Adsorption of remazol yellow FG from aqueous solution on chitosan-linked P-T-Butylcalix[4]Arene

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Abstract. Chitosan-liked p-t-butylcalix[4]arene can be applied as an adsorbent of dye Remazol Yellow FG because it has an active group of hydroxy (-OH) and amine (-NH$_2$). Adsorption had done by comparing to chitosan. Adsorption was carried out in a batch system. Several variables including pH, contact time, and initial concentration of dye Remazol Yellow FG were determined. The optimum adsorption conditions of dye Remazol Yellow FG by chitosan dan chitosan-liked p-t-butylcalix[4]arene occurred at pH 4 and a contact time of 135 minutes. The adsorption kinetics of dye Remazol Yellow FG using chitosan and chitosan-liked p-t-butylcalix[4]arene followed Ho kinetics model, pseudo-second order and the rate constant of adsorption was 2.42 x 10$^{-4}$ g/mg.menit and 3.63 x 10$^{-4}$ g/mg.menit. The isothermal study showed that adsorption of dye Remazol Yellow FG using chitosan and chitosan-liked p-t-butylcalix[4]arene tends to follow the Langmuir isotherm, with adsorption energy was 24.92 kJ/mol and 32.21 kJ/mol.

1. Introduction

The development of the textile industry has a positive impact that can improve the welfare of the community. In another hand, development of the textile industry could also have a negative impact that environmental pollution when the wastewater from the textile dyeing process settled into rivers or sewers without treatment processing. Batik industrial waste water is originating from the dyeing, washing, printing and finishing the process. Waste staining of batik industry contains several components such as a residual dye, salt and additive materials such as urea, sodium alginate, sodium bicarbonate and water (residual staining and washing) [1].

Residual dye was the most dominant component of the waste dyed batik industry. Classification of dyes based on their use that was an acid dye, basic, direct, mordant, metal complexes, azoat, sulphur, vessel, dispersions and reactive [2]. Reactive dyes are often used in the batik industry include Procion, Cibracon, Drimaren, and Lavafix, which can hold a substitution reaction with the fiber, and azo dyes are Remazol, forecasts allowing, and Primaxin, which can hold an addition reaction [3].

Remazol Yellow FG is an azo dye which is a kind of synthesis of dyes are quite important and widely used. More than 27.2% of the textile industry uses Remazol Yellow FG dye. Azo dye has a chromophore system of the azo group (-N=N-), which binds to the aromatic group. Reactive dye chromophore is usually the azo and anthraquinone systems with relatively small molecular weight. Absorption of the fiber was not great so that the dye does not react with the fibers easily removed [4].
Many methods have been developed for the treatment of waste water, including precipitation, extraction, separation with membranes [5], ion exchange [6], and adsorption. Precipitation method was the most economical method, but it was not efficient to the aqueous solution, ion exchange method, and reverse osmosis are generally effective, but requires equipment and operating costs are relatively high. Adsorption method was one potential alternative method because the process is relatively simple, can work at low concentrations, can be recycled, and the costs involved are relatively inexpensive [7].

Adsorption method has been proven effective to reduce the concentration of the dye in water as reported by various studies, including the adsorption of the dye textile waste types BR Red HE 7B using rice straw [8]. Adsorption used the fly ash [9]. The use of natural adsorbent which cheap and abundant certainly very profitable, but to know the active compound which acts as the adsorbent of such materials was difficult, it can be difficult to explain the phenomenon of adsorption occurs. It was, therefore, necessary to find another adsorbent whose structure was known with certainty, and this can be obtained from the synthesis.

One group of synthetic compounds that have great potential to be developed as an adsorbent was chitosan. Chitosan is the result of deacetylation of chitin which has undergone the removal of acetyl groups. Acetyl group was missing from the process of deacetylation leaving a free amino group that causes the chitosan was polycationic [10]. Research on the application of chitosan as an adsorbent has been widely studied, including Rakhmawati (2007) [4] which successfully applying chitosan as an adsorbent dye. Mahatmanti (2003) [11] was using chitosan as an adsorbent for the adsorption of methyl orange dye. Chitosan which has specific properties such as biocompatibility, a non-toxic and renewable biopolymer made of chitosan as serious attention to continue to be developed and researched. Improving the ability of chitosan can be crosslinked on macromolecular compounds namely crown ether p-t-butylcalix[4]arene. p-t-butylcalix[4]arene has a geometry such as baskets and hollow, can be used in guest-host systems (guest host) [12]. Modification of chitosan has to improve as an adsorbent that is by p-t-butylcalix[4]arene attached to the chitosan. In this research, dye adsorption Remazol Yellow FG by using research results Hand (2014) [13] p-t-butylcalix[4]arene tied to generate chitosan, chitosan-p-t-butylcalix[4]arene. Chitosan-p-t-butylcalix[4]arene was expected to effectively and efficiently so it can be useful to reduce environmental pollution, especially in the textile industry.

2. Research Methods

2.1. Effect of solution pH Remazol Yellow FG

A total of 25 mL of Remazol Yellow FG at a concentration of 100 ppm respectively set the initial pH to 1.5; 2; 4; 6; 8; 10 with HNO$_3$ and NaOH. Then into each solution was added 20 mg of chitosan-p-t-butylcalix[4]arene. The chitosan-p-t-butylcalix[4]arene was synthesized based on the previous research [4]. The mixture was stirred at a speed of 200 rpm for 2 hours. Afterward, the solution was filtered, and the filtrate was analyzed by UV-Vis spectroscopy. Equal treatment performed on chitosan as a comparison.

2.2. Effect of Stirring Time

A total of 25 mL of Remazol Yellow FG each with a variation of time at 5, 15, 45, 135, 405 minutes was set at optimum pH. Then into a solution, the the 20 mg of chitosan-p-t-butylcalix[4]arene adsorbent was added and stirred for optimum time with a speed of 200 rpm. The solution is then filtered and analyzed by UV-Vis spectroscopy (Optima SP-300). Equal treatment performed on chitosan as a comparison.

2.3. Influence of Solution Concentration Remazol Yellow FG

A total of 25 mL of Remazol Yellow FG each with varying concentrations of 100, 150, 200, 250, 300 ppm was set at optimum pH. Then into a solution, 20 mg of chitosan-p-t-butylcalix[4]arenes
adsorbent was added and stirred for optimum time with a speed of 200 rpm. The solution is then filtered and analyzed by UV-Vis spectroscopy. The same treatment was done for chitosan as a comparison. Morphological analysis was conducted by Scanning Electron Analysis (SEM) JEOL JSM 6360 equipped with an elemental analysis of EDX (JED-2200). Meanwhile, the functional group analysis was conducted by FTIR analysis (Prestige-21 Shimadzu).

3. Results And Discussion

3.1. Determination of Optimum pH

Effect of pH was very important in the process of adsorption, adsorption processes depending on the type of adsorbent, the adsorbed species and the type of solvent. Variations initial pH of the solution at pH 1.5, 2, 4, 6, 8 and 10, get results as shown in Figure 1.

![Figure 1. Concentration of Dye Absorbed Remazol Yellow FG on the variation of pH](image)

Based on the data in Figure 1 shows that both adsorbent experience optimum absorption at pH 4, so that it can be said that the optimum pH-absorption occurs at pH 4. The phenomenon that occurs possibly because, at pH 4, the atmosphere is not strongly acidic, proton (H+) was used to protonated D-SO₂CH₂CH₂OSO₃Na group into vinyl sulphone (D-SO₂-CH=CH₂) groups did not take place completely. Vinyl sulphone group formed perfectly leads to reduced interaction with the chitosan and chitosan-p-t-butylcalix[4]arene as an adsorbent.

Sakkayawong (2005) [5] suggested that at acidic conditions the hydrogen atoms (H+) in solution can protonate primary amine group (R-NH₂) of chitosan becomes (R-NH₃⁺). Similarly, on the chitosan-p-t-butylcalix[4]arene adsorbent, hydrogen atoms (H+) in solution can protonate secondary amine group (R-R’-NH). In aqueous solution, the dye will dissolve, and sulphonate groups on reactive dye Remazol Yellow FG dissociated and transformed into ions. The adsorption process was then generated from the interaction between the dye with an adsorbent.

Adsorption process which takes place at pH 1.5 and pH 2 has a low adsorption efficiency value; it was possible proton (H⁺) are used for protonated D-SO₂CH₂CH₂OSO₃Na group into vinyl sulphone group (-SO₂-CH=CH₂) has complete, so that the interaction between chitosan and chitosan-p-t-butylcalix[4]arene adsorbent was reduced.

Adsorption of Remazol Yellow FG dye by chitosan and chitosan-p-t-butylcalix[4]arene at pH 8 and pH 10 had a small adsorption value. This was because the highly alkaline pH condition, D-SO₂CH₂CH₂OSO₃Na group into vinyl sulphone group (-SO₂-CH=CH₂) was complete. As at pH 6, the atmosphere was not too alkaline vinyl sulphone group formation is not running perfectly, so still have
a sulphonate group in the reactive dye Remazol Yellow FG, which dissociates and transformed into ions, then interact with the adsorbent.

3.2. Effect of Contact Time and Parameter Kinetics

The contact time was the time required adsorbent to absorb dye Remazol Yellow FG. Variation of the contact time in this study was 5, 15, 45, 135 and 405 minutes. Effect of contact time on the amount of dye adsorbed can be seen in Figure 2.

![Concentration of Dye Absorbed Remazol Yellow FG on the variation of contact time](image)

**Figure 2.** Concentration of Dye Absorbed Remazol Yellow FG on the variation of contact time

Based on data from the influence of contact time, then it can be studied adsorption kinetics. Results of the adsorption kinetics study of both adsorbents shown in Table 1.

**Table 1.** Assessment of the dye adsorption kinetics of Remazol Yellow FG

| Adsorption kinetics | Adsorbent | Adsorbent |
|---------------------|-----------|-----------|
|                     | Chitosan  | chitosan-p-t-buthylcalix[4]arene |
| Lagergren:          |           |           |
| K (min⁻¹)           | 0.012     | 0.015     |
| R²                  | 0.979     | 0.791     |
| Ho:                 |           |           |
| K (g mg⁻¹ min⁻¹)    | 2.42 x 10⁻⁴ | 3.63 x 10⁻⁴ |
| R²                  | 0.999     | 0.966     |

Based on the linearity calculation, it can be concluded that kinetics equation Lagergren pseudo first-order less suitable to be applied as adsorption kinetics model for both adsorbents, while the second order equation pseudo-Ho had high linear coefficient so that both of adsorbent was likely to follow a pseudo second order Ho.

Rate constants adsorption value of second order Ho equation for both chitosan and chitosan-p-t-buthylcalix[4]arene adsorbent was 2.42 x 10⁻⁴ g/mg.min and 3.63 x 10⁻⁴ g/mg.min, respectively. Based on the adsorption rate constant value, capabilities interaction of chitosan-p-t-buthylcalix[4]arene faster than with chitosan.

3.3. Effect of Initial Concentration Dyes and Parameter Isotherm

The influence of the initial concentration of Remazol Yellow FG against the adsorbent was shown in Figure 3.
Figure 3. Initial concentration of Dyes variation Remazol Yellow FG on the initial concentration of dye

Figure 3 shown the concentration of adsorbed solution tends to increase with increasing adsorbate concentration. This was because an increase in competition between the adsorbate with the active adsorbent side. The adsorption process was also influenced by the surface area of the adsorbent for adsorption availability. The surface area of the adsorbent was determined by the size and magnitude of the adsorbent pores, the greater of the surface area, the greater on the adsorption had done. Handayani [14] states that the chitosan-p-t-buthylcalix[4]arene adsorbent had an outer surface of 16.352 m$^2$/g, while chitosan according to Cahyaningrum et al. [16] mentions that the surface area is 0.847270 m$^2$/g, and Kelesorgu [17] states that the specific surface area of chitosan was 4.45 m$^2$/g. From these results it can be seen that the surface area of chitosan-p-t-buthylcalix[4]arene adsorbent was larger than the specific surface area of chitosan, this causes the adsorption of chitosan-p-t-buthylcalix[4]arene more than chitosan.

Study of adsorption isotherms was tested to determine whether the dye adsorption with adsorbent followed Langmuir isotherm or Freundlich isotherm using absorbance calculation data. The isotherm study results for adsorption Remazol Yellow FG dye using adsorbents chitosan and chitosan-p-t-buthylcalix[4]arene were presented in Table 2.

Based on Table 2, the linearity graph adsorption level of Langmuir isotherm models was higher than Freundlich isotherm for both chitosan and chitosan-p-t-buthylcalix[4]arene, with a linearity value of 0.975 and 0.910 for chitosan adsorbent and 0.998 and 0.746 for the chitosan-p-t-buthylcalix[4]arene adsorbent. Thus the dye adsorption isotherm Remazol Yellow FG on chitosan and chitosan-p-t-buthylcalix[4]arene more appropriate and tend to follow the model of the Langmuir adsorption isotherm, which showed that both adsorbent chitosan and chitosan-p-t-buthylcalix[4]arene occurred in monolayer, which assumes that the maximum adsorption occurs when all of the active sites of the adsorbent filled by adsorbate forming monolayer. In addition Langmuir models indicated that the adsorption process happening was chemisorption. Adsorption process which influenced by the bond between the active group of dyes that react with a hydroxyl group (OH) on the adsorbent.
Table 2. The dye adsorption isotherms Remazol Yellow FG with adsorbent

| Adsorbent                     | Chitosan | Chitosan-p-t-butylcalix[4]arene |
|-------------------------------|----------|---------------------------------|
| Langmuir:                     |          |                                 |
| \(q_m\) (mg/g)                | 188.31   | 187.28                          |
| \(K\) (L/mol)                 | 21897.37 | 406114.46                       |
| \(E_{adsorpo}\) (kJ/mol)      | 24.92    | 32.21                           |
| \(R^2\)                       | 0.975    | 0.998                           |
| Freundlich:                   |          |                                 |
| \(n\)                         | 2.39     | 6.41                            |
| \(K\) (mol/gr)                | 110.92   | 790.68                          |
| \(R^2\)                       | 0.910    | 0.746                           |

Comparison of optimum adsorption capacity from adsorbent that has been used to adsorb Remazol Yellow FG dye, chitosan and chitosan-p-t-butylcalix[4]arene adsorbent have optimum adsorption capacity greater than other adsorbents, as shown in Table 3.

Table 3. Adsorption Remazol Yellow FG dye by several adsorbent

| Adsorbent                                      | \(q_m\) (mg/gr) |
|------------------------------------------------|-----------------|
| Active water hyacinth [18]                     | 4.43            |
| Reeds activated NaOH                           | 7.85            |
| Copoly(Eugenol-DVB)-Calix[4]resorsinarene      | 12.26           |
| Chitosan                                       | 188.31          |
| Chitosan-p-t-butylcalix[4]arene                | 187.28          |

The optimum adsorption capacity value between the chitosan and chitosan-p-t-butylcalix[4]arene adsorbent had a great optimum capacity value at chitosan adsorbent of 188.31 mg/g and 187.28 mg/g for chitosan and chitosan-p-t-butylcalix[4]arene. This phenomenon allegedly because chitosan-p-t-butylcalix[4]arene adsorbent had bonding process occurs with chitosan causes the adsorbent was increasingly full or bulky, so the adsorption capacity tends less than chitosan without bound. In addition to the chitosan adsorbent adsorption mechanism not only chemisorption but accompanied by physisorption, can be seen from the determination coefficient value on chitosan which was not too far from Langmuir and Freundlich models. Physisorpsi adsorption process involves intermolecular forces (Van der Waals force), and the adsorbed substances were relatively easily separated which allows the desorption.

The determination coefficient \(R^2\) in the chitosan-p-t-butylcalix[4]arene adsorbent was 0.998 which indicated that the adsorption process takes place in Chemisorption, the chemical bonding that occurs between chitosan adsorbent chitosan-p-t-butylcalix[4]arene with Remazol Yellow FG dye. This was supported by \(K\) value that Langmuir provision was a provision related to the free energy or adsorption enthalpy. Low \(K\) value indicates that low adsorption energy and the desorption process rate is larger the rate of the sorption processes. The \(K\) values of chitosan are 21897.37 L/mol, and the \(K\) value of chitosan-p-t-butylcalix[4]arene is 406114.46 L/mol. It indicates that the desorption of chitosan was larger than the desorption from the chitosan-p-t-butylcalix[4]arene.

Determination of adsorption isotherms can also be done by calculating the adsorption energy. In which, if the energy of adsorption is less than 20 kJ/mol, the adsorption follows Freundlich isotherm, while adsorption energy at > 20 kJ/mol follows the Langmuir isotherm [18]. Based on calculations, the adsorption energy of chitosan adsorbent was 24.92 kJ/mol, while the adsorption energy of chitosan-p-t-butylcalix[4]arene adsorbent was 32.21 kJ/mol, which states that chitosan adsorbent and chitosan-p-
t-butylcalix[4]arene follows the Langmuir isotherm. Adsorption energy value can be determined by the Gibbs free energy equation. Gibbs, free energy was negative indicates the adsorption process takes place spontaneously [13], from the calculation of the energy obtained adsorption for the both adsorbent was negative. Thus, adsorption process of chitosan and chitosan-p-t-butylcalix[4]arene adsorbents were spontaneous.

3.4. Adsorbent characterization With FTIR
Characterization of adsorbent was using an infrared spectrophotometer has been conducted to identify the functional groups contained in the adsorbent. FTIR spectra results of Remazol Yellow FG dye as well as a combination of both chitosan before and after being used to adsorb dye Remazol Yellow FG can be seen in Figure 4.

![Figure 4. FTIR spectrum of Remazol Yellow FG dye (a), chitosan before (b) and after (c) adsorption Remazol Yellow FG dye.](image)

Based on FTIR spectra can be obtained information for functional groups contained within the adsorbent. FTIR spectra in Figure 4 can be interpreted that after being used in the adsorption, chitosan provides a wide absorption at 3369.64 cm\(^{-1}\) region that showed the hydrogen bonds. That hydrogen bonding occurs between chitosan adsorbent and Remazol Yellow FG dye.
Adsorption peak on the wave number 1082.07 and 1031.92 cm\(^{-1}\) indicated a C-O bond, the wavelength of 1253.73 cm\(^{-1}\) indicated a S=O bond and a wavelength of 763.61 cm\(^{-1}\) indicated the presence of the -Cl bond on adsorbent which has adsorbed with Remazol Yellow FG dye [20]. The groups contained in Remazol Yellow FG dye. This shows that the chitosan adsorbent can absorb the Remazol Yellow FG dye. The other peaks that are in the dye structure do not appear in clearly due to its low intensity.

Remazol Yellow FG FTIR analysis of chitosan-p-t-butylcalix[4]arene before and after used to adsorb Remazol Yellow FG dye can be seen in Figure 5.

![FTIR spectra](image)

**Figure 5.** FTIR spectra of the dye Remazol Yellow FG (a), chitosan-p-t-butylcalix[4]arene before adsorption, and (b) after adsorption. The adsorbate is the Remazol Yellow FG (c)

FTIR spectrum in Figure 5 shows that the chitosan-p-t-butylcalix[4]arene adsorbent after adsorption showed broad absorption at 3441.01 area. This indicated the presence of hydrogen bonding that occurs between the adsorbent with Remazol Yellow FG dye, besides the difference in the pattern with the advent of peaks at wave number 1060.85; 1031.92; 1006.84 is the group C=S, peak at around the wave number 1201.65 is a group S=O and peak at wave number around 783.10; 742.59 was a -Cl groups [20].
The groups contained in Remazol Yellow FG dye there was also appeared in the adsorbent which had adsorbed. This shows that the chitosan-p-t-butylcalix[4]arene adsorbent can absorb the Remazol Yellow FG dye. Other peaks that are in the dye structure does not appear in clearly because it had a low intensity thus covered by the peaks of chitosan-p-t-butylcalix[4]arene.

3.5. Adsorbent characterization By SEM - EDX

Chitosan adsorbent morphology before and after adsorption were characterized using Scanning Electron Microscopy (SEM) as shown in Figure 6. Based on Figure 6, visible differences between the structure of chitosan adsorbent before and after adsorbed. Chitosan adsorbent which has not been adsorbed was shown in Figure 6a, shows a slotted structure which allows the adsorbate dye can meet the gap on the surface of chitosan. Chitosan adsorbent which has adsorbed shown in Figure 6b, where the visible surface structure has been covered by Remazol Yellow FG dye. This is supported by the results which showed an increase EDX atoms Na, S, and Cl in chitosan adsorbent.

![Figure 6. SEM Results of chitosan Before Adsorption (a), after Adsorption (b)](image)

SEM analysis result of chitosan-p-t-butylcalix[4]arene adsorbent before and after the adsorption was shown in Figure 7. Based on Figure 7 visible differences between the structure of adsorbent chitosan-p-t-butylcalix[4]arene before and after adsorbed. Chitosan-p-t-butylcalix[4]arene adsorbent that has not adsorbed shown in Figure 7a shows the structure more porous compared to chitosan, which allows adsorbate dye can fulfill porous more than chitosan. Chitosan-p-t-butylcalix[4]arene adsorbent that has been adsorbed shown in Figure 7b, where the visible surface structure has been coated with Remazol Yellow FG dye. This was also supported by EDX results which showed an increase of Na, S and Cl atoms in the chitosan-p-t-butylcalix[4]arene adsorbent.

![Figure 7. SEM Results of chitosan-p-t-butylcalix[4]arene before Adsorption (a), after Adsorption (b).](image)
4. Conclusion
Adsorption of the dye Remazol Yellow FG using chitosan and chitosan-p-t-butylcalix[4]arene following the adsorption pseudo second order kinetics of the Ho equation, while the isotherm adsorption test for both adsorbents tends to follow the Langmuir isotherm.

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