Utilization of C-Cinnamal Calix[4] Resorcinarene as Adsorbent for Methanil Yellow

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Abstract. Rapid population growth causes many environmental problems. One of them is the pollution of methanil yellow in the water. One of the effective methods in controlling water pollution caused by dyes is the adsorption method with a batch system. C-Cinnamal Calix [4] Resorcinarene (CCCR) compound is a compound synthesized from cinnamon oil waste that has great potential to be developed as adsorbent for dangerous dyes. The purpose of this study is to determine the maximum absorption capacity of CCCR towards methanil yellow using optimum conditions parameters (concentration and contact time). Absorption of methanil yellow in solution by C-Cinnamal Calix [4] resorcinarene (CCCR) compounds is carried out at the optimum pH of 3 with concentration variations of 20, 50, 100, 150 and 200 mg/L. The amount of methanil yellow reaches an absorption capacity of 1.83 mg/g at a concentration of 150 mg/L, while for the contact time is carried out at the optimum pH and concentration with variations in contact time of 30, 60, 90, 120, 150, and 180 minutes. The Results show that the optimum contact time was 150 minutes with an absorption capacity of 2.1375 mg /g.

1. Introduction

The rapid development of the textile industry in Indonesia has had a negative impact on health due to environmental pollution. Wastewater discharged into the environment such as rivers, sewers and waters without being treated first will cause changes in the quality of river water and sewage water so that it cannot be used according to its function. Lately, most of the textile industry uses synthetic dyes for reasons that are durable, cheap and easy to obtain, but the resulting waste is still colored and difficult to degrade. 15 to 20\% of the dyes used will remain in the waste water which will eventually enter the surrounding environment. To protect the public from the dangers caused by these dangerous dyes, the Indonesian Ministry of Health has regulated it.

The uncontrolled handling of industrial waste disposal systems causes environmental pollution by hazardous materials from the textile, paper, pigment and paint industries, then this industrial activity releases harmful dyes and enters through the food chain so that it has a bad impact on human health. Methanil yellow is a water-soluble synthetic yellow dye chemical, and can cause tumors in various tissues of the liver, bladder, digestive tract, cancer and skin tissue. The substance of methanil yellow is in the form of a powder and is toxic. The chronic dangers of using methanil yellow in the long term cause health problems in liver function, bladder disorders and cancer \cite{1}.

Several studies on methanil yellow that have been carried out include research on the absorption of the dye methanil yellow by batch method using pensi shell biosorbent (Corbicula moltkiana). The
optimum conditions for absorption occurred at pH 4 and an initial concentration of 100 mg/L [2] and research on the development of azo dye (methanyl yellow) removal process that dissolves in water using adsorbent under ash and de-oiled soybeans. Development of a water-soluble azo (methanyl yellow) dye removal process using bottom ash adsorbent and de-oiled soybean. The optimum pH is at pH 2 and the optimum concentration is at 100 mg/L [3].

There are many methods for treating this waste, including nano filtration, electrochemical and coagulation, but these methods are less efficient and expensive. For this reason, researchers used the adsorption method, because it is cheaper and safer [2].

Calixarene (Calixarene) is an organic compound that has great potential to be used as an adsorbent. Calixarene is a cyclic oligomeric compound composed of aromatic units connected by a methylene bridge. Calix because it has a basket-like and hollow geometry. The derivative of calixarene is calix [4] resorcinene. Calix [4] resorcinene is a synthetic macromolecule which is a resorcinol residue in a cyclic series and is connected by a methylene bridge [4] The reaction of resorcinol with various aldehydes and acid catalysts can synthesize calx [4] and the aldehydes used are cinamaldehyde, benzaldehyde, and acetaldehyde.

The use of C-Sinamalkaliks [4] resorcinene (CCCR) as an adsorbent has been carried out by [5], [6] and [7] using heavy metal cations, namely Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, and Cr$^{3+}$. Where the optimum pH for Cu$^{2+}$ metal is pH 4, the optimum contact time obtained is 90 minutes and the optimum concentration obtained is 80 ppm. For Cd$^{2+}$ metal, the optimum pH obtained was pH 3, the contact time obtained was 120 minutes, and the concentration obtained was 80 ppm. For Pb$^{2+}$, the optimum pH obtained was pH 4, the contact time obtained was 60 minutes, and the concentration obtained was 40 ppm. For Cr$^{3+}$, the optimum pH obtained was 4, the optimum contact time was 150 minutes, and the optimum concentration was 100 ppm. Therefore, the researcher wanted to know whether the C-Sinamalkalik compound [4] resorcinene (CCCR) could be used as an adsorbent for the dye methanyl yellow.

This study aims to determine the optimum conditions (pH, concentration and contact time) of methanyl yellow by using the synthesized CCCR absorbent agent and to determine the optimum absorption capacity of methanyl yellow against CCCR using a UV-VIS spectrophotometer.

2. **Materials and Methods**

2.1. **Material and Equipments**

The equipments used in this research are reflux set, buchner funnel, FTIR (Jasco 460 plus Spectroscopy), rotary evaporator (Heidolph Laborota 4000), Desiccator, Ultraviolet Spectroscopic Agilent 8453 UV-Vis. For pH measurement, a Hitachi-Horiba Model M-5 glass electrode pH meter was used. The materials are NaOH 0.1 M (merck), HNO3 0.1 M (merck), Synthesized CCCR, and methanyl yellow.

2.2. **Sample Preparation**

This study used CCCR which was synthesized in the previous study which was refined using a mortar and pestle. CCCR which has been refined with a particle size of 75 µm.

2.3. **Research Treatment Using Batch Method**

2.3.1. **Determine the maximum λ of methanyl yellow absorption.** Measuring the maximum wavelength used a 10 ppm methanyl yellow solution, then measured with a UV-Vis spectrophotometer and obtained the maximum wavelength.

2.3.2. **Solution pH.** The maximum pH measurement used 10 ml of methanyl yellow solution with a concentration of 10 ppm with a variation of pH 2, 3, 4, 5, 6, 7, and 8, then each solution was contacted with 0.1 gram of CCCR using the Batch method, then the solution was in the shacker at a speed of 200 rpm for 60 minutes. The solution is filtered and the filtrate is collected. The concentration of methanyl
yellow absorbed by the filtrate was measured by a UV-Vis spectrophotometer, so that the optimum pH was obtained.

2.3.3. Concentration of Solution. The effect of the maximum concentration was used a solution of 25 ml of methanyl yellow with various concentrations of 10, 50, 100, 150, and 200, ppm at the optimum pH. Then each solution was contacted with 0.1 gram of CCCR using a batch system, the solution was in the shacker at a speed of 200 rpm for 60 minutes. Then the solution is filtered and the filtrate is stored. The filtrate was measured for the concentration of metanyl yellow which was not absorbed by a UV-Vis spectrophotometer, so that the optimum concentration was obtained.

2.3.4. Contact Time. A total of 0.1 gram of CCCR was contacted with 25 ml of methanyl yellow solution with optimum pH and concentration. Then each solution was contacted using a batch system, the solution was shaker at a speed of 200 rpm for 30, 60, 90, 120, 150, and 180 minutes. Then the solution is filtered and the filtrate is accommodated. The filtrate was measured for the concentration of metanyl yellow which was not absorbed by a UV-Vis spectrophotometer. So that the optimum contact time is obtained.

3. Results and Discussion

3.1. Determination of the Maximum Wavelength (λ max) of Methanyl Yellow

Determination of the maximum wavelength was carried out by taking the main solution of 1000 mg/L of methanyl yellow dye which had been diluted to 10 mg/L. The results of the UV-Vis spectrophotometer analysis with the wavelength range used were 350-600 nm. The maximum wavelength of the methanyl yellow solution was 436 nm.

3.2. FTIR spectra analysis from CCCR

FTIR Spectra analysis is very important to do which aims to determine the functional groups of the adsorbents involved in the adsorption process of the dye methanyl yellow and to predict the absorption mechanism between the adsorbent and the dye [2]. The CCCR used in this study is the synthesis CCCR from previous research [7] that has been characterized. The results of CCCR characterization using FT-IR (Fourier Transform InfraRed) spectroscopy showed a wide and strong peak at 3306.68 cm⁻¹ which indicated the presence of an O–H group. Then at wave numbers 1610.56 cm⁻¹ and 1495.95 cm⁻¹ which indicate the presence of the -C = C aromatic group. At the wave number 1110 cm⁻¹ there is an absorption band which indicates a vibration of O = S = O (SO₂), the presence of the O = S = O (SO₂) vibration indicates the presence of the –SO₃H group in the CCCR compound [8]. Furthermore, the absorption at the fingerprint wave number 971.98 cm⁻¹ - 836.05 cm⁻¹ indicates the presence of –C = C bending. The results of CCCR characterization of pure cinnamaldehyde showed the same results as the CCCR characterization of isolated cinnamaldehyde and almost the same as the CCCR that has been contracted.

CCCR that had been contacted with methanyl yellow showed a slight change in uptake in each functional group. The OH- functional group appears at wave number 3334.26 cm⁻¹, then in the -C = C aromatic group the absorption band is at wave numbers 1615.14 cm⁻¹ and 1441.35 cm⁻¹, while the group O = S = O (SO₂) the absorption band is at the wave number 1283.85 cm⁻¹.

3.3. Optimum pH of Methanyl Yellow

The pH value of the dye solution is very important in the adsorption process, the pH of the solution greatly affects the surface of the adsorbent and the adsorbate or dye molecules [2]. The effect of pH of the solution on the adsorption of methanyl yellow dye was carried out in a pH range of 2, 3, 4, 5, 6, 7, and 8 with a concentration of 10 mg/L of methanyl yellow solution. The relationship between the adsorption capacity and the pH variation of methanyl yellow can be seen in Figure 1.
Figure 1. Graphic Effect of Methanyl Yellow pH on CCCR

The optimum pH occurs at pH 3 with an absorption capacity of 0.17 mg/g. The initial absorption capacity increases from 0.15 mg/g to 0.17 mg/g at pH 2 to 3. The adsorption capacity increases at acidic pH due to an increase in H⁺ ions which will encourage electrostatic attraction with the methanyl yellow anion. Furthermore, from pH 3 to 8 there was a decrease in the adsorption capacity with the absorption capacity of metanyl yellow at pH 4 of 0.08 mg/g, pH 5 of 0.09 mg/g, pH 6 is 0.07 mg/g, pH 7 is 0.06 mg/g and pH 8 is 0.03 mg/g can be seen in Figure 1. Meanwhile, alkaline pH decreases the adsorption capacity due to an increase in OH⁻ ion. The presence of OH⁻ ion causes a new competitor to compete with the anion of the dye methanyl yellow to fill the active site resulting in a decrease in the adsorption capacity due to electrostatic repulsion between the anion of the dye methanyl yellow and the adsorbent surface [2].

3.4. Optimum Concentration of Methanyl Yellow

The concentration of adsorbate (dye) is one of the factors that influence adsorption because the initial concentration of the dye provides a driving force in the transfer process of dye molecules between the liquid and solid phases so that it affects the interaction between adsorbent and adsorbate [9]. In this study, the effect of the concentration of methanyl yellow on CCCR was carried out in the range of 10, 50, 100, 150 and 200 mg/L with optimum pH conditions pH 3. From the results, the optimum absorption of the dye methanyl yellow by CCCR was achieved at a concentration of 150 mg/L with an adsorption capacity of 1.83 mg/g. The effect of the optimum concentration of methanyl yellow on CCCR can be seen in Figure 2.
Figure 2 shows the 10 mg/L methanyl yellow concentration, the absorption of methanyl yellow was 0.33 mg/g, at a concentration of 50 mg/L to 150 mg/L, the absorption capacity increased by 0.91 mg/g, 1.7 mg/g and 1.83 mg/g. Meanwhile, at a concentration of 200 mg/L, the absorption capacity decreased to 1.26 mg/g. The higher the dye concentration will increase the adsorption capacity due to the increased electrostatic interaction between the active site on the adsorbent surface and methanyl yellow molecules. There is a decrease in adsorption capacity at higher concentrations because many dye molecules are not absorbed due to the active site which is not proportional to the amount of adsorbate so that the active side of the adsorbent is saturated [10]. The adsorption capacity is proportional to the increase in concentration.

3.5. Optimum Contact Time for Methanyl Yellow

Contact time is an important thing in the adsorption process, because the contact time allows the diffusion and binding process of the adsorbate molecules to take place. In this study, the variations in contact time used were 30, 60, 90, 120, 150 and 180 minutes which aimed to determine the optimum contact time at pH 3, the concentration of methanyl yellow solution 150 mg/L, the volume of the dye solution 25 ml and the mass of the adsorbent. 0.1 gram. From the research results obtained contact time The optimum absorption of methanyl yellow by CCCR is 150 minutes with an absorption capacity of 2.1375 mg/g. The effect of contact time on the absorption of methanyl yellow can be seen in Figure 3.
The decrease in adsorption capacity shows that the active side of CCCR is saturated so that it is unable to absorb more methanyl yellow. The decrease in adsorbate absorption by the adsorbent is due to the desorption process. Desorption is the process of releasing ions or adsorbate molecules that have bound to the active groups on the adsorbent surface [11].

4. Conclusion
The optimum conditions for absorption of methanyl yellow against CCCR were obtained at pH 3, concentration 150 mg/L, contact time 150 minutes. The optimum absorption capacity of methanyl yellow dye against CCCR is 1.83 mg/g.

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