study kinetic rhodamin b onto c-hidrokxy phenylcalix-4-recorcinarena

by Tamimah Tamimah

Submission date: 04-Sep-2021 09:50PM (UTC+0700)
Submission ID: 1641326158
File name: STUDY_OF_THE_ADSORPTION_KINETICS_OF_RHODAMIN_B_ONTO.docx (386.4K)
Word count: 7142
Character count: 39527

STUDY OF THE ADSORPTION KINETICS OF RHODAMIN B ONTO 2-HYDROXYPHENYLCALIX-4-RESORCINARENE

Santi Nur Handayani[1, (a)], Irmanto[1, (b)], Tamimah Sufi Widianti[1, (c)]

Author Affiliation
[1]*Faculty of Mathematics and Science, Universitas Jenderal Soedirman*
Jl. Dr. Soeparno no. 6, Karangwangkal, Purwokerto Utara,
Kabupaten Banyumas, Indonesia. 53122

Author Emails
[a)]*santi.handayani@unsoed.ac.id*
[b)]*irmantoz@gmail.com*
[c)]*tamimah.sufiwidii@gmail.com*

Abstract. The textile industry produces liquid waste that contains dyes. One of the dyes that are often used in the textile industry is rhodamine B. Waste containing dyes must go through processing before being discharged into the water because it can cause quite dangerous impacts. The method that is considered quite effective in treating dyestuff waste is the adsorption method. In the present study, the adsorben used is the 2-hydroxyphenylcalix[4]resorcinarene is a derivative of calixarenes synthezided from 2-hidroxy-benzaldehide and resorcinol. The yield of product was 84.7% and its ability to adsorb rhodamine B dye. The removal of Rhodamine B by the compound was investigated in the present study. The adsorbtion studies were performed by batch experiments. The effect of pH, time of contact and concentration of dye were investigation. The synthesized compounds were characterized by FTIR spectrophotometry, ^{1}H-NMR spectrometry, and BET analysis. In addition, from the BET analysis, it was found that the surface area of ompound was 14.102 m^2/g, the total pore volume was 8.733 × 10-2 cm^3/g, and the average pore radius size was 123.852 Å. The Rhodamine B adsorption has optimum conditions at pH 4, contact time 180 minutes, and follows second order Pseudo adsorption kinetics. Rhodamine B adsorption isotherm follows the Langmuir and Freundlich isotherms with a Langmuir maximum adsorption capacity (q_{max}) of 19.26 mg/g and an adsorption energy (E) of 20.57 kJ / mol.

INTRODUCTION

The textile and apparel industry shows growth from year to year (Ministry of Industry, 2020). The increase in the amount of production in the textile and textile product sector also increases the amount of textile production waste. One of the liquid wastes produced is dye waste. The dyes used usually use synthetic dyes because they are cheap, easy to obtain, and easy to use. One of the dyes that are often used in the textile industry is rhodamine B. Rhodamine B is often used in the textile industry because this dye produces attractive and varied colors (Hindryawati, 2020).

Rhodamine B compound is an unsaturated organic compound containing an auxochrome group and a chromophore group which can give color in the form of a solution (Heaton, 1994). Rhodamine B has an aromatic structure that makes this dye difficult to degrade naturally. In addition, rhodamine B also contains chlorine compounds (Cl-) making this dye toxic and carcinogenic. Therefore, waste containing these compounds must undergo further treatment before being released into the waters. Currently, various techniques or methods in dealing with textile waste have been developed. Some of them are coagulation, flocculation, ozonation, and adsorption. However, the adsorption method is more in demand because the treatment is relatively easy, efficient, economical, and can be used on a large scale (Santos et al., 2013). Various kinds of adsorbents have been widely applied to rhodamine B, one of which is from the banana peel with an adsorption capacity of 4.55 mg/g (Musafira et al., 2019) and hemicellulose fiber of 0.047 mg/g (Putri et al., 2019). In addition, other adsorbents can be used as an alternative for the adsorption of rhodamine B dye, one of which is calix[4]resorcinarene. Kaliks[4]resorcinarene has an active group, namely a polyhydroxy group so that it has the potential to become an

adsorbent (Jumina, et al., 2020), a polyhydroxy group so that it can interact with cations contained in dyes and is not soluble in water but can still be distributed in water evenly. evenly so that it has the potential as an adsorbent. Calix[4]resorcinarene melts at temperatures above 300°C (Eddaif et al., 2019), this physical property can be exploited in the textile industry dye waste treatment which usually uses temperatures below the melting point of calix[4]resorcinarene.

The use of kalix[4]resorcinarene as an adsorbent has been carried out by Ethics (2020), namely the compound C-Sinamalkaliks[4]resorcinarene as an adsorbent for rhodamine B dye with an adsorption capacity of 1.6234 mg/g. In addition, Wulandari et al. (2015) synthesized the compound C-4-ethoxy-3-methoxyphenylcalyx[4] resorcinarene and applied it as an adsorbent for remazol brilliant blue R. dye with an adsorption capacity of 6.51 x 10-5 mol/L. The synthesis of the compound C-2-hydroxyphenylcalix[4]resorcinarene has been carried out by Handayani et al. (2016) which was applied as an antioxidant compound. Based on the description of the background above, research will be conducted on the application of the compound C-2-hydroxyphenylcalix[4]resorcinarene from the reaction of 2-hydroxybenzaldehyde and resorcinol with an acid catalyst as an adsorbent for rhodamine B dye which has not been reported. The results of the synthesis of C-2-hydroxyphenylcalix[4]resorcinarene were further identified by FTIR, 1H-NMR, and BET spectrophotometers. Several parameters such as variations in pH, contact time, and concentration will also be carried out to determine the ability of C-2-hydroxyphenylcalix[4]resorcinarene to adsorb rhodamine B dye.

TOOLS AND MATERIALS

Tools used in this study were reflux kit, hot plate, three neck flask, thermometer, beaker glass, measuring cup, spatula, stirring rod, dropper, measuring pipette, filler, buchner funnel, oven, watch glass, measuring flask, capillary tube, pH meter, analytical balance (ohaus PA224), spectrophotometer UV-Vis (Shimadzu UV-1800), spectrophotometer infrared (IR Shimadzu FTIR-8201 PC, Gadjah Mada University), Surface Area Analyzer (Quantachrome Nova 1200e, Semarang State University), proton nuclear magnetic spectrometer (^{1}H-NMR Jeol JNM-ECZ500R/S1, Indonesian Institute of Sciences). Materials used in this study were resorcinol (Merck, Germany), 2-hydroxybenzaldehyde (Merck, Germany), HCl, ethanol (Merck, Germany), aquadest, rhodamine B (Merck, Germany), NaOH, filter paper, KLT plate, aceton, and hexane.

METHODS

Synthesis of C-2-hydroxyphenylcalix[4]resorcinarene

A total of 1.1 grams of resorcinol (10 mmol) was dissolved in 100 mL of ethanol. After that, 1.22 grams (10 mmol) of 2-hydroxybenzaldehyde and 1 mL of HCl were added dropwise. Then the mixture was refluxed for 24 hours then cooled and analyzed using TLC. The resulting synthesis was washed with distilled water, filtered using filter paper. The solid obtained was dried in an oven at 100°C. The solid obtained was washed again using ethanol solvent, filtered and the solid obtained was dried again using an oven. The yield solids obtained were weighed, then characterized using an IR spectrophotometer, ^{1}H-NMR spectrometer, and BET Surface Area Analyzer (SAA-BET).

Thin-layer chromatography (TLC) test

The TLC plate was cut to a size of 3×5 cm. The TLC plate was prepared in an oven for 10 minutes at 100°C. Then marked the upper and lower limits of 0.5 cm each. The synthesized compound, 2-hydroxybenzaldehyde, and resorcinol were spotted on the TLC plate using a capillary tube and then dried. The TLC plate was placed in a vessel that was saturated with eluent steam of acetone: n-hexane (7:1) in the expansion vessel. The elution process was carried out until the eluent reached the upper limit mark on the TLC plate. After the elution process was completed, the TLC plate was viewed under UV light at a wavelength of 254 nm and the spots that appeared were marked and then the Rf value was determined.

Formation of Rhodamine B in concentreation 1000 ppm

A total of 0.1 grams of rhodamine B was put into a 20 mL beaker. Then dissolved with distilled water. The solution was put into a 100 mL volumetric flask and then added distilled water to the mark and homogenized.

Maximum wavelength determination

The maximum wavelength was determined by making a solution of rhodamine B with a concentration of 2 ppm and measured with a spectrophotometer UV-Vis in the wavelength range of 500 – 600 nm.

Rhodamine B calibration curve

Calibration curves were made using a solution of rhodamine B with a concentration variation of 1; 1.5; 2; 2.5; and 3 ppm then the absorbance was measured with a spectrophotometer UV-Vis at the maximum wavelength that was obtained. After that, the calibration curve was determined using the concentration (x-axis) and absorbance (y-axis).

Determination of optimum pH and contact time

A total of 0.02 grams of C-2-hydroxyphenylcalyx[4]resorcinarene was added to 20 mL of 10 ppm Rhodamine B solution in a beaker. Treatment of the degree of acidity (pH) of the solution was adjusted, namely pH 2, 3, 4, 5, 6, 7, and 8 using NaOH and HCl solutions. The solution was stirred using a magnetic stirrer for 60 minutes according to a variable hereinafter referred to as optimum pH, the solution was adsorption with time variations at the optimum pH of 5, 10, 15, 30, 60, 120, 180, 360, and 720 minutes with a stirring speed maintained at 500 rpm. The temperature of the solution was set at 25°C. At the end of equilibrium, the solution was centrifuged and the adsorbent was filtered using filter paper. The concentration of rhodamine B in the filtrate was analyzed using a UV-Vis spectrophotometer. This treatment was repeated three times. Then the adsorption data on the determination of the optimum contact time was used to determine the adsorption reaction kinetics using a pseudo-first-order equation, namely:

$$\ln(qe - qt) = \ln qe - \frac{kt}{2{,}303}$$

qe = concentration at equilibrium (mg/g)
k = adsorption rate constant (g/mg.minute)
t = time (minute)

and for pseudo second-order equations, the equations are :

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{k.qe^2}$$

t = time (minute)
qe = concentration at equilibrium (mg/g)
k = adsorption rate constant (g/mg.minut
qt = concentration of adsorbed substance at time (mg/g)

The value of qe and k in pseudo-first order can be determined by making a linear regression equation between ln (qe-qt) vs t. Whereas in pseudo-second-order, the values of qe and k can be determined by plotting t/qt vs t on the linear regression equation.

Determination of adsorption isotherm

A total of 20 mL of rhodamine B solution with various concentrations of 5, 10, 15, 20, 25, and 30 ppm was added with 0.02 gram of C-2-hydroxyphenylcalyx[4]resorcinarene set at the optimum pH and stirred at the optimum time. After that, the solution was centrifuged and filtered then analyzed using a spectrophotometer UV-Vis. This treatment was repeated three times. Then the type of adsorption isotherm is determined whether it is following the Langmuir or Freundlich adsorption isotherm. Determination of the type of Langmuir adsorption isotherm is determined based on the following equation:

$$q = \frac{b.k.Ce}{1 + k.Ce}$$

The constants k and b can be found by plotting $\frac{Ce}{q}$ with Ce on the linear regression equation. The value of $\frac{Ce}{q}$ can be determined by the equation :

$$\frac{Ce}{q} = \frac{1}{qmax}Ce + \frac{1}{k.qmax}$$

q = sorbate mass absorbed (mg/g)
Ce = equilibrium concentration of adsorbate in solution after adsorption (mg/L)
k = empirical constant

while for the determination of the type of Freundlich adsorption isotherm is determined based on the following equation :

$$\log q = \frac{1}{n}\log Ce + \log k$$

q = adsorbate mass absorbed (mg/g)

Ce = equilibrium concentration of adsorbate in solution after adsorption (mg/L)
k = Freundlich capacity factor (mol/gram)
n = Freundlich intensity factor

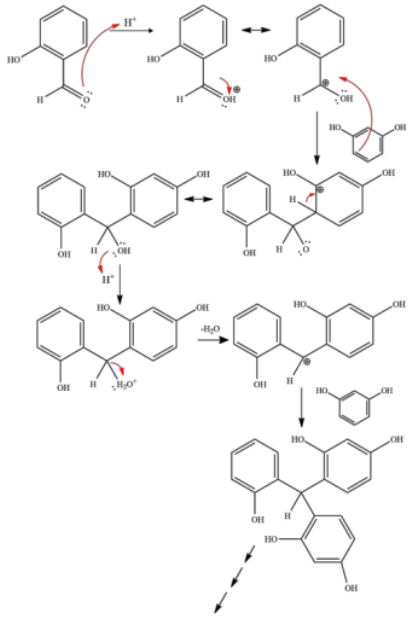
A total of 30 mL of rhodamine B solution with a concentration of 10 ppm was adjusted to the optimum pH and then added with 0.15 grams of C-2-hydroxyphenylcalyx[4] resorcinarene and interacted at the optimum time. After that, the solution was filtered and the filtrate was analyzed using a UV-Vis spectrophotometer. Meanwhile, the solid C-2-hydroxyphenylcalix[4]resorcinarene that has been used is then washed using ethanol and dried in an oven. The washed C-2-hydroxyphenylcalix[4]resorcinarene was reused to determine its adsorption capacity on repeated use.

RESULTS AND DISCUSSIONS

Synthesis of C-2-hydroxyphenylcalix[4]resorcinarene

The compound C-2-hydroxyphenylcalix[4]resorcinarene is a tetramer compound resulting from the reaction product between resorcinol and 2-hydroxybenzaldehyde with an acid catalyst. Resorcinol or m-dihydroxybenzene is a benzene derivative compound that has two hydroxyl groups (-OH) in the meta position. The compound 2-hydroxybenzaldehyde or salicylaldehyde is an aromatic aldehyde group compound and is one of the isomers of hydroxybenzaldehyde. This compound has a hydroxyl group (-OH) and an aldehyde group (-COH) which are quite reactive so that it can increase the reactivity of the synthetic target compound to be used as an adsorbent.

The synthesis of the compound C-2-hydroxyphenylcalyx[4]resorcinarene was carried out by dissolving resorcinol in ethanol to produce a brownish-red solution. Next, the resorcinol solution was mixed with 2-hydroxybenzaldehyde which had been reacted with concentrated HCl dropwise. The reaction process was carried out at the boiling point of the solvent at 78°C for 24 hours. The process of forming the compound C-2-hydroxyphenylcalyx[4]resorcinarene is through an electrophilic substitution reaction (Etika et al., 2018), where the H+ ion from the HCl catalyst protonates the oxygen atom present in the carbonyl group of 2-hydroxybenzaldehyde, causing oxygen bonding to the group becomes unstable and makes the electrons in the carbonyl bond shift to the oxygen atom and makes the carbon atom in the carbonyl group a positive charge. The carbocation resulting from this protonation process makes 2-hydroxybenzaldehyde act as an electrophile and can be attacked by resorcinol which acts as a nucleophile. The reaction mechanism for the synthesis of C-2-hydroxyphenylcalix[4]resorcinarene can be seen in Figure 1.



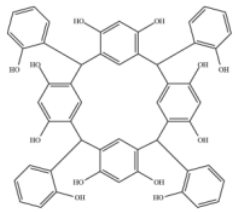


FIGURE 1 The reaction mechanism of the synthesis of C-2-hydroxyphenylcalix[4] resorcinarene (Handayani et al., 2016)

Based on the synthesis of C-2-hydroxyphenylcalix[4]resorcinarene from resorcinol and 2-hydroxybenzaldehyde, an orange-colored precipitate was obtained. The resulting product is separated from the solvent mixture because it is not soluble in the ethanol solvent used. The precipitate was then washed with distilled water to remove residual acid. Then washed again with ethanol to remove the remaining water and other impurities. Then filtered, dried, and then calculated the yield. Based on research conducted by Tuzahiroh, (2020) the compound C-2-hydroxyphenylcalix[4]resorcinarene is insoluble in water, ethanol, methanol, n-hexane, and ethyl acetate but is soluble in DMSO.

Analysis of thin-layer chromatography

Thin-layer chromatography is a technique for separating analytes in a compound that is distributed between two phases, namely the stationary phase and the mobile phase. A thin layer chromatography test in this study was conducted to determine whether the synthesized product still contained reactants or impurities or not. The characterization of the TLC test was carried out on the synthesis product of C-2-hydroxyphenylcalix[4]resorcinarene against resorcinol and 2-hydroxybenzaldehyde after 24 hours of synthesis. Identification was carried out with three samples, namely resorcinol, 2-hydroxybenzaldehyde as a reactant, and C-2-hydroxyphenylcalyx[4]resorcinarene as a 24-hour synthesized product. TLC test was carried out on unpurified synthesized compounds, 2-hydroxybenzaldehyde and resorcinol as comparisons which were spotted on the plate. The plate is allowed to stand until the sample dries and then put into a developer vessel which is saturated with eluent steam in the form of acetone: n-hexane 7:1 (Handayani et al., 2016). The elution process was carried out until the eluent reached the upper limit mark on the TLC plate. After the elution process is complete, the TLC plate is dried and the stain can be seen under UV light at a wavelength of 254 nm then the stain formed is marked with a pencil so that the Rf value can be calculated. Following are the results of thin-layer chromatography of C-2-hydroxyphenylcalix[4]resorcinarene.

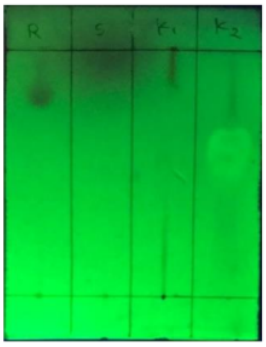


FIGURE 2 The result of TLC (a) resorcinol, (b) 2-hydroxybenzaldehyde, (c) calix before washing (d) calix after washing

Figure 2 is the result of thin-layer chromatography of resorcinol, 2-hydroxybenzaldehyde, and C-2-hydroxyphenylcalyx[4]resorcinarene. Resorcinol and 2-hydroxybenzaldehyde respectively produced Rf values of 0.85 and 0.9, while for C-2-hydroxyphenylcalyx[4] resorsinarene from the synthesis of the stain formed was an

impurity, so it needed to be purified by washing. Based on the stains formed on the TLC results, this is a sign that the reaction can be stopped within 24 hours.

Analysis of infrared spectrophotometry

Analysis of the synthesized C-2-hydroxyphenylcalix[4]resorcinarene was characterized using an FTIR spectrophotometer to determine the absorption of the functional groups present in the compound. The FTIR spectrum of the compound C-2-hydroxyphenylcalix[4]resorcinarene can be seen in Figure 3.

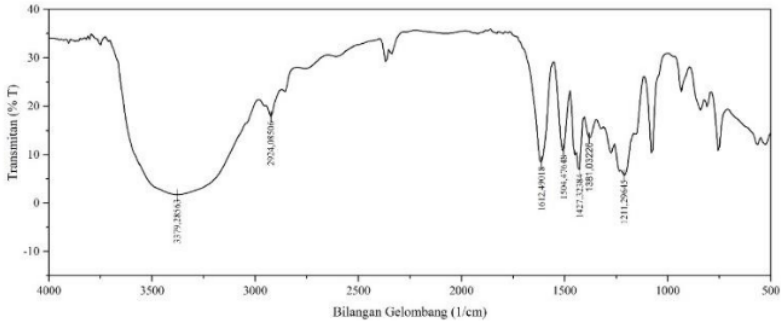


FIGURE 3 FTIR spectrum of C-2-hydroxyphenylcalix[4]resorcinarene

Based on the results of the FTIR analysis in Figure 3, it can be seen that several absorptions are indicating the presence of functional groups contained in the analysis results. Strong and wide absorption in the 3379 cm-1 regions indicates the presence of vibrations from the hydroxyl group (-OH). Absorption in the area of 2924 cm-1 and 1381 cm-1 indicated the presence of Csp2-H. Another typical absorption of calix[4]resorcinarene compounds is indicated by the presence of a methine bridge (C-H) that appears in the 1427 cm-1 region, absorption at this wave number indicates that the cyclization process in the synthesis has occurred. Strong absorption in the area of 1612 cm-1 and 1504 cm-1 indicates an aromatic ring absorption (C=C). The absorption that appears in the 1211 cm-1 region indicates the presence of C-O bonds. Based on the interpretation of the results of the FTIR spectrum of the compound C-2-hydroxyphenylcalix[4]resorcinarene, there are several absorptions in the same group as in the spectrum of the compound synthesis that has been carried out by (Handayani et al., 2016). In addition, there was no absorption from the CH aldehyde group in the 2734 - 2800 cm-1 area and the absorption from the C=O carbonyl group in the 1700 cm-1 area which indicated that the condensation product between 2-hydroxybenzaldehyde and resorcinol had formed a C-2- compound. hydroxyphenylcalix[4]resorcinarene.

Analysis of proton nuclear magnetic spectrometer (^{1}H-NMR)

The results of the synthesis of C-2-hydroxyphenylcalix[4]resorcinarene were analyzed using a 1H-NMR spectrometer to support the results of the FTIR spectrum analysis. The analysis performed with a 1H-NMR spectrometer can provide information in the form of the type, number, and arrangement of hydrogen atoms in a molecule so that it can provide an overview of the structure of the C-2-hydroxyphenylcalix[4]resorcinarene formed. The following is the 1H-NMR spectrum of C-2-hydroxyphenylcalix[4]resorcinarene.

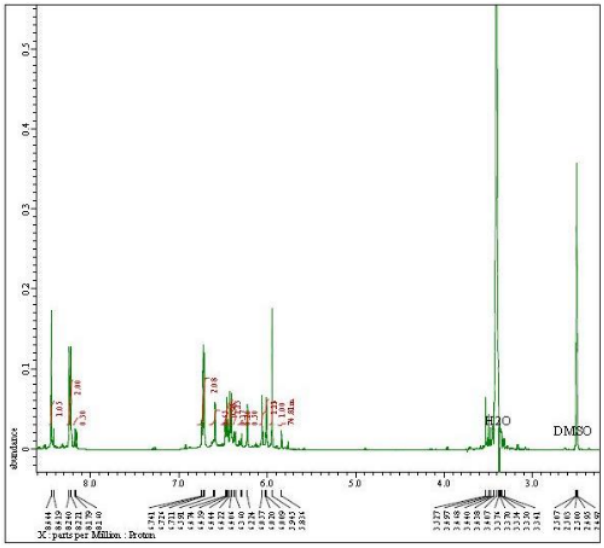


FIGURE 4 ^{1}H-NMR spectrum of C-2-hydroxyphenylcalix[4]resorcinarene

Based on Figure 4, it can be seen that there are several shift signals formed. The proton signal in the 2.4 ppm H region is the DMSO solvent used and the signal in the 3.4 ppm H region is the absorption of H2O which is dissolved in the DMSO solvent. The proton signal from the methine bridge is seen in the H region of 5.945 ppm (i) with singlet multiplicity. The presence of a signal peak from the methine bridge indicates that the cyclization process has occurred to form C-2-hydroxyphenylcalyx compounds [4]. The proton signal from the aromatic ring appears in the H 6,741 region; 6,726; and 6,711 ppm (c) with triplet multiplicity, then in the H region 6,474; 6,459; 6.444 ppm (e) with triplet multiplicity, then in the H region 6.422 and 6.406 ppm (f) with duplet multiplicity, and in the H area 6.591 (d); 6,224 (g); 6.057 ppm (h) with singlet multiplicity. The proton signal of the hydroxyl group seen in the H region of 8.444 ppm (a) with duplet multiplicity and the signal in the H region of 8.221 and 8.240 ppm (b) with duplet multiplicity, this signal has a greater chemical shift because the O in the electron group has a higher electronegativity. high so that nearby proton are not shielded and will shift towards the downfield. The proton signal results obtained were compared with the research conducted by Handayani et al., (2016) as shown in Table 1.

TABLE 1 Comparison of chemical shift (δ) ^{1}H-NMR of C-2-hydroxyphenylcalyx[4]resorcinerene

Label	Proton Type	Synthesis Result	Handayani et al., (2016)
a	-OH	8,444 ppm	8,1336 – 8,4124 ppm
b	-OH	8,221 ppm 8,240 ppm	
c	C_{sp2}-H phenyl group	6,741 ppm 6,726 ppm 6,711 ppm	6,0595 – 6,7288 ppm
d	C_{sp2}-H phenyl group	6,591 ppm	
e	C_{sp2}-H phenyl group	6,474 ppm 6,459 ppm 6,444 ppm	
f	C_{sp2}-H phenyl group	6,422 ppm 6,406 ppm	
g	C_{sp2}-H meta group –OH	6,224 ppm	
h	C_{sp2}-H orto group –OH	6,057 ppm	
i	=C-H Metin bridge	5,945 ppm	5,9492 ppm

Analysis of BET

BET analysis (Brunauer Emmett Teller) is used to determine the specific surface area and also the pore size of a sample which is an important parameter because it is used to determine the structural properties of an adsorbent (Virtanen et al., 2020). BET analysis was carried out by flowing nitrogen gas onto the sample surface for 3 hours at 300°C. The dissolution rate of nitrogen gas in the sample is proportional to the specific surface area. The nitrogen gas adsorption-desorption isotherm and the pore radius distribution curve for the compound C-2-hydroxyphenylcalix[4]resorcinarene analyzed at 77.3 K are shown in Figure 5.

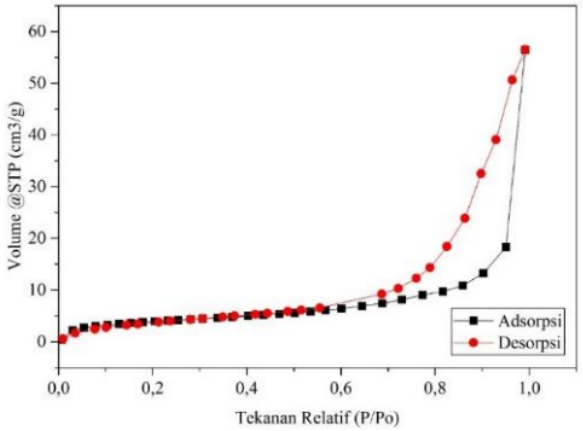


FIGURE 5. Nitrogen adsorption-desorption isotherms and distribution of C-2-hydroxyphenylcalyx[4]resorcinarene

Based on Figure 5, the nitrogen adsorption-desorption isotherm belongs to type IV, where the synthesis product will be used as a narrow gap adsorbent. From the results of BET analysis, the surface area of the adsorbent C-2-hydroxyphenylcalix[4]resorcinarene is 14,102 m2/g, the total pore volume is 8,733 × 10-2 cm3/g, and the average pore radius is 123.852.

The maximum wavelength of rhodamine B

The wavelength used to measure the absorbance of the sample is the maximum wavelength. The maximum wavelength is determined to get the absorptivity value that gives the highest measurement sensitivity. The maximum wavelength also has a relatively constant molar absorptivity of the compound so that a linear calibration curve is obtained. The maximum wavelength can be determined by plotting the absorbance with the wavelength of the standard solution at a certain concentration (Pescok, et al. 1976).

Determination of the maximum wavelength of rhodamine B using a standard solution with a concentration of 2 ppm in the wavelength range of 400-800 nm. The absorption of the colored solution is in the visible light wavelength range, which is between 400-750 nm. Rhodamin B is a dye that has a chromophore group in the form of a xanthene group and an auxochrome group in the form of a dimethylamine group which causes this compound to give color so that it can be analyzed by UV-Vis spectrophotometer.

The maximum wavelength of rhodamine B obtained was 554 nm. The results of this measurement are following the results of measurements made by (Rahayu et al., 2020) where rhodamine B has a maximum wavelength of 554 nm. The graph of the spectrum of the UV Vis spectrophotometer solution of rhodamine B at a concentration of 2 ppm can be seen in Figure 6.

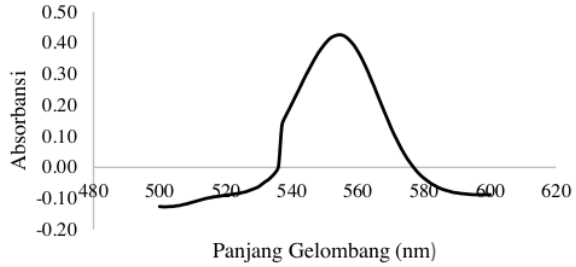


FIGURE 6 Spectrum UV-Vis maximum wavelength of rhodamine B

Rhodamine B is a chemical compound consisting of a chromophore group in the form of a xanthene group and an auxochrome group in the form of a diethylamine group. A chromophore group is a group of radical compounds consisting of conjugated double bonds that must bind to another group, namely auxochrome to be colored. This auxochrome group works by activating the work of the chromophore group and providing binding power to the fiber (Rahayu et al., 2021).

Calibration curve of rhodamine B

The rhodamine B calibration curve was determined by measuring the absorption of various dilutions of solutions with a concentration of 1; 1.5; 2; 2.5; and 3 ppm at a maximum wavelength of 544 nm. Then a linear curve of the relationship between concentration (x) and absorbance (y) is made to determine the regression equation. This regression equation was used to determine the concentration of rhodamine B before and after adsorption. The calibration curves of standard solutions of rhodamine B at various concentrations are presented in Figure 7.

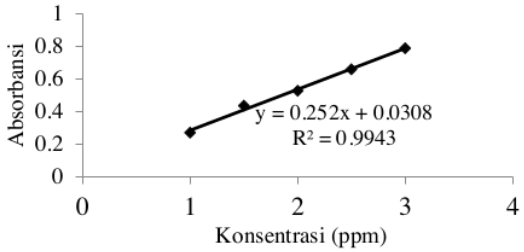


FIGURE 7 Calibration curve of rhodamine B

The absorbance resulting from the standard solution is in the range of 0.2-0.8. absorbance range between 0.2-0.8 can provide an acceptable percentage of analytical error between 0.5-1.05%. This number can be used to minimize systematic errors (Harjito, 2019). Based on the results of the regression calculation from the calibration curve, the equation of the line y = 0.252x + 0.0308 and R2 is 0.9943. The value of R2 is used to determine the linearity of the absorbance results of a standard solution with a certain concentration. According to (Harjito, 2019), the value of R2 which is close to 1 is perfect linearity. Values a, b and R2 from the linear equation were used to measure the concentration of rhodamine B before and after adsorption.

Determination of optimum pH and contact time

One of the factors that can affect the adsorption process is pH. Because the pH state of the adsorption process can cause changes in the surface properties of the adsorbent, the molecular properties of the adsorbate, changes in the composition of the solution, and can also affect the interaction between the adsorbate and the adsorbent (Puriyandari et al., 2019). The pH variations used in this study were pH 2, 3, 4, 5, 6, 7, and 8. The optimum pH as indicated by the condition of the most adsorbed adsorbate. The curve of the relationship between pH and adsorption percentage can be seen in Figure 8.

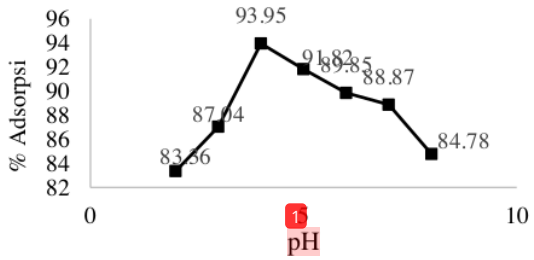


FIGURE 8 Effect of pH on the adsorption of Rhodamine B by C-2-hydroxyphenylcalyx[4]resorcinarene

Based on Figure 8, it can be seen that the amount of rhodamine B adsorbed by C-2-hydroxyphenylcalix[4]resorcinarene is influenced by pH where the percentage of adsorption increases from pH 2 to 4, and the percentage of adsorption decreases from pH 4 to 8. According to Goto et al. al., (2020), under conditions of pH 4 rhodamine B will release Cl- ions and create a positively charged chromophore group, then rhodamine B will turn into zwitter ions at pH 3.6. While C-2-hydroxyphenylcalix[4] resorcinarene has a hydroxy group that will be positively charged in acidic conditions because the –OH group changes to R-OH2+, whereas if it is in an alkaline condition the surface of the adsorbent will tend to be negatively charged (Anwar et al., 2016). The optimum pH occurred at pH 4 with an adsorption percentage of 93.95%. This is because, at pH 4, rhodamine B will turn into a zwitter ion which has a negatively charged group and can interact with C-2-hydroxyphenylcalyx[4] resorcinarene which is positively charged. This interaction indicates an electrostatic attraction between C-2-hydroxyphenylcalyx[4] resorcinarene and rhodamine B (Anwar et al., 2016). Meanwhile, if the adsorption process is in a state of pH 4 the zwitter rhodamine B ion will decrease as the pH increases so that the interaction between the adsorbent and the adsorbate will be weaker and cause the percentage of adsorption to be smaller.

Contact time is an important thing in the adsorption process to determine the presence of the binding event of the adsorbate molecule (Aminullah et al., 2021). The optimum contact time can be determined by varying the contact time at a known optimum pH. In this study, the variations in contact time used were 5, 10, 15, 30, 60, 120, 180, 360, and 720 minutes. The effect of contact time on the adsorption percentage can be seen in Figure 9.

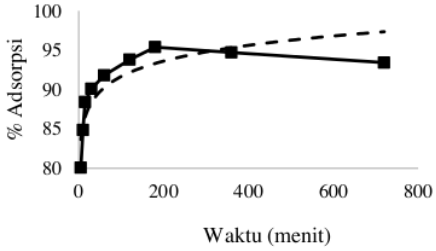


FIGURE 9 Chart of adsorption of rhodamine B by C-2-hydroxyphenylcalyx[4] resorcinarene on variations in contact time

Based on Figure 9, it can be seen that the longer the interaction between C-2-hydroxyphenylcalix[4]-resorcinarene and rhodamine B, the percentage of adsorption tends to continue to increase. At 180 minutes, the equilibrium time is obtained where the absorption tends to remain until 720 minutes. This is because the adsorbent is already saturated with dye ions so that slowly the active site of C-2-hydroxyphenylcalix[4]resorcinarene which binds to rhodamine B begins to release ions from rhodamine B back into the solution so that the addition of contact time can no longer be used. increase the percentage of adsorption (Aminullah et al., 2021). The interaction that occurs between the adsorbent C-2-hydroxyphenylcalyx[4]resorcinarene and rhodamine B is estimated by comparing the results of the FTIR analysis of the adsorbent C-2-hydroxyphenylcalyx [4]resorcinarene before and after the adsorption process is depicted in Fig 10.

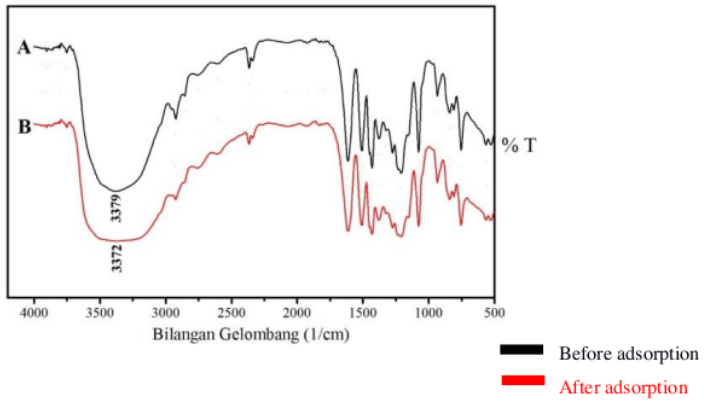


FIGURE 10 FTIR adsorbent C-2-hydroxyphenylcalix[4]resorcinarene before and after adsorption

Based on Figure 10, it can be seen that there has been a shift in the absorption peak of the –OH group from 3379 cm-1 to 3372 cm-1 which indicates that the adsorbent C-2-hydroxyphenylcalix[4]resorcinarene has interacted with rhodamine B. This indicates a strong interaction. match between the $–OH_2+$ group of the adsorbent and the –COO- group of rhodamine B.

Adsorption kinetics

Adsorption kinetics shows the rate of absorption that occurs between the adsorbent and the adsorbate. The dynamics of rhodamine B absorption in an adsorbent occurs in several stages including; 1) The transfer of dye from the solution to the surface boundary layer of the adsorbent and the active site on the surface of the adsorbent begins to open, 2) The dye spreads in through the surface layer of the adsorbent and begins to interact with the open active site, 3) intraparticle diffusion begins where the dye begins to enter the pores of the adsorbent, 4) begins to interact between the adsorbate and the adsorbent at the active site and in the pores of the adsorbent (Yu et al., 2009). The characteristics of the adsorption ability of an adsorbent can be seen from the speed of the adsorbent against the contact time. The adsorption rate can be determined from the adsorption rate constant (k) and the reaction order resulting from an adsorption kinetics model (Widihati et al., 2012). The adsorption kinetics of rhodamine B with C-2-hydroxyphenylcalix[4]resorcinarene was determined based on the equations of the first order pseudo system developed by Lagergen and the second-order pseudo system developed by Yuh Shan Ho (Ho, 2006). Pseudo first order and second order pseudo equations each have different equations (Equation (2.1) and equation (2.2)). The value of k can be determined by making a linear regression equation between ln (qe-qt) vs t. The relationship curve between ln (qe-qt) vs t can be seen in Figure 11.

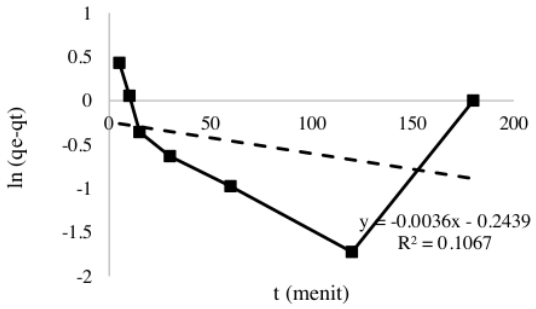


FIGURE 11 Pseudo first order curve

Based on Figure 11, it can be seen that the value of y = -0.0036x - 0.2439 and the value of R2 = 0.1067. While the second-order pseudo can be determined by plotting t/q vs t on the linear regression equation. The relationship curve between t/qt and t can be seen in Figure 12.

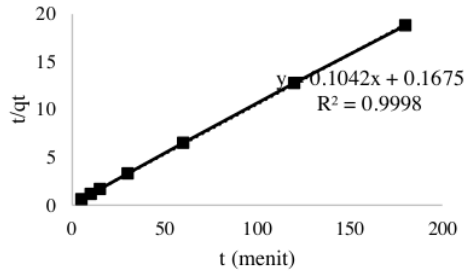


FIGURE 12 Pseudo second order curve

Based on Figure 12, it can be seen that the value of y = 0.1042x + 0.1675 and the value of R2 = 0.9998. Based on the regression equation of the first order pseudo and second-order pseudo it can be seen the comparison of several parameters between the first order pseudo and second-order pseudo as shown in Table 2.

Table 2 Adsorption kinetics of rhodamine B by C-2-hydroxyphenylcalix[4]resorcinarene

Adsorption kinetics	First order	Second order
R^2	0,1067	0,9998
K (g/mg.minute)	0,0082	0,0648
Q (mg/g)	0,7836	9,5969

Based on Table 2, it can be seen that the R2 value of the first-order pseudo-pseudo is lower than the second-order pseudo-pseudo. This indicates that the adsorption of rhodamine B by C-2-hydroxyphenylcalyx[4] resorcinarene follows a second-order pseudo. The results of the suitability of the second-order Pseudo kinetic model in this study are supported by several previous studies (Badri et al., 2020). The adsorption process that followed the second-order pseudo-adsorption showed that the rate of absorption of C-2-hydroxyphenylcalyx[4] resorcinarene against rhodamine B per unit time was directly proportional to the capacity of the adsorbent that was still empty so that at the beginning of the adsorption process there was a drastic reduction in the concentration of the solution, then adsorption continues to decrease until equilibrium conditions are reached (Hasan et al., 2021)

Determination of adsorption isotherm

The adsorption isotherm is the relationship between the amount of adsorbed substance and the equilibrium pressure or equilibrium concentration (Puriyandari, et al., 2019). The adsorption model used in this study is the Langmuir isotherm and the Freundlich isotherm. The Langmuir isotherm and the Freundlich isotherm each have different similarities. Determination of the adsorption isotherm was carried out at the optimum pH, namely pH 4 at the optimum equilibrium time for 180 minutes with various concentrations of 5, 10, 15, 20, 25, and 30 ppm with a volume of rhodamine B as much as 20 mL and the adsorbent used as much as 0.02 grams.

The Langmuir isotherm shows that during the adsorption process, a homogeneous layer is formed on the surface and can only adsorb one molecule of adsorbate for each molecule of the adsorbent so that there will be no repeated interactions between the adsorbed molecules (Kadirvelu et al., 2015). The Langmuir isotherm can be determined by plotting Ce/q with Ce on the linear regression equation. The relationship curve between Ce/q and Ce can be seen in Figure 13.

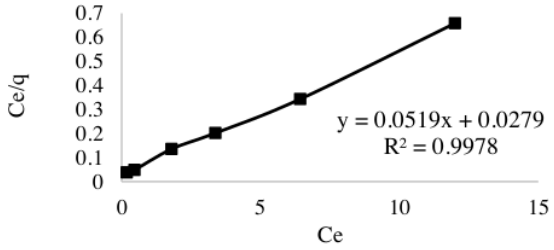


FIGURE 13 Isoterm Langmuir curve

Based on Figure 13, it can be seen that the value of y = 0.0519x + 0.0279 with R^2 of 0.9978. The maximum adsorption capacity (qmax) obtained from this isotherm model is 19.26 mg/g with adsorption energy (E) of 20.57 kJ/mol. The Freundlich isotherm shows that during the adsorption process more than one layer is formed on the surface which is heterogeneous which makes a difference in the binding energy of each active site (Kadirvelu et al., 2005). The Freundlich isotherm can be determined by plotting log q with log Ce on the linear regression equation. The relationship curve between log q and log Ce can be seen in Figure 14.

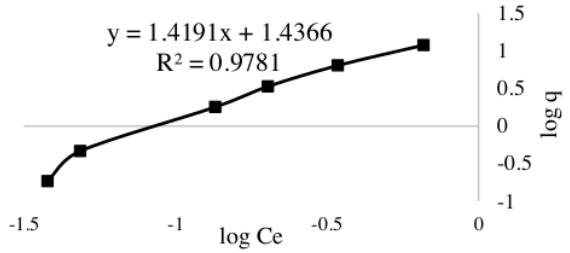


FIGURE 14 Isoterm Freundlich curve

Based on Figure 14, it can be seen that the value of y = 1.4191x + 1.4366 with an R2 value of 0.9781. The maximum adsorption capacity obtained based on the Freundlich isotherm model was 0.704 L/g with adsorption energy (E) of 0.021 J/mol. Based on the regression equation of the Langmuir isotherm and the Freundlich isotherm can be seen that the comparison of several calculation results from the regression equation of each model is as shown in Table 3.

Table 3 Comparison of adsorption isotherm parameters

Parameters	Langmuir	Freundlich
Intersep	0,0279	1,4366
Slope	0,0519	1,4191
R^2	0,9978	0,9781
E	20.575,0 J/mol	0,0217 J/mol

The value of R2 is the coefficient of determination which has a range from 0 to 1. The higher the value of R^2, the better the regression equation for a particular model (Hasan et al., 2021). Based on Table 3, it can be seen that the R^2 value of the Freundlich isotherm model is quite high, this indicates that the adsorption process occurs on a heterogeneous surface and does not only adsorb one adsorbate molecule for each adsorbent molecule. However, the R^2 value of the Langmuir isotherm model is greater than that of the Freundlich isotherm. According to (Ouachtak et al., 2020) an interaction occurs where the adsorbate that is already bound to the adsorbent binds to other adsorbates to form a surface that does not only consist of 1 layer. The adsorption mechanism between rhodamine B and C-2-hydroxyphenylcalyx[4]resorcinarene occurs electrostatic interaction between the negatively

charged carboxyl group on rhodamine B (=COO-) and the positively charged active group on the adsorbent C-2-hydroxyphenylcalyx[4]resorcinarene. This electrostatic interaction indicates chemical adsorption. In addition, hydrogen bonding interactions occur between rhodamine B and the adsorbent C-2-hydroxyphenylcalix[4]-resorcinarene. This electrostatic interaction and hydrogen bonding indicate chemical adsorption (Ouachtak et al., 2020).

The energy required in the adsorption process of rhodamine B with C-2-hydroxyphenylcalix[4]resorcinnarene can be calculated using the equation E = RT ln K. Based on the calculations, the adsorption of rhodamine B with C-2-hydroxyphenylcalyx[4] resorcinarene requires energy of 20.57 kJ/mol and qmax from the adsorption process were 19.26 mg/g. This qmax value is greater than the adsorption of rhodamine B from banana peel adsorbent with an adsorption capacity of 3.8 mg/g (Singh et al., 2018), activated carbon adsorbent from sago waste with an adsorption capacity of 16.2 mg/g (Kadirvelu et al., 2005), and adsorbent activated carbon from willow leaves with an adsorption capacity of 1.94 mg/g (Qu et al., 2015).

Desorption

The adsorbent C-2-hydroxyphenylcalix[4] resorcinarene has the advantage of its ability to be used repeatedly in the adsorption process. Desorption is the process of releasing an adsorbate which is absorbed by the adsorbent (Crawford & Quinn, 2017). The desorption process carried out in this study began with the initial interaction of C-2-hydroxyphenylcalix[4]resorcinarene with rhodamine B at optimum pH and time, then the initial absorption was measured. Furthermore, the contacted C-2-hydroxyphenylcalix[4]resorcinarene was separated from the filtrate, then washed with ethanol. After that, C-2-hydroxyphenylcalyx[4]resorcinarene was reused for the adsorption process of rhodamine B. The results of adsorption of rhodamine B by C-2-hydroxyphenylcalyx[4] resorcinarene can be seen in Figure 16.

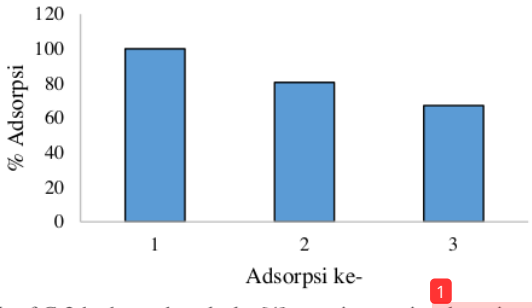


FIGURE 16 Reusable of C-2-hydroxyphenylcalyx[4]resorcinarene in adsorption of rhodamine B

Based on Figure 16, it can be seen that in the first adsorption the percentage of adsorption was 100%, in the second adsorption it was obtained 80.56%, and in the third adsorption, it was obtained 67.18%. Furthermore, calculations were carried out where the percentage of desorption for 3 times reuse of the adsorbent C-2-hydroxyphenylcalix[4]resorcinarene was 100%; 80.56%; and 67.19%. These results indicate that the adsorbent C-2-hydroxyphenylcalix[4]resorcinarene is still effectively used 3 times because the desorption percentage obtained is not less than 50%.

CONCLUSIONS

1. Synthesis of the compound C-2-hydroxyphenylcalix[4]resorcinarene resulted in an orange solid with a yield of 84.7%. The results of the FTIR analysis show that there is absorption at the wavenumber of 1427 cm-1 which is the hallmark of the methine bridge. The results of the 1H-NMR analysis showed that there was a proton signal at H 5.945 ppm which was a signal from the proton bridge methine (=CH-). The results of the BET analysis showed that the surface area of C-2-hydroxyphenylcalyx [4] resin was 14,102 m2/g, the total pore volume was 8,733×10-2 cm3/g, and the average pore radius was 123.852 .
2. Adsorption of rhodamine B by C-2-hydroxyphenylcalix[4]resorcinarene has a maximum condition at pH 4 with an optimum time of 180 minutes. The adsorption kinetics of rhodamine B by C-2-hydroxyphenylcalyx[4] resorcinnarene followed the second-order pseudo kinetics model. The adsorption of rhodamine B by C-2-hydroxyphenylcalix[4]resorcinarene was carried out according to the Langmuir isotherm model and also the Freundlich isotherm with the maximum adsorption capacity (qmax) for the Langmuir isotherm of 19.26 mg/g and the adsorption energy (E) of 20.57 kJ/mol.

ACKNOWLEDGMENTS

This research was supported by Research and Community Service (LPPM) of Universitas Jenderal Soedirman through 'Riset Peningkatan Kompetensi 2020'

REFERENCES

1. Aliabadi, M., Morshedzadeh, K., & Soheyli, H. Removal of Hexavalent Chromium from Aqueous Solution by Lignocellulosic Solid Wastes. *International Journal of Environmental Science & Technology*, *3*(3), 321-325. (2006).
2. Aminullah, Etika, S. B., & Amelia, F. Optimasi Kecepatan Pengadukan dan Waktu Kontak Zat Warna Metanil Yellow Terhadap C-sinamalkaliks[4]resorsinarena (CSKR). *Periodic*. 10(1). 7–11. (2021).
3. Anwar, C., Jumina, Siswanta, D., Santosa, S. J., Dewi, R. K., & Mardjan, M. I. D. Adsorption Study of Pb (II), Cd (II), Hg (II) and Cr (III) Onto Calix[4]resorcinarene Derivative. *Oriental Journal of Chemistry*. 32(6). 2881–2887. (2016).
4. Badri, A. F., Palapa, N. R., Mohadi, R., Mardiyanto & Lesbani, A. Mg-Cr Layered Double Hydroxide with Intercalated Oxalic Anion for Removal Cationic Dyes Rhodamine B and Methylene Blue. *Journal of Environmental Treatment Techniques*. 9(1). 85–94. (2020).
5. Crawford, C. B., & Quinn, B. The Interactions of Microplastics and Chemical Pollutants. *Microplastic Pollutants*, 131–157. (2017).
6. Eddaif, L., Trif, L., Telegdi, J., Egyed, O., & Shaban, A. Calix[4]resorcinarene Macrocycles: Synthesis, Thermal Behavior and Crystalline Characterization. *Journal of Thermal Analysis and Calorimetry*. 137(2). 529–541. (2019).
7. Etika, S. B., Nasra, E., & Rilaztika, I. Synthesis and Characterization of C-cinnamalcalix[4]resorsinarena from Cinnamon Oil Waste West Sumatra. *IOP Conference Series: Materials Science and Engineering*. 335(1). 1–8. (2018).
8. Etika, S. B., Nasra, E., Hafids, A., & Sari, T. K. Utilization of C-cinnamalcalix[4]resorcinarene as Adsorbent for Rhodamin B and Methanil Yellow. *Advances in Biological Science Research*. 10. 234–237. (2020).
9. Goto, Y., Nema, Y., & Matsuoka, K. Removal of Zwitterionic Rhodamine B Using Foam Separation. *Journal of Oleo Science*. 69(6). 563–567. (2020).
10. Handayani, S. N., Jumina, Mustofa, & Swasono, D. R. T. Antioxidant Assay of C-2-hydroxyphenylcalix[4]resorcinarene Using DPPH Method. *International Journal of ChemTech Research*. 9(2). 278–283. (2016).
11. Harjito. Perbandingan Metode Kurva Kalibrasi / Standar dan Metode Adisi Standar pada Pengujian Chrom Total dalam Bahan Makanan Menggunakan Spektrometri Serapan Atom (SSA). *Jurnal Inovasi Dan Pengelolaan Laboratorium*. 1(1). 26–30. (2019).
12. Hasan, A., Yerizam, M., & Yahya, M. H. Mekanisme Adsorben Zeolit dan Manganese Zeolit Terhadap Logam Besi (Fe). *Jurnal Kinetika*. 12(1). 9–17. (2021).
13. Heaton, A. *The Chemical Industry 2th edition*. London: Blackie Academic and Profesional, Chapman & Hal London. (1994).
14. Hindryawati, N. *Fotokatalis dalam Pengolahan Limbah Tekstil*. Yogyakarta: Budi Utama. (2020)
15. Ho, Y. S. Review of Second-order Models for Adsorption Systems. *Journal of Hazardous Materials*. 136(3). 681–689. (2006).
16. Jumina, Priastomo, Y., Setiawan, H. R., Mutmainah, Kurniawan, Y.S., Ohto, K. Simultaneous Removal of Lead (II), Chromium (III), and Copper (II) Heavy Metal Ions Through an Adsorption Process using C-phenylcalix[4]pyrogallolarene Material. *Journal of Environmental Chemical Engineering*. 8(4). 103971. https://doi.org/10.1016/j.jece.2020.103971. (2020).
17. Kadirvelu, K., Karthika, C., Vennilamani, N., & Pattabhi, S. Activated Carbon from Industrial Solid Waste as an Adsorbent for the Removal of Rhodamine-B from Aqueous Solution: Kinetic and Equilibrium Studies. *Chemosphere*. 60(8). 1009–1017. (2005).
18. Kementerian Perindustrian. *Sepanjang 2019, Sektor Industri Unggulan Tumbuh Melesat*. Kementerian Perindustrian Republik Indonesia. diakses pada 21 November 2020. https://kemenperin.go.id/artikel/21492/Sepanjang-2019,-Sektor-Industri-Unggulan-Tumbuh-Melesat. (2020)
19. Musafira, Adam, N. M. & Puspitasari, D. J. Pemanfaatan Limbah Kulit Buah Pisang Kepok (Musa paradisiaca) Sebagai Biosorben Zat Warna Rhodamin B. *Kovalen*. 5(3). 308–314. (2019).
20. Ouachtak, H., El Haouti, R., El Guerdaoui, A., Haounati, R., Amaterz, E., Addi, A. A., Akbal, F., & Taha, M. L. Experimental and Molecular Dynamics Simulation Study on the Adsorption of Rhodamine B Dye on Magnetic Montmorillonite Composite γ-Fe2O3@Mt. *Journal of Molecular Liquids*. 309. 1–18. (2020).
21. Pescok, R. L., Shields, L. D., Cairns, T., & Mc. William, I. G. *Modern Methods of Chemical Analysis 2nd edition*. New York: Jhon Wiley and Sons. (1976).

22. Puriyandari, D., & Laksono, P. J. Pengaruh Ion Cr (VI) pada Variasi pH Terhadap Serapan Ion Cu (II) Oleh Adsorben Kulit Kacang Tanah dengan Spektrofotometri Serapan Atom. *Orbital: Jurnal Pendidikan Kimia*. 3(1). 15–29. (2019).
23. Putri, S. A., Asnawati, & Indarti, D. Optimalisasi Adsorpsi Zat Warna Rhodamin B pada Hemiselulosa dalam Sistem Dinamis. *Berkala Saintek*. 7(1). 1–6. (2019).
24. Qu, J., Zhang, Q., Xia, Y., Cong, Q., & Luo, C. Synthesis of Carbon Nanospheres Using Fallen Willow Leaves and Adsorption of Rhodamine B and Heavy Metals by Them. *Environmental Science and Pollution Research*. 22(2). 1408–1419. (2015).
25. Rahayu, S., Herawati, N., & Wijaya, M. Sintesis Nanopartikel Mangan Oksida dengan Metode Sol Gel dan Uji Aktivitas Katalitik terhadap Degradasi Zat Warna Rhodamin B. *Chemica: Jurnal Ilmiah Kimia Dan Pendidikan Kimia*. 21(2). 190–199. (2020).
26. Rahayu, A. P., Sulmartiwi, L., & Kurnia, K. A. Overview of the Impact of Different Concentration of Acid Solutions in the Production of Adsorbents from Shrimp Waste and the Capacity to Eliminate Textile Colours. *IOP Conference Series: Earth and Environmental Science*. 718(1). 1–4. (2021).
27. Santos, O. A. A. D., Castelli, C. Z., Oliveira, M. F., Neto, A. F. D. A., & De Silva, M. G. C. Adsorption of Synthetic Orange Dye Wastewater in Organoclay. *Chemical Engineering Transactions*. 32. 307–312. (2013).
28. Singh, S., Parveen, N., & Gupta, H. Adsorptive Decontamination of Rhodamine-B from Water Using Banana Peel Powder: A biosorbent. *Environmental Technology and Innovation*. 12. 189–195. (2018).
29. Tuzahiroh, A. Sintesis C-hidroksifenilkaliks[4]resorsinarena serta Uji Aktivitas Antibakteri Terhadap Bakteri *Staphylococcus aureus*. *Skripsi*. Purwokerto : Universitas Jenderal Soedirman. (2020).
30. Virtanen, T., Rudolph, G., Lopatina, A., Al-Rudainy, B., Schagerlöf, H., Puro, L., Kallioinen, M., & Lipnizki, F. Analysis of Membrane Fouling by Brunauer-Emmet-Teller Nitrogen Adsorption/Desorption Technique. *Scientific Reports*. 10(1). 1–10. (2020).
31. Widihati, I. A. G., Suastuti, N. G. A. M., & Nirmalasari, M. A. Y. Studi Kinetika Adsorpsi Larutan Ion Logam Kromium (Cr) Menggunakan Arang Batang Pisang (Musa Paradisiaca). *Jurnal Kimia*. 6(1). 8–16. (2012).
32. Wulandari, R., Jumina, & Siswanta, D. Adsorption of Remazol Brilliant Blue R (RBBR) by C-4-ethoxy-3-methoxyphenylcalix[4]resorcinarene Triphenylphosphonium Chloride. *Advanced Materials Research*. 1101. 290–293. (2015).

study kinetic rhodamin b onto c-hidrokxy phenylcalix-4-recorcinarena

ORIGINALITY REPORT

16%	1%	15%	1%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	S N Handayani, Irmanto, N N Indriyani. "Removal of rhodamine b using 4-hydroxy-3-methoxyphenylcalix[4]resorcinarene", Journal of Physics: Conference Series, 2020 Publication	14%
2	Submitted to Udayana University Student Paper	1%
3	Kadek Novi Sri Budhiary, Indro Sumantri. "Langmuir and Freundlich isotherm adsorption using activated charcoal from banana peel to reduce total suspended solid (TSS) levels in tofu industry liquid waste", IOP Conference Series: Materials Science and Engineering, 2021 Publication	1%
4	neptjournal.com Internet Source	1%

Exclude quotes	Off	Exclude matches	< 1%
Exclude bibliography	On		