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Adsorption of Methylene Blue on Fix Bed Column Using Adsorbent from Tea Waste

Novi Sylvia*, Rozanna Dewi, Fitriani, Lukman Hakim, Nasrul Zainal Abidin, Rizki Ramadhan, Nur Asiah Indah Rahayu

Department of Chemical Engineering, Malikussaleh University, Lhokseumawe 24351, Indonesia

Corresponding Author Email: novi.sylvia@unimal.ac.id

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ABSTRACT

Printing and dyeing wastewater with a high salt content makes it difficult to process industrial wastewater, one of them is Methylene Blue (MB). MB waste is a dye commonly used in the textile industry which is harmful to the environment and threatens public health. MB removal can be done by adsorption method using tea waste adsorbent. This study aims to characterize and analyze the efficiency of tea waste in absorbing methylene blue using an adsorption column. The adsorption process was carried out with various concentrations of adsorbate (15 and 30 ppm), various bed heights (8, 12, and 16 cm), and various operating times (15, 30, 45, 60, 75, and 90 minutes), with the flow rate of 6 $L.min^{-1}$ in the column. The kinetic model data were analyzed using simple first order and pseudo second order. The results showed that the highest absorption efficiency of 99.48% was obtained at adsorbate concentration of 30 $mg.L^{-1}$, contact time of 75 minutes and bed height of 16 cm. The appropriate adsorption equilibrium mechanism is the Langmuir isotherm as evidenced by the correlation coefficient (R^2) of 0.998, while the resulting kinetic model is Pseudo Second Order, with R^2 of 0.999, qe of 1.933 $mg.g^{-1}$, and k2 of 19,947 mg^{-1} min^{-1}. This can be seen from the correlation value (R^2) which is close to 1.

1. INTRODUCTION

Processes in the industry always produce liquid waste as a by-product [1-5]. Generally, the liquid waste produced includes dyestuffs. Dyes are organic or inorganic compounds that give color to textiles, food, beverages, medicines, and cosmetics [6]. There are two types of dyes; natural and synthetic dyes, but synthetic dyes are more widely used [7, 8]. Natural dyes are found in nature, both from animals and plants, while synthetic dyes, also called artificial dyes, are usually processed by applying sulfuric acid or nitric acid, which are often contaminated by arsenic or other toxic heavy metals. Every year, nearly one million tons of synthetic dyes are produced worldwide to meet industry demand [9].

Industries, such as the textile industry, plastics, paper, paints, and other sectors, use synthetic dyes [10, 11]. Among all sectors, the textile industry produces the most waste, about 54% of the total dye waste [4, 12]. The resulting debris will be disposed of in the environment so that it can cause environmental pollution, especially in the aquatic environment.

Methylene Blue (MB) is a dye widely used in the textile industry. MB is a toxic aromatic hydrocarbon compound, a cationic dye with extreme adsorption power, and has the chemical formula of C16H18ClN3S. In the textile dyeing process, MB is usually only used for about 5%, while the remaining 95% is disposed of as waste [13-15]. Because it is non-biodegradable, MB is the leading waste in the water. MB is dangerous because it can cause mild irritation, dizziness, headache, increased sweating, nausea, and diarrhea [3]. Even at low concentrations, it will also harm aquatic ecosystems [12]. MB has a complex dye structure, is stable, and cannot be decomposed naturally. Based on PP No. 20 of 1990 concerning water pollution control, the maximum limit of MB in waters is 0.5 $mg.L^{-1}$. If this wastewater is not treated effectively, it can seriously impact the environment and threaten public health [4]. Therefore, MB dye wastewater treatment development is significant and urgently needed [16, 17].

Various methods have been widely used to remove MB dyestuffs, including coagulation, ion exchange, adsorption, electro flotation, and ozonation. However, forms other than adsorption have limitations in the process. Currently, the adsorption method is preferred because it is practical, simple in design, has low operational costs, the processing is relatively simple, and the efficiency is quite high. It can use alternative adsorbents from biomass and does not harm the environment [18].

Biomass is an ideal material for adsorbents due to its wide availability and low cost, especially biomass based on agricultural and forestry residues [19-28]. The use of biomass as an absorber of methylene blue dyes as alternative adsorbents is currently widely developed because it is more selective, effective, and cheap, such as bagasse [10], activated lignin- chitosan [7], rice husks [28], Balanites Aegyptiaca [29], and other materials containing cellulose.

One of the materials considered as adsorbents is tea waste [2, 9, 30, 31]. Tea waste is organic waste that comes fresh that has undergone shading. According to Ali et al. [32], tea waste leaves are leftovers from tea that have undergone a dissolving process with water so that the fibers left behind are more dominant in the form of insoluble fibers. Tea has been recognized as the second most consumed drink in the world,

and the annual yield of tea is estimated at more than 4 million tons [9, 24, 32]. Currently, the use of tea waste is still minimal, where it is used as a raw material for compost and particleboard.

Most of the tea waste is burned or thrown into landfills. Indonesia Bureau of Statistics reported that national tea production was 94.1 tons in 2021. This number increased by 20.3% from the previous year of 78.2 tons. It is certainly evitable the dreg produced is the same as tea production in Indonesia. Undoubtedly the amount of tea waste wasted is huge during consumption, leading to serious environmental problems. Tea waste is considered a potential ingredient of adsorbent. This is supported by the content of tea waste, such as cellulose compounds (37%), hemicellulose and lignin (14%), and polyphenols (25%). Cellulose contains functional groups such as hydroxyl, methyl, and carbonyl groups which can play a role in the spring dyestuffs in waste [1, 33].

Tea waste is a significant trend in biomass utilization. Tea waste-based adsorbent preparations have increased interest due to their characteristics involving surface structure, functional groups, contact surface area, and stable absorption effect.

For this reason, this study aims to utilize tea waste as adsorbents useful for absorbing MB in liquid waste. Studies on the absorption of MB using tea waste have been carried out, but they have been carried out in batches [4, 8, 9, 16, 26, 31, 33, 34].

In this study, the MB absorption process was carried out using a fixed-bed column. The MB solution, at a constant flow rate with variations in initial concentration, was passed through a column with variations in the height of the tea waste bed. Variations in contact time are also used as a consideration for adsorption efficiency and capacity. Adsorption isotherms and adsorption kinetics are also calculated, and characterization of tea waste is performed using characterization methods, such as scanning electron microscopy (SEM) and Fourier transform infrared (FTIR).

2. RESEARCH METHODS

2.1 Research tools and materials

Adsorbents were applied to acrylic pipes as adsorption columns with a diameter of 6.4 cm and a length of 30 cm, as shown in Figure 1 which was performed on one column. Additional equipment used was an oven (Memmert UN 30), a 20 mesh sieve (AMB No 20), desiccator, spatula, 500 mL beaker, 100 mL measuring cup, 1000 ml glass beaker, sample bottle, stirring rod, bucket, aluminum foil, measuring flask, funnel, analytical balance, stopwatch, Scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDX, CARL ZEISS type EVO MA 10), and Fourier Transform Infra-Red (FT-IR, IR Prestige 21) UV-Vis Spectrophotometer (UV-1800) spectrophotometer (UV-1800). The materials used were the dregs from several coffee shops in Lhokseumawe, aquadest, 0.1 N HCl solution, and methylene blue.

2.2 Research procedure

2.2.1 Making tea waste as adsorbent

The tea waste was obtained from a coffee shop in Lhokseumawe, then washed with running water at a temperature of 70℃ until the filtrate was clear. Furthermore, the tea waste was soaked with water at a temperature of 100℃ for ±20 minutes, then filtered. The tea waste was then dried at a temperature of 105℃ until a constant mass was obtained; then, the tea waste was activated.

The activation process was carried out using 250 grams of dried tea waste which then put into a 1000 ml beaker glass and HCl 0 solution. 1 N of 1000 ml of dreg was wholly submerged for ±24 hours. Waste of soaked tea was then filtered and rinsed with aquadest until a neutral pH was obtained. Then the tea waste was dried in the oven at 105℃.

2.2.2 Making of methylene blue solution

Adsorbate was prepared using methylene blue with a concentration of 15 and 30 ppm. The making of methylene blue solution for concentrations of 15 ppm and 30 ppm was by dissolving 15 mg of methylene blue powder into 1000 ml of aquadest with a measuring flask of 1000 ml. As for the concentration of 30 ppm, by dissolving 30 mg of methylene blue powder into 1000 ml of aquadest with a measuring flask of 1000 ml. Each operation requires a solution of 3 liters. Therefore, 45 mg of methylene blue was dissolved in 3 liters of aquadest. Likewise, for methylene blue of 30 ppm, 90 mg of methylene blue was dissolved into 3 liters of aquadest.

2.2.3 Adsorption process

The adsorption process used columns with a diameter of 6.4 cm and height of 50 cm made of acrylic pipes. In the initial stage, the activated adsorbent was placed in an adsorption column with a bed height of 8 cm (44.76 gr), 12 cm (69.18 gr), and 16 cm (93.54 gr). Furthermore, MB was flowed into a column with a flow rate of 6 L/min, and MB concentrations were varied (15 mg/L and 30mg/L) in a down flow, and contact times were varied by 15; 30; 45; 60; 75; 90 mins, as shown in Figure 1. After that, the efficiency and capacity of adsorption with Eqns. (1) and (2) were carried out. The adsorption sample was then analyzed with a UV-Vis spectrometer.

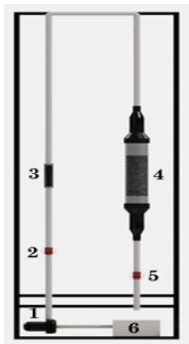


Figure 1. Adsorption column

Information:

1. Pump
2. Inlet Valve
3. Flow Meter
4. Fixed bed column
5. Outlet Valve
6. Source

2.2.4 Data analysis methods

The data analysis was carried out by measuring absorption efficiency and capacity. The initial data was obtained from

samples that had gone through the adsorption process, and then the adsorption result samples were analyzed with a UV-Vis spectrometer. The absorbance of the adsorbate was determined with a spectrophotometer wavelength of 665 nm. Analysis of adsorbent characteristics was carried out using FTIR and SEM / EDX tools on tea waste before activation, after activation, and after the adsorption process. The calculation of efficiency and adsorption capacity was done using Eqns. (1) and (2) [35].

$$\text{efficiency} = \frac{Co_{MB} - Ce_{MB}}{Co_{MB}} \text{ x } 100\% \quad (1)$$

$$qe = \frac{Flowrate\,(Co_{MB} - Ce_{MB})}{m} \quad (2)$$

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

2.2.5 Adsorption kinetics analysis

Based on the experimental conditions above, the flow rate of 6 $L.min^{-1}$ MB solution with an initial concentration of 15 $mg.L^{-1}$ flowed in columns with contact time variations of 15; 30; 45; 60; 75; 90 min with a tea waste bed height of 8 cm (44.76 gr). Samples were taken according to contact time for analysis using a UV-Vis spectrometer at 665 nm. Then, MB adsorbed on the tea waste was calculated. Different kinetic models were applied to fit the adsorption process. The data obtained were analyzed using Simple First order and Pseudo-second-order kinetic models. The sorption kinetics is of great importance in evaluating the efficiency of sorption, exploring the mechanisms and rates of MB adsorption on the surface of tea waste. Simple First order and Pseudo-second-order kinetic models are expressed in Eqns. (3) and (4) [4, 36, 37].

$$C_t = C_0 e^{k_1 t} \quad (3)$$

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \quad (4)$$

where, q_t ($mg.g^{-1}$) is the number of MB adsorbed at time t, k_1 (min^{-1}) and k_2 ($mg^{-1}\,min^{-1}$) are the rate constants of simple first order dan Pseudo-second-order, respectively. OriginPro software (version 2021, OriginLab) was used to plot data on individual isotherm and kinetic models. The data plot aims to perform nonlinear analysis fittings.

2.2.6 Adsorption isotherm analysis

Based on the experimental conditions above, the flow rate of 6 $L.min^{-1}$ MB solution with an initial concentration of 15 $mg.L^{-1}$ flowed in a column with a contact time variation of 15; 30; 45; 60; 75; 90 min with a tea waste bed height of 8 cm (44.76 gr). Samples were taken according to contact time for analysis using a UV-Vis spectrometer at a wavelength of 665 mn. Then, the number of MB adsorbed on the tea waste was calculated. Different isotherm models were used to describe the process.

Isotherm adsorption is an adsorption process that takes place at a fixed temperature. The most common and widely used adsorption isotherm models in adsorption are the Langmuir and Freundlich isotherm models [38-40] shown in Eqns. (5) and (6).

$$q = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (5)$$

$$q = k_f C_e^{\frac{1}{n}} \quad (6)$$

where, q is the number of MB adsorbed per unit weight of tea waste at equilibrium, and C_e is the concentration of unabsorbed MB in effluent at equilibrium ($mg.L^{-1}$). k_L is the Langmuir equilibrium constant, qm is the number of MB adsorbed with monolayer coverage, k_F is the Freundlich constant, and n is the Freundlich exponent.

3. RESULTS AND DISCUSSION

3.1 Adsorbent activation

The activation process is a treatment of dreg, which aims to enlarge pores by breaking hydrocarbons or oxidizing surface molecules so that the tea waste undergoes changes in both physical and chemical properties. The formed modifications are to the surface area in the adsorption power. The greater the adsorbent surface area, the more the adsorption ability will increase [11]. The activation carried out in this study uses an acidic solution that can release impurities or metal ions such as Ca^{2+}, K^{+}, and Mg^{2+}, which partially cover the pores of the adsorbent, so that the pores of the adsorbent have a clean and wide surface. The active group contained in the adsorbent is more reactive when binding to dyestuffs.

Several solutions can be used as activators in the activation process, such as H_2SO_4 [10], H_3PO_4 [20], and NaOH [27]. Activation of tea waste with HCl solution was chosen because HCl solution can dissolve impurities better than other activators so that more pores are formed, and the adsorbate absorption process is maximized. After being activated using an acidic solution, tea waste was drained to reduce the moisture content. The higher water content will reduce the quality of the tea waste adsorbent because it will cover the pores of the adsorbent so that it can reduce absorption.

On the contrary, the lower the moisture content in activated carbon, the more places in the adsorbent pores can be occupied by adsorbate so that adsorption can take place optimally [37].

3.2 Adsorption efficiency

Adsorption efficiency is the ability of adsorbents to absorb adsorbates [41]. The purpose of testing the absorption capacity of tea waste against methylene blue is to determine the ability of tea waste to adsorb methylene blue. The effect of contact time and bed height on adsorption efficiency can be seen in Figure 2.

Based on Figure 2, it can be seen that contact time dramatically affects absorption efficiency. The longer the contact time, the greater the absorption efficiency. This is because the longer the contact time, the more collisions occur, so absorption takes place faster. The adsorption process also has a maximum contact time so that the adsorbent will experience saturation, resulting in decreased methylene blue absorption at a contact time of 70 minutes. The results of this study are those reported [15] that adsorption continues to run until the maximum adsorption is achieved.

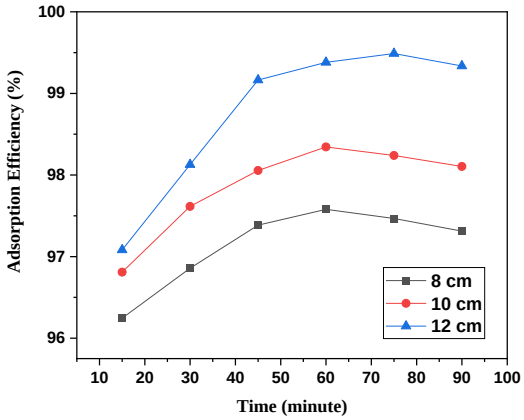


Figure 2. Correlation between contact time and MB adsorption efficiency graph at different bed heights

3.3 Adsorption capacity

The adsorption capacity states the number of adsorbates capable of accumulating on the surface of the adsorbent [4]. Figure 3 shows the analysis results on various variations of methylene blue concentration, tea waste mass, and contact time. The greater the contact time, the greater the value of its absorption capacity against methylene blue. This is because, with the increase in contact time, the contact between adsorbents and methylene blue is getting longer, which results in methylene blue being absorbed more and more.

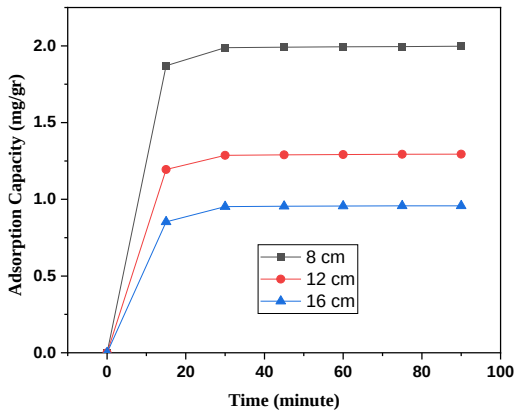


Figure 3. Correlation between contact time and MB adsorption capacity graph at different bed heights

The maximum adsorption capacity was obtained at a bed height of 8 cm and a contact time of 90 minutes. Similarly, in the adsorbent mass, the greater the dreg of tea, the greater the adsorption capacity against methylene blue.

3.4 Effect of adsorbate concentration

This discussion was taken on the high backside of the adsorbent and at the same operating time differing only methylene blue concentrations. The concentration of methylene blue used was 15 and 30 ppm. The adsorbent bed height was 8 cm with a contact time of 15, 30, 45, 60, 75, and 90 minutes [22]. The relationship between absorption content efficiency and adsorption capacity with methylene blue concentrations can be seen in Figures 4 and 5.

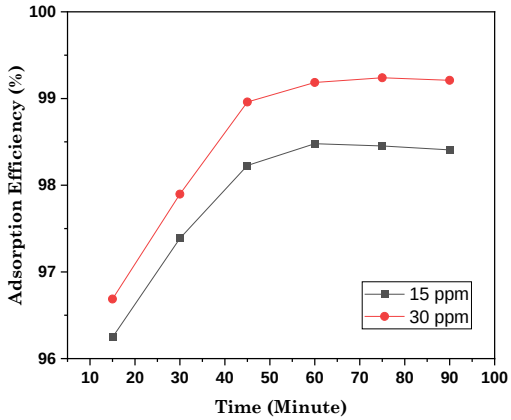


Figure 4. Correlation between contact time and adsorption efficiency graph at different MB concentration

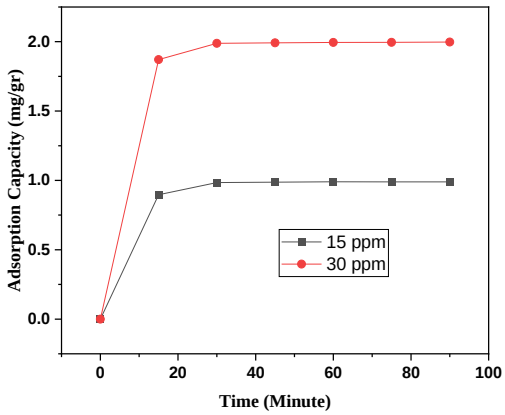


Figure 5. Correlation between contact time and MB adsorption capacity graph at different MB concentration

Figures 4 and 5 show that at the same bed height and operating time, the difference in concentration dramatically affects the absorption efficiency and adsorption capacity. From the graph, it can be concluded that the higher the concentration of methylene blue, the greater the value of efficiency absorption and adsorption capacity produced.

3.5 Isotherm adsorption

Langmuir isotherm defines that the maximum adsorbent capacity occurs due to a single layer (monolayer) of adsorbate on the surface of the adsorbent. Meanwhile, Freundlich Isotherm describes adsorption as a type of physics where adsorption occurs in several layers, and the bond is not strong [40]. The occurrence of Langmuir or Freundlich isotherm can be seen from the correlation value (R^2) generated in the isotherm equation model [37].

Figure 6 is a patterned curve of Langmuir and Freundlich isotherm carried out by plotting between Ce and qe; the results of the curve plot from the data obtained show that the Langmuir isotherm graph is close to the experimental data. Table 1 shows that the tests of the Langmuir and Freundlich equations have different linearization. Based on these linear values, it can be concluded that the column adsorption process on tea waste follows the Langmuir isotherm model.

Table 1. Langmuir and Freundlich isotherm parameters for MB adsorption in tea waste

Type	Parameters	Unit	Equation non-Linear
Langmuir			
q_m	1.942	mg.g^{-1}	$q = \frac{q_m k_L C_e}{1 + k_L C_e}$
k_L	429.19	-	
R^2	0.998	-	
Freundlich			
k_F	1.901	-	$q = k_f C_e^{\frac{1}{n}}$
1/n	0.0303	-	
R^2	0.956	-	

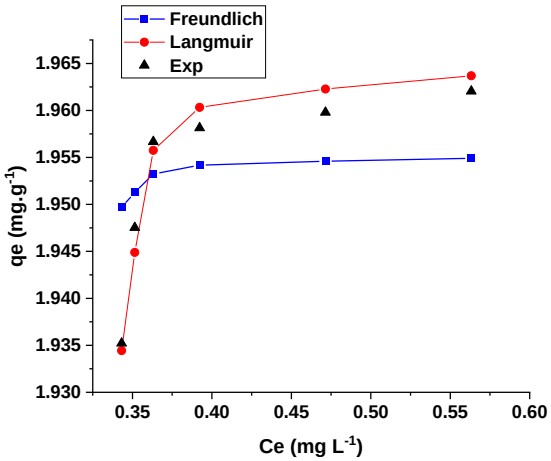


Figure 6. Isotherm adsorption curve

This is evidenced by linearization and a correlation value (R^2) close to 1. This statement corresponds to studies [42, 43] who reported that the corresponding adsorption isotherm was shown from a correlation value (R^2) close to 1.

3.6 Adsorption kinetics

Kinetics studies are time-dependent factors for determining the equilibrium time against specific adsorbents, which will help in the design process of industrial wastewater treatment [32, 41]. This kinetics process aims to see the rate of the adsorption process carried out by the adsorbent against the adsorbate and to see the suitability between the experimental data and the correlation value of the model. Data suitability testing was carried out using several kinetic models, including the Simple First Order (SFO) and the Pseudo Second Order Model (PSO) [38]. The Kinetics model data is shown in Table 2.

The kinetic analysis of the Simple First Order *(*SFO) model is a linear plot between the C_t log and the time (minutes). Based on the SFO equation, the value of the coefficient of toleration (R^2) was 0.877, the adsorption rate constant (k_1) was 0.006 min^{-1}, and C_0 was 0.574 mg. L^{-1}.

Analysis of adsorption kinetics using the Pseudo Second Order Model (PSO) model is performed by creating a linear plot between t/qt and time (minutes). Based on the Pseudo Second Order Model (PSO) equation, it was obtained that the value of the coefficient of toleration (R^2) was 0.999, and for the constant, the adsorption rate (k_2) was 19.947 mg^{-1} min^{-1}, and qe was 1.933 mg.g^{-1}. Based on the correlation coefficient obtained, it can be concluded that the adsorption process using tea waste adsorbent meets the Pseudo Second Order kinetic model, so that the process that occurs in the process of adjusting where the assumed kinetic rate is chemisorption. MB adsorption studies using black tea waste were performed in batches following the Pseudo Second Order kinetic model [9, 34]. This conclusion is based on the value of the coefficient of toleration (R^2) which approached the value of 1. Aurich et al. [23] stated that the kinetics model k estimates the behavior of adsorption during the course of the adsorption process.

Table 2. Kinetic model parameter for MB adsorption of 15 mg/L in tea waste

Kinetic models	Parameters	Unit	Equation non-Linear
SFO			
k_1	0.006	min^{-1}	$C_t = C_0 e^{k_1 t}$
C_0	0.574	mg.L^{-1}	
R^2	0.877		
PSO			
k_2	19.947	mg^{-1}	$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$
q_e	1.933	min^{-1}	
R^2	0.999	mg.g^{-1}	

3.7 Characteristics of using FT-IR

Adsorbent samples of tea waste before chemical activation using HCl, after activation using HCl, and after the adsorption process were analyzed using the FTIR method. FT-IR analysis aims to determine the functional groups present in adsorbents [22]. Qualitative testing of functional groups was carried out by interfacing the absorption peaks from the infrared spectrum, and the resulting range can be seen in Figure 7.

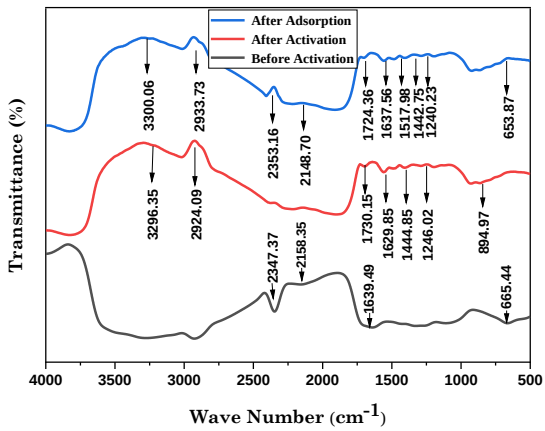


Figure 7. FT-IR spectrum on tea waste adsorbent

Figure 7 shows the difference between adsorbents before and after activation using HCl. Adsorbents of tea waste that have been activated and the contained functional groups undergo modification [19]. Of all the FTIR spectra that appear after activation, there was an uptake of several wave numbers. The presence of an absorption band at wave number 3296 cm^{-1} is the focal vibration of the hydroxyl group (-OH). The peaks at 2924 cm^{-1} were caused by the symmetrical and asymmetrical C-H aliphatic group. Peaks in 1730 and 1629.8 cm^{-1} were caused by asymmetric strains C=O, aromatic C=C, and C=O/C=C stretching of the amide group. Cluster function was shifted after MB adsorption on tea waste. The main subdistrict at the apex of the spectrum is shown for functional groups such as –OH (3296→3 300.6), C–H (2924→ 2933.7), C=O (1730→ 1724), C=C (1629.8→ 1637). The changes are also shown in Table 3. Therefore, it can be concluded that MB

interacts with functional groups in tea waste and involves the formation of complexes. Adsorption of dye MB is shown at 2933.7 cm^{-1}. These results correspond to the peak of adsorption reported by other researchers conducting MB absorption bands in the range of 2500-3000 cm^{-1} [3]. Thus, tea waste can be used as an adsorbent because of its function group characteristics and presence in the nature, which is very easy to find.

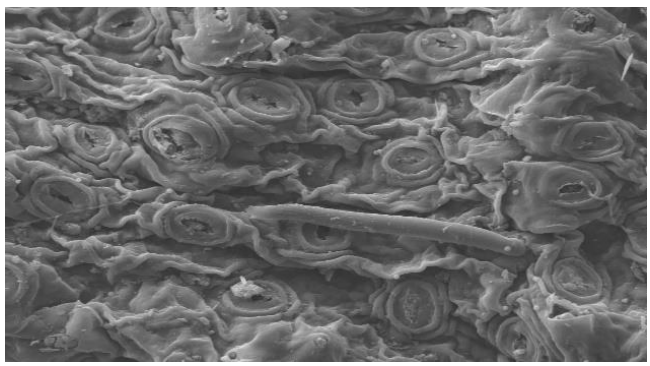
Table 3. Functional groups before adsorption and after adsorption

Tea waste		Assignment
Before adsorption	**After adsorption**	
3296.35	3300.6	Bonded–OH
2924.09	2933.73	Aliphatic C–H
1730	1724	C=O stretching
1629.8	1637	Aromatic C=C
1246.02	1240.03	$–SO_3$ stretching

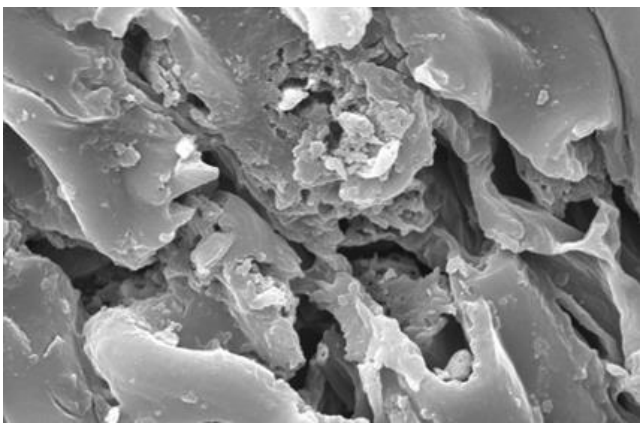
3.8 Analyzes SEM /EDX

The adsorbents were characterized to find their physical and chemical properties. Tea waste adsorbents were characterized using Scanning Electron Microscopy (SEM). SEM analysis determines a substance's morphological structure [38].

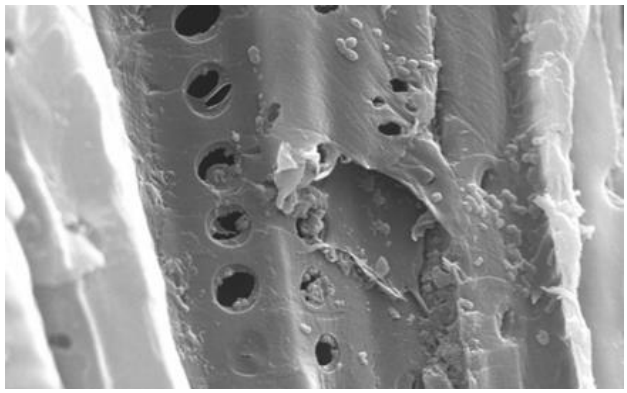
The results of absorbent characterization using SEM can be observed in the structure and shape of the surface that scales more smoothly, equipped with EDX, which can detect elements in the sample, and also the surface observed through electron conductors [9]. The three types of adsorbent morphological structure were analyzed using SEM (Scanning Electron Microscopy) with 1,000 magnifications, as shown in Figure 8.



a. Tea waste before activation



b. Tea waste after activation



c. Tea waste after adsorption process

Figure 8. SEM analysis results (Scanning electron microscopy)

The SEM analysis results on the three adsorbent samples had different morphological structures. Figure 8a shows the pores of the tea waste before activation, which still has many impurities, with a minor average pore diameter of 10.154 μm. However, Figure 8b shows the tea waste that has been activated, the pore size of the tea waste is much bigger and cleaner, which ranges from 14 to 20 μm, so it is good to be used as an adsorbent. Meanwhile, Figure 8 c shows the pores of the tea waste that have undergone an adsorption process so that the pores are covered by methylene blue. This is demonstrated by the increasingly smaller adsorbent pores ranging from 2 to 4 μm. The larger the adsorbent surface area, the better the adsorption ability [32].

Tea waste adsorbents show wider absorbent pores after chemical activation than physically activated adsorbents alone, and adsorbents have larger functional groups after adsorption. This indicates the large number of particles from methylene blue absorbed. This shows that chemical activation enlarges pores in adsorbent absorption, and the adsorption process also takes place quite well.

EDX analysis was carried out to determine the components of the adsorbent material or atomic composition in the tea waste adsorbent before activation, after activation, and during the adsorption process. The results of the EDX Analysis can be seen in Table 4.

Table 4. SEM EDX adsorbent analysis results before activation, after activation, and after adsorption

No	Element	Atom (%)		
		Before Activation	**After Activation**	**After Adsorption**
1	Carbon	75.62	76.04	59.21
2	Oxygen	23.41	23.23	38.08
3	Aluminum	0.26	-	0.5
4	Calcium	0.71	0.5	1.72
5	Copper	-	-	0.46
6	Chlorine	-	0.23	-
7	Nitrogen			7.6

The results of the EDX analysis on tea waste are shown in Table 4. Table 4 shows that the components of tea waste are C, O, Al, Ca, Cu, and Cl elements. The members of the highest composition are carbon and oxygen. After activation, a chlorine element was found as the tea waste is activated using HCl, and adsorbent washing after the activation process was not optimal resulting in the presence of chlorine elements. While in the tea waste, there was an element N after the

adsorption process which indicates that MB is absorbed in the tea dregs, because the N element is present in methylene blue.

4. CONCLUSION

Based on the data and results obtained, it can be concluded that the more the initial concentration of methylene blue is used, the greater the efficiency value and adsorption capacity. The greater the mass of an adsorbent, the greater the efficiency value and absorption capacity of methylene blue. Based on the best conditions, adsorbent operation time used with an adsorbate concentration of 15 $mg.L^{-1}$ at bed heights of 8, 12, and 16 cm were 45 minutes, 60 minutes, and 75 minutes with absorption efficiency of 98.47%, 99.34%, and 99.48%, respectively. The isotherm model obtained in this study is Langmuir, while the kinetic model is Pseudo Second Order model. Therefore, tea waste can be used to absorb MB.

For further research, it is recommended to optimize the flow rate, contact time, and bed height so that in the future we can design columns with process variables to obtain optimum adsorption results.

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REFERENCES

[1] Abeer I.A., Ali J.J., Zainab Z.I. (2020). New application of eco-friendly biosorbent giant reed for removal of reactive dyes from water followed by sustainable path for recycling the dyes-loaded sludge in concrete mixes. Journal of Material Cycles and Waste Management, 4: 1036-1046. https://doi.org/10.1007/s10163-020-00998-4

[2] Amjad, M., Hussain, S., Javed, K., Rehman Khan, A., Shahjahan, M. (2020). The sources, toxicity, determination of heavy metals and their removal techniques from drinking water. World Journal of Applied Chemistry, 5(2): 34-40. https://doi.org/10.11648/j.wjac.20200502.14

[3] Li, G., Zhu, W., Zhang, C., Zhang, S., Liu, L., Zhu, L., Zhao, W. (2016). Effect of a magnetic field on the adsorptive removal of methylene blue onto wheat straw biochar. Bioresource Technology, 206: 16-22. https://doi.org/10.1016/j.biortech.2015.12.087

[4] Liu, L., Fan, S., Li, Y. (2018). Removal behavior of methylene blue from aqueous solution by tea waste: kinetics, isotherms, and mechanism. International Journal of Environmental Research and Public Health, 15(7): 1321. https://doi.org/10.3390/ijerph15071321

[5] Grace Pavithra, K., Jaikumar, V., Kumar, P.S., SundarRajan, P.S. (2019). A review on cleaner strategies for chromium industrial wastewater: Present research and future perspective. Journal of Cleaner Production, 228: 580-593. https://doi.org/10.1016/J.JCLEPRO.2019.04.117

[6] Alrubaiea, J.F., Latteiff, F.A., Mahdi, J.M., Atiya, M.A., Majdi, H.S. (2021). Desalination of agricultural wastewater by solar adsorption system: A numerical study. International Journal of Renewable Energy Development, 10(4): 901-910. https://doi.org/10.14710/ijred.2021.38798

[7] Albadarin, A.B., Collins, M.N., Naushad, M., Shirazian, S., Walker, G., Mangwandi, C. (2017). Activated lignin-chitosan extruded blends for efficient adsorption of methylene blue. Chemical Engineering Journal, 307: 264–272. https://doi.org/10.1016/j.cej.2016.08.089

[8] Nasuha, N., Hameed, B.H. (2011). Adsorption of methylene blue from aqueous solution onto naoh-modified rejected tea. Chemical Engineering Journal, 166(2): 783-786. https://doi.org/10.1016/j.cej.2010.11.012

[9] El-Azazy M., El-Shafie, A.S., Al-Shaikh Yousef, B. (2021). Green tea waste as an efficient adsorbent for methylene blue: Structuring of a novel adsorbent using full factorial design. Molecules. 26(20): 6138. https://doi.org/10.3390/molecules26206138

[10] Nurhasni, N., Harahap, S., Fathoni, A., Hendrawati, H. (2021). Synthesis of Adsorbent from Bagasse for Methylene Blue Adsorption. Jurnal Kimia Valensi, 7(2): 188-195. https://doi.org/10.15408/jkv.v7i2.20916

[11] Panigrahi, T., Santhoskumar, A.U. (2020). Adsorption process for reducing heavy metals in Textile Industrial Effluent with low-cost adsorbents. Progress in Chemical and Biochemical Research, 3(2): 135-139. https://doi.org/10.33945/sami/pcbr.2020.2.7

[12] Daneshvar, E., Vazirzadeh, A., Niazi, A., Kousha, M., Naushad, M., Bhatnagar, A. (2017). Desorption of Methylene blue dye from brown macroalga: Effects of operating parameters, isotherm study, and kinetic modeling. Journal of Cleaner Production, 152: 443-453. https://doi.org/10.1016/j.jclepro.2017.03.119

[13] Altenor, S., Carene, B., Emmanuel, E., Lambert, J., Ehrhardt, J.J., Gaspard, S. (2008). Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation. Journal Hazardous Material, 165: 1029-1039. https://doi.org/10.1016/j.jhazmat.2008.10.133

[14] Rakesh, K.G., Deb, P.R., Sanjoy, D., Avisek, T., Ipsita, D. (2019). Optimization of process parameters for methylene blue removal by jute stick using response surface methodology. Environmental Progress & Sustainable Energy, 5: 1314. https://doi.org/10.1002/ep.13146

[15] Rashtbari, Y., Afshin, S., Hamzezadeh, A., Abazari, M., Poureshgh, Y., Fazlzadeh, M. (2020). Application of powdered activated carbon coated with zinc oxide nanoparticles prepared using a green synthesis in removal of reactive blue 19 and reactive black-5: Adsorption isotherm and kinetic models. Desalination and Water Treatment, 179: 354-367. https://doi.org/10.5004/dwt.2020.25020

[16] Santosa, S.J., Kunarti, E.S., Aprilita, N.H., Wulandari, B., Bawani, D.N. (2019). Sorption mechanism and performance of peat soil humin for Methylene blue and p-Nitrophenol. Indonesian Journal of Chemistry, 19(1): 198-210. https://doi.org/10.22146/ijc.33635

[17] Sud, D., Mahajan, G., Kaur, M.P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—A review. Bioresource Technology, 99: 6017-6027. https://doi.org/10.1016/j.biortech.2007.11.064

[18] Vargas, A.M.M., Cazetta, A.L., Kunita, M.H., Silva, T.L., Almeida, V.C. (2011). Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): Study of adsorption isotherms and kinetic models. Chemical Engineering Journal, 168: 722-730. https://doi.org/10.1016/j.cej.2011.01.067

[19] Rusdiarso, B., Basuki, R., Santosa, S.J. (2016). Evaluation of Lagergren kinetics equation by using novel kinetics expression of sorption of Zn2+ onto horse dung humic acid (HD-HA). Indonesian Journal of Chemistry, 16(3): 338-346. https://doi.org/10.22146/ijc.1158

[20] Shamsuddin, M.S., Yusoff, N.R.N., Sulaiman, M.A. (2016). Synthesis and characterization of activated carbon produced from kenaf core fiber using H3PO4 activation. Procedia Chemistry, 19: 558-565. https://doi.org/10.1016/j.proche.2016.03.053

[21] Shao, Y., Zhou, L., Bao, C., Ma, J., Liu, M., Wang, F. (2016). Magnetic responsive metal–organic frameworks nanosphere with core–shell structure for highly efficientremoval of methylene blue. Chemical Engineering Journal, 283: 1127-1136. https://doi.org/10.1016/j.cej.2015.08.051

[22] Ahmad, M.A., Eusoff, M.A., Oladoye, P.O., Adegoke, K.A., Bello, O.S. (2021). Optimization and batch studies on adsorption of Methylene blue dye using pomegranate fruit peel based adsorbent. Chemical Data Collections, 32: 100676. https://doi.org/10.1016/j.cdc.2021.100676

[23] Aurich, A., Hofmann, J., Oltrogge, R., Wecks, M., Gläser, R., Blömer, L., Mauersberger, S., Müller, R. A., Sicker, D., Giannis, A. (2017). Improved isolation of microbiologically produced (2R,3S)-Isocitric acid by adsorption on activated carbon and recovery with methanol. Organic Process Research and Development, 21(6): 866-870. https://doi.org/10.1021/acs.oprd.7b00090

[24] Indira, D., Das, B., Bhawsar, H., Moumita, S., Johnson, E.M., Balasubramanian, P., Jayabalan, R. (2018) Investigation on the production of bioethanol from black tea waste biomass in the seawater-based system, Bioresource Technology Reports, 4: 209-213. https://doi.org/10.1016/j.biteb.2018.11.003

[25] Yin, W.Q., Dai, D., Hou, J.H., Wang, S.S., Wu, X.G., Wang, X.Z. (2019). Hierarchical porous biochar-based functional materials derived from biowaste for Pb(II) removal. Applied Surface Science, 465: 297-302 https://doi.org/10.1016/j.apsusc.2018.09.010

[26] Hu, Y., Zhang, Y., Hu, Y., Chu, C.-Y., Lin, J., Gao, S., Lin, D., Lu, J., Xiang, P., Ko, T.H. (2019). Application of wasted oolong tea as a biosorbent for the adsorption of methylene blue. Journal of Chemistry, 2019: 1-10. https://doi.org/10.1155/2019/4980965

[27] Twang, S.M., Zaini, M.A.A., Salleh, L.M., Yunus, M.A.C., Naushad, M., Zaini, M.A.A., Salleh, L.M., Azizi, M., Yunus, C., Naushad, M. (2017). Potassium hydroxide-treated palm kernel shell sorbents for the efficient removal of methyl violet dye. Desalination and Water Treatment, 84: 262-270. https://doi.org/10.5004/dwt.2017.21206

[28] Mobolaji, M.J., Olatunde, S.D., Joshua, N.E. (2021). Sequestration of hazardous dyes from aqueous solution using raw and modified agricultural waste. Adsorption Science & Technology, 2021: 1-21. https://doi.org/10.1155/2021/6297451

[29] Ibrahim, A.A., Salma, M.H., Fatima, H.A., Mohamed, Y.N., Fatima, A.A. (2021). Removal of methylene blue using Balanites Aegyptiaca bark powder as a low-cost and eco-friendly biosorbent. Research Journal of Textile and Apparel, 1: 1-17. https://doi.org/10.1108/rjta-07-2020-0075

[30] Azapagic, A., Bore, J., Cheserek, B., Kamunya, S., Elbehri, A. (2016). The global warming potential of production and consumption of Kenyan tea, Journal of Cleaner Production, 112: 4031-4040. https://doi.org/10.1016/j.jclepro.2015.07.029

[31] Hussain, S., Saima, K.P.A., Hassan, T., Brat, P. (2018). Tea waste as a novel adsorbent: a review. Applied Water Science, 8(6): 1-16. https://doi.org/10.1007/s13201-018-0824-5

[32] Ali, A., Siddique, M., Chen, W., Han, Z., Khan, R., Bilal, M., Waheed, U., Shahzadi, I. (2022). Promising low-cost adsorbent from waste green tea leaves for phenol removal in aqueous solution. International Journal of Environmental Research and Public Health, 19(11): 6396. https://doi.org/10.3390/ijerph19116396

[33] Khalil, U., Bilal Shakoor, M., Ali, S., Rizwan, M., Nasser Alyemeni, M., Wijaya, L. (2020). Adsorption-reduction performance of tea waste and rice husk biochars for Cr(VI) elimination from wastewater. Journal of Saudi Chemical Society, 24(11): 799-810. https://doi.org/10.1016/j.jscs.2020.07.001

[34] Lin, D., Wu, F., Hu, Y., Zhang, T., Liu, C., Hu, Q., Xue, Z., Han, H., Ko, T.H. (2020). Adsorption of dye by waste black tea powder: parameters, kinetic, equilibrium, and thermodynamic studies. Journal of Chemistry, 2020: 1-13 https://doi.org/10.1155/2020/5431046

[35] Chen, W.S., Chen, Y.C., Lee, C.H. (2022). Modified activated carbon for copper ion removal from aqueous solution. Processes, 10(1): 150 https://doi.org/10.3390/pr10010150

[36] Chu, K.H. (2021). Fixed bed adsorption of chromium and the Weibull function. Journal of Hazardous Materials Letters, 2: 100022. https://doi.org/10.1016/j.hazl.2021.100022

[37] Zhai, Q.Z. (2020). Studies of adsorption of crystal violet from aqueous solution by nano mesocellular foam silica: process equilibrium, kinetic, isotherm, and thermodynamic studies. Water Science and Technology, 10: 2092-2108. https://doi.org/10.2166/wst.2020.267

[38] Sylvia, N., Fitriani, F., Dewi, R., Mulyawan, R., Muslim, A., Husin, H., Yunardi, Y., Reza, M. (2021). Characterization of bottom ash waste adsorbent from palm oil plant boiler burning process to adsorb carbon dioxide in a fixed bed column. Indonesian Journal of Chemistry, 21(6): 1454-1462 https://doi.org/10.22146/ijc.66509

[39] Mendiretta, M.M., Mudliar, S.L., Bharati, A.V. (2022). Physico-chemical key parameters, freundlich and langmuir isotherm, rate constant studies on the removal of divalent nickel using delonix regia fruit pod as low cost bioadsorbent. IOP Conference Series: Materials Science and Engineering, 1221(1): 012024. https://doi.org/10.1088/1757-899x/1221/1/012024

[40] N'diaye, A.D., Kankou, M.S.A., Hammouti, B., Nandiyanto, A.B.D., Al Husaeni, D.F. (2022). A review of biomaterial as an adsorbent: From the bibliometric literature review, the definition of dyes and adsorbent, the adsorption phenomena and isotherm models, factors affecting the adsorption process, to the use of typha

species waste as adsorbent. Communications in Science and Technology, 7(2): 140-153. https://doi.org/10.21924/cst.7.2.2022.977

[41] Bommavaram, K., Bhattacharjee, A., Yadav, D., Andra, N., Pandey, P., Ibrahim, H. (2020). Tea residue as a bio-sorbent for the treatment of textile industry effluents. International Journal of Environmental Science and Technology, 7: 3351-3364. https://doi.org/10.1007/s13762-020-02628-w

[42] Manyangadze, M., Chikuruwo, N.H.M., Narsaiah, T.B., Chakra, C.S., Radhakumari, M., Danha, G. (2020). Enhancing adsorption capacity of nano-adsorbents via surface modification: A review. South African Journal of Chemical Engineering, 31: 25-32. https://doi.org/10.1016/j.sajce.2019.11.003

[43] Dada, A.O., Olalekan, A.P., Olatunya, A.M., Dada, O. (2012). Langmuir, freundlich, temkin, and dubinin–radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry, 3(1): 38-45. https://doi.org/10.9790/5736-0313845