Synthesis of Silica Xerogel based Bagasse Ash as a Methylene Blue Adsorbent on Textile Waste

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Abstract. The textile industry is one of the fastest growing industries in Indonesia. One of the important components in the textile industry is methylene blue dye. In the process of dying, methylene blue is only tied at 5%, while 95% as waste. The non-biodegradable methylene blue properties make it as a contaminant in the water. Therefore, it is necessary to handle methylene blue in the textile industry waste to reduce the level of contamination in the waters. One of material that can be used as an adsorbent is bagasse ash. The high silica content in bagasse ash allows bagasse as a raw material for the manufacture of silica xerogel which acts as a blue methylene adsorbent. The synthesis of silica xerogel was done through two stages of extraction and sol-gel. The silica xerogel obtained was a white-colored powder to be used for adsorption of a methylene blue solution. The initial step for the adsorption process was to test the methylene blue solution using UV-vis spectroscopy. The results showed that the maximum λ of methylene blue solution was at 665 nm and the correlation coefficient (R²) was 0.9980. The adsorption capacity of the xerogel silica increases with the increase of adsorption contact time and the optimum contact time at 60 minutes. The increased initial concentration of methylene blue further increases the adsorption capacity. Under the equilibrium conditions, the adsorption capacity increased 2.18 mg / g to 10.53 mg / g. Adsorption of blue methylene by silica xerogel following Langmuir adsorption isotherm model, takes place spontaneously and exothermically.

Keywords: Silica xerogel, bagasse ash, methylene blue, adsorbent, textile waste.

1. Introduction
The development of fashion trends has pushed the textile industry to grow rapidly. Around 15% of the total dye production in the world is used by the textile industry and its waste is discharged into the environment [1]. Textile dyes in the form of organic compounds that are nonbiodegradable. One of the common dyes is methylene blue (C₁₆H₁₈N₃SCI). Methylene blue has several advantages such as the price is relatively cheap, easy to obtain, good solubility, and is a basic dye. In the coloring process, methylene blue is bonded about 5% while the remaining 95% is wasted as waste, so the methylene blue waste in the aquatic environment is very large [2]. Methylene blue waste in addition to damaging aquatic ecosystems can disrupt human health as well [3].

Various ways have been applied to reduce the level of contamination of dye waste in waters, such as chemical oxidation, coagulation-flocculation, biological treatment and filtration [4]. Another effective method of reducing dye contamination in waters is adsorption. Types of adsorbents used include active carbon and silica. Silica adsorbents can be obtained from ash waste bagasse. Bagasse is a solid sugar
cane obtained as waste from sugar cane processing in the sugar processing industry. The results show that bagasse ash contains more than 50% silica and the silica has an amorphous phase. The amorphous silica in bagasse ash can be taken by alkaline extraction to form sodium silicate solution followed by sol-gel method [5]. The content of silica in a high bagasse ash has the potential to become the raw material for the manufacture of silica xerogel used as a blue methylene adsorbent.

2. Materials and Methods
The materials used in this research are bagasse ashes from Krebet II New Sugar Factory Malang; Standard methylene blue solution; NaOH; HCl; Water demineralization; Whatman-42 filter paper; And universal indicators. Tools used include balance sheet; Pumpkin powder; beaker; Erlenmeyer; pipette; funnel; Stirring rod; Hotplate; Magnetic stirring bar; oven; Crucial; A crucial clamp; And spray bottles.

The silica extraction step is carried out by inserting 10 g of bagasse ash into 60 mL sodium hydroxide 2 M. The mixture was heated at its boiling temperature for 1 hour while constantly stirring using a magnetic stirrer to dissolve the silica. The mixture was cooled and filtered using Whatman-42 ashless filter paper and produce the sodium silicate solution. The next step was the synthesis of xerogel silica, which was 10 mL of the extracted filtrate fed into 30 mL of a pH 2 cation exchange resin with stirring for 30 min. The mixture was further filtered and the filtrate was produced in the form of silicic acid. The 10 mL silicate acid was added dropwise ammonium hydroxide 2 M to form a gel. Hydrogel formed then aging at room temperature for 18 hours. The gel was washed with demineralized water until it was clean and the pH neutral. The resulting gel was dried at 80 °C for 24 hours. Characterization of the silica xerogel was done using FTIR (8400 S, Shimadzu) and analysis methylene blue was using spectrophotometer UV-Vis (BIO-RAD).

3. Results and Discussion
Silica xerogel obtained in the form of white powder. The following is the result of the xerogel silica formed on the sol-gel process.

![Figure 1. Silica Xerogel](image)

Silica xerogel based bagasse ash synthesis was characterized by X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FT-IR) spectroscopy. The results of the XRF test is shown in Table 1. Based on the table, it can be seen that the most elemental content in silica xerogel is silicon with a percentage of 92.8%. This indicates that the most compound in silica xerogel is a silicon compound. To know what functional group is contained in silica xerogel, further characterization was done in the form of FT-IR characterization as shown in Figure 2.

The silica xerogel spectrum shows the absorption bands at wave numbers 3444,87 cm⁻¹ to 3224,98 cm⁻¹ and 1633,71 cm⁻¹ indicating the O-H vibration of the silanol (Si-OH) group. In the wave number 1085, 92 cm⁻¹ appears an absorption band that indicates the vibration of the Si-O-Si bond. This signal indicates that the silica xerogel has been successfully prepared. The silica xerogel is further used as a blue methylene adsorbent. The following is the result of the xerogel silica application as a methylene blue adsorbent.
Table 1. The Results of XRF Silica Xerogel

| Component | Mass (%) |
|-----------|----------|
| Si        | 92.8     |
| Ca        | 1.97     |
| Ti        | 0.23     |
| Cr        | 0.11     |
| Fe        | 0.52     |
| Ni        | 2.83     |
| Cu        | 0.39     |
| Zn        | 0.06     |
| Ba        | 0.2      |
| Re        | 0.35     |

Figure 2. The FT-IR Silica Xerogel Spectrum

The application of xerogel silica as a blue methylene adsorbent is carried out by studying the effect of contact time variation on adsorption capacity. Based on Table 2, the xerogel silica adsorption capacity increases with the increase of adsorption contact time. At the contact time of 60 minutes, the adsorption capacity increase is not very significant, so it can be stated that the optimum contact time is 60 minutes.

Table 3 shows that with the increased initial concentration of methylene blue, the adsorption capacity also increases. An increase in the initial concentration of methylene blue leads to increased competition between the adsorbate molecules to be absorbed into the adsorbent bed, thereby increasing the interaction between blue methylene with silica xerogel which will result in a higher adsorption capacity.

Table 2. Methylene Blue adsorbed on Contact Time Variation

| Time (min) | Concentration (mg/L) | Methylene Blue adsorbed (%) | qt (mg/g) |
|------------|----------------------|----------------------------|-----------|
|            | C₀                  | C₁                         |           |
| 10         | 6                   | 2.804                      | 98.668    | 7.99      |
| 20         | 6                   | 2.789                      | 98.662    | 8.03      |
| 30         | 6                   | 2.411                      | 98.505    | 8.97      |
| 40         | 6                   | 1.780                      | 98.242    | 10.55     |
| 50         | 6                   | 1.517                      | 98.132    | 11.21     |
| 60         | 6                   | 1.368                      | 98.070    | 11.58     |
| 90         | 6                   | 1.368                      | 98.070    | 11.58     |
| 120        | 6                   | 1.187                      | 97.994    | 12.03     |
Table 3. Methylene Blue adsorbed on Adsorbent Concentration Variation

| Concentration (mg/L) | Methylene Blue adsorbed (%) | qt (mg/g) |
|----------------------|-----------------------------|-----------|
| C₀                   | Cₜ                          | 87.081    | 2.18    |
| 1                    | 0.129                       | 88.038    | 4.40    |
| 2                    | 0.239                       | 91.069    | 6.83    |
| 3                    | 0.268                       | 85.048    | 8.50    |
| 4                    | 0.598                       | 84.211    | 10.53   |

Thermodynamics that can be calculated during the adsorption process are the free energy changes Gibbs (ΔG°), enthalpy changes (ΔH°), and entropy changes (ΔS°). Based on the calculation, the values obtained at ΔG°, ΔH°, and ΔS° as presented in Table 4.

Table 4. The Thermodynamic Parameters

| T (K) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/mol) |
|-------|--------------|--------------|-------------|
| 308   | -4.805       | -18.848      | -45.960     |
| 318   | -4.013       | -18.848      | -45.960     |
| 328   | -3.900       | -18.848      | -45.960     |

In Table 4 an increasingly negative ΔG° value was obtained with a decrease in temperature, indicating that the methylene blue adsorption by silica xerogel runs spontaneously and is better at low temperatures. The negative value of ΔH° indicates that the adsorption is exothermic, while the ΔH° value is -18.848 kJ/mol (<80 kJ/mol) indicating that the adsorption type is physical adsorption. The value of the ΔS° entropy change shows a negative value indicating that there is a decrease in irregularity in the adsorption process [6]. The adsorption isotherm describes the relationship between adsorption capacity and the concentration of adsorbate at a constant temperature. In summary, the Langmuir and Freundlich adsorption isotherm values of the calculations are presented in Table 5.

Table 5. The Parameters of Langmuir and Freundlich Isotherms Model

| Temperature (°C) | Isoterm Langmuir | Isoterm Freundlich |
|------------------|-------------------|-------------------|
|                  | R²                | Q₀ (mg/g) | b_L (L/mg) | R² | k_f | n |
| 35               | 0.937             | 14.085    | 4.4375     | 0.924 | 16.319 | 2.053 |
| 45               | 0.977             | 14.493    | 2.0294     | 0.915 | 15.578 | 2.278 |
| 55               | 0.875             | 15.625    | 1.1852     | 0.652 | 14.481 | 2.924 |

Based on Table 5, it shows that the Langmuir isotherm model gives a correlation coefficient value (R²) better than the Freundlich isotherm model. Therefore, the Langmuir isotherm model is better used in explaining the blue methylene adsorption process by silica xerogel. It also proves that the surface of the xerogel silica is a homogeneous side.

The kinetic parameter is used to determine the absorption rate in the adsorption process through the influence of contact time and this parameter to explain the efficiency characteristics of the adsorption occurring. The data in the adsorption kinetics study were taken from the influence of contact time data on the percentage of methylene blue adsorbed, the data used at 10-60 minutes. The following Table 6 is presented to compare two possibilities of a pseudo-first order and pseudo-second order adsorption kinetics model.
Table 6. The Parameters of Pseudo-First Order and Pseudo-Second Order

| $q_e$ (mg/g) | Pseudo-first order | Pseudo-second order |
|-------------|-------------------|--------------------|
| $q_e$ cal  (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ | $q_e$ cal  (mg/g) | $k_2$ (g/mg.min) | $R^2$ |
| 12.03       | 1.142             | 0.866             | 12.897       | 0.051             | 0.965 |

Based on Table 6 it can be seen that the value of the adsorption capacity of the pseudo order ($q_e$ cal) approaches the value of the experimental adsorption capacity ($q_e$) of 12.897 mg/g. This indicates that the methylene blue adsorption process with silica xerogel can be well explained using a pseudo-second order model. The statement is also proved by the value of the pseudo-second order coefficient ($R^2$) which is closer to 1 than the pseudo-first order one [7].

4. Conclusion
Silica xerogel in the form of white-colored powder is used for adsorption of methylene blue solution. The adsorption capacity of silica xerogel increased with increasing of adsorption contact time and optimum contact time at 60 minutes. The more amount of the initial concentration of methylene blue, increases the more the adsorption capacity also increases. Under equilibrium conditions, the adsorption capacity increased 2.18 mg/g to 10.53 mg/g. The adsorption of blue methylene by silica xerogel following Langmuir adsorption isotherm model takes place spontaneously and exothermically.

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