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Optimization of Dyes Pollutant Adsorption Using KOH-Activated Eucalyptus Leaf Waste with Isotherm Adsorption Model

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ABSTRACT

As with the rest of the production, the Batik industry hurts people's lives due to dyes. When discharged into the river, this dye will directly cause environmental pollution, one of which is the disruption of photosynthesis of aquatic plants and can cause disease for living things. Therefore, it is necessary to make efforts to overcome this. This study aims to determine the effect of adsorbent time variation and dose variation on methylene blue and malachite green adsorption. Adsorption is the absorption of solution molecules that occur on an adsorbent surface. The adsorbent used is Eucalyptus distillation leaf waste with KOH activation treatment using the Freundlich and Langmuir adsorption isotherm model. The measurement method uses UV-Vis spectrophotometry to analyze methylene blue and malachite green levels at the maximum wavelength. The results showed that the best % removal to adsorb methylene blue was 52.84% and malachite green 88.03% at a dose of 0.2 gram, and the optimum contact time to adsorb malachite green and methylene blue was 20 minutes. The adsorption Model in this study followed the Isotherm of Freundlich and Langmuir adsorption on malachite green with R^2 *of 0.872 and 0.612 for non-activation and 0.964 and 0.095 for KOH activation, while methylene blue obtained 0.636 and 0.143 for non-activation and 0.850 and 0.545 for KOH activation. Based on the study results, it was concluded that the distillation of Eucalyptus leaf waste is more effective in adsorbing malachite green.*

1. Introduction

Scientific and technological progress pushes humanity to meet its needs. One of the human needs is clothing, which triggered the establishment of the textile industry. The textile industry is an industry that processes raw cotton materials into the fabric, which, in the production process, produces liquid waste containing hazardous and toxic materials that can interfere with biological processes and cause other damage [1]. Liquid waste produced by the textile industry contains dyes consisting of acid dyes, azo dyes, and alkaline dyes that are thick in color so that they kill aquatic organisms and cause smell [2]. Wastewater from textile, paint and dye manufacturing, and metal plating discharged untreated into rivers can drastically reduce water quality, eventually detrimental to the survival of life on earth [3]. The Textile dyes often used in industry are methylene blue and malachite green dyestuffs. Methylene blue is a thiazine class dye which includes cationic dyes. Direct contact with the skin causes several health problems, including cyanosis, irritation, and digestive tract disorders [4], [5]. When dissolved in water, methylene blue dye will ionize into $C_{16}H_{18}N_3S^+$ and Cl^- and can interact physically and chemically [6]. The second textile dye that is often used is green malacite. Green malachite is a toxic dye that can cause mammal tumors when consuming fish containing this dye. The maximum concentration of green malachite in water is 0.01 ppm [7]. Methylene blue and malachite green, when entering the river body, will interfere with the photosynthesis of algae [8]. Adsorption of dyes from the environment is important to the ecosystem, and developing effective and cost-effective technologies is an ongoing effort [9]. The adsorption process is an absorption technique for capturing contaminants from solutions by placing them precisely on the surface of the adsorbent [10]. *Eucalyptus* oil mill is an essential oil industry that uses distillation to extract the oil in the leaves and produce waste. This distillation waste is only used to fuel the furnace and cause piles of waste that pollute the environment. *According to their structure, Eucalyptus leaves contain cellulose, which* can be used to adsorb dyes. Some previous studies using biomaterials to adsorb methylene blue and malachite green [11] utilize cocoa fruit to adsorb green malachite at a maximum wavelength of 617 nm, utilize activated carbon and activated zeolite [12]. The longer the contact time, the more the substance is adsorbed. Previous research [6] utilized a mixture of rice husks to adsorb methylene blue with a concentration of 20 ppm to 0.23 ppm. Harahap reported that using activated bagasse can open the pores of the adsorbent so that it can adsorb more. Previous research [13] reported that NaOH-activated fly ash can adsorb methylene blue concentration of 0.3 g/L at a dose of 0.2 gram with a percent removal of 100%. Based on the above conclusions, the danger of textile dyes is that they pose a toxic hazard if not treated properly; in this study, leaf waste Eucalyptus distillation is used to adsorb methylene blue and malachite green.

2. Research Methodology

2.1. Materials

This study uses several tools, including a blender, sieve 60 mesh, measuring flask, Erlenmeyer, beaker glass, measuring cup, hot plate, magnetic stirrer, analytical balance, MS-1 Intelligent Shaker, spectrophotometer UV-Visible Genesys 10S, and others. The materials used are malachite green, methylene blue, aquades, KOH solution, and *Eucalyptus* leaf waste size 60 mesh.

2.2. Preparation and Treatment of *Eucalyptus* Leaf Waste

The adsorbent was used in this study as leaf waste refining eucalyptus. The adsorbent smoothes the waste leaves of Eucalyptus distillation using a blender; then, the adsorbent is sifted using a sieve size 60 mesh. Then, activation treatment to adsorbent using KOH solution. Meni can do the activation process of the adsorbent and then give activation treatment to the adsorbent using a KOH solution. The adsorbent activation process can be done by weighing 20 grams of Eucalyptus leaf distillation waste, which is then mixed with a KOH solution of 250 mL and allowed to stand for 24 hours. After 24 hours, the solution is washed using aquades to a neutral pH. The activated adsorbent is then dried, pulverized, and ready for use.

2.3. Calibration Curve

This study's calibration curve was determined by making a mother solution of malachite green and methylene blue with a concentration of 1 g/L. The solution is diluted from 10-100 ppm by 100 mL. Then, the absorbance measurement was carried out using a UV-visible spectrophotometer Genesys 10S with a wavelength of 617 nm for green malacite and 670 nm for methylene blue. After determining the absorbance value of the solution, the concentration of each solution will be obtained by using the equation:

$$y = mx + c \quad (1)$$

2.4. Absorbance Values of Malachite Green and Methylene Blue with Variation Adsorbent Dose

This study used KOH-activated and KOH-inactivated *Eucalyptus* leaf waste adsorbent. Weighed absorbent nonactivation and KOH activation of 0.01, 0.05, 0.1, 0.15, and 0.2 grams. The absorbent is mixed with 50 mL of green malacite solution at 20 ppm, then in a shaker at 250 rpm for 10 minutes. Then, malachite green absorbance was measured using a UV-visible spectrophotometer Genesys 10s. The same treatment was also carried out for the adsorbate in a 30 ppm methylene blue solution. Based on the optimum absorbance values, the best results are shown at doses of 0.05 and 0.1 grams, and then the dose will be used for research with variations in contact time.

2.5. Absorbance Values of Malachite Green and Methylene Blue with Time Variation

This study used KOH-activated and KOH-inactivated *Eucalyptus* leaf waste adsorbent. Non-activating and KOH-activating adsorbents weighed 0.05 and 0.1 grams, respectively. The adsorbent was mixed with 50 mL of malachite green solution 20 ppm, then in a shaker at a speed of 250 rpm with variations in contact time for 10, 15, and 20 minutes. Then, measured malachite green absorbance using a UV-visible spectrophotometer Genesys 10S and recorded the results. The same treatment was carried out for methylene blue 30 ppm.

2.6. Isotherm Adsorption Model

Adsorption is a widely applied separation process, especially in environmental improvement, because of its low cost and high efficiency. Adsorption isotherm models can provide information about the mechanism of the adsorption process, which is important for adsorption system design. Adsorption isotherms are classified into empirical adsorption isotherms, chemisorption isotherms, physical adsorption isotherms, and ion exchange models [14].

In this paper, the adsorption isotherm model is a single-layer chemical model and a multi-layer physical model with KOH-activated and KOH-inactivated *Eucalyptus* leaf waste adsorbent with a dose of 0.05 grams. The adsorbent is mixed with 50 mL of green malachite solution concentration 10-50 ppm, then in a shaker at a speed of 250 rpm with variations in contact time for 10 minutes. Then, measured malachite green absorbance using a UV-visible spectrophotometer Genesys 10S and recorded the results. The same treatment is carried out for adsorbate in methylene blue solution with a 10-50 ppm concentration.

2.7. Absorption Efficiency

The absorption efficiency of the adsorbent to the solution can be calculated using equation [10]. C_O is the solution concentration before adsorption (ppm), and Ce is after adsorption (ppm).

$$\%removal = \frac{Co - Ce}{Co} \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Preparation and Treatment of *Eucalyptus* Leaf Waste

Preparation for this *Eucalyptus* leaf waste by reducing the leaf area. this is intended to increase the absorbency of the dye. This study used 60 mesh *Eucalyptus* leaf waste adsorbent. the goal is to expand the surface of the adsorbent so that the absorption produced is greater [11]. The adsorbent was given two treatments, non-activation and activation with KOH. Activation treatment of adsorbents to enlarge pores and remove impurities in the adsorbent [15].

3.2. Calibration Curve

This study used two different dyes, malachite green, and methylene blue. the first step is to make malachite green dye with a concentration of 1 ppm. The wavelength is 616,5 nm for malachite green. The mother liquor used in this study was 1 g/L. The solution was diluted to 10-100 ppm by 100 mL. Then, the solution was measured in absorbance using a UV-visible spectrophotometer Genesys 10S. The results of determining the calibration curve can be seen in Fig.1. It is also done for methylene blue, which is the same as malachite green, and the wavelength for methylene blue is 670 nm.

Fig. 1. (a) and (b), the graph is per Lambert-Beer law, which states that the greater the concentration of malachite green and methylene blue, the higher the absorbance value produced. The result of equation y = 12.445 x -0.0014 and R^2 is 0.9973 for malachite green solution, while methylene blue solution produces equation y =11.76 x + 0.0298 and R^2 is 0.999. Where y in the equation is the absorbance, x is the concentration of malachite green and methylene blue. The resulting regression result (R^2) is close to 1, so it can be said that the graph is linear [15].

3.3. Absorbance Value of Malachite Green and Methylene Blue with Adsorbent Variation Dose

This study used two dye solutions, malachite green 20 ppm and methylene blue 30 ppm, and adsorbents with two treatments of non-activation and activation of KOH. Variations of adsorbent dose used are 0.01, 0.05, 0.1, 0.15, and 0.2 grams with a time of 10 minutes. The measurement results in this study can be seen in Fig. 2., Table 1 and Table 2.

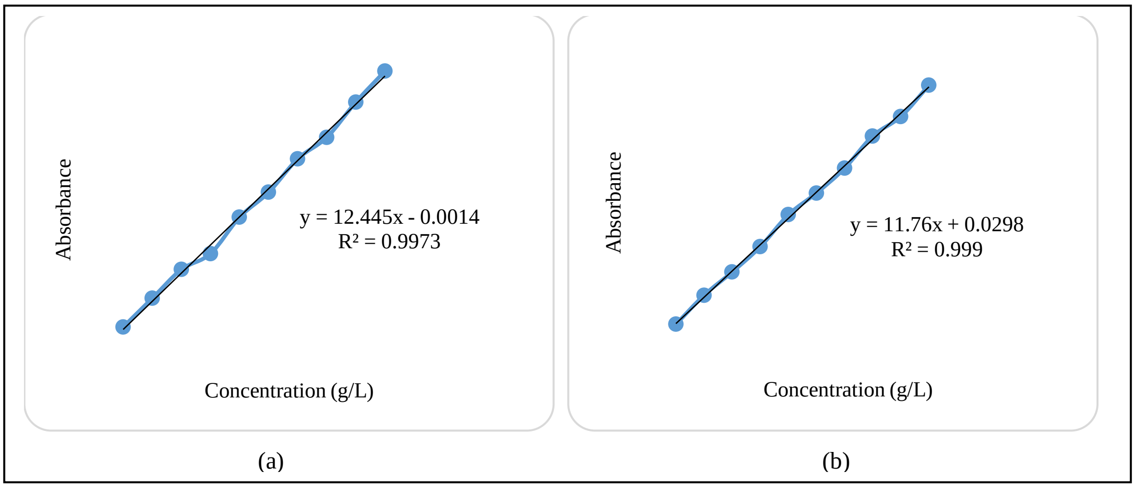

Fig. 1. (a) Calibration curve of malachite green solution; (b) Calibration curve of methylene blue solution

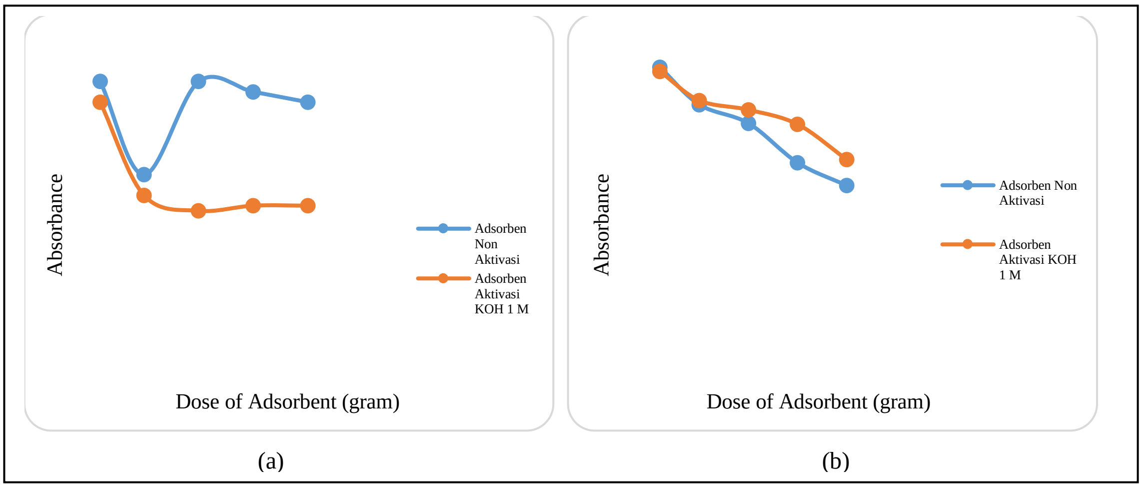

Fig. 2. (a) Adsorbance value of malachite green solution (b) Adsorbance value of methylene blue solution

Table 1. Correlation of Adsorbent Dose Variation to Absorption Efficiency of Malachite Green

Dose of Adsorbent (gram)	% Removal for Non-Activated Adsorbent	% Removal for KOH Activated Adsorbent
0.01	78.8872	80.4116
0.05	85.7470	87.2713
0.1	78.8872	88.4146
0.15	79.6494	88.0335
0.2	80.4116	88.0335

Table 2. Correlation of Adsorbent Dose Variation to Absorption Efficiency of Methylene Blue

Dose of Adsorbent (gram)	% Removal for Non-Activated Adsorbent	% Removal for KOH Activated Adsorbent
0.01	27.2832	28.4319
0.05	37.6221	36.4733
0.1	42.7915	39.0580
0.15	53.7048	43.0787
0.2	60.0230	52.8432

Fig. 2. (a) and (b) show that the more adsorbent dose used, the lower the absorbance value. Because the more adsorbent the dose is, the greater the surface area for absorption. Tables 1 and 2 show the % removal for KOH activation adsorbent at a dose of 0.2 gram in malachite green solution of 88.03%

and in methylene blue of 52.84%. The results showed that KOH activation adsorbent with a dose of 0.2 gram has the greatest absorption. This KOH is a strong base that can destroy compounds that can close the pores on the adsorbent.

3.4. Absorbance Value of Malachite Green and Methylene Blue with Time Variation

This study used two dye solutions, malachite green 20 ppm and methylene blue 30 ppm, and adsorbents with two treatments: non-activation and activation of KOH. The dose of adsorbent used is 0.05 and 0.1 grams with a variation of contact time of 10, 15, and 20 minutes. The measurement results can be shown in Fig. 3. and Fig. 4.

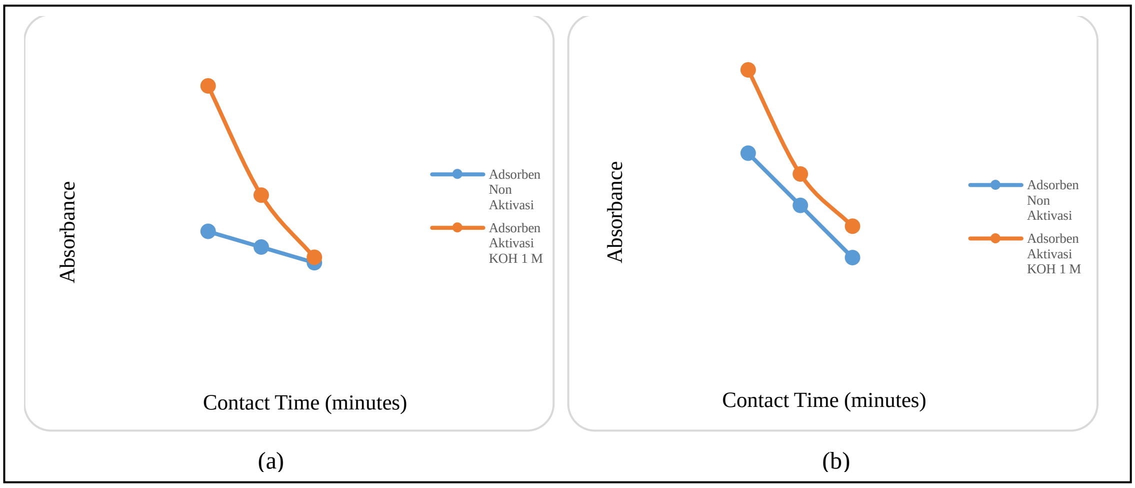

Fig. 3. (a) variation of contact time of 0.05 gram dose in malachite green solution; (b) variation of contact time of 0.1 gram dose in malachite green solution

Fig. 3. (a) and (b) show that the longer the contact time, the absorbance value produced is getting down. This result occurs because the longer the contact time used, the more malachite green is absorbed [9]. Increased absorption can be achieved by the activation process using a KOH solution. This is because KOH is a strong base that can destroy the impurity compounds that cover the pores. After the adsorbent is activated, it can increase the number of pores, increasing the adsorbent absorption of the malachite green solution. The optimum contact time for adsorbing malachite green substances is 20 minutes.

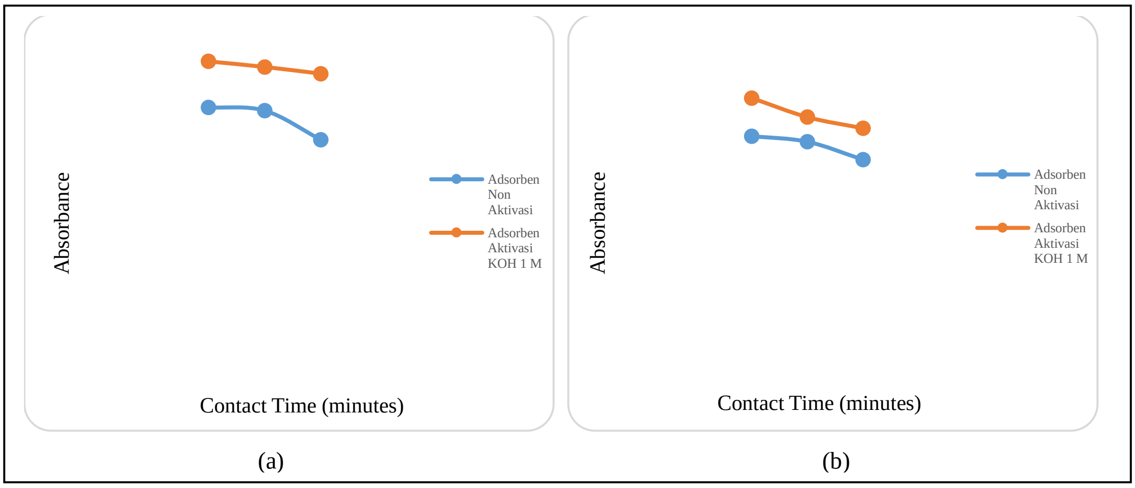

Fig. 4. (a) variation of 0.05 gram dose contact time in methylene blue solution; (b) variation of 0.1 gram dose contact time in methylene blue solution

Fig. 4. (a) and (b) show that the longer the contact time, the absorbance value produced is getting down. This result occurs because the longer the contact time, the more methylene blue is absorbed [9]. Increasing adsorbent absorption can be done through an activation process using a KOH solution. This happens because KOH is a strong base that can destroy the impurities that cover the pores, so after the adsorbent is activated, it can increase the number of pores that can increase the adsorbent

absorption of methylene blue solution. The optimum contact time for adsorbing the Blue methylen substance is 20 minutes.

3.5. Adsorption Isotherm Model

1) Adsorption Isotherm Model on Malachite Green

The adsorption isotherm model is a graph that describes the adsorbate distribution on the adsorbent's surface at a constant temperature and pressure. The adsorption isotherms used in this study are Langmuir and Freundlich adsorption isotherms. Langmuir and Freundlich's adsorption isotherms are two main methods that are very important to overcome environmental improvement and adsorption techniques. The following is the adsorption isotherm of malachite green solution:

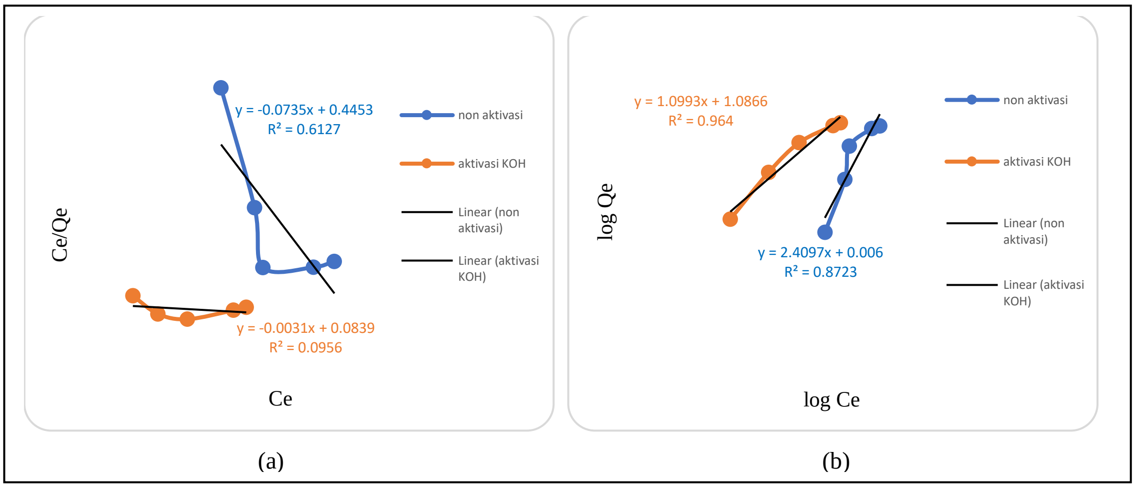

Fig. 5. (a) Isotherm Langmuir Curva (b) Isotherm Freundlich Curva

Fig. 5. (a) and (b) is an adsorption isotherm modeling to adsorb green malasite. Based on the graph, R2 of 0.613 and 0.872 were obtained for the non-activation adsorbent. In contrast, the KOH activation adsorbent has R^2 of 0.096 and 0.964, and it can be concluded that the activated and non-activation adsorbent following the modeling of Freundlich adsorption isotherm where the following data are obtained:

Table 3. Freundlich Adsorption Isotherm on Malachite Green

Adsorbent	Freundlich Constant			
	1/n	***n***	***ln k***	***K***
Non Activated	2.409	0.4151	0.006	1.006
KOH Activated (1 M)	1.099	0.909	1.086	2.962

2) Adsorption Isotherm Model on Methylene Blue

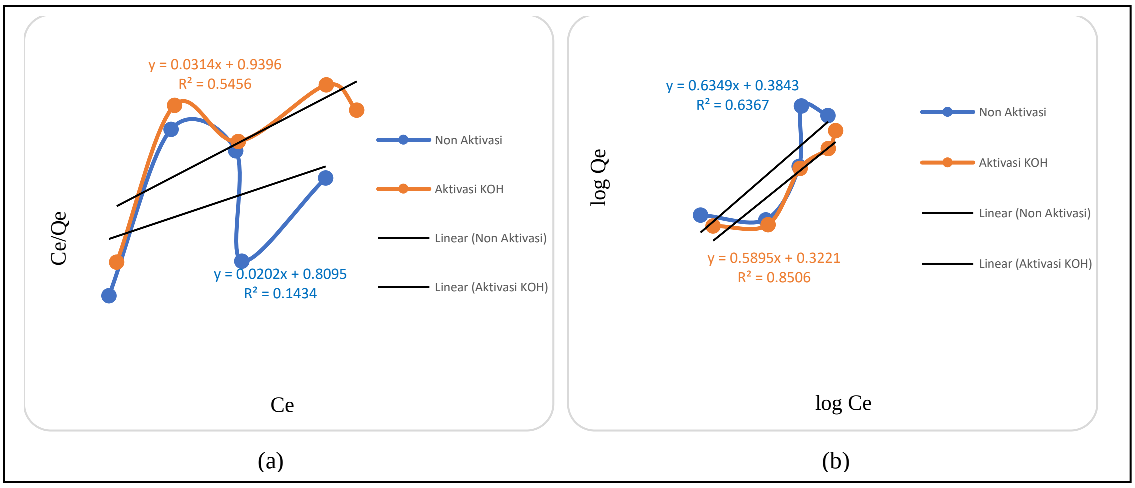

Fig. 6. (a) Isotherm Langmuir Curva (b) Isotherm Freundlich Curva

Fig. 6. (a) and (b) an adsorption isotherm modeling to adsorb Methylene Blue. Based on the graph obtained, R^2 is 0.143 and 0.637 for the non-activation adsorbent, while the KOH activation adsorbent has R^2 of 0.546 and 0.851; it can be concluded that the activated and non-activation adsorbent follow the modeling of adsorption Isotherm Freundlich where obtained the following data

Table 4. Freundlich Adsorption Isotherm on Methylene Blue

Adsorbent	**Freundlich Constant**			
	1/n	***n***	***ln k***	***K***
Non Activated	0.634	1.577	0.384	1.4681
KOH Activated (1 M)	0.589	1.6977	0.322	1.379

Freundlich adsorption isotherm modeling describes the adsorption of adsorbate on the surface of *Eucalyptus* leaf waste adsorbent, where adsorption is formed by more than one adsorbate layer (multilayer). In this type of isotherm, the binding energy of each site is different, and absorption occurs physically [15].

4. Conclusion

The research results show that the more adsorbent the dose, the greater the absorption power. The greatest absorption was shown in the adsorbent of KOH activation *Eucalyptus* distillation leaf waste at 0.2 grams of 88.03% for malachite green and 52.84% for methylene blue. The longer the contact time given, the resulting absorbance value decreases. This is because the absorption capacity produced is greater. The optimum contact time for adsorbing malachite green and methylene blue dyes is 20 minutes. The adsorption isotherm model that satisfies is the Freundlich adsorption isotherm. Based on the research, it can be concluded that E*ucalyptus* leaf distillation waste adsorbent effectively absorbs malachite green.

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