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Adsorption of Metanil Yellow Dye with Sugarcane Bagasse (*Saccharum officinarum* L.) Activated Carbon Modified with Cetyl Trimethyl Ammonium Bromide (CTAB) Surfactant

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ABSTRACT

Environmental pollution caused by textile industry wastewater containing synthetic dyes such as Metanil Yellow has become a serious concern due to its carcinogenic nature. This study aims to determine the adsorption capacity of activated carbon derived from sugarcane bagasse waste (*Saccharum officinarum* L.), which was activated using Potassium Hydroxide (KOH) and modified with the cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB). The activated carbon was produced through carbonization at 500 °C for 2 minutes, followed by chemical activation using 5N KOH and surface modification with CTAB. FTIR characterization showed spectral changes with the appearance of new functional groups such as --CH_2 vibrations (2961 and 2849 cm^{-1}), --C--N (1020 cm^{-1}), and quaternary ammonium $\text{--N}^+(\text{CH}_3)_3$ (1470 cm^{-1}), indicating successful interaction of CTAB molecules on the carbon surface. The adsorption results showed that optimum conditions were achieved at an adsorbent mass of 1.5 grams, Metanil Yellow concentration of 25 ppm, and a contact time of 30 minutes, with an adsorption efficiency of 94%.

Keywords: Activated Carbon, Sugarcane Bagasse, CTAB, Adsorption, Metanil Yellow

1. INTRODUCTION

Indonesia is one of the many countries that are rapidly developing in the industrial sector such as the textile industry which exists in almost every region in Indonesia. However, the textile industry has a negative impact on the environment with the disposal of textile waste that guides hazardous chemicals into the waters. Textile effluents contain highly complex contaminants with high color intensity. Most of the pollutants contained in textile effluents are textile dyes, especially synthetic dyes ¹. Synthetic dyes are one of the organic pollutants that are difficult to degrade, generally made from azo compounds and their derivatives from the benzene group. If azo compounds are too long in the environment, they will become a source of disease because they are carcinogenic. The synthetic dyes that contain azo compounds are Metanil Yellow. Metanil yellow can cause irritation, tumors of various liver tissues, bladder, digestive tract, or skin tissues and even cancer if consumed in the long term. Metanil yellow also acts as a tumor promoting agent and can cause liver damage ².

One of the currently developing dye wastewater treatment processes is the adsorption method. This method is widely used because it is safe, has no harmful side effects, requires simple and inexpensive equipment, is easy to operate, is recyclable, and is efficient and economical ³. Activated carbon is a highly potent adsorbent in adsorption systems due to its large surface area and high adsorption capacity. Activated carbon is produced from agricultural waste such as sugarcane bagasse. Sugarcane bagasse has a very high carbon content, namely 50% cellulose. This indicates that sugarcane bagasse has the potential to be used as a material for making activated carbon through carbonization and activation. According to ⁴, the cellulose contained in sugarcane bagasse determines the adsorption capacity, where cellulose contains carboxyl (-COO-) and hydroxyl (-OH) groups.

One of the efforts to increase the absorbency of activated carbon can be modified by the addition of surfactants. Modification of the adsorbent surface with the addition of a surfactant is one way to maximize the adsorption ability ⁵. Some studies also show that modifying the orange peel adsorbent can maximize the adsorption process, including research ⁶ that the best adsorption process on methyl orange is using Cetyl Trimethyl Ammonium Bromide (CTAB) modified orange peel adsorbent with the best optimum amount of dye at minute 50 which is equivalent to 13.34 ppm. In the study, ⁵, Silica gel modified Cetyl Trimethyl Ammonium Bromide (CTAB) with gelation pH variation 3 is the best pH variation for Rhodamine B adsorption with an adsorption ability of 89.28% at 120 ppm Rhodamine B concentration. This research aims to investigate the adsorption capability of activated carbon derived from sugarcane bagasse waste (*Saccharum officinarum* L.), which was activated using Potassium Hydroxide (KOH) and modified with the cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB), in removing Metanil Yellow dye.

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

The equipment used in this research are grinder, 100 mesh sieve, furnace, porcelain crucible, magnetic hot plate stirrer, thermometer, oven, glassware (Pyrex), desiccator, spatula, aluminum foil, and Ultraviolet-Visible Spectrophotometer (UV-Vis), and Fourier Transform Infra-Red (FTIR) instruments. The materials used in this research are Potassium Hydroxide (KOH) (e- Merck), distilled water, Whatman No. 1 filter paper, Sugarcane Bagasse, Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant and Metanil Yellow dye.

2.2. Research Procedure

2.2.1 Preparation and Carbonization of Sugarcane Bagasse with KOH Activation

Sample preparation was carried out by washing bagasse first to remove impurities that were still attached to the bagasse. Next, the bagasse was dried under the sun for 7 days (7x12 hours) to reduce the moisture content. The dried bagasse was cut into 2-3 cm pieces ⁷. Then the bagasse was reduced in size using a grinder and sieved using a 100 mesh sieve. The carbonization process is carried out by weighing the sugarcane bagasse that has been hollowed out, then the bagasse is put in the furnace and heated at 500 °C for 2 minutes ⁸. The carbonated bagasse was then activated using 5N Potassium Hydroxide (KOH) ⁹. The 5N Potassium Hydroxide (KOH) solution was taken according to the ratio of the mass of activating agent to the mass of carbon used, which is 4:1. Sugarcane bagasse carbon was immersed in Potassium Hydroxide solution (KOH) for 24 hours ⁸. Then stirred the mixture of carbon and Potassium Hydroxide (KOH) with a rotation of 200 rpm using a magnetic stirrer until homogenized while heated at 80°C for 4 hours. Then the mixture was allowed to stand for 24 hours. The carbon was filtered to separate the precipitate and filtrate. The filtrate was discarded while the precipitate obtained was washed with st water repeatedly until the pH of the filtrate was neutral ¹⁰. The carbon was then heated in an oven at 105 °C for about 2 hours ¹¹.

2.2.2 Modification of Activated Carbon with CTAB (Cetyl Trimethyl Ammonium Bromide) surfactant

The adsorbent modification of Cetyl Trimethyl Ammonium Bromide (CTAB) was adapted from the method of⁶. 5 g of activated carbon was soaked in 100 mL of 1% Cetyl Trimethyl Ammonium Bromide (CTAB) for 24 hours and filtered. The precipitate obtained was dried in an oven at 75°C for 6 hours.

2.2.3 Adsorbent Characterization

Characterization was carried out using Fourier Transform Infra-Red (FTIR) to determine the functional groups present in carbon, activated carbon and activated carbon modified with Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant.

2.2.4 Determination of Maximum Wavelength of Metanil Yellow

Determination of wavelength aims to determine the absorption area in the form of adsorbance value. Analyzed by using UV-Visible Spectrophotometer (UV-Vis) with a length range between 400-500 nm to get the absorption wavelength of Metanil Yellow. Determination of wavelength using Metanil Yellow with 30 ppm solution preparation.

2.2.5 Determination of Optimum Mass of the Absorption Power of Metanil Yellow Dye Solution

Determination of optimal mass in KA-CTAB. Put each into 100 mL of Metanil Yellow 25 ppm solution. Each KA-CTAB is varied from 0.5 g, 1 g, 1.5 g and 2 g². Next, it is stirred at a speed of 100 rpm at room temperature with a contact time of 30 minutes. After that, the mixture was separated and the filtrate was analyzed using Ultraviolet-Visible (UV-Vis) at the maximum wavelength that had been obtained to determine the adsorption capacity.

2.2.6 Determination of Optimum Concentration of Metanil Yellow Dye Solution Adsorption Capacity

Determination of optimum concentration in KA-CTAB. 100 ml of metanil yellow solution of 10, 15, 20, and 25 ppm was put into a 250 mL beaker. The optimum mass of CTAB modified activated carbon was then put into the beaker at each concentration. Next, it was stirred at a speed of 100 rpm at room temperature for 30 minutes. After that, the mixture was separated and the filtrate was analyzed using Ultraviolet-Visible (U V-Vis) at the maximum wavelength that had been obtained to determine its adsorption capacity.

2.2.7 Determination of Optimum Contact Time for the Absorption Power of Metanil Yellow Dye Solution

Determination of the optimal contact time of KA-CTAB. 100 mL of metanil yellow solution with optimal concentration was added and KA-CTAB carbon with optimum mass was added, then stirred at a speed of 100 rpm at room temperature with variations in contact time used, namely 30, 60, 90, and 120 minutes². After that, the mixture was separated and the filtrate was analyzed using Ultraviolet-Visible (U V-Vis) at the maximum wavelength that had been obtained to determine its adsorption capacity.

3. RESULTS AND DISCUSSION

3.1. Preparation and Carbonization of Sugarcane Bagasse with Activation of Potassium Hydroxide (KOH)

The bagasse was obtained from a sugarcane ice seller in Jl. Tempuling, Medan Tembung, Medan City, North Sumatra. The bagasse taken was then cleaned using running water, then the bagasse was dried under the sun for 7 days (7x12 hours) to reduce the water content in the bagasse. The dried bagasse was cut into 2-3 cm pieces to facilitate the grinding process⁷. Grinding is a process to grind or reduce the size of bagasse into finer particles. After that, the fine particles are sifted again using a 100 mesh sieve. With this refinement, the bagasse carbonization process will be more evenly distributed because the smaller (finer) the size of the bagasse, the greater the carbonization process. The carbon that has been activated is then neutralized by washing it using aqueous repeatedly until the pH approaches 7.

Neutralization aims to remove or neutralize unwanted substances or contaminants that are absorbed on the surface of the activated carbon after activation. The neutral activated carbon is dried in the oven at a temperature of 105°C for 2 hours.

3.2. Modification of Activated Carbon with CTAB (Cetyl Trimethyl Ammonium Bromide) surfactant

After activated carbon is activated, it is then modified with surfactant Cetyl Trimethyl Ammonium Bromide (CTAB), used to change carbon activated carbon with the goal of maximizing the adsorption capacity of activated carbon on metanil yellow dye effluent. A total of 5 grams of sugarcane bagasse activated carbon was contacted with 100 mL of Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant, with a Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant concentration of 1% for 24 hours at low pressure. Then filtered using filter paper. Thus, the use of Cetyl Trimethyl Ammonium Bromide (CTAB) is better for removing anionic dyes, due to the presence of the N element of the ammonium group of Cetyl Trimethyl Ammonium Bromide (CTAB) because this group has a positive partial charge which causes Cetyl Trimethyl Ammonium Bromide (CTAB) to have cationic properties so that it is easier to attract anionic dyes ⁶.

3.3. Adsorbent Characterization

Characterization using *Fourier Transform Infrared* (FTIR) spectroscopy aims to identify the functional groups found on the surface of activated carbon before and after modification with CTAB (*Cetyl Trimethyl Ammonium Bromide*). The figure 1 is the result of characterization using FTIR spectroscopy conducted to identify the presence of functional groups on the surface of activated carbon. KOH-activated activated carbon from bagasse and activated carbon modified using CTAB surfactant.

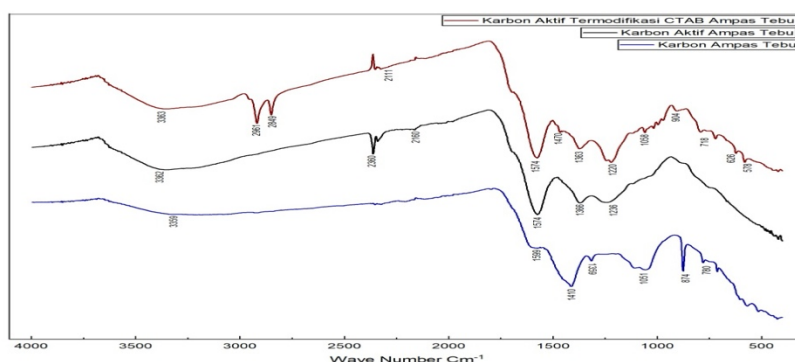


Figure 1. FTIR results of carbon, KA, KA-CTAB sugarcane bagasse

Based on Fourier Transform Infrared (FTIR) analysis, the results of sugarcane bagasse carbon show several absorption bands indicating the presence of active functional groups. The absorption band at wave number 3359 cm^{-1} indicates the presence of hydroxyl groups -OH from bound water or alcohol. The absorption at 1599 cm^{-1} indicates the presence of aromatic $\text{C}=\text{C}$ bonds, while the band at 1051 cm^{-1} is related to the C-O group. The absorption at 1315 cm^{-1} and 1410 cm^{-1} indicates the presence of alkane C-H bonds. The absorption at 780 cm^{-1} and 874 cm^{-1} indicates the presence of aromatic C-H bonds ¹². The Fourier Transform Infrared (FTIR) spectrum of activated carbon following Potassium Hydroxide (KOH) activation shows changes in the functional group characteristics compared to unactivated carbon. The absorption band at 3362 cm^{-1} indicates the presence of -OH groups from hydroxyl compounds. The band at 3362 cm^{-1} also supports the presence of strong hydrogen bonds. The absorption at 2360 cm^{-1} can be attributed to adsorbed CO_2 groups. The absorption at 2160 cm^{-1} can be attributed to $\text{C}\equiv\text{C}$ triple bonds. The wavelength of 1574 cm^{-1} indicates the presence of aromatic $\text{C}=\text{C}$ bonds, while 1326 and 1236 cm^{-1} are associated with C-H and C-O groups from phenolic or ether compounds ¹².

The Fourier Transform Infrared (FTIR) spectrum of sugarcane bagasse activated carbon modified with Cetyl Trimethyl Ammonium Bromide (CTAB) shows several important changes in the surface functional groups. The absorption band at 3360 cm^{-1} indicates the presence of -OH groups from hydroxyl compounds. There are absorption bands in the 2961 and 2849 cm^{-1} regions which indicate the presence of C-H groups from the aliphatic methyl and methylene chains, which originate from the CTAB compound. This indicates that Cetyl Trimethyl Ammonium Bromide (CTAB) is successfully bound or adsorbed on the surface of activated carbon. Strong bands in the 1574 and 1220 cm^{-1} regions indicate the presence of aromatic C=C groups, C-N groups from amines, which are strengthened due to the interaction between Cetyl Trimethyl Ammonium Bromide (CTAB) and the carbon surface.

In addition, the appearance of absorption around 1470 cm^{-1} which refers to the bending vibration of the -CH_2 group or quaternary ammonium group, further strengthens the evidence that Cetyl Trimethyl Ammonium Bromide (CTAB) has been adsorbed or effectively bonded to the carbon surface. The absorption band at 1058 cm^{-1} is related to the C-O group. Absorption at 578 and 621 cm^{-1} indicates the presence of a C-Br bond, while the bands at 718 and 904 cm^{-1} are related to the Aromatic C-H group ⁶. The presence of these functional groups indicates that carbon from bagasse still contains residual organic compounds and has undergone the formation of aromatic structures that have the potential to increase adsorption ability.

3.4 Determination of Maximum Wavelength of Metanil Yellow

Based on the image 3 with the UV-Vis spectrophotometer, the Metanil Yellow solution shows the highest absorption level at a wavelength of 494 nm .

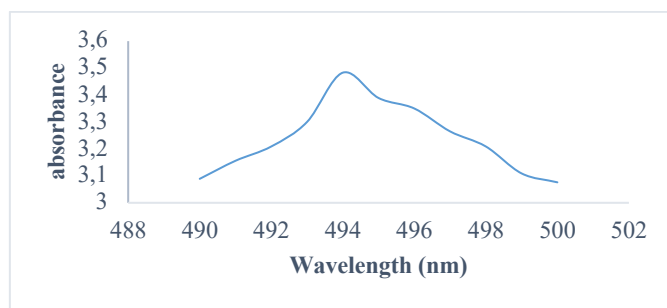


Figure 3. Maximum wavelength of Metanil Yellow

This wavelength was chosen because it is the area with the most absorption produced by the dye molecule, which is used as a reference in measuring concentration. The importance of using the maximum wavelength is to obtain precise data and in accordance with the principle of the Lambert-Beer law, which states that the level of absorption is proportional to the concentration. This λ_{max} value of 494 nm is also almost the same as that reported by ¹³, who found that Metanil Yellow has a maximum wavelength of 484 nm . This small difference is still within the tolerance limit and can be influenced by factors such as the state of the solution, the level, and the type of solvent applied in each study. Thus, the value of 494 nm is considered appropriate to be used as the maximum wavelength in this study.

3.5 Determination of Optimum Mass, Concentration, and Time on Adsorption of Metanil Yellow

Figure 4 shows the relationship between the weight variation of activated carbon from bagasse and the absorption efficiency of metanil yellow dye.

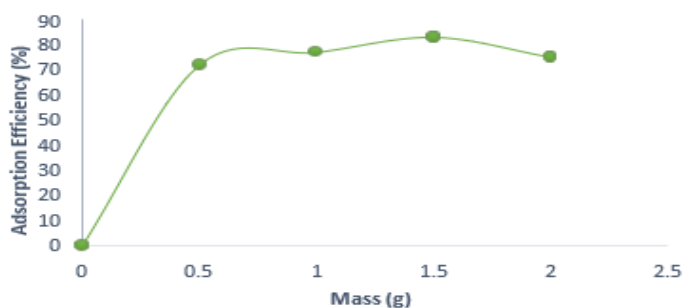


Figure 4. Optimum mass of metanil yellow adsorption

Based on the information presented, the absorption efficiency was seen to increase with increasing adsorbent weight until it reached its highest point at 1.5 grams, with the maximum efficiency reaching 83%. This indicates that the heavier the adsorbent used, the more active sites are available to bind the methane yellow molecules in the solution. However, after reaching the optimum point at 1.5 grams, increasing the weight to 2 grams actually resulted in a decrease in absorption efficiency.

This decrease may be due to the clumping of activated carbon particles, which results in a reduction in the available active surface area and inhibits the diffusion process of adsorbate molecules into the adsorbent pores. The same phenomenon was also mentioned by ¹⁴, Increasing the weight of the adsorbent can cause the adsorbent to reach the saturation point if the adsorbent surface has been filled with adsorbate. Increasing adsorbent weight can cause the adsorbent to reach saturation point if the adsorbent surface has been filled with adsorbate.

Figure 5 shows the relationship between the initial concentration of metanil yellow and the adsorption efficiency using activated carbon derived from bagasse.

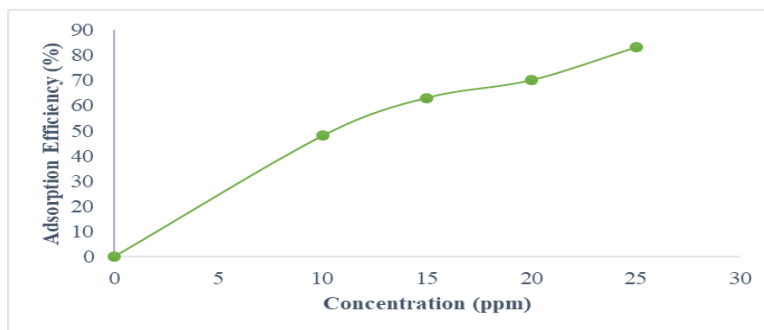


Figure 5. Optimum concentration of Metanil Yellow adsorption

From the figure 5, it can be seen that the adsorption efficiency increases as the solution concentration increases, reaching a peak at 25 ppm with an efficiency close to 83%. This occurs due to the increase in the number of metanil yellow molecules that can interact with active sites on the adsorbent surface, so that more molecules can be bound.

The adsorption process is influenced by the concentration of the adsorbate (dye) because the initial concentration of the dye provides the driving force in the process of transfer dye molecules between the liquid and solid phases thus affecting the interaction between the adsorbent and adsorbate ³. Therefore, it can be concluded that the best concentration for metanil yellow in the adsorption process with activated carbon from bagasse is 25 ppm. Determining the optimal concentration plays an important role so that the adsorption process can take place optimally with the use of chemicals that are efficient and environmentally friendly. However, the concentration of 25 ppm cannot be said to be the optimum concentration because the adsorbate molecules have not filled all the available active sites on the adsorbent surface. Greater adsorption ability is still possible at higher concentrations.

Figure 6 shows the relationship between contact time and the effectiveness of methane yellow adsorption using activated carbon from sugarcane waste.

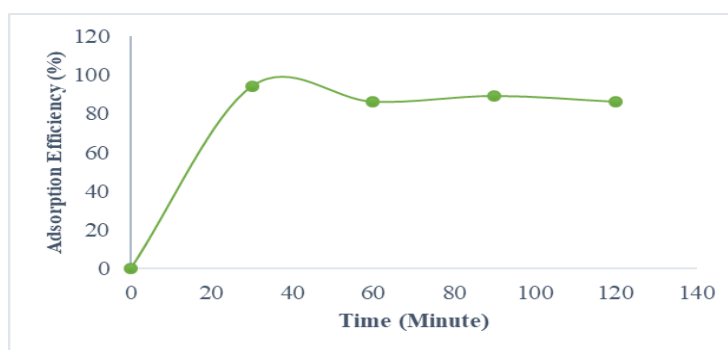


Figure 6. Optimum Adsorption Time of Metanil Yellow

Figure 6 shows the relationship between contact duration and the effectiveness of metanil yellow absorption using activated carbon from sugarcane waste. From the graph, it can be seen that the highest absorption effectiveness occurs at a duration of 30 minute, with an efficiency level reaching around 94%. This indicates that at duration, the interaction between the methane yellow molecules and the active surface of the carbon adsorbent is optimal.

The increase is quite high because at the beginning of adsorption the entire pore surface is still empty and the dye molecules will stick and form a layer on the surface so that the rate is fast. This shows that the longer the contact time, the empty surface will decrease so that the ability of the adsorbent to absorb dye molecules decreases, at the same time the rate of re-release of dye molecules increases until it reaches an equilibrium. This can also be caused because when it has reached the optimum contact time, the adsorbent experiences too much desorption due to the available active side on the adsorbent surface decreasing because the dye solution forms a new layer on the adsorbent surface so that it covers the adsorbent layer ¹⁵. Thus, it can be stated that the most effective contact time for the absorption of methanil yellow by activated carbon from sugarcane waste is 30 minutes, because it provides the highest absorption efficiency before a decrease occurs.

4. CONCLUSION

The FTIR characterization results showed the presence of new groups in the modified carbon such as $-\text{CH}_2$ (2961 and 2849 cm^{-1}), $-\text{C}-\text{N}$ (1020 cm^{-1}), and quaternary ammonium groups $-\text{N}^+(\text{CH}_3)_3$ (1470 cm^{-1}). The optimum adsorbent mass that provided the highest adsorption efficiency for metanil yellow dye was 1.5 grams, with an adsorption efficiency of 83% . The optimum concentration of metanil yellow dye that provided the highest adsorption efficiency was 25 ppm , with an adsorption efficiency of 83% . The optimum contact time for the metanil yellow adsorption process using activated carbon was 30 minutes, with the highest adsorption efficiency of 94% .

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