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Removal efficiency of methylene blue using activated carbon from waste banana stem: Study on pH influence

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Abstract. The effort to remove methylene blue in artificial solution had been conducted using adsorption process. The abundant banana stem waste was utilized as activated carbon precursor. This study aimed to analyse the influence of solution pH to removal efficiency of methylene blue using activated carbon from banana stem as adsorbent. Activated carbon from banana stem was obtained by chemical activation using H_3PO_4 solution. Proximate analysis result showed that the activated carbon has 47.22% of fixed carbon. This value exhibited that banana stem was a potential adsorbent precursor. Methylene blue solutions were prepared at initial concentration of 50 ppm. The influence of solution pH was investigated with the use of 0.2 g adsorbent for 100 mL dye solution. The adsorption was conducted using shaker with at a constant rate of 100 rpm at room temperature for 90 minutes. The results showed that solution pH influenced the adsorption. The activated carbon from banana stem demonstrated satisfying performance since removal efficiencies of methylene blue were higher than 99%.

1. Introduction

The occurrence of synthetic dyes gives negative effects to aquatic organism and human health when discharge directly to environment. The dyes consist of poisonous and complex components with slow degradation rate. Furthermore, the presence of dyes components affects the undesirable color change in water. The unfavorable impact is not only from esthetics point of view but also from the decline of sun light penetration, thus reducing photosynthetic activity [1, 2].

Dye is used widely in industries such as textile, food, paper and textile. The annual production of synthetic dye is about 70,000 tons with 100,000 types of dye. During the production process, about 15-20% are lost and carried away in wastewater [3]. Methylene blue ($C_{16}H_{18}N_3SCl$, C. I. No. 52015) is one of cationic dyes that most frequently used in industry [4]. Concerning the quantity and its harmful impacts, it is necessary to make efforts to reduce the dye components before discharging to environment.

The removal of methylene blue from wastewater were reported by using numerous methods such as liquid-liquid extraction, reverse osmosis, advanced oxidation process, electrocoagulation, electrochemical oxidation, ozonation, and membrane filtration . However, adsorption method offers some advantages due to its simple design, high efficiency and low costs with unhazardous byproducts [2, 5].

The utilization of activated carbon obtained from agricultural wastes as adsorbent has stimulated the interest of researchers, because it provides both low cost adsorbent and solve agricultural waste problem altogether.

Banana stem is one of lignocellulose waste and exist abundantly in Indonesia. Banana production in Indonesia increases annually and reached 6.862 ton in 2014 [6]. From the total production, banana stem takes the largest portion of 60%, whereas 30% is fruit and the rest is banana leaf [7]. The composition of cellulose, hemicellulose and lignin in banana stem is 43.3%, 20.6% and 27.8% respectively [8]. At this composition, the utilization of banana stem as the source of activated carbon becomes potential.

In this study, the analysis of removal efficiency of methylene blue was analyzed using activated carbon from banana stem as adsorbent. The activated carbon was prepared by chemical activation with H_3PO_4 solution. The adsorption was conducted in various pH of dye solution in order to investigate the influence of pH on removal efficiency of methylene blue.

2. Experimental Procedure

2.1. Activated Carbon Preparation and Characterizations

The activated carbon from banana stem was prepared with the same method as previously published [9, 10]. The first outer layer and the white middle part of banana stem were omitted from raw material. The sample was cut and washed several times. Afterwards, the sample was dried under sun light for 5 days and followed by oven drying at 105 °C until the constant mass was achieved. The samples were grinded and then sieved to 32 mesh. Sieved samples were impregnated in H_3PO_4solution at sample to solvent ratio of 1:1 and left overnight. Pyrolysis reactor equipped with nitrogen (N_2) flow was operated at 400 °C for 15 minutes. The produced activated carbon was washed with warm distilled water until solution reached neutral pH and then dried. Proximate analysis was carried out to obtain the moisture content, ash content and volatile matter content.

2.2. Adsorption of Methylene Blue

The adsorption of methylene blue was studied in batch mode. The solution was prepared at initial concentration (C_0) of 50 ppm. At this concentration, the pH of solution was 7 (neutral). The influence of solution pH was investigated in the range of 4-9. The pH was adjusted using 0.1 N HCl and 0.1 N NaOH. The dose of adsorbent was 0.2 g [2] for each 100 mL dye solution. The adsorption processes were conducted using shaker at 100 rpm at room temperature for 90 minutes. The concentration of methylene blue after adsorption (C_e) was measured using UV-VIS spectrophotometer in triplicate. Removal efficiency (R) of methylene blue was calculated using Eq. 1.

$$R=\frac{C_0 - C_e}{C_0} \quad (1)$$

3. Result and Discussion

3.1. Characteristics of Activated Carbon

Based on proximate analysis, the dried activated carbon had of 7.5% moisture, of 10.64% ash and of 34.64% volatile matter. The total amount of moisture, ash, volatile matter and fixed carbon content should be 100%. Therefore, the fixed carbon content in the activated carbon was 47.22%.

Based on SNI (Indonesian National Standard) for activated carbon [11], maximum value of moisture, ash and volatile matter content are 5%, 10% and 25% respectively, and minimum value for fixed carbon is 65%. Thus, only moisture and ash content of the activated carbon that met the requirements of SNI. However, previous study reported that proximate analysis of activated carbon from apple pulp was 15.11%, 15.35%, 62.69% and 6.56% respectively for moisture, ash, volatile matter and fixed carbon content. Whereas the value of moisture, ash, volatile matter and fixed carbon content of apple peel activated carbon were 12.27%, 7.43%, 72.89% and 7.40% respectively [12]. Both activated carbons of apple pulp and apple peel were applied to adsorb methylene blue with removal efficiency of up to 94.6%. Therefore, the potency of activated carbon from banana stem would merit further investigation.

3.2. Standard Curve

The measurement of methylene blue concentration in final solution was initiated with searching the maximum wavelength. From UV-VIS spectrophotometer result, it was observed that maximum peak was acquired at 664 nm. Subsequently, methylene blue solutions at various concentrations were prepared and analyzed at 664 nm. The standard curve was obtained by plotting the recorded absorbance from spectrophotometer versus the prepared concentration of solution. The accuracy was excellent with coefficient correlation (R^2) of 0.9975 (Fig. 1).

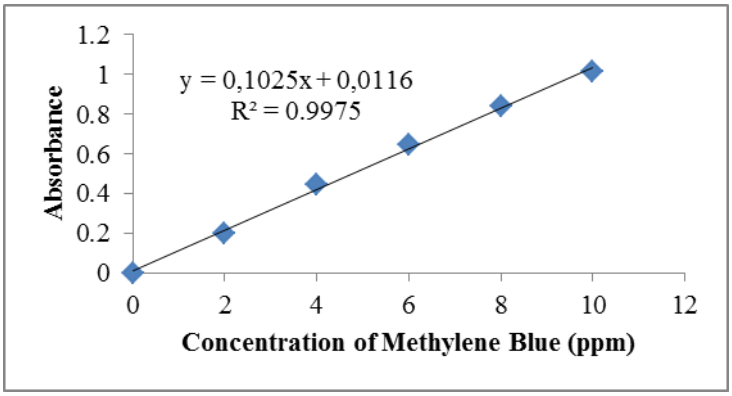

Figure 1. Standard Curve for Methylene Blue Solution

3.3. Solution pH Influence on Removal Efficiency

Fig. 2 showed the influence of solution pH on final concentration of methylene blue. After 90 minutes of adsorption process, the concentration of methylene blue in solution decreased dramatically in the range of pH 4-9 (Fig. 2a). Thus, the removal efficiency of methylene blue could be calculated using Eq. 1 and showed excellent results that were higher than 99% (Fig. 2b).This was also confirmed with the change of solution color from dark blue to bright and clear color (Fig. 3). Besides that, the solution pH decreased 1 level after adsorption process.

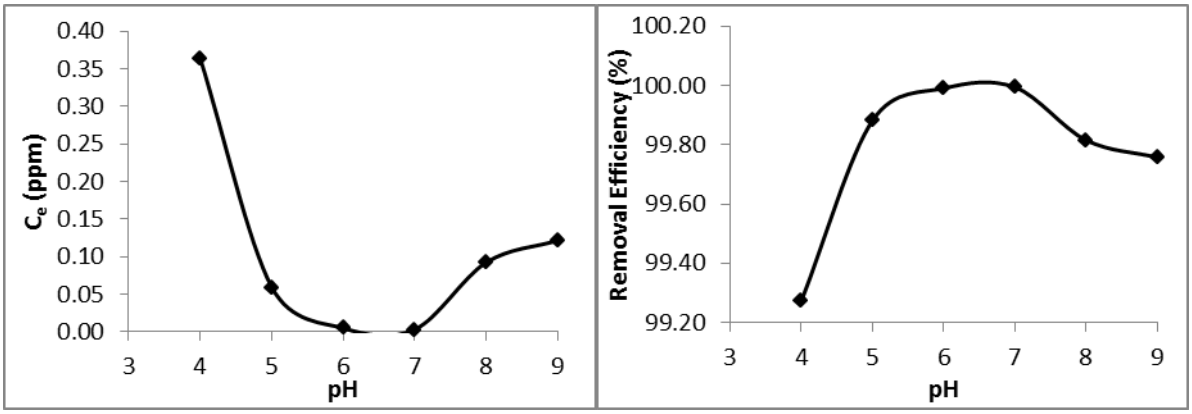

Figure 2. Influence of pH on (a) final concentration of methylene blue and (b) removal efficiency of methylene blue in adsorption process using activated carbon from banana stem

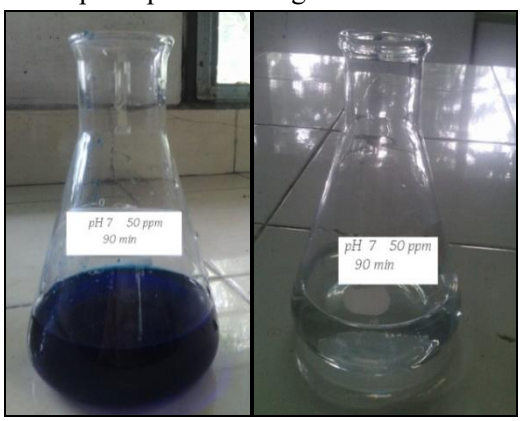

Figure 3. Color of methylene blue solution (a) before and (b) after adsorption process at pH = 7

The removal efficiency increased with the increasing pH of solution from 4 to 7, then decreased at pH 8 and 9. Methylene blue is cationic dye that generally demonstrates the positively charged ions when dissolved in water. The increasing of removal efficiency in the range of pH 4 to 7 might be because of the presence of acidic medium. The adsorbent surface may contain positive charge that does not attract the positively charged methylene blue in the solution [13]. As the pH of methylene blue solution increases, the adsorbent surface attains the negative charge that increases the adsorption capacity of activated carbon from banana stem. This is due to the formation of electrostatic interaction between the positively charged methylene blue and the negatively charged activated carbon [2].

Hence, the maximum removal of methylene blue using activated carbon from banana stem in this study was obtained at pH 7. However, the removal efficiency increased slightly with the rise of pH. Previous study reported that the best removal efficiency was also obtain at solution pH 7 for methylene blue adsorption using microwave assisted corncob activated carbon [2]. Whereas use of *Ficus carica* bast activated carbon showed that maximum methylene blue removal was obtained at pH 7.8 [14]. Both studies showed that adsorption of methylene blue were pH dependent.

In this study, the use of adsorbent dose of 0.2 g showed excellent performance of banana stem as activated carbon precursor in removing methylene blue in 100 mL solution with initial concentration of 50 ppm. The highest methylene blue removal in this study was 99.99%. A former study that used the same adsorbent dose showed almost the same removal efficiency. However, the treated initial concentration of methylene blue was smaller i.e. 25 ppm [2].The use of 0.5 g *Ficus carica* bast activated carbon in 100 mL methylene blue solution with initial concentration of 50 ppm gave about 85% removal efficiency [14]. These results showed that banana stem activated carbon is a promising adsorbent that can remove methylene blue effectively.

4. Conclusion

The increase of pH of the solution improved the removal efficiency of methylene blue using adsorbent of banana stem activated carbon. The maximum removal efficiency of 99.94% was achieved at pH 7. Methylene blue concentration dramatically decreased after contacting for 90 minutes with the adsorbent. This was also confirmed by significant color change of solution. Excellent performance was obtained when applying only a little amount of adsorbent mass in this study. Hence, banana stem activated carbon is a promising adsorbent in removing methylene blue.

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