

DETERMINATION OF THE ADSORPTION KINETICS FOR ADSORPTION METHYLENE BLUE DYE WITH C-4-HYDROXY- 3- METHOXYPHENYLCALIX[4]RESO RCINARENE

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**DETERMINATION OF THE ADSORPTION KINETICS FOR ADSORPTION
METHYLENE BLUE DYE WITH C-4-HYDROXY-3-
METHOXYPHENYLCALIX[4]RESORCINARENE**

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ABSTRACT

Abstract. Adsorption kinetics is part of adsorption and discusses the adsorption rate of an adsorbent on the adsorbate. Adsorption kinetics has an equation to determine the rate constant of adsorption, namely the pseudo-first order and pseudo-second order. In this study, methylene blue was adsorbed using a C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene adsorbent. The aim of this study to determine the effect of process parameters (concentration, pH, and processing time) on the process adsorption, with the Langmuir and Freundlich adsorption isotherm model approach, and to determine the adsorption kinetics of methylene blue with CHMFKR. Ten mL of methylene blue solution with various concentrations of 5, 6, 8, 10, and 11 ppm with a solution pH of 7 was added to as much as 0.001 gram of CHMFKR adsorbent and stirred at 600 rpm for 40 minutes. The solution was measured, and its absorbance was measured using the UV-Vis Spectrophotometer. The results show that the adsorption kinetics follow pseudo second order with an adsorption rate of 0.7217 ± 0.4 g/mg.s. The adsorption isotherm follows the Langmuir equation, and the maximum adsorption amount is 114.94 ± 2.04 mg/g.

Keyword: methylene blue, C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene, adsorption

INTRODUCTION

According to the World Bank in 2017, the development of the textile industry has increased significantly. Indonesia has grown from 149.88 trillion in 2010 to 151.77 trillion. This is due to the increase in the number of textile companies from 2880 to 2980, or about 3.5%. Reactive dyes are often used in the textile industry due to their different colors and textures. This increase affects the amount of waste generated. The waste from the textile industry, in particular, contains dangerous dyes and is therefore considered a potential source of pollution (Ngapa and Ika, 2020). Disposal of such dye-contaminated wastewater from the textile industry is a major problem (Karmakar *et al.*, 2019).

Synthetic dyes are commonly used in textile dyeing processes. This is because synthetic dyes are larger and easier to use than natural dyes and have different colors. More than 700.000 tons of textile industry waste contain synthetic dyes (Adegoke and Bello, 2015). Dyes contained in textile wastewater have a complicated molecular structure and are difficult to remove by conventional wastewater treatment. They are fairly light and thermally stable and resist biodegradation, a challenge for traditional physicochemical and biological treatment methods (Sanghi and Verma, 2013).

However, the contents of the waste must be treated before they can be removed from the environment. This is because waste generally contains substances that are harmful to living organisms. One of them is the content of low-degradable organic compounds that are difficult to decompose, such as methylene blue dye in waste. The dye methylene blue is widely used in the textile industry. Methylene blue is part of the cationic dye group, which has a very strong adsorption power (Velásquez-Silva *et al.*, 2017). In fact, only 5% was used in the methylene blue staining process, while the remaining 95% was wasted (Rizqi and Purnomo, 2014).

An easy method that can be used to treat textile waste is the adsorption method. Adsorption is a surface phenomenon due to the accumulation of chemical species at the solid-liquid surface boundary (Hadayani *et al.*, 2015). The adsorption process is one of the most frequently used separation and purification processes, where adsorption occurs through the formation of physical or chemical bonds between a porous solid medium and a mixture of liquid or gaseous multi-component fluids. Taking into account the equilibrium data and adsorption properties of both the adsorbent and the adsorbate, the adsorption isotherm model can explain the mechanism of interaction between the adsorbent and the adsorbate at a constant temperature. Therefore, understanding the modelling of equilibrium data is a very

important way to predict the adsorption mechanism of various adsorption systems (Al-Ghouti and Da'ana, 2020).

An exponential kinetics model has been proposed to model the adsorption kinetics at the solid-solution interface. This new equation is compared to the pseudo-first-order (PFO) and pseudo-second-order (PSO) equations, two well-known parametric models. It has been shown that new and pseudo-quadratic models of homogeneous solid surfaces can be used based on data points (t, q) numerically generated using the statistical velocity theory equations of homogeneous surfaces (Haerifar and Azizian, 2013).

Supramolecular chemistry is an interdisciplinary scientific discipline that covers the chemical, physical, and biological properties of species that are more complex than the molecule itself. Calixarenes/Calixresorcinarene is a macrocyclic compound composed of "n" phenol/resorcinol units bound by a methylene bridge. These macrocycles are often used for molecular recognition. Therefore, different changes can be made at both the bottom and top, allowing the construction of well-defined multi-valued buildings (Eddaif et al., 2019a). Calixresorcinarene and calixarenes are widely used as receptors for cations, anions, and even neutral molecules (Eddaif et al., 2019b). Calix[4]resorcinarene is a calixarene derivative. Calix[4]resorcinarene can be synthesized from resorcinol or its derivative compounds and various types of aldehydes, both aliphatic and aromatic aldehydes (Handayani, *et al.* 2016a; Handayani et al., 2022). Calix[4]resorcinarene derivatives can be used as adsorbents. Several studies using Calix[4]resorcinarene as an adsorbent used C-Cinnamal-Calix[4]resorcinarene as an adsorbent for methanil yellow, with an optimum contact time of 150 minutes and an absorption capacity of 2.1375 mg/g (Etika et al., 2018). Another application of Calix[4]resorcinarene as an adsorbent is the adsorption of remazol yellow FG using chitosan-linked P-T-Butylcalix[4]Arene by Handayani, *et al.*, (2016b), adsorption of sodium dodecylbenzene sulfonate (DBS) by C-3,4-di-methoxyphenylcalix[4]resorcinarene triphenylphosphonium chloride by Wulandari (2018), and adsorption of reactive blue (RB-19) dye using Calix[4]arene-based adsorbent by Junejo *et al.*, (2019).

Based on this, it is necessary to research to determine the adsorption kinetics of the derivate Calix[4]resorcinarene as an adsorbent for methylene blue dye with varying pH and contact time.

EXPERIMENTAL SECTION

Tools and Materials

The tools used include a set of reflux equipment, 250 mL beaker, dropper, 100 mL measuring cup, watch glass, stirring rod, A&E Lab Spectrophotometer, funnel, test tube, vial bottle, magnetic stirrer, hotplate, 100 measuring flask. mL, O Hauss analytical balance, oven, Buchner funnel, thermometer, pH meter, FTIR Spectrophotometer 8201 PC Shimadzu, and ¹H-NMR Jeol JNM-ECZ500R / S1 500.1599 MHz.

Pro-analyst chemicals such as vanillin, resorcinol, hydrochloric acid, sodium hydroxide, ethanol, and methylene blue were purchased from Merck.

C-4-hydroxy-3-methoxyphenylcalyx[4]resorcinene Synthesis (Handayani et al., 2020a)

HMFKR was synthesized using the method described by (Handayani et al., 2020a). Vanillin (0.04 mol) was dissolved in 50 mL ethanol, then mixed with resorcinol (0.04 mol), and 1 mL hydrochloric acid was added. The solution was refluxed at 78°C for 24 hours. The solution was washed with distilled water and filtered using a Buchner funnel. The solid is dried in the oven. The dried solid was washed with ethanol: distilled water (1:1) and dried again. The obtained solid content yields were calculated and analyzed using an FTIR Spectrophotometer 8201 PC Shimadzu, and ¹H-NMR Jeol JNM-ECZ500R / S1 500.1599 MHz.

Determination of the maximum wavelength and calibration curve

The maximum wavelength of the methylene blue solution was determined using a 4 ppm methylene blue solution using an A&E Lab spectrophotometer in the wavelength range of 500-700 nm. Then the curve is calibrated using a solution of methylene blue at 1, 5; 2; 2.5; 3 and 3.5 ppm as measured at the maximum wavelength. Calibration curves were created by plotting concentrations and absorbances. The experiment was carried out with three repetitions.

Determination of the optimum pH

A 10 ppm methylene blue solution was interacted with 0.01 gram of CHMFKR adsorbent at pH variations of 4, 5, 6, 7, and 8 with added amounts of hydrochloric acid 0.1 M or sodium hydroxide 0.1 M. The solution is then stirred at a rate of 600 rpm for 30 minutes. After the adsorption process is complete, the solution is filtered using filter paper, and the absorbance is measured using a UV-Vis spectrophotometer. The concentration of the solution is obtained

by plotting the absorbance against the calibration curve. Percent (%) adsorption can be determined using Equation 1.

$$\% \text{ adsorption} = \frac{C_0 - C_t}{C_t} \times 100\% \dots\dots\dots 1$$

C_0 = initial concentration (mg/L)

C_t = final concentration (mg/L)

Determination of the optimum contact time

A 10 ppm methylene blue solution was made at optimum pH and interacted with a 0.025 gram CHMFKR adsorbent. Then the solution is stirred for a variation of 10, 20, 25, 30, and 50 minutes at a rate of 600 rpm. After the adsorption process is complete, the solution is filtered using filter paper, and the absorbance is measured using a UV-Vis spectrophotometer. The concentration of the solution is obtained by plotting the absorbance against the calibration curve. % Adsorption can be determined using Equation 1.

Determination of the adsorption isotherm and kinetics isotherm

Methylene blue solutions with various concentrations of 5, 6, 8, 10, and 11 ppm were made at optimum pH and interacted with a 0.001 grams CHMFKR adsorbent. The solution is then stirred at the optimum time at a speed of 600 rpm. After the adsorption process is complete, the solution is filtered using filter paper, and the absorbance is measured using a UV-Vis spectrophotometer at a maximum wavelength of 664 nm.

Adsorption kinetics generally correspond to the first-order pseudo-kinetic model developed by Lagergren (Ho and Mc Kay, 1999) and the second-order pseudo-kinetic model developed by Ho (2006). The first order pseudo equation can be seen in Equation 2.

$$\ln(q_e - q_t) = \ln q_e - \frac{kt}{2.303} \dots\dots\dots 2$$

The values of q_e and k can be known by graphing the relationship between $\ln(q_e - q_t)$ vs t . Meanwhile, in the pseudo-second order, the values of q_e and k can be determined by plotting t/q_t vs t . The pseudo second-order equation can be seen in Equation 3.

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{kq_e^2} \dots\dots\dots 3$$

q_e = concentration at equilibrium (mg/g)

q_t = concentration at time t mg/g

k = adsorption rate constant (g.mg-1min-1)

t = time (minutes)

The adsorption isotherm is a function of the concentration of the solute adsorbed on the solid to the concentration of the solution. This type of isotherm is used to study adsorption mechanisms. According to Atkins (1999), the most commonly found isotherms include the Langmuir and Freudlich isotherms. The Langmuir adsorption isotherm equation can be derived theoretically by assuming the equilibrium between the adsorbed substance molecules on the surface of the adsorbent and the non-adsorbed substance molecules as follows Equation 4:

$$q = \frac{b \cdot k \cdot C_e}{1 + k \cdot C_e} \dots\dots\dots 4$$

The constants k and b can be determined based on the C_e/q relationship curve with the Equation 5:

$$\frac{C_e}{q} = \frac{1}{q_{maks}} C_e + \frac{1}{k \cdot q_{maks}} \dots\dots\dots 5$$

Information:

q = mass of adsorbed adsorbate/gram of adsorbent (mg/g)

C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L)

k = empirical constant

Freundlich adsorption isotherm is adsorption where the adsorption process occurs heterogeneously on the surface, and not all adsorbent surfaces have adsorption capacity. This model shows the adsorbate layer on the surface of the adsorbent in a multilayer manner (Husin and Rosnelly, 2007). The form of the equation on the Freundlich adsorption isotherm is as follows Equation 6:

$$\log q = \frac{1}{n} \log C_e + \log k \dots\dots\dots 6$$

Information:

q = amount of adsorbed substance per gram of adsorbent (mg/g)

C_e = equilibrium concentration of adsorbate in the solution phase (mg/L)

k = Freundlich capacity factor (mol/g)

n = Freundlich intensity factor

The amount of dye adsorbed, the distribution ratio and the selectivity coefficient can be determined by the following Equation 7:

$$q = (C_o - C_e) V/W \dots\dots\dots 7$$

Information:

q = amount of adsorbed substance (mg/g)

C_o = initial concentration before adsorption (mg/L)

Ce = final concentration after being adsorbed (mg/L)

W = adsorbent mass (g)

V = volume of dye solution (L) (Buhani et al., 2010)

RESULTS AND DISCUSSION

² C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene Synthesis

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Synthesis of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinol using vanillin, resorcinol, ethanol as a solvent, and hydrochloride acid as a catalyst. Hydrochloride acid is used to allow vanillin to form its carbocation. Vanillin is electrophilic, and resorcinol acts as a nucleophile (Utomo, 2014).

The results showed CHMFKR synthesis in cream-colored solid form with a yield of 85.707% and a melting point of above 380°C. These synthesis products are characterized using FTIR and ¹H-NMR.

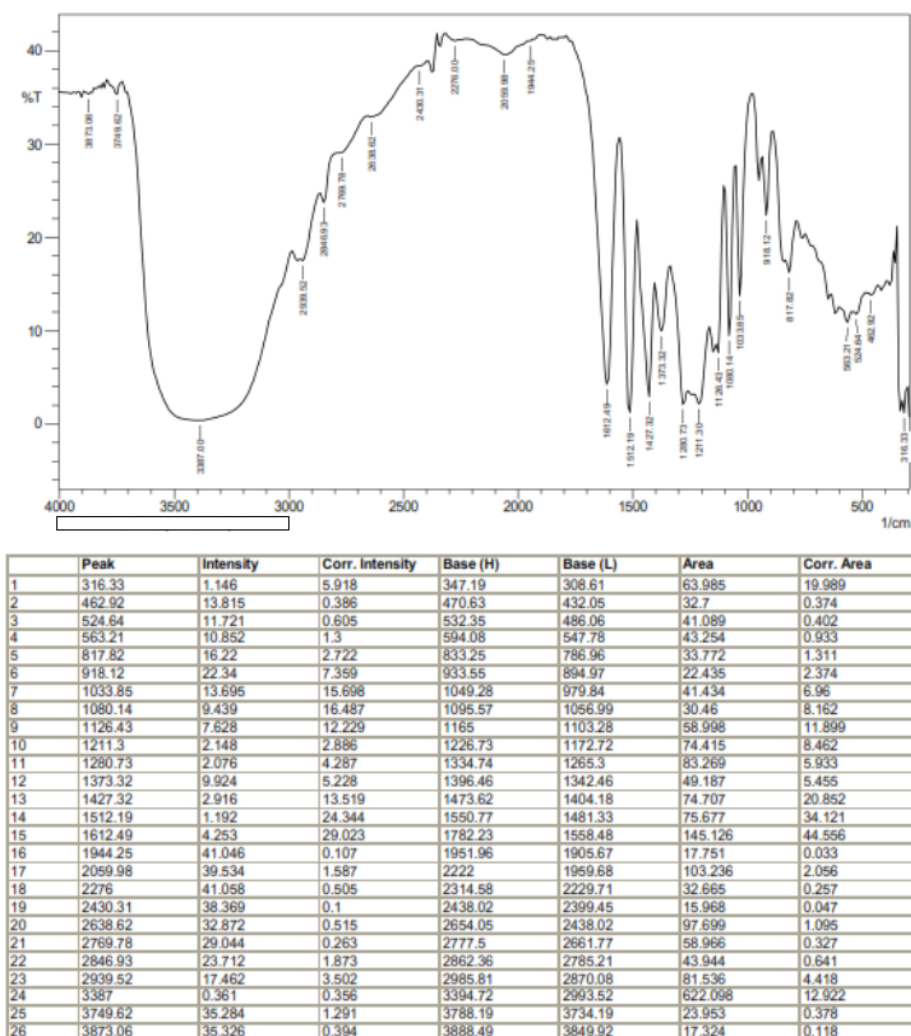


Figure 1. The FTIR spectrum of CHMFKR

Figure 1 shows the Ftir spectrum from CHMFKR. Absorption at a wave number of 3402 cm^{-1} shows the presence of an OH group. On the other hand, the absorption in the regions 1612 cm^{-1} and 1427 cm^{-1} regions indicates an aromatic ring. There is also absorption in the of 2939 cm^{-1} , 2846 cm^{-1} and 1373 cm^{-1} ranges, corresponding to the aliphatic $\text{C}_{\text{sp}^3}\text{-H}$ range. This $\text{C}_{\text{sp}^3}\text{-H}$ derived from CH_3 of methoxy and C-H methyne formed by the cyclization process of CHMFKR (Handayani *et al.*, 2020a, and Handayani *et al.*, 2020b). Vanillin-derived methoxy groups also appeared in the 1280 cm^{-1} and 1211 cm^{-1} regions (Fatoni *et al.*, 2018). During that time, the absorption of vanillin-derived aldehyde groups, which typically

occurs in the 2850 cm^{-1} and 2750 cm^{-1} regions is not appear. Similarly, uptake of carbonyl groups ranging from 2850 cm^{-1} to 2750 cm^{-1} . This indicates that the aldehyde group has reacted with resorcinol to form a methylene bridge at the CHMFKR junction.

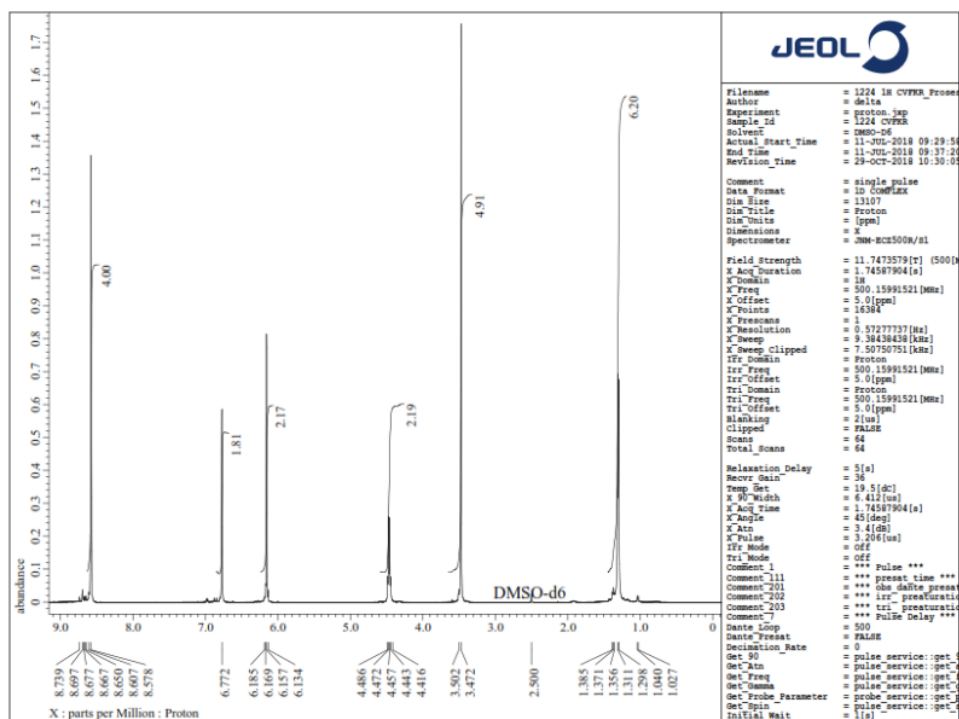


Figure 2. The ^1H -NMR spectrum of CHMFKR

Figure 2 shows the ^1H -NMR CHMFKR spectrum. Seven signals are displayed based on Figure 2. This signal shows that there are 7 protons from CHMFKR in different environments. Signals in the range of δ 1.3 ppm are the H_2O signal as well as H_2O soluble in the DMSO. The signals from methoxy derived from vanillin appear at the range of δ 3.5-3.8 ppm because these protons are far from the benzene ring experience the anisotropic effect (Wade 2006). While in the region of δ 4.4 ppm, there is a signal from the methine bridge with a singlet peak. This methine bridge is one of the important groups showing the formation of CHMFKR compounds. Absorption at δ 6.1 ppm and δ 6.8 ppm is the absorption from the aromatic rings. On the other hand, the hydroxyl group appeared in the range of δ 8.5 ppm.

Calibration Curves

The calibration curve is a curve that shows the relationship between the concentration measured at the maximum wavelength and the absorbance. Methylene blue has a maximum wavelength 664 nm. On the other hand, the concentration of the methylene blue solution used is 1.5-3.5 ppm. Figure 3 shows the calibration curve of the methylene blue solution.

From Figure 3 we can see that the regression equation is $y = 0.225x + 0.035$ and R^2 is 0.994.

The correlation coefficient (R^2) value satisfies the requirements of $0.9 < r < 1$ so that can be used as a standard curve in measurement. The value of the correlation coefficient being close to 1 indicates a relationship between absorbance and concentration that has a linear correlation where all the points lie on one straight line.

The regression equation is used to determine the concentration of the methylene blue solution before and after adsorption so that later the optimum conditions, adsorption kinetics, and adsorption isotherms can be known.

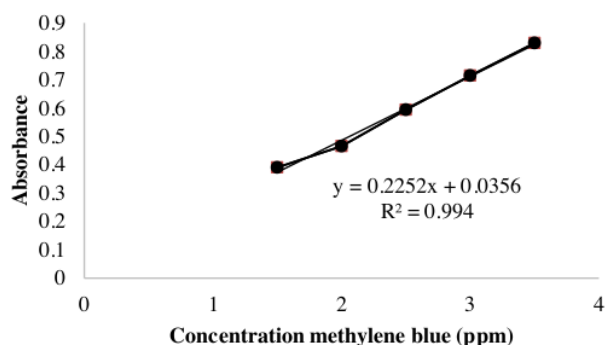


Figure 3. Calibration curve solution of Methylene blue

Optimum pH

The following are the results of the analysis of the methylene blue solution at various pH. The optimum pH value is the pH condition at which the adsorbent concentration is maximized. Determining the optimum pH is important as it can affect the chemical equilibrium of the adsorbate and adsorbent. The pH value affects the charge on the surface of the adsorbent, the degree of ionization and the species that can be absorbed during the adsorption process (Nasution et al., 2016). The variations of pH from the methylene blue solution used were 4, 5, 6, 7 and 8. The analysis results of the analysis of the methylene blue solution at various pH values are shown in Fig 4.

From figure 4, we can see that the % adsorption of the methylene blue solution by the adsorbent CHMFKR increase from pH 4 to pH 7 and then decreased to pH 8. The maximum % adsorption was at pH 7, and the number of adsorptions was 98.91%. Methylene blue belongs to the group of cationic dyes. Low or acidic pH is considered saturated with excess H^+ ions. This reduces the positive charge on the surface of the adsorbent and promotes the formation of hydroxyl radicals from the adsorbent (Sapawe et al. 2013).

Whereas at high or alkaline pH values, there is OH^- that promotes OH radicals. The CHMFKR adsorbent adsorbed methylene blue at pH 7 due to the change added to the adsorbent surface. This increased the electrostatic interaction between the CHMFKR adsorbent and methylene blue (Wahyu and Dini 2014). On the other hand, if the pH is too high, many OH^- ions will be present, creating a repulsive force between the hydroxy and methoxy groups of CHMFKR and the OH^- ions (Atikah, 2017).

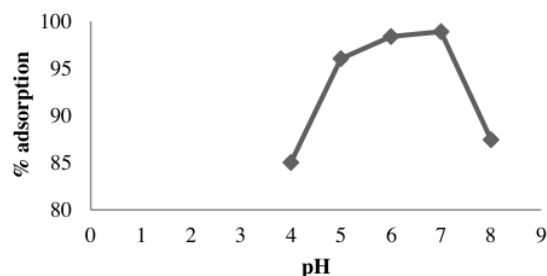


Figure 4. Graph % adsorption solution methylene blue using adsorbent CHMFKR at various pH

Optimum Contact Time

Contact time is an important parameter that determines the time it takes for the adsorbent and adsorbate to interact in the adsorption process. The time variations used in the adsorbing of the methylene blue solution with the CHMFKR adsorbent was 10, 20, 30, 40 and 50 minutes. Figure 5 is a graph of % adsorption of methylene blue solution using CHMFKR at variations of time.

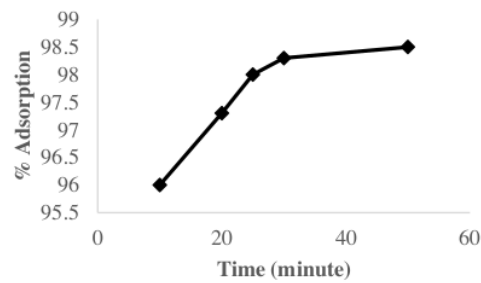


Figure 5. Graph of the adsorption of methylene blue using CHMFKR at variations of time

Figure 5 shows that the longer the interaction between the adsorbent and the adsorbate the higher the adsorption %. However, when kinetic equilibrium conditions are reached, the interaction time is 40 minutes and the adsorbent tends to remove adsorbates, which reduces adsorption (Nasution et al., 2016). This indicates that the CHMFKR adsorbent is saturated.

Adsorption Kinetics

The adsorption rate in this study was determined based on Equation 2 and 5. The reaction sequence and the rate of a chemical reaction are the rates at which the reaction occurs. The resulting adsorption rate data can be used to determine the dynamics of the adsorption process based on the adsorption order (Handayani et al., 2020a).

Methylene blue adsorption kinetics using the adsorbent CHMFKR determined based on a pseudo-first order and the pseudo-second order with 10, 20, 30, 40, and 50 minutes contact time variations. First-order pseudo kinetics are obtained by creating a curve between $\ln(q_e - q_t)$ vs t . Below is the curve of the relationship between $\ln(q_e - q_t)$ vs t in first order pseudo kinetics.

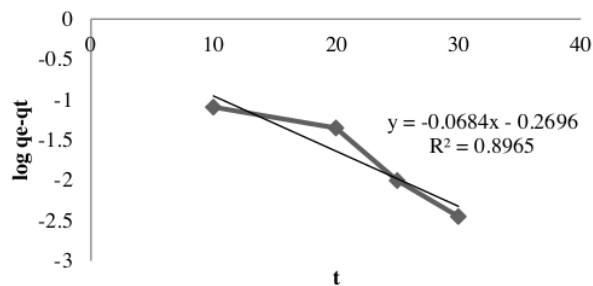


Figure 6. First-order pseudo adsorption kinetics

Based on Figure 6, we can obtain the regression equation of the pseudo first order adsorption kinetics: $y = -0.068x - 0.269$ and $R^2 = 0.896$. Based on the linear equation, the slope value is -0.068 and the intercept value is 0.896 . The value of k_1 is determined by the expression $b = \frac{k_1}{2.303}$ and the value of q_1 is determined by the expression $\ln q_1 = a$.

On the other hand, the second-order pseudo adsorption kinetics was obtained by plotting t/qt vs t . Below is the t/qt vs t relationship curve in second-order pseudo adsorption kinetics.

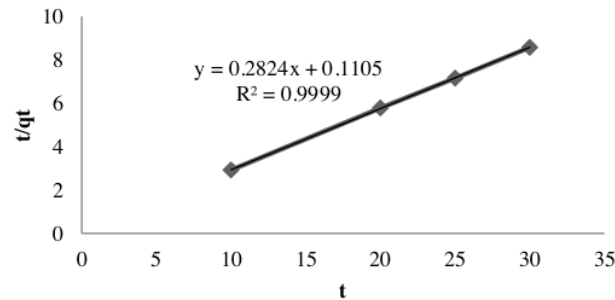


Figure 7. Second order pseudo adsorption kinetics

Based on the figure 7, regression adsorption kinetics may be known. The pseudo second order is $y = 0.282x + 0.110$ and R^2 is 0.999 . Based on the regression equation, we can see that the slope value is 0.282 and the intercept is 0.110 . The value of k_2 can be determined by the expression $b = \frac{1}{q_2}$ and the value of q_2 can be determined by the expression $a = \frac{1}{k_2 q^2}$.

Based on the results of linear regression (R^2), the rate constant (k) reaction, q value of the adsorption kinetics, pseudo first order and pseudo second order as shown in Table 1.

Table 1. Comparison of the instantaneous adsorption value of methylene blue adsorption using CHMFKR

Adsorption Kinetics	First-order pseudo	Second order pseudo
R^2	0.8965	0.9999
K	0.1575	0.7217
Q	0.7636	3.5410

The order in which they are used can be determined by examining the value of R^2 . When the value of R^2 was close to 1, the adsorption pseudo second-order kinetics rate was 0.9999 . It is amplified by the value of the second order reaction rate constant (k) of the two orders. The

value of k in the pseudo second order is greater than the value of k in the pseudo first order. Therefore, the process of adsorbing a methylene blue solution using the CHMFKR adsorbent follows the second-order pseudo equation.

Adsorption Isotherm

The adsorption isotherms can provide information about the adsorption mechanism that occurs. This adsorption isotherm can be determined based on the Freundlich isotherm equation and The Langmuir isotherm can be determined by plotting C_e/q_e vs C_e . Where C_e is the equilibrium concentration of adsorbate (mg/L) and q_e is the amount of adsorbate (mg/g). Equilibrium data were described using the Langmuir and Freundlich models to determine thermodynamic parameters, Gibbs free energy ΔG° , enthalpy change ΔH° , and entropy ΔS° . Negative values of ΔH indicate that the adsorption is exothermic. Positive values of ΔG° at all temperatures investigated indicate that adsorption is a spontaneous process (Alsenani, 2014). Below is the curve of the relationship between C_e/q_e vs C_e in the Langmuir isotherm.

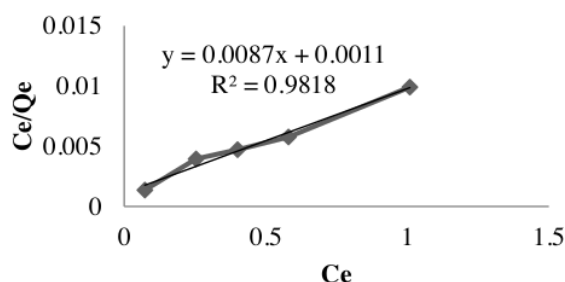


Figure 8. Langmuir's adsorption isotherm

Based on the figure 8, we can see the regression equation of Langmuir adsorption isotherm of is $0.008x + 0.001$ and R^2 is 0.981. Based on the regression equation, the slope value (b) is 0.008 and the intercept value (a) is 0.001, so that the q_{max} value in equation $b = \frac{1}{q_{maks}}$ and the k_1 value (adsorption rate constant) with the equation $a = \frac{1}{k_1 \times q_{maks}}$. So that the max q value is 114.94 mg/g and the k_1 value = 35.30 mol / g. The results of the adsorption of methylene blue using CHMFKR produce a higher max value when compared to some adsorbents. Research conducted by Baunsele and Missa (2020), using Fe_2O_3 impregnated corncob activated carbon adsorbent is available Langmuir isotherm with Langmuir constant and adsorption capacity/the maximum (q_m) obtained were 0.49 and 15.38 mg/L, respectively. The research using coconut coir adsorbent showed that the adsorption of

methylene blue using coconut coir adsorbent followed the model pseudo second order reaction kinetics with adsorption constant rate of 0.01 gram $\text{mg}^{-1} \text{ minute}^{-1}$ (Ristianingsih et al., 2020). This indicates that the absorption capacity of methylene blue by CHMFKR is greater.

The Freundlich isotherm can be determined by plotting $\log q_e$ vs $\log C_e$, where C_e is the equilibrium concentration of adsorbate (mg/L) and q_e is the amount of adsorbate adsorbed (mg/g). Below is the graph showing the relationship between $\log C_e$ vs $\log q_e$ in the Freundlich isotherm.

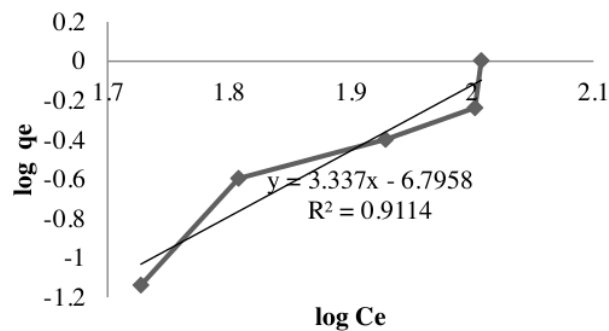


Fig 9. Freundlich's adsorption isotherm

Based on Figure 9, we can get the regression equation where $y = 3.337x - 6.795$ and R^2 is 0.911. Based on the regression equation, we can see that the gradient (b) value is 3.337 and the intercept (a) is 6.795. Therefore, the value of n (Freundlich's intensity coefficient) is given by the expression $b = \frac{1}{n}$ and k_2 with the equation $\log k_2 = a$. This gives the values $n = 0.2996 \text{ g/L}$ and $k_2 = 19.536 \text{ mol/g}$ is obtained. Table 2 shows a comparison of the Langmuir isotherm and the Freundlich isotherm values.

Table 2. Comparison of adsorption isotherms on adsorption of methylene blue using CHMFKR

Parameter	Isotherm	
	Langmuir	Freundlich
Intercept	0.0011	- 6,7958
Slope	0.0087	3.337
R^2	0.9818	0.9114
E	- 87458.29 J/mol	- 7363.985 J/mol

Table 2 shows that the R^2 values for the Langmuir and Freundlich isotherms are close to one, with the R^2 Langmuir being greater than the R^2 Freundlich. This indicates that the adsorption of methylene blue by the adsorbent CHMFKR is performed according to Langmuir isotherms. Negative energy values of -87458.29 J/mol, on the other hand, indicate that the reaction process is spontaneous.

CONCLUSION

The optimum conditions for adsorption of methylene blue using the adsorbent C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene were obtained at pH 7 with a contact time of 40 minutes. The results show that the adsorption kinetics follow pseudo-second order with an adsorption rate of 0.7217 ± 0.4 g/mg.s. The adsorption isotherm follows the Langmuir equation, and the maximum adsorption amount is 114.94 ± 2.04 mg/g.

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REFERENCES

- Adegoke, K. A., and Bello, O. S. (2015). Dye Sequestration Using Agricultural Wastes as Adsorbents. *Water Resources and Industry*, 12, 8–24. doi: 10.1016/j.wri.2015.09.002.
- Al-Ghouti, M. A., and Da'ana, D. A. (2020). Guidelines for the Use and Interpretation of Adsorption Isotherm Models: A Review. *Journal of Hazardous Materials*, 393, 122383. doi: 10.1016/j.jhazmat.2020.122383.
- Alsenani, G. (2014). Removal of Congo Red Dye from Aqueous Solution by Date Palm Leaf Base. *American Journal of Applied Sciences*, 11(9), 1553–57. doi: 10.3844/ajassp.2014.1553.1557.
- Atikah, W. S. (2017). Karakterisasi Zeolit Alam Gunung Kidul Teraktivasi Sebagai Media Adsorben Pewarna Tekstil. *Arena Tekstil*, 32(1), 17–24. doi: 10.31266/at.v32i1.2650.
- Baunsele, A. B., and Missa, H. (2020). Kajian Kinetika Adsorpsi Metilen Biru Menggunakan Adsorben Sabut Kelapa. *Akta Kimia Indonesia*, 5(2), 76. doi: 10.12962/j25493736.v5i2.7791.
- Buhani, Suharso and Sumadi. (2010) adsorption Kinetics and Isoterm of Cd(II) Ion on *Nanochloropsis sp* Biomass Imprinted Ionic Polymer. *Desalination*, 259(1), 140-146. <https://doi.org/10.1016/j.desal.2010.04.019>

- Eddaif, L., Shaban, A., and Telegdi, J. (2019a). Application of Calixresorcinarenes as Chemical Sensors. P. 6166 in *Proceedings of 1st Coatings and Interfaces Web Conference*. Vol. 137. Basel, Switzerland: MDPI.
- Eddaif, L., Shaban, A., and Telegdi, J. (2019b). Application of Calixresorcinarenes as Chemical Sensors. P. 6166 in *Proceedings of 1st Coatings and Interfaces Web Conference*. Basel, Switzerland: MDPI.
- Etika, S. B., E. Nasra, and I. Rilaztika. (2018). Synthesis and Characterization of C-Cinnamal Calix [4] Resorsinarena from Cinnamon Oil Waste West Sumatra. *IOP Conference Series: Materials Science and Engineering* 335(1). doi: 10.1088/1757-899X/335/1/012028.
- Fatoni, A., Hariani, P. L., Hermansyah, and Lesbani, A. (2018). Synthesis and Characterization of Chitosan Linked by Methylene Bridge and Schiff Base of 4,4-Diaminodiphenyl Ether-Vanillin. *Indonesian Journal of Chemistry*, 18(1), 92–101. doi: 10.22146/ijc.25866.
- Handayani, L.W., Riwayati, I., and Ratnani, R. (2015). Adsorpsi Pewarna Metilen Biru Menggunakan Senyawa Xanthat Pulpa Kopi. *Jurnal Momentum UNWAHAS*, 11(1), 114174. doi: 10.36499/jim.v11i1.1077.
- Haerifar, M., and Azizian, S. (2013). An Exponential Kinetic Model for Adsorption at Solid/Solution Interface. *Chemical Engineering Journal*, 215–216, 65–71. doi: 10.1016/j.cej.2012.11.017.
- Handayani, D. S., Amin, Z. A. A., Kusumaningsih, T., and Masykur, A. (2016a). Synthesis and Characterization of C-Hexyl Calix[4]Resorcinarena From Resorcinol-Heptanal Condensation. *ALCHEMY Jurnal Penelitian Kimia*, 10(1), 49. doi: 10.20961/alchemy.v10i1.730.
- Handayani, D. S., Purnawan, C., Pranoto, Hastuti, S., and Hilmiyana, D. (2016b). Adsorption of Remazol Yellow FG from Aqueous Solution on Chitosan-Linked P-T-Butylcalix[4]Arene. *IOP Conference Series: Materials Science and Engineering* 107(1). doi: 10.1088/1757-899X/107/1/012011.
- Handayani, S. N., Irmanto, and Indriyani, N. N. (2020a). Removal of Rhodamine b Using 4-Hydroxy-3-Methoxyphenylcalix[4]Resorcinarene. *Journal of Physics: Conference Series*, 1494 (1). doi: 10.1088/1742-6596/1494/1/012022.
- Handayani, S. N., Ekowati, H., Irmanto, Aprilia, D. N. A., and Utami, S. (2020b). Synthesis of Phenylcalix[4]Resorcinarene Sulfonate and It's Application as an Antioxidant. *AIP Conference Proceedings* 2237(June). doi: 10.1063/5.0006139.
- Handayani, S. N., Irmanto and Widiyanti, T. S. 2022. Study of the Adsorption Kinetics of Rhodamine B onto C-2-Hydroxyphenylcalix[4]resorcinarene *AIP Conference Proceedings* 2553, 020049. <https://doi.org/10.1063/5.0103723>
- Ho, Y.S., and McKay, G. (1999). Pseudo-second Order model for sorption processes,

Prosess Biochemistry, 34, 451-465. Elsevier.

- Husin, H and Rosnelly, C.M. (2007). Studi Kinetika Adsorpsi Larutan Logam Timbal (Pb) Menggunakan Karbon Aktif dari Batang Pisang. *Jurnal Hasil Penelitian Industri*, 20(1). 1-10.
- Nasution, H., Mayudendi, and Siregar, S. H. (2016). Penentuan Waktu Kontak Dan PH Optimum Penyerapan Zat Warna Direct Yellow Menggunakan Abu Terbang (*Fly Ash*) Batubara. *Semirata* 2015 0(0), 747-56. doi: <https://jurnal.untan.ac.id/index.php/semirata2015/article/view/14296>.
- Junejo, R., Memon, S., Memon, F. N., and Memon, A. A. (2019). Thermodynamic and Kinetic Studies for Adsorption of Reactive Blue (RB-19) Dye Using Calix[4]Arene-Based Adsorbent. *Journal of Chemical & Engineering Data*, 64(8), 3407-15. doi: 10.1021/acs.jced.9b00223.
- Karmakar, S., Roy, D., Janiak, C., and De, S. (2019). Insights into Multi-Component Adsorption of Reactive Dyes on MIL-101-Cr Metal Organic Framework: Experimental and Modeling Approach. *Separation and Purification Technology*, 215, 259-75. doi: 10.1016/j.seppur.2019.01.013.
- Ngapa, Y. D., and Ika, Y. E. (2020). Optimasi Adsorpsi Kompetitif Pewarna Biru Metilena Dan Metil Oranye Menggunakan Adsorben Zeolit Alam Ende-Nusa Tenggara Timur (NTT). *Indonesian Journal of Chemical Research*. 8(2), 151-58. doi: <https://doi.org/10.30598/ijcr.2020.8-ydn>.
- Ristianingsih, Y., Istiani, A., and Irfandy, F. (2020). Keseimbangan Adsorpsi Zat Warna Metilen Blue Dengan Adsorben Karbon Aktif Tongkol Jagung Terimpregnasi Fe₂O₃. *Jurnal Teknologi Agro-Industri*, 7(1), 47-55. doi: 10.34128/jtai.v7i1.115.
- Rizqi, H. D., and Purnomo, A. S. (2014). Biodegradasi Pewarna Metilen Biru oleh *Daedalea dickinsii*. *Jurnal Seni Dan Sains*. 2(1). 1-6. doi: <https://repository.its.ac.id/1584/1/1410100065-Abstract.pdf>.
- Sanghi, R., and Verma. P. (2013). Decolorisation of Aqueous Dye Solutions by Low-cost Adsorbents: A Review. *Coloration Technology*, 129(2), 85-108. doi: 10.1111/cote.12019.
- Sapawe, N., Jalil, A. A., Triwahyono, S., Sah, R. N. R. A., Jusoh, N. W. C., Hairom, N. H. H., and Efendi, J. (2013). Electrochemical Strategy for Grown ZnO Nanoparticles Deposited onto HY Zeolite with Enhanced Photodecolorization of Methylene Blue: Effect of the Formation of SiOZn Bonds. *Applied Catalysis A: General*, 456, 144-58. doi: 10.1016/j.apcata.2013.02.025.
- Utomo, S. B. (2014). Rekayasa Molekul Makrosiklis untuk Aplikasi Lingkungan Dan Medis. 4-15. *Prosiding Seminar Nasional Kimia dan Pendidikan Kimia VI*, UNS.
- Velásquez-Silva, A., Cortés, B., Rivera-Monroy, Z.J., Redondo, A. P., and Maldonado, M. (2017). Crystal Structure and Dynamic NMR Studies of Octaacetyl-Tetra(Propyl)Calix[4]Resorcinarene. *Journal of Molecular Structure*, 1137(4), 380-86. doi: 10.1016/j.molstruc.2017.02.059.

- Wade, L. (2006). *Organic Chemistry, 6th Ed.* New Jersey: Pearson Education International.
- Wahyu, E., and Dini, P. (2014). Degradasi Metilen Blue Menggunakan Fotokatalis ZnO-Zeolit, 7(1), 29–33. doi: 10.35799/cp.7.1.2014.4852.
- Wulandari, R. (2018). Adsorption of Sodium Dodecylbenzene Sulfonate (DBS) by c-3,4-Di-Methoxyphenylcalix [4]Resorcinarene Triphenylphosphonium Chloride. *Jurnal Riset Teknologi Pencegahan Pencemaran Industri*, 9(1), 1–8. doi: 10.21771/jrtppi.2018.v9.no1.p1-8.

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