_3 + 0.0001X_2X_3 + 0.0021X_1^2 + 4.947E-06X_2^2 + 0.006X_3^2 \quad (6)$$

Where: Y₁= Removal Efficiency, Y₂ = Adsorption Capacity, X₁ = bed height (cm), X₂ = contact time (minutes), X₃= flow rate (L/min).

Table 4 illustrates that the quadratic model exhibits an R² value close to 1 for predicting both removal efficiency and adsorption capacity as response variables, along with smaller standard deviations across all models. When the R² value approaches 1, it signifies a smaller standard deviation, indicates a better model for response prediction (Kutluay et al., 2020). Specifically, Table 4 displays that the quadratic model showcases a comparatively diminutive standard deviation of 9.37, a relatively high R² value of 0.844, and predictive value R² (-1.495), and an adjusted R² value of 0.643. Furthermore, analysis from the table indicates that the quadratic model for response Y₂ is not aliased, affirming its applicability in

Table 4. Regression optimization statistics for removal efficiency (%) model summary statistics.

Source	Std. Dev.	R^2	Adj. R^2	Pred R^2	
Linear	16.02	0.1543	-0.0409	-0.4553	
2FI	16.16	0.3380	-0.0592	-1.0914	
Quadratic	9.37	0.8440	0.6435	-1.4956	Suggested
Cubic	0.0000	1.0000	1.0000		Aliased

Table 5. Regression Optimization Statistics for adsorption capacity (mg/g)

Source	Std. Dev.	R^2	Adj. R^2	Pred R^2	
Linear	0.0332	0.5712	0.4723	0.2418	
2FI	0.0338	0.6597	0.4555	-0.1690	
Quadratic	0.0193	0.9221	0.8219	-0.2470	Suggested
Cubic	0.0000	1.0000	1.0000		Aliased

Table 6. Analysis of variance (ANOVA) data removal efficiency (%).

Source	Sum of squares	df	mean square	F-value	p-value	
Model	3327.79	9	369.75	4.21	0.0357	significant
X ₁ -Bed height	72.50	1	72.50	0.8253	0.3938	
X ₂ -Contact time	527.86	1	527.86	6.01	0.0440	
X ₃ -Flow rate	7.81	1	7.81	0.0889	0.7742	
X ₁ X ₂	420.05	1	420.05	4.78	0.0650	
X ₁ X ₃	172.16	1	172.16	1.96	0.2043	
X ₂ X ₃	132.25	1	132.25	1.51	0.2595	
X ₁ ²	612.03	1	612.03	6.97	0.0335	
X ₂ ²	175.39	1	175.39	2.00	0.2006	
X ₃ ²	1024.57	1	1024.57	11.66	0.0112	
Residual	614.97	7	87.85			
Lack of fit	614.97	3	204.99			
Pure error	0.0000	4	0.0000			
Cor total	3942.76	16				

describing the relationship between the Y response and interaction variables.

Similarly, Table 5 also illustrates the effectiveness of the quadratic model, showing a relatively small standard deviation of 0.0193, a moderately high R^2 value of 0.922, a predictive R^2 value of (-0.2470), and an adjusted R^2 value of 0.8219. Consistent with Table 4, examination of Table 5 confirms that the quadratic model for response Y_2 is suggested, supporting its suitability in describing the relationship between response Y and the interaction variables (Ghosh et al., 2019; Kutluay et al., 2020).

Table 6 shows the results of the analysis of variance (ANOVA) for the quadratic model of methylene blue removal efficiency. The ANOVA for the quadratic model in Table 4 shows that the probability values (Prob > F) for variables X_1^2 and X_3^2 are smaller than 0.05. This indicates that the quadratic model (2nd order), where variables X_1^2 and X_3^2 significantly affect the removal efficiency of methylene blue. The interaction variables X_1X_2 , X_1X_3 and X_2X_3 as well as the quadratic variables X_2^2 and X_3^2 were not significant. This indicates that statistically these variables have little influence on the methylene blue removal efficiency, but are still included in the model, given the possibility of these

Table 7. Analysis of variance (ANOVA) data adsorption capacity (mg/g).

Source	Sum of squares	df	mean square	F-value	p-value	
Model	0.0309	9	0.0170	9.20	0.0040	significant
X ₁ -Bed height	0.0170	1	0.0021	45.69	0.0003	
X ₂ -Contact time	0.0021	1	2.004E-08	5.62	0.0496	
X ₃ -Flow rate	2.004E-08	1	0.0024	0.0001	0.994	
X ₁ X ₂	0.0024	1	0.0003	641	0.0392	
X ₁ X ₃	0.0003	1	0.0003	0.7789	0.4068	
X ₂ X ₃	0.0003	1	0.0048	0.7596	0.4124	
X ₁ ²	0.0048	1	0.0001	12.94	0.0088	
X ₂ ²	0.0001	1	0.0033	0.2239	0.6505	
X ₃ ²	0.0033	1	0.0004	8.74	0.0212	
Residual	0.0026	7	0.0009			
Lack of fit	0.0026	3	0.0000			
Pure error	0.0000	4	0.0170			
Cor total	0.0335	16				

variables having a significant influence on adsorption (Mofarrah et al., 2014).

The Model F-value of 4.21 implies the model is significant. There is only a 3.57% chance that an F-value this large could occur due to noise. P-values less than 0.05 indicate model terms are significant. In this case X₂, X₁², X₃² are significant model terms. Values greater than 0.10 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.

Table 7 shows the results of the analysis of variance (ANOVA) for the quadratic model of methylene blue adsorption capacity. The ANOVA for the quadratic model in Table 4 shows that the probability values (Prob > F) for variables X₁ and X₂ are smaller than 0.05. This indicates that the quadratic model (2nd order), where variables X₁² and X₃² significantly affect the methylene adsorption capacity. The interaction variable X₁X₂, and the quadratic variables X₂² and X₃² appeared significant. This indicates that statistically these variables have little effect on the adsorption capacity of methylene blue, but are still included in the model, given the possibility of these variables having a significant effect on adsorption.

Figure 2 shows the contour plot graph and three-dimensional response surface graph describing the methylene blue absorption efficiency with variations in bed height, contact time, and flow

rate. The three-figure show that the surface response graph and contour plot have a maximum shape. Based on the figure, it can be seen that the response optimization of methylene blue absorption efficiency of 98.45% is at a bed height of 16 cm, contact time of 150 minutes and flow rate of 2 L/min. Optimum adsorption capacity of 0.115 mg/g (Dbik et al., 2022; Elmoubarki et al., 2017).

The higher the bed, the greater the concentration of methylene blue adsorbed, and reversely. This happens because the higher the bed, the greater the contact surface area between fly ash and methylene blue, so that the adsorption increases. Fly ash requires sufficient contact time in order to adsorb methylene blue optimally. Therefore, the longer the contact time, the more opportunity for the adsorbent, fly ash, to come into contact with the methylene blue bound within the pores of the FA. The parameter desirability function DF was used to determine the optimal operating conditions for the independent variables to achieve maximum methylene blue absorption efficiency, based on the research presented above. If the DF is close to one, then the target response is optimal. On consideration of the DF value and methylene blue absorption efficiency, solution number 1 was chosen to represent the optimal response variable (Azzouni et al., 2023).

From the optimization results in Table 8, it can be seen that the combination of independent variable levels that can provide the optimal

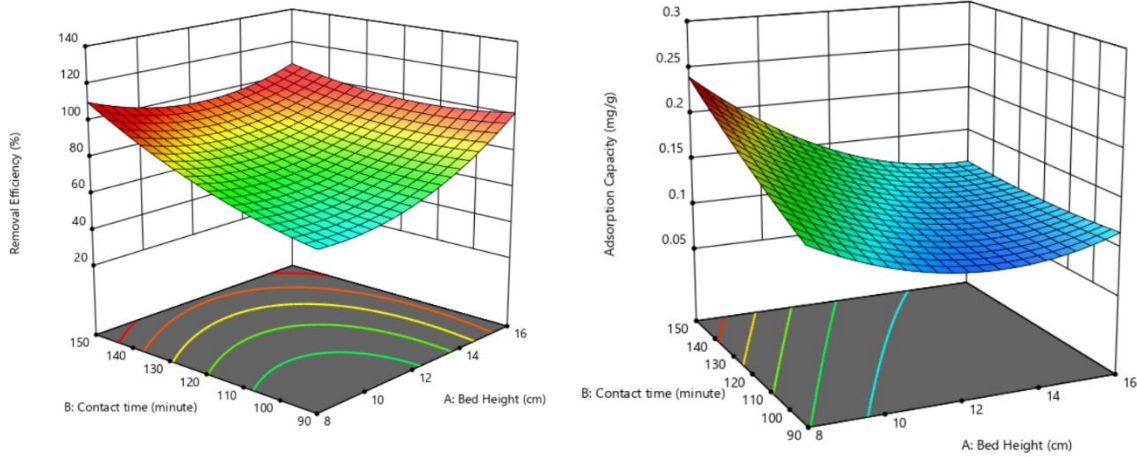


Figure 2. Response surface plots showing influences contact time, bed height and flow rate.

Table 8. Analysis of optimization with constraints on adsorption using FA adsorbent.

Alternative	X ₁ - Bed height	X ₂	X ₃	Removal Efficiency (%) Prediction	Removal Efficiency (%) Experiment	Adsorption capacity (mg/g) Prediction	Adsorption capacity (mg/g) Experiment	Desirability
1	16	150	2.00	99.139	98.45	0.111	0.115	0.945
2	16	145	2.00	97.706	96.20	0.109	0.111	0.895

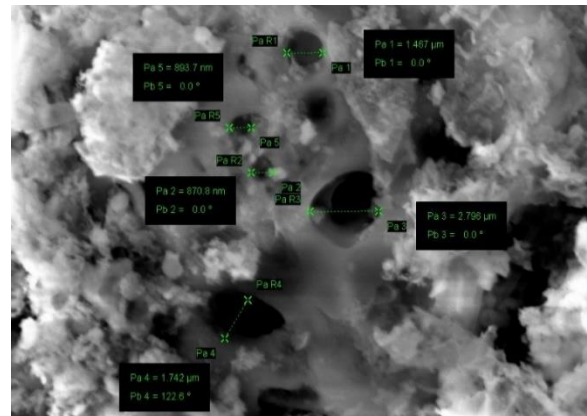
response value is at a bed height of 16 cm, a contact time of 150 minutes and a flow rate of 2 L/min. based on the DF value, the design expert software produces 2 solutions, as shown in Table 5. On consideration of the DF value and methylene blue absorption efficiency, solution number 1 was chosen to represent the optimal response variable (Azzouni et al., 2023).

Characterisation of adsorbent

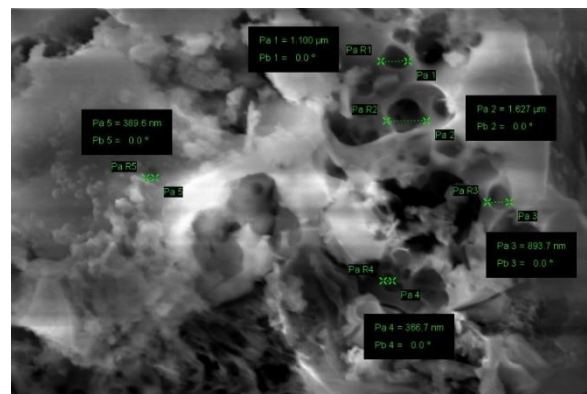
The adsorbent was characterized to determine its physical and chemical properties, the FA adsorbent was characterized using Scanning Electron Microscopy (SEM). SEM analysis determines the morphological structure of a substance (Sylvia et al., 2021).

The results of adsorbent characterization using SEM can be observed finer scaly surface structure and shape, equipped with EDX that can detect elements in the sample, and also the surface observed through electron conductors. The three types of adsorbent morphological structures were analyzed using SEM (Scanning Electron Microscopy) with a magnification of 1,000 times as shown in Figure 4.

The morphological structures of the three adsorbent samples determined by SEM analysis are distinct. Figure 4a demonstrates that the pore size



(a)



(b)

Figure 4. SEM Analysis Results (Scanning Electron Microscopy).

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

No	Element	Atom (%)	
		Before Adsorption	After Adsorption
1	Carbon	6.86	56.04
2	Oxygen	50.36	23.23
3	Magnesium	2.17	-
4	Aluminium	0.46	0.5
5	Silicon	23.81	0.5
6	Phosphorus	1.14	-
7	Pottasium	7.81	-
8	Calcium	6.49	1.72
9	Iron	0.90	-
10	Chlorine	-	8.41
11	Nitrogen	-	9.6

of activated FA is significantly larger and cleaner, spanning from 1 to 2 μm , making it suitable for use as an adsorbent. While Figure 4b depicts the pores of FA that has undergone an adsorption process so that the pores are covered with methylene blue, Figure 4a depicts the pores of FA that has not undergone an adsorption process. This is indicated by the finer adsorbent particles in the range of 396 to 893 nm. The greater the adsorbent's surface area, the greater its adsorption capacity (Chong et al., 2022)

Before and during the adsorption process, the components of the adsorbent material or atomic composition of the FA refuse adsorbent were determined by EDX analysis. The outcomes of the EDX analysis are displayed in Table 6 (Hamzah et al., 2019).

The results of EDX analysis on FA are shown in Table 6. Table 6 shows that the components of FA are elements C, O, Al, Ca, Mg, Si and K. The highest composition members are silicon and oxygen. After adsorption, chlorine, and nitrogen were found. While in the FA there were element N and Cl after the adsorption process which indicates that MB is absorbed in the FA because element N and Cl are found in methylene blue. Surface area BET of fly ash is $40.4954 \text{ m}^2/\text{g}$, pore volume of fly ash is $0.0019 \text{ cm}^3/\text{g}$.

CONCLUSION

The DF approach was used to optimise the process variables of bed height (8, 12, and 16 cm), contact time (90, 120, and 150 min) and flow rate (2, 4, and 6 L/min) on MB removal efficiency and adsorption capacity. The optimum condition was

obtained at a removal efficiency of 98.45% and adsorption capacity of 0.115 mg/g under fixed column conditions, i.e. at a bed height of 16 cm, contact time of 150 min, and flow rate of 2 L/min.

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