Preparation of Activated Carbon from Gnetum gnemon Shell Waste by Furnace-NaCl Activation for Methylene Blue Adsorption

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Abstract. A low-cost activated carbon from waste biomass has been yielded and applied for dye removal. Gnetum gnemon shell from local agriculture and waste biomass was used as a carbon source. The activated carbon powder was yielded after Gnetum gnemon shell waste heating in furnace at temperature of 400°C and it was then activated with NaCl. Parameter effects such as contact time and pH on methylene blue dye adsorption were evaluated. The optimum methylene blue dye adsorbed on prepared activated carbon was achieved at contact time of 20 minutes and pH 8. Langmuir isotherm model was appropriate to describe the dye adsorption by prepared activated carbon. In this study, a maximum absorption capacity (Qmax) of 62.5 mg g⁻¹ was obtained which indicated a potential activated carbon-based adsorbent for dye adsorption.

1. Introduction

Intensive industrial activities have led to the negative impact on the environment caused by wastewater disposal without treatment. Industrial plants such as textile industry, discharge wastewater containing liquid dye waste from the coloring process into water resource. Liquid dye waste can contain highly toxic chemicals that are harmful to human life and other living things as well as to the ecosystem. Methylene blue (MB) is one a widely dyes in the textile industry which was known as a non-biodegradable, mutagenic and carcinogenic that can cause harmful effect to human health [1].

Numerous physical and chemical methods such as adsorption, ion exchanges, ultrafiltration, photodegradation and biodegradation techniques have been applied for MB removal. Among various method, adsorption process onto solid adsorbents is the most extensively applied method for handling of MB dye due to its simplicity and effectiveness [2]. Adsorption technique using various adsorbent materials is known as a low cost and an environmentally friendly method for reducing dyes from wastewater.

Various adsorbent material such as rice husk, fly ash, zeolite, bentonite, chitosan, and activated carbon have been studied and applied to treat liquid waste. Among them, activated carbon is one of the powerful adsorbent materials in eliminating dyes from wastewater [3]. However, activated carbon that is obtained commercially is expensive so that an alternative activated carbon-based adsorbent material is needed. In decade, many researches have been conducted to obtain a low cost activated carbon
material from agricultural and waste biomass for MB removal including Ficus carica bast [4], cashew nut shell [5], mango seed [6], walnut shell [7], date press cake [8].

Gnetum gnemon shell waste is one of abundant waste biomass which can be utilized as an alternative carbon source dealing with MB adsorption. In previous study, we have evaluated the MB adsorption by heat-treated Gnetum gnemon shell waste particles and obtained a Qmax of 35.58 mg g⁻¹ [9]. However, the use of activated carbon-based adsorbent prepared from Gnetum gnemon shell waste by furnace-NaCl activation has not been intensively reported. Therefore, in this work, we aimed to prepare activated carbon by furnace-NaCl activation method using Gnetum gnemon shell as a carbon sources for MB adsorption of in aqueous solution. In order to study the performance of prepared adsorbent for MB removal, the effect of contact time, pH, and initial concentration were investigated. The obtained adsorbent was characterized by SEM-EDS and FTIR techniques.

2. Method

2.1 Activated carbon preparation
Gnetum gnemon shell waste (GSW) was obtained from the local area in Aceh. Indonesia. Collected GSW (1 kg) was rinse with distillate water for impurities removal. Washed GSW was then applied into an oven at a temperature of 105°C for 1 hour. Obtained GSW was then grinded into particles and sieved with a 100-mesh sieve. Furthermore, GSW particles were carbonized with furnace (Barnstead-Thermolyne Furnace-1300) on temperature of 400°C for about 1 hour. The carbon obtained was then added into 100 ml erlenmeyer containing 25 mL of 4% NaCl and then soaked for 1 hour. The gnetum gnemon derived-activated carbon (GSW-AC) obtained was filtered and washed several times using distilled water.

2.2 Adsorption study
The batch adsorption experiments were conducted in order to investigate the performance of GSW-AC on its capability on MB removal. 0.05 gram of GSW-AC particles were applied to each shaker glass which has been fill out with 15 mL of MB 50 mg L⁻¹, then shaken it for 10 minutes with a shaker (Memmert) with a speed of 250 rpm. Obtained filtrate was applied to a Shimadzu-UV mini 1240 UV-Vis spectrophotometer to monitor the MB concentration at 665 nm. The percentages of MB removal (%R) and the amounts of MB adsorbed at equilibrium (Q, mg g⁻¹) were calculated as follows [10]:

\[
% R = \frac{C_0 - C_e}{C_0} \times 100 
\]

\[
Q = \frac{C_0 - C_e}{m} \times V \quad (2)
\]

where, \(C_0\) was MB initial concentration, \(C_e\) was MB final concentration, \(V\) was volume of MB solution and \(m\) was mass of adsorbent. Langmuir (Eq.-3) and Freundlich (Eq.-4) equations were used as adsorption isotherm models [2] in order to study the equilibrium adsorption of MB by GSW-AC

\[
\frac{C}{Q} = \frac{1}{K_Q Q_{max}} + \frac{C}{Q_{max}} \quad (3)
\]

\[
\log Q = \log K_f + \frac{1}{n} \log C \quad (4)
\]
3. Results and Discussion

3.1. Characterization of GSW-AC

Fig. 1 and Fig. 2 show the characterization results of the activated carbon prepared from Gnetum gnemon shell waste (GSW-AC). Fig. 1(a) displays scanning electron microscopy (SEM) image of prepared activated carbon GSW-AC. As shown in Fig. 1(a), the surface morphology of GSW-AC particles is amorphous, irregular and porous activated carbon which indicates a potential activated carbon-based adsorbent. EDS analysis performed on the GSW-AC adsorbent shows that the obtained adsorbent is composed mostly of carbon (71.15%) and oxygen (24.85%) (Fig. 1(b)). EDS results also demonstrate that elements such Na (1.55%), Cl (1.04%), Mg (0.25%) and K (1.16%) are contained in GSW-AC

![Figure 1. SEM image (a) and EDS result (b) of prepared activated carbon GSW-AC.](image)

Fourier Transform Infra-Red (FTIR) analysis is aimed to observe the functional groups of prepared adsorbents. Fig. 2 shows FTIR spectrum of prepared activated carbon GSW-AC. The FTIR result showed that the broad absorption bands at a 3586 cm⁻¹ and 3200 cm⁻¹ are attributed to stretching of the O-H group, confirming the presence of free and bonded OH groups on the GSW-AC adsorbent surface [11]. Another characteristic strong peak is observed at 1722 cm⁻¹ which might attributed to C=O stretching of carboxylic acid [1]

![Figure 2. FTIR spectrum of GSW-AC](image)
3.2 Adsorption study

3.2.1 Effect of contact time. The activated carbon prepared from Gnetum gnemon shell waste by furnace-NaCl activation method (GSW-AC) was investigated their adsorption performance on MB removal in aqueous solution. In order to evaluate the effect of contact time on removal of MB by prepared GSW-AC, the experiments were carried out with varying contact time ranged to 5 - 30 minutes. The results are depicted in Fig.3. As can be seen from Fig.3, the adsorption of MB by GSW-AC increased as contact time was increased. The MB remove by GSW-AC was faster at the 20 min initial contact time and tend to be constant at later stages. The adsorption capacity of MB by GSW-AC increased from 14.32 (mg/g) to 14.88 (mg/g) with the increased of contact time from 5 to 20 minutes, while the adsorption capacity decreased with increased of the contact time up to 30 minutes. It may presumably be attributed to the desorption of adsorbed MB onto solution.

![Figure 3. Effect of contact time on MB adsorbed by GSW-AC](image)

3.2.2 Effect of pH. The initial pH of MB solution affects the surface nature of the GSW-AC adsorbent. In order to investigate the optimum pH for MB removal by GSW-AC, pH of MB solution was varied from pH 2.0 to 12. Fig. 4 exhibits the effect of pH of MB solution on the adsorption capacity of MB by GSW-AC. Fig. 4 revealed that high adsorption capacity of MB by GSW-AC was achieved at pH 8.0 with 14.88 mg g⁻¹ of MB adsorbed and 99.20% removed. Meanwhile, a low removal efficiency was observed under acidic solution. It might be due to increased repulsion between the positively charged H⁺ ions present in the solution and the positively charge of MB. Similar result was also obtained by Shakoor et al. [1]

![Figure 4. Effect of pH of MB solution on adsorption capacity of MB by GSW-AC](image)
3.2.3 Effect of initial concentration of methylene blue. In order to investigate the effect of MB initial concentration on adsorption capacity of MB by GSW-AC, the adsorption experiment was carried out by varying different initial MB concentration (30, 50, 70 and 100, 200, 300 mg L$^{-1}$). The result was denoted in Fig. 5. It can be observed from Fig. 5 that the amount MB adsorbed increased with the increasing of the MB concentration up to 200 mg L$^{-1}$, while the adsorption capacity progressively slow down with increased beyond concentration of 300 mg L$^{-1}$. The adsorption capacity increased from 8.57 to 63.40 mg g$^{-1}$ with the increased of MB concentrations from 30 to 300 mg L$^{-1}$. In order to describe the maximum concentration adsorbed by GSW-AC adsorbent, Langmuir and Freundlich adsorption isotherm equation (Eq.3 and 4) were applied. Parameter of Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of methylene blue onto GSW-AC was summarized in Table 1. The values of coefficient square of determination (R$^2$) indicated that the adsorption of MB by GSW-AC adsorbent was agreeable to Langmuir isotherm equation model with an obtained maximum adsorption capacity (Qmax) of 62.5 mg g$^{-1}$.

![Figure 5](image_url)

**Table 1.** Parameter of Langmuir and Freundlich isotherm models for MB adsorption by GSW-AC adsorbent.

| Sampel/Isotherm model | Langmuir | Freundlich |
|-----------------------|----------|------------|
|                       | Qmax (mg g$^{-1}$) | $K_l$ | $R^2$ | $K_f$ (mg g$^{-1}$) | $n$ | $R^2$ |
| GSW-AC                | 62.5     | 0.0909     | 0.9283 | 5.508 | 0.720 | 0.9034 |

4. Conclusion
A low-cost activated carbon-based adsorbent derived from Gnetum gnemon shell waste has been produced and applied for MB removal. The activated carbon powder was obtained after heating Gnetum gnemon shell waste in furnace at temperature of 400$^\circ$C and activated with NaCl. The adsorption performance of prepared adsorbent for MB removal was investigated by varying parameter contact time, pH, and initial concentration. The result showed that the optimum adsorption performance of prepared adsorbent was achieved at pH 8 and contact time of 20 minutes. Methylene blue adsorption by prepared activated carbon adsorbent follow the Langmuir isotherm model with an obtained maximum adsorption capacity (Qmax) of 62.5 mg g$^{-1}$. 
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