Removal of rhodamine b using 4-hydroxy-3-methoxyphenyl-calix[4]resorcinarene

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Abstract. Rhodamine B is one of the dyes that is widely used in the textile industry. However, the rhodamine B waste produced is dangerous for the environment. So, it must be treated properly. Adsorption is a simple method that can be used in waste water treatment. In the present study, the adsorbent used is 4-hydroxy-3-methoxyphenyl-calix[4]resorcinarene (CHMFKR) which is synthesis from vanillin and resorcinol. The yield of product was synthesis is 85.707%. The removal of rhodamine B by calix[4]resorcinarene was investigated in the present study. Adsorption studies were performed by batch experiments. The effect of contact time, pH, initial dye concentration was explored. The optimum conditions at contact time 75 minutes and pH 7. The adsorption kinetics of rhodamine B using calix[4]resorcinarene followed second pseudo order. The isotherm study showed that adsorption rhodamine B using 4-hydroxy-3-methoxy-calix[4]resorcinarene followed Freundlich isotherm with adsorption energy of -33598.02 J/mol, kᵢ value 1.29 x 10⁻⁶ L/mol and qₚₓₜₗₐ₃ₕₖₐ₅, 6.157 mg/g.

Keyword: 4-Hydroxy-3-methoxyphenyl-calix[4]resorcinarene, Adsorption, Rhodamine B

1. Introduction

The textile industry is experiencing rapid development due to the increasing needs of people's clothing. This causes the need for dyes to increase. Most textile industries use synthetic dyes in the production process because of low prices, easily obtained, durable and easy to use [1]. Rhodamine B is a synthetic dyestuff produced by the reaction between methanlinylate and alanine. Manufacture of synthetic dyes generally by giving sulfuric acid and nitric acid. However, the process is often contaminated with heavy metals such as arsenic or other metals that are toxic. In addition, the process of making organic dyes must go through intermediates which are often dangerous. The reaction process will form new compounds that are dangerous and left behind in the dye as residues [2]. Even though 10-15% of the dyes that have been used cannot be reused and must be discarded [3]. This is clearly dangerous if the Rhodamine B dye waste is not treated and discharged directly into waters such as rivers.
Various methods have been developed to overcome the problem of dye waste. Commonly used methods are coagulation, precipitation, ozonation and ion exchange. However, the use of these methods is still considered ineffective because it requires quite expensive costs and equipment that is not simple. Precipitation is one of the economical methods, but this method is not efficient for water solvents [4].

One alternative that can be applied to overcome these problems is to use the adsorption method. The adsorption method is a simple method that uses an adsorbent to adsorb a compound, one of which is rhodamine B. This method is simple, can work at low concentrations, the adsorbent can be reprocessed and the cost is inexpensive [4]. Various kinds of adsorbents have been developed, for example rhodamine B adsorbents from the shell of Kluwak with an adsorption capacity of 3.05 mg / g and cocoa with an adsorption capacity of 1.572 mg / g [5]. Therefore, it is necessary to do an innovation in finding the type of adsorbent that can be known both the capacity and mechanism of action. One of them uses Calix[4]resorcinarene.

Calix[4]resorcinarene can be applied as a host or receptor for anions [6], cations [7] or neutral molecules. This is due to the ability of calix[4]resorcinarene which is able to be a host molecule and guest ion because of its macrocyclic form. In addition, the presence of polyhydroxy groups that can interact with cations of dyes and are not soluble in water but distributed evenly in water so that it has the potential as an adsorbent. Calix[4]resorcinarene also has a high melting point of around 380°C so that it can be used in the processing of textile dye wastes which are generally at high temperatures [4]. Several studies that have been carried out regarding the application of calix[4]resorcinarene are chitosan-p-t-butyl-calix[4]arenas as an adsorbent of remazol yellow FG. This compound is capable of adsorbing remazol yellow FG dyes with an adsorption capacity of 187.28 mg/g [8].

Based on this background, a study was conducted to determine the ability of calix[4]resorcinarene to adsorb rhodamine B dyes. This study used a solution of rhodamine B made at certain concentrations to determine the ability of calix[4]resorcinarene to adsorb rhodamine B. Some dyes Factors that can affect adsorption such as pH, contact time and also concentration will be studied to determine the type of adsorption isotherm and its kinetics.

2. Materials and Methods

2.1 Research Material

The materials used in this experiment were resorcinol p.a, acetone p.a, vanillin p.a, HCl p.a, ethanol 95% p.a, Rhodamine B p.a, aquades, NaOH p.a, and filter paper.

2.2 Research Tool

The tools used in this study are a set of glassware, a set of reflux apparatus, thermometer, capillary tube, pH meter, UV-Vis A & E Lab spectrophotometer, spatula, O Hauss analytical balance, measuring flask 100 mL, Buchner funnel, oven, 8201 PC Shimadzu FTIR Spectrophotometer, 1H-NMR Jeol JNM-ECZ500 r/s1 500.1599 MHz.

2.3 Research procedure

2.3.1 Synthesis calix[4] resorcinarene

Ethanol (50 mL) was put into a three-neck flask. After that, vanillin (0.04 mol) is added. After dissolving, resorcinol (0.04 mol) and HCl (1 mL) are added dropwise, then refluxed for 24 hours and cooled. The solution is then added with distilled water, filtered using filter paper and the obtained solid is dried using an oven at 70°C. The obtained solid is washed using ethanol : aquades (1:1), filtered and dried using an oven. After that, the yield is calculated and characterized using FTIR spectrophotometer and 1H-NMR spectrometer.
2.3.2 Preparation of Rhodamine B 1000 ppm
Rhodamine B (0.1 gram) is put into a beaker glass 20 mL and added with distilled water, stirring until dissolved. The solution was put into a 100 mL measuring flask and added with distilled water to mark the limit and homogenized.

2.3.3 Determination of Maximum Wavelength
The maximum wavelength is determined by making a rhodamine B solution with a concentration of 2 ppm and measured with a UV-Vis spectrophotometer in the wavelength range of 400-600 nm.

2.3.4 Determination of the Calibration Curve
Calibration curves were made using rhodamine B solution with a concentration variation of 2; 2.5; 3; 3.5; and 4 ppm absorbance was then measured with a UV-Vis spectrophotometer at maximum wavelength. After that, the calibration curve is determined by plotting the concentration with absorbance.

2.3.5 Determination of optimum pH
Rhodamine B solution of 10 mL with a concentration of 10 ppm is adjusted to pH 4, 5, 6, 7 and 8 with HCl and NaOH. Then into each solution added with 0.05 g calix[4]resorcinarene. The mixture is stirred at 200 rpm for 90 minutes. After that, the solution is filtered and the filtrate is analyzed using a UV-Vis spectrophotometer at the maximum wavelength.

2.3.6 Determination of Optimum Time
A total of 10 mL of 10 ppm Rhodamine B solution with time variations of 15, 30, 45, 60, 75 and 360 minutes is set at the optimum pH. In each solution added with 0.05 g calix[4]resorcinarene and stirrer for each time variation with a speed of 200 rpm. The solution was filtered and analyzed using a UV-Vis spectrophotometer.

2.3.7 Determination of Adsorption Isotherms
Rhodamine B (10 mL) with variations in concentrations of 6, 8, 10, 12 and 14 ppm plus 0.05 g calix[4]resorcinarene is adjusted at the optimum contact time and pH. After that, the solution is filtered and analyzed using a UV-Vis spectrophotometer. Then the adsorption isotherm is determined.

3. Results and Discussion

3.1 Synthesis calix[4]resorcinarene
Synthesis of calix[4] resorcinarene using aldehydes in the form of vanillin (4-hydroxy-3-methoxybenzaldehyde) and resorcinol (m-dihydroxybenzene) produce C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene (CHMFKR). Vanillin is used because it belongs to the aromatic aldehyde group found mostly in nature. In addition, in the vanillin compound there are hydroxy (-OH) and methoxy (-OCH₃) groups which are quite reactive groups so that they can increase the reactivity of the CHMFKR produced when acting as an adsorbent. Synthesis was carried out by dissolving vanillin with ethanol solvent then reacted with resorcinol (1: 1) and refluxed at 78°C for 24 hours. In this reaction an acid catalyst, HCl is used. The acidic atmosphere of concentrated HCl requires vanillin to form its carbocation. Vanillin acts as electrophilic while resorcinol acts as a nucleophile [7]. Vanillin substitution in resorcinol occurs in positions 4 and 6 which are free from steric obstructions [9].

Based on the results of CHMFKR synthesis from resorcinol and vanillin obtained solids, the product is separated from the reaction mixture because it is insoluble in the ethanol solvent used. This is because CHMFKR has low solubility. The following physical characteristics of CHMFKR obtained can be seen in Table 1.
Table 1. Characterization physical of CHMFKR.

| Characterization physical | CHMFKR          |
|---------------------------|-----------------|
| Weight                    | 8.365 gram      |
| Type                      | Solid phase     |
| Colour                    | Light yellow    |
| Rendemen                  | 85.707%         |

3.2 Characterization of Calix[4]resorcinarene

3.2.1 FTIR spectrophotometer

The synthesized CHMFKR was characterized using FTIR to determine the active groups contained in CHMFKR. Fig. 1 is the CHMFKR spectrum using FTIR spectrophotometer. Based on Fig. 1, it can be seen several uptake which shows some groups contained in the results of the analysis using FTIR spectrophotometer. Strong and wide absorption at 3402 cm\(^{-1}\) indicates the vibration of the O-H group. The uptake in the areas of 2939 cm\(^{-1}\) and 2846 cm\(^{-1}\) and 1373 cm\(^{-1}\) is the Csp\(^{3}\)-H aliphatic range. Csp\(^{3}\)-H is derived from CH\(_3\) in methoxy and CH methyl formed in the CHMFKR cyclization process. In addition, there is also absorption in of 1612 cm\(^{-1}\) and in the area of 1427 cm\(^{-1}\) which shows the presence of aromatic rings. The C-O-C symmetry range is also found in 1280 and 1211 cm\(^{-1}\). In addition, the uptake of aldehyde groups (CH aldehydes) originating from the vanillin reactants in 2850 and 2750 cm\(^{-1}\) did not appear and there was no absorption of carbonyl groups (C=O) in the area around 1740-1720 cm\(^{-1}\) indicating absence of aldehyde groups (CHO) [10] (Fessenden & Fessenden, 1986). This shows that the aldehyde group (CHO) has reacted with resorcinol to form a methine bridge in the CHMFKR compound. The CHMFKR spectrum using FTIR spectrophotometer can be seen in Fig. 1.

3.2.2 \(^1\)H NMR Spectrometer

Based on Fig. 2 can be seen 7 different signals. This different signal shows that there are 7 protons with different environments. The signals are methoxy (O-CH\(_3\)), methylene bridge (-CH\(_2\)-), aromatic ring (Ar-H) and hydroxyl (-OH), DMSO (solvent) and H\(_2\)O. Proton signals from methoxy (O-CH\(_3\)) can be seen in areas \(\delta \) 3.5 ppm. The signal in the region \(\delta \) 1.3 there is an absorption of H\(_2\)O which is dissolved in the DMSO solvent used. While the signal from the metin bridge is in the region of \(p4.4\) ppm with the peak of the singlet. This methane bridge is one of the important groups that shows the formation of CHMFKR compounds. The aromatic ring (Ar-H) it self is located in the region
of δ 6.1 ppm and in the area of δ 6.8 ppm. While the hydroxyl group (–OH) appears in the area of δ 8.5 ppm [11]. Each proton signal produces a single absorption (singlet). This is because each H proton does not have a neighboring H atom. The following $^1$H-NMR spectrum of CHMFKR can be seen in Fig. 2.

![Figure 2. CHMFKR $^1$H-NMR spectrum.](image)

### 3.3 Rhodamine B adsorption study by CHMFKR

**Maximum Wavelength of Rhodamine B**

Wavelengths used in quantitative analysis use maximum wavelengths. This is because at this maximum wavelength the maximum absorption of light occurs so that maximum absorbance is obtained which results in greater accuracy and sensitivity. The maximum wavelength is obtained by plotting the absorbance with the wavelength of the standard solution with a certain concentration [12]. The maximum wavelength of Rhodamine B solution obtained is 544 nm. Rhodamine B calibration curve shown figure 3.

![Figure 3. Standard curves of Rhodamine B.](image)

Rhodamine B calibration curves are made using a solution with a concentration of 2; 2.5; 3; 3.5; and 4 ppm measured using a maximum wavelength of 544 nm. Then the concentration curve (x) and absorbance (y) are made. Making the calibration curve aims to obtain a regression equation that will be used to determine the concentration of Rhodamine B before and after treatment. The following absorbance results from various concentrations of Rhodamine B solution
Based on the results of the regression calculation of the calibration curve obtained by the equation \( y = 0.2124x - 0.0047 \) and \( R^2 \) of 0.9991. \( R^2 \) is a measure of perfection between absorbance and concentration that forms a straight line and shows linearity. Linearity is said to be perfect if the value of \( R^2 \) approaches 1 [13]. This regression equation is then used to determine the initial and final concentrations of Rhodamine B when interacted with CHMFKR adsorbents.

**Effect of pH on the adsorption of Rhodamine B**

The factor that influences the adsorption process is pH. This is due to changes in pH resulting in changes in the nature of the surface of the adsorbent, changes in the composition of the solution and changes in the nature of the adsorbate molecule so that it is one of the important factors determined in this study [14]. This optimum pH indicates the conditions where the highest adsorbed concentration. The optimum pH can be determined by varying the pH of the solution. This study uses variations in pH 4, 5, 6, 7 and 8.

The results obtained from the calculation are at pH 4 to 8, respectively, producing % rhodamine B adsorption of 79.799%; 83.329%; 83.805%; 84.747% and 58.027%. The graph of the relationship between pH and % rhodamine B adsorption can be seen in Figure 4.

![Figure 4. Effect of pH on the adsorption of Rhodamine B by CHMFKR.](image)

Based on Figure 4 it can be seen that the % rhodamine B adsorbed by CHMFKR is influenced by the pH where the pH of the solution increases, rhodamine B which is adsorbed rises to the optimum pH of 7. After that, at pH 8 the amount of rhodamine B that is adsorbed decreases. Rhodamine B belongs to the group of cationic dyes which will ionize to release Cl\(^-\) when the atmosphere is acidic and produce cationic chromophore groups [15] (Fang, 2008). Whereas CHMFKR has a hydroxy and methoxy group will release the H\(^+\) which causes CHMFKR to be negatively charged [16]. Therefore, Rhodamine B can interact with CHMFKR electrostatically.

Whereas at high pH (bases) there are a lot of OH\(^-\) ions. This causes competition between OH\(^-\) ions and rhodamine B which is negatively charged to bind to CHMFKR so that the adsorption process decreases. The adsorption of rhodamine B by CHMFKR tends to be stable at low pH (acidic) to neutral until an optimum pH is obtained at pH 7. This is because the pH is not only influenced by H\(^+\) ions but also because rhodamine B compounds have optimum pH ranging from 6-7 [17].

**Effect of contact time on the adsorption of Rhodamine B**

Contact time is needed in the adsorption process to achieve adsorption equilibrium [14]. This contact time can be determined by varying the adsorption process time at the known optimum pH. The time variation used in the process of adsorption of rhodamine B by CHMFKR is 15, 30, 45, 60, 75 and 360 minutes. Rhodamine B adsorption increases with increasing contact time and will experience equilibrium after reaching optimum contact time. The influence of contact time on Rhodamine B % adsorption can be seen in Figure 5.
Based on Figure 3.6 it can be seen that the longer the interaction between rhodamine B solution and the CHMFKR adsorbent, the higher the adsorption of rhodamine B. However, at 75 minutes an equilibrium time is obtained where the uptake tends to remain constant or even decrease. This is because the bond between rhodamine B and CHMFKR is getting weaker because the adsorbent is saturated with rhodamine B adsorbate so that rhodamine B tends to defend itself in solution [18].

**Adsorption of Rhodamine B Isotherms with CHMFKR**

Isothermal adsorption is a description of the equilibrium in the concentration of adsorbent on the surface of the adsorbent. The equilibrium model that is often used is to use the Langmuir and Freundlich equations. The determination of this adsorption isotherm was carried out at pH 7 and 75 minutes contact time with variations in the concentration of rhodamine B 4, 6, 8, 10, 12 and 14 ppm with a volume of 10 mL and using 0.05 grams of CHMFKR adsorbent.

The Langmuir isotherm and the Freundlich isotherm each have different similarities. Next is the Langmuir isotherm equation

\[
\frac{C_e}{q} = \frac{1}{q_{max}} C_e + \frac{1}{k q_{max}} 
\]

where \(C_e\) is the concentration of the adsorbate (mg/L), \(q\) is the amount of adsorbate adsorbed (mg/g), and \(k\) is the Langmuir constant. The Langmuir isotherm can be determined by making a relationship curve between \(C_e/q\) vs \(C_e\). Next is the Langmuir adsorption isotherm curve.

**Figure 5.** Effect of time on the adsorption of rhodamine B by CHMFKR.

**Figure 6.** Langmuir adsorption isotherm curve.

Figure 6 is the Langmuir Rhodamine B adsorption isotherm curve by CHMFKR. Based on the 4.10 figure, it can be seen that the value of \(y = 0.624x + 0.5396\) and \(R^2 = 0.9736\). Whereas the Freundlich isotherm has the following equation

\[
\log q = \frac{1}{n} \log C_e + \log k \]

where \(q\) is the amount of substance adsorbed per gram of adsorbent (mg/g), \(1/n\) is a heterogeneity factor related to the capacity and intensity of adsorption and \(C_e\) is the equilibrium concentration (mg/L). The
Freundlich isotherm can be determined by creating a log q vs. log Ce curve. The following curve is the relationship log \( q_e \) vs Ce.

**Figure 7** represents the isotherm curve of the adsorption of Freudlich rhodamine B with CHMFKR.

Based on Figure 7, it can be seen that the value of \( y = 1.3815x - 0.2085 \) and the value of \( R^2 = 0.9992 \). Based on the regression equation of the Langmuir isotherm and the Freudlich isotherm above, it can be seen the comparison of several parameters between the Langmuir isotherm and the Freudlich isotherm as in **Table 2**.

**Table 2.** Langmuir and Freundlich Parameters for rhodamine B adsorption by CHMFKR

| Parameter | Isoterm    |
|-----------|------------|
|           | Langmuir   | Freundlich |
| Intersep  | 0.5396     | -0.2085    |
| Slope     | 0.1624     | 1.3815     |
| \( R^2 \) | 0.9736     | 0.9992     |
| \( E \)   | 725.1 J/mol | -33598.02 J/mol |

The value of \( R^2 \) is the coefficient of determination that has a range between 0 to 1 \((0 \leq R^2 \leq 1)\). If the value of \( R^2 \) is greater or closer to 1, then the regression model is getting better [19]. Based on calculations, the \( R^2 \) value of the Langmuir isotherm is 0.9736. While the value of \( R^2 \) in the Freundlich isotherm obtained a value of 0.9992. Based on these results it can be seen that the value of \( R^2 \) in the Freundlich isotherm is greater than the value of \( R^2 \) in the Langmuir isotherm which shows Rhodamine B adsorption by CHMFKR following the type of Freundlich isotherm which means that Rhodamine B adsorption by CHMFKR occurs physically.

The energy needed in the rhodamine B adsorption process by CHMFKR which follows the Freundlich isotherm equation can be calculated through the equation \( E = RT \ln K \). Based on the calculation of rhodamine B adsorption by CHMFKR it releases energy of \(-33598.02\) J/mol. While the \( q_{max} \) of the rhodamine B adsorption process by CHMFKR based on the calculation is 6.157 mg/g. This \( q_{max} \) value is greater than the adsorption of rhodamine B using kluwak shell adsorbent with adsorption capacity of 3.05 mg/g and cocoa adsorbent with adsorption capacity of 1.57 mg/g [5].

**Adsorption Kinetics**

The kinetics of adsorption are the adsorption reaction rate of adsorbate by adsorbents. Adsorption kinetics can be used to determine the rate of adsorption that occurs in the adsorbent to the adsorbate which is affected by contact time. The kinetics of Rhodamine B adsorption by CHMFKR...
can be determined based on the first-order Pseudo equation developed by Lagergren [20] (and the second-order Pseudo developed by Ho [21]. The following is the first-order Pseudo equation

\[
\ln(q_e - q_t) = \ln q_e - \frac{kt}{2.303} \ldots \ldots (3)
\]

where \( q_e \) is the concentration when equilibrium (mg/g), \( k \) is the constant and \( t \) is the time of minutes). First-order pseudo can be determined by making a relationship curve between \( \ln (q_e - q_t) \) vs \( t \). Here is the relationship curve between \( \ln (q_e - q_t) \) vs \( t \)

![Figure 8](image)

**Figure 8.** is the relationship curve between \( \ln (q_e - q_t) \) vs \( t \).

Based on the curve above it can be seen the value of \( y = 0.0056x - 0.9656 \) and the value of \( R^2 = 0.0871 \). Whereas the second-order Pseudo can be determined by plotting \( t / Qt \) vs \( t \). Next is the second-order Pseudo equation

\[
\frac{t}{Qt} = \frac{1}{q_e^2} t + \frac{1}{kq_e^2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)
\]

where \( t \) is the time (minutes), \( q_e \) is the concentration at equilibrium (mg/g), \( q_t \) is the concentration at time \( t \) (mg/g). Based on the plot of \( t / Qt \) vs \( t \) the following curve is obtained.

![Figure 9](image)

**Figure 9** is the relation curve of \( t / Qt \) vs \( t \) rhodamine B with CHMFKR.

Based on the curve above it can be seen the value of \( y = 0.534x + 2.0511 \) and the value of \( R^2 = 0.9979 \). Based on the regression equation of first-order Pseudo and second-order Pseudo, it can be seen the comparison of several parameters between first-order and second-order Pseudo as shown in **Table 3**.

**Table 3.** Comparison of first and second order Pseudo values in rhodamine B adsorption kinetics by CHMFKR

| Kinetic Adsorption | First pseudo order | Second pseudo order |
|--------------------|--------------------|---------------------|
| \( R^2 \)         | 0.087              | 0.9979              |
| \( K \)           | -0.029             | 7.193               |
| \( Q \)           | 0.108              | 1.873               |
Based on Table 3 it can be seen that the $R^2$ value of the second-order Pseudo higher than the first-order Pseudo $R^2$. This shows that the adsorption of Rhodamine B dyes by CHMFKR follows the second-order Pseudo. Second-order pseudo shows that the reaction rate is directly proportional to the square of the active position on the adsorbent that has not been used to interact. Therefore, adsorption takes place mostly at the beginning of the interaction when the active position of the adsorbent that is still empty is in the most condition [4].

4. Conclusion

Based on the results of the research conducted obtained the following conclusions:

1. Synthesis of calix[4]resorcinarene from vanillin and resorcinol can be carried out using the reflux method at a temperature of 78 °C for 24 hours. The results of the synthesis in the form of brownish cream solids with a rendemen of 85.707%.

2. Adsorption of rhodamine B by calix[4]resorcinarene has an optimum pH of 7 with a contact time of 75 minutes. Adsorption of Rhodamine B dyes by calix[4]resorcinarene follows the Freundlich isotherm equation with a value of $1.29 \times 10^{-6}$ L/mol and an adsorption energy of $-33598.02$ J/mol and a qmax of 6.157 mg/g. The kinetics of adsorption of calix[4]resorcinarene to rhodamine B followed the second-order Pseudo kinetics.

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