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Study on Methylene Blue Dye Adsorption in Aqueous Solution by Heat-Treated *Gnetum gnemon* Shell Waste Particles as Low-Cost Adsorbent

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Abstract. In this present study, a low-cost adsorbent from *Gnetum gnemon* shell waste has been prepared for methylene blue adsorption from aqueous solution in a batch system. The adsorbent particles were obtained after heat treatment of *Gnetum gnemon* shell waste at variation temperatures of 250, 300, 350 and 400°C. The optimum adsorption capacity of 14,37 mg/g and percentage removal of 95.80% were obtained at heat temperature of 300°C. The effect of experimental condition such as contact time and pH on adsorption capacity of methylene blue were also investigated. The result showed that the optimum experimental conditions was acheived at pH 6 and contact time of 25 minutes. Adsorption of methylene blue dye by heat-treated *Gnetum gnemon* shell waste particles fitted the Langmuir isotherm adsorption model with a maximum absorption capacity (Qmaks) of 35.58 mg/g which suggested that heat-treated *Gnetum gnemon* shell waste particles is a good potential adsorbent for methylene blue removal.

INTRODUCTION

The development of domestic industries has a positive influence in the form of increasing the national economy. However, the development of the industry such as textile industry has a negative effect, namely the deterioration of the quality of the aquatic environment. Rapid development poses a problem for the environment, especially the problem caused by staining liquid waste. The liquid waste contains toxic and dangerous ingredients. The presence of liquid waste in the aquatic environment can block the penetration of sunlight to the aquatic system, thus disrupting the biological processes that occur in it [1]. The use of cationic dyes in the textile industry is known to be quite extensive [2], where one type that is widely used is methylene blue [3]. Methylene blue can cause irritation to the digestive tract if ingested, causing cyanosis if inhaled and irritated to the skin if touched by the skin [4].

There are various methods of dye removal such as membrane filtration, coagulation, precipitation, electrolysis, chemical oxidation, ion exchange, adsorption and several other biological techniques. According to various literatures, adsorption method is the most widely used method in liquid waste treatment because it is effective in absorbing various types of pollutant, especially dyes that are non-biodegradable [2,5,6]. The adsorption method using various adsorbent materials has some advantages. It is one of the easiest methods, low cost and also known as an environmentally friendly for reducing dyes from wastewater [7,8].

Several material of adsorbents have been developed and applied for adsorption process on dye wastewater treatment such as silica, bentonite, chitosan, activated alumina, activated charcoal, zeolite [9]. Many studies have been carried out to produced inexpensive alternative material of adsorbents such as rice husk ash eggshell membrane, fiber, and activated carbon from rice husk. Many agricultural wastes have been used as an effective and inexpensive adsorbent. Preparation of adsorbents from pinecone for cationic dye removal has been investigated by Momcilic et

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al. [10]. Yenti & Zultiniar [11] have applied adsorbent from sugarcane bagasse to adsorb methylene blue. The use of coconut frond as adsorbent for removal of methylene blue has also been investigated by Mohammad et al. [12]

Another agricultural waste that can also be used as a carbon-based adsorbent for removal of methylene blue is *Gnetum gnemon* (Melinjo) waste. *Gnetum gnemon* seed peel has been used as a heavy metal adsorbent by Shinta [13]. However, the use of *Gnetum gnemon* seed shell waste as a carbon-based adsorbent for removing methylene blue has not been widely reported. Therefore, this study aimed to used heat-treated gnetum gnemon shell waste as a low cost adsorbent particle for methylene blue dyes adsorption. In this study, we investigated the effect of heat treatment of gnetum gnemon sell waste particles on their adsorption performance on removal of methylene blue. The adsorption performance of was evaluated by varying contact time, pH, and initial concentration of methylene blue.

EXPERIMENTAL

Materials

Methylene blue (MW: 319.86, MF: C16H18ClN3S) used in this study was of commercial purity and used without further purification. *Gnetum gnemon* shell waste was collected from the local area in Pidie, Aceh. Indonesia.

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Preparation of heat-treated adsorbent

One kilogram of collected *Gnetum gnemon* shell waste sample was washed with distillate water thoroughly to remove impurities attached to the surface of the *Gnetum gnemon* shell. Washed *Gnetum gnemon* shell waste was then dried in an oven at a temperature of 105^{o}C for 1 hour. The dried *Gnetum gnemon* shell waste was crushed into particles and sifted with a 100-mesh sieve and then weighed as much as 500g. Furthermore, *gnetum gnemon* shell waste particles were heated with furnace (Barnstead-Thermolyne Furnace-1300) on temperature variation of 250^{o}C, 300^{o}C, 400^{o}C and 500^{o}C for 1 hour.

Adsorption Study

In order to study the effect of heat-treated of *gnetum gnemon* shell waste particles on its ability for methylene blue removal, 1 gram of each heated gnetum gnemon shell waste particles (250oC, 300oC, 400oC and 500^{o}C) and *gnetum gnemon* shell waste particles without heated treatment were added to each erlenmeyer glasses containing 15 mL of 50 ppm of methylene blue solutions, then stirred using a shaker (Memmert) at 250 rpm for 10 minutes. The filtrate obtained was analysed using a UV-Vis spectrophotometer (Shimadzu-UV mini 1240), at maximum wavelength of 665 nm. 1000 mg/L stock solution of methylene blue was prepared by dissolving 1 gram of methylene blue in 1000 mL of distilled water. Calibration curve was obtained by varying concentrations of methylene blue ranged from 0.5 to 7.0 mg/L. Furthermore, the percentages of removal which are percent of absorbed substances are calculated using the following formula [14]:

$$Q = \frac{C_0 - C_e}{m} \times V \% \quad (1)$$

$$\% \, Adsorbed = \frac{C_0 - C_e}{C_0} \times 100 \% \quad (2)$$

Where, C_0 was initial concentration of the methylene blue, Ce was final concentration of methylene blue, V was volume of solution and m was mass of adsorbent. In order to study the equilibrium adsorption of methylene blue by heat-treated gnetum gnemon shell waste particles, Langmuir (Eq.-3) and Freundlich (Eq.-4) equations were used as adsorption isotherm models [15].

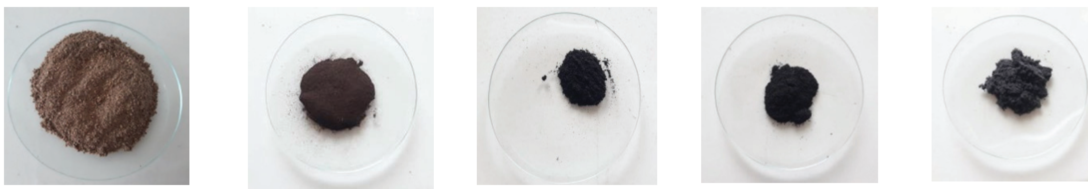
$$\frac{C}{Q} = \frac{1}{K_L Q_{max}} + \frac{C}{Q_{max}} \quad (3)$$

$$log\ Q = log\ log\ K_f + \frac{1}{n} log\ log\ C \quad (4)$$

RESULT AND DISCUSSION

Preparation of Heat-treated Adsorbent

Heat-treated adsorbent was obtained by heat treatment of gnetum gnemon shell waste particle in furnace with variation temperatures of 250^{o}C, 300^{o}C, 400^{o}C and 500^{o}C. The results were depicted in Figure1. It can be observed that the heat treatment of gnetum gnemon shell waste particles produced an adsorbent that have physically different color. Adsorbent with a heat temperature of 250oC has a brownish color which means it has not been evenly carbonized, Meanwhile, the increase in temperature of the heat treatment generated a more solid black color of obtained adsorbent due to the organic compound decay. The yield of adsorbent particles obtained was 61.22%.



(a) (b) (c) (d) (e)

FIGURE 1. Heat-treated gnetum gnemon shell waste at temperature of (without heat treatment) (b) 250^{o}C, (c) 300^{o}C, (d) 400^{o}C dan (e) 500^{o}C.

Adsorption study of methylene blue by heat-treated *gnetum gnemon* shell waste

The heat-treated gnetum gnemon shell waste particles obtained by varied heat temperature was evaluated their adsorption capacity on removal of methylene blue in aqueous solution. The effect of heat treatment temperature of gnetum gnemon shell waste particles on adsorption capacity (Q) and percentage of methylene blue removal was illustrated in Figure 2. It was observed that the adsorption capacity of heat-treated adsorbent increased by increasing the heat temperature of adsorbent up to 300^{o}C whereas gnetum gnemon shell waste particles without heat treatment showed low adsorption capacity and removal percentage of methylene blue. An increase methylene blue adsorption capacity was achieved at heat treatment temperature of 300^{o}C. Heat temperature of obtained adsorbent particles at 250^{o}C resulting a lower percentage removal of methylene blue due to a lower active side available on surface of adsorbent particles [16]. Meanwhile, the heat treatment temperature above 300^{o}C resulting a decrease in absorption capacity of adsorbent on methylene adsorption. Rahmi and Lelifajri [16] have reported that as heat treatment temperature increased, the active side of heat-treated adsorbent was reduced and resulted a lower adsorption performance. Therefore, the optimum heat treatment of adsorbent was chosen at 300^{o}C for the subsequent analysis.

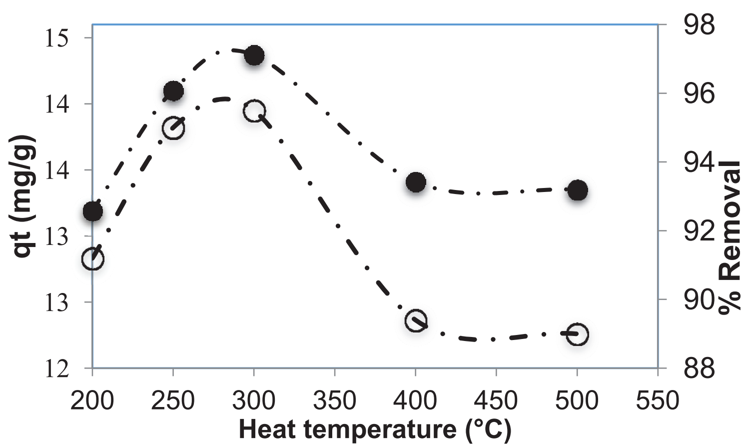


FIGURE.2: Effect of heat treatment temperature of adsorbent on adsorption capacity and percentage of methylene blue removal.

Effect of contact time

In order to study the effect of contact time on adsorption performance of methylene blue removal by heat-treated *gnetum gnemon* shell waste particles which were heated at 300^{o}C, the contact time was varied from 5 to 30 minutes. The results are illustrated in Figure-3. It could be observed from the figure that the adsorption capacity of methylene blue by heat-treated *gnetum gnemon* shell waste particles increased as contact time was increased. The amount methylene blue adsorbed on heated-treated adsorbent was faster at the 25 min initial stages but progressively slowed down at the later stages beyond this contact time. The adsorption capacity of methylene blue by heat-treated *gnetum gnemon* shell waste particles increased from 13.86 (mg/g) to 14.35 (mg/g) with increasing contact time from 5 to 25 minutes. It was attributed to at a longer contact time, a longer active sites of heat-treated *gnetum gnemon* particles contacted with methylene blue molecules resulting an increase adsorption capacity. However, the increase of contact time up to 30 minutes decreased the adsorption capacity.

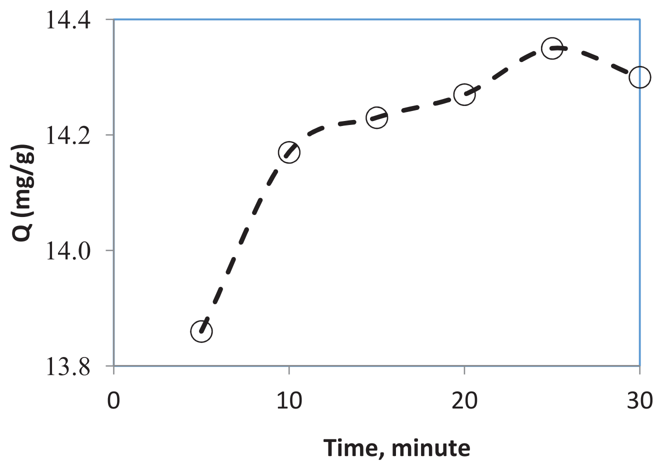


FIGURE 3: Effect of contact time on the adsorption capacity of methylene blue by heat-treated gnetum gnemon shell waste particles

Effect of pH

The pH value is very influential in the adsorption process because it affects the interaction between adsorbent and adsorbate as well as affect the nature of the surface charge of the adsorbent [17]. Fig .4 shows that heat treatment process of gnetum gnemon shell waste particles produced a material with a good methylene blue removal efficiency, over a wide range of pH (4-12). Meanwhile, heat-treated gnetum gnemon shell waste particles have poor absorption capacity at very low pH (pH 2). The low absorption capacity at low pH is attributed to the large amount of H+ ions present in the solution so that competition occurs with methylene blue which is also positively charged [16].

A good removal efficiency of heat-treated adsorbent particles was achieved above pH 6 to 10 with absorption capacity of 14,38 mg/g. The optimum adsorption of methylene blue at relatively high pH was also found in the study of Derakhsan et al. [3] (pH = 10, adsorbent: pumice) and research by Momcilovic et al. [10] (pH = 10, adsorbent: active pinecone). Several studies [6,18]) have shown that adsorption of cationic dyes can occur well under conditions of pH of the solution which tends to be alkaline. In basic conditions, a negative charge on the surface of the heat-treated gnetum gnemon shell waste particles was increased which that it increases the electrostatic force that occurs between the negative surface charge of the adsorbent and the positive charge of methylene blue. For further analysis, pH 6 (initial pH) is used for other parameters.

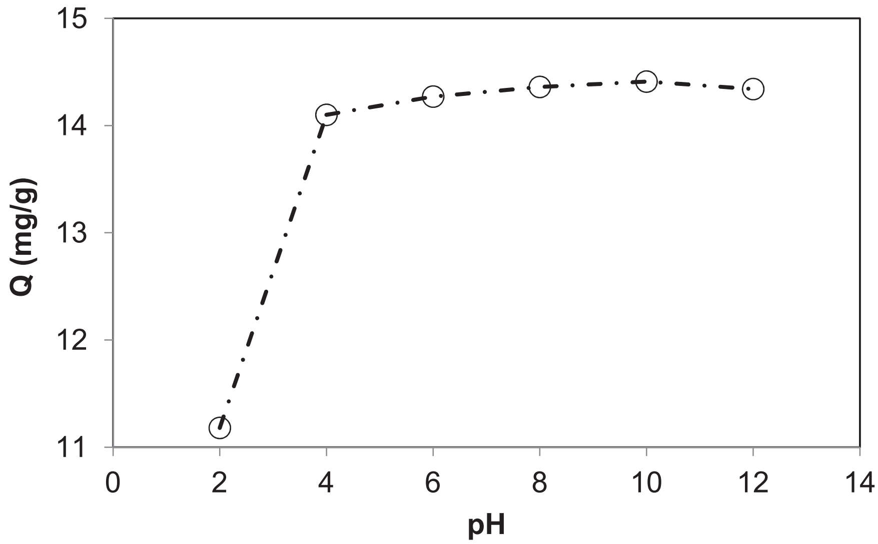


FIGURE 4: Effect of pH on the adsorption capacity of methylene blue by heat-treated *gnetum gnemon* shell waste particles

Effect of initial concentration of methylene blue

The adsorption of methylene blue by heat-treated *gnetum gnemon* shell waste particles was studied at different initial methylene blue concentration (30, 50, 70 and 100 mg L^{-1}). Figure 5. shows the effect of various initial methylene blue concentration on the adsorption capacity of heat-treated *gnetum gnemon* shell waste particles. As can be seen from the figure, the adsorption capacity of heat-treated adsorbent increased with increase in the initial concentration of methylene blue from 30 to 100 mg L^{-1}. It is attributed to the increased mass transfer with increase in the initial concentration of methylene blue. The Langmuir and Freundlich adsorption isotherm have been used to describe the maximum concentration of the adsorption process by the heat-treated *gnetum gnemon* shell waste particle.

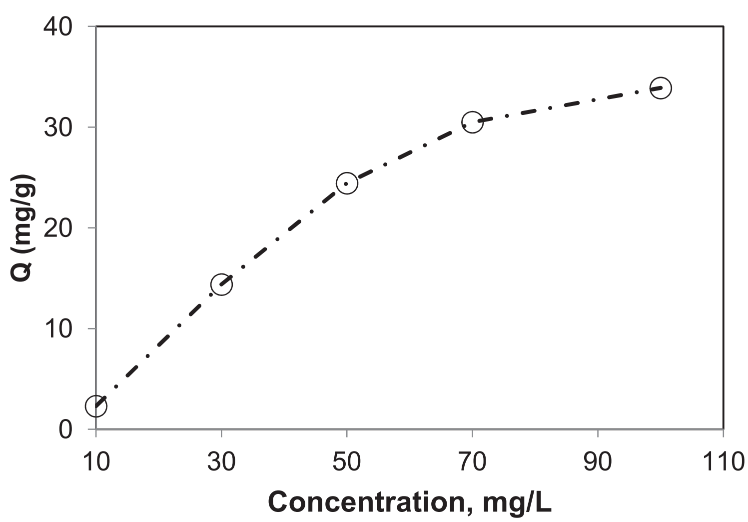


FIGURE 5: Effect of initial concentration on the adsorption capacity of methylene blue by heat-treated gnetum gnemon shell waste particles

The parameters of Langmuir and Freundlich models as well as the correlation coefficients indicating the agreement between the experimental and the calculated data by these two models are summarized in Table 4.4. Based on the coefficient square of determination (R2) obtained for both, this adsorption study is closer to the Langmuir adsorption equation because the R2 value in the Langmuir adsorption equation was more convenient than Freundhlich equation model in describing the adsorption of methylene blue by heat-treated gnetum gnemon shell waste particles. Langmuir isotherm assumes that the surface of adsorbent is homogenous and covered by monolayer of adsorbate and homogeneous [19]. The maximum adsorption capacity of methylene blue by heat-treated *gnetum gnemon* shell waste particles obtained in this study was 35.58 mg/g. The qmax value obtained was comparable with other adsorbents reported by Rahmi and Lelifajri [15] (0,35 mg/g) and Muhammad et al. [12] (18,69 mg/g) which suggested as a potent adsorbent for the removal of methylene.

TABLE 1. Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of methylene blue onto heat-treated *gnetum gnemon* shell waste particles.

Sampel	Langmuir Isotherm			Freundlich Isotherm		
	Qmaks (mg/g)	K_l	R^2	Kf (mg/g)	n	R^2
Heat-treated gnetum gnemon	35,58	0,448	0,9823	10,127	1,321	0,8922

CONCLUSION

The optimum adsorption capacity of 14,37 mg/g and percentage removal of 95.80% were obtained at heat temperature of 300^{o}C. The effect of experimental condition such as contact time and pH on adsorption capacity of methylene blue were also investigated. The optimum experimental conditions were achieved at pH 10 and contact time of 25 minutes. Adsorption of methylene blue dye by heat-treated *Gnetum gnemon* shell waste particles fitted the Langmuir isotherm adsorption model with a maximum absorption capacity (Qmaks) of 35.58 mg/g.

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