Application of kepok banana peel activated carbon prepared by conventional and microwave heating for malachite green adsorption

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Abstract. Kepok banana peel as an agricultural waste has been used as a precursor in the production of activated carbon with NaOH activation. In this sense, the effect of heating technique (e.g. conventional and microwave heating) to the character and adsorption performance of the activated carbon was investigated. The obtained activated carbon was characterized by pore structural analysis, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM), then it used to remove malachite green from aqueous solution. It was found that microwave assisted NaOH activated carbon possessed high surface area and uniform pore structure. The surface area of activated carbons produced by conventional and microwave heating were 10.95 and 187.66 m\textsuperscript{2}/g, respectively. The optimum malachite green adsorption occurred at pH 10 and the equilibrium reached after 180 min. The adsorption behavior was well described by the Freundlich isotherm model.

1. Introduction

Wastewater released from textile, paint and printing industries generally contains a large number of dyestuff. If it enters into the water body, it can inhibit photosynthesis process of plants in the water [1]. The dyes have a complex aromatic structure that is stable to biodegradation and photodegradation. In addition, several dyes are toxic, carcinogenic and mutagenic. Considering the danger caused by the dyes, it must be removed from wastewater before discharged into the stream. Several methods such as electrochemical treatment [2], coagulation [3] and adsorption [4] have been used to remove dyes in aqueous solution. Among them, adsorption using activated carbon is the promising method due to its simplicity and high performance [5]. Recently, the use of lignocellulose-based activated carbon is preferred due to low cost and its abundant availability [6-8]. In this study, kepok banana (Musa paradisiaca) peel waste was used as a precursor in the preparation of activated carbon due to it has a high content of hemicellulose (74.9%), lignin (7.9%) and cellulose (7.5%).

In general, physical or chemical activation methods are used in the synthesis of activated carbon. In contrast to the physical activation where the resulting char is activated in the presence of CO\textsubscript{2} or steam [9], in chemical activation, char is impregnated with activating agents such as ZnCl\textsubscript{2} [10] and H\textsubscript{3}PO\textsubscript{4} [11]. In this sense, conventional heating using a furnace is usually adopted. Recently, microwave technique becomes a promising alternative for conventional heating due to it has several advantages including uniform temperature distribution, shorter time and lower energy [12]. To the best of our knowledge, no literature have been reported on the preparation of kepok banana peel activated carbon by microwave-assisted NaOH activation. Therefore, the objectives of this study were to (1) prepare...
and characterize activated carbon from kepok banana peel with NaOH activation using conventional and microwave heating (2) investigate adsorption characteristics of malachite green onto the activated carbon and (3) determine isotherm model for malachite green-activated carbon system.

2. Materials and methods

2.1. Preparation of activated carbon

Kepok banana peel used as a precursor in this study was obtained from a traditional market in Semarang, Indonesia. The banana peel was washed and heated at 110°C in an oven to remove moisture content. The dried sample was then blended to a powder. Furthermore, char was produced through a carbonization process by heating the sample in a furnace at a temperature of 500°C for 2 hours. The obtained char was mixed with NaOH and 10 mL of distilled water in a vertical reactor and stirred for 2 hours at room condition. The ratio of NaOH:char was 3:1. Afterward, the sample dried at 130°C for 4 hours. There are two heating techniques. First, using a furnace at a temperature of 700°C for 1 hour. Second, using a microwave oven with a frequency of 2.45 GHz at 600 W for 7 min, under a stream of N2 with a flow rate of 0.25 L/min. The obtained activated carbon was washed with 0.1 M HCl and distilled water until the filtrate pH was around 7. Furthermore, it was dried at 110°C for one hour.

A scanning electron microscope ((Phenom Pro X Desktop, UK) was used to analyze the surface morphology of char, conventional heated activated carbon (CAC) and microwave heated activated carbon (MAC) while the surface area was characterized through adsorption of N2 at 77K using gas sorption apparatus (Quantachrome, USA) and calculated by Brunauer-Emmet-Teller (BET) method. The surface organic structure of the adsorbents was characterized by Fourier transform infrared (FTIR) spectroscopy (Shimadzu, Japan) using KBr pellet method at wave number 400-4000 cm⁻¹.

2.2. Adsorption studies

Malachite green (chemical grade reagent) used as adsorbate was obtained from U.D. Indrasari Semarang and used without further purification. The sample solution was prepared by dissolving the malachite green powder with distilled water to the required concentration.

Batch adsorption experiments were conducted in six Erlenmeyer (100 mL size) containing 0.1 g of adsorbent and 50 mL of malachite green solution (100 mg/L). The adsorption was carried out at various pH (2, 4, 6, 8, 10 and 12) with added 0.1 N HCl or 0.1 N NaOH. The suspensions were shaken using a shaker apparatus at 120 rpm for 180 min. All suspended solids were filtered using Whatman paper and the filtrates were then analyzed for residual malachite green using a UV-Visible spectrophotometer at λmax 618 nm. The effect of contact time toward the quantity of malachite green adsorbed was studied at various contact time (10, 20, 30, 40, 50, 60, 120, and 180 min) at solution pH of 10 and malachite green concentration of 100 mg/L. Adsorption isotherm was studied through various malachite green concentration (5, 10, 20, 30, 40, 50, 100, 200, 300, 400, and 500 mg/L) at solution pH of 10 for 180 min. The malachite green uptake at equilibrium per unit mass adsorbent (mg/g) was calculated by Eq. (1) as follows [13]:

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  

(1)

where \( C_0 \) and \( C_e \) (mg/L) are concentrations of malachite green in the liquid-phase at initial and equilibrium, respectively, \( M \) (g) is the mass of adsorbent used and \( V \) (L) is the volume of solution.

3. Results and discussion

3.1. Characterization of char, CAC and MAC

Figure 1 describes SEM micrographs of char, CAC, and MAC. It can be observed that the char (Figure 1a) has a dense and constricted surface due to the pores were blocked by tarry substances. While, after the activation process with NaOH, the porosity of the activated carbon increased (Figure 1b and 1c). In this sense, pore development through three stages including the opening of the blocked pores,
widening of the existing pores and formation of new pores. In conventional heating, material (i.e. char) was heated by conduction and convection mechanism from a heat source located outside material bed. It led to a temperature gradient in the bed until a steady state condition was reached. As a result, the pore size was very diverse (Figure 1(b)). In contrast to the conventional heating, in the microwave heating, material received heat through dipole rotation and ionic conduction mechanism. As a result, MAC surface (Figure 1(c)) had a highly porous structure with more uniform pore size.

Figure 1. SEM micrographs of (a) char, (b) CAC and (c) MAC

To confirm the presence of functional groups which were capable to adsorb malachite green, FTIR analysis was conducted. Figure 2 describes the FTIR spectra of dried banana peel, char, and MAC. The wide absorption peak around 3400-3700 cm\(^{-1}\) with a maximum at 3430 cm\(^{-1}\) (Figure 2(a)) indicated the O-H stretching mode of hydroxyl groups derived from cellulose and lignin in the banana peel. While the absorption peak at 2924.56 cm\(^{-1}\) indicated the presence of the C-H group. The bands at 1642.28 cm\(^{-1}\) may be attributed to the C=C stretching vibration of olefinic groups, whereas the presence of C-OH groups derived from lignin was indicated by absorption peak at 1037.03 cm\(^{-1}\). The existence of C-O-H twist bending vibration from cellulose was indicated by the presence of an absorption peak around 607 cm\(^{-1}\). After the carbonization and activation process, the position and intensity of some peaks being changed (Figure 2(b) and 2(c)). Peak around 3400-3700 cm\(^{-1}\), 1642 and 607 cm\(^{-1}\) became shallower which suggested the decrease of cellulose and lignin content.

Figure 2. FTIR spectra of (a) dried banana peel, (b) char, and (c) MAC

BET surface area of CAC and MAC was 10.946 m\(^{2}\)/g and 187.664 m\(^{2}\)/g, respectively. It suggests that microwave heating increased surface area compared to conventional heating. Thus, there was a
good agreement with the result of SEM micrographs which described that the pore size of CAC was smaller than that of MAC and several pores in CAC was blocked.

3.2. Adsorption of malachite green

The adsorption uptake of malachite green onto MAC linearly increased from pH 4 to 10, but it was nearly constant between pH 10 to 12 (Figure 3(a)). In the acid medium (i.e. presence of H⁺), the phenolic groups contained in the MAC will be protonated to R-O⁻H₂. As a result, no ionic interaction between MAC and the malachite green cations. It led to a decrease in the amount of malachite green adsorbed. While, at higher solution pH, the negatively charged species start dominating in the MAC surface. As a result, the amount of malachite green adsorbed increased due to the electrostatic attraction between positively charged of malachite green and negatively charged of MAC. Between solution pH 10 to 12, adsorption was nearly constant due to the formation of carbinol complexes.

Figure 3(b) depicts that the quantity of malachite green adsorbed increased rapidly in the first 10 min and thereafter it gradually slows down till the equilibrium was reached. It may be due to a large number of vacant sites were available to the adsorption process during the initial stage.

![Figure 3. The effect of (a) pH and (b) contact time toward quantity of malachite green adsorbed](image)

3.3. Adsorption isotherm study

Adsorption isotherm, that is used to optimize the design of adsorption system, describes the equilibrium of adsorbate molecules between liquid and solid (i.e. adsorbent) phase. It is characterized by specific constants that describe the affinity of adsorbent toward adsorbate molecules. In this study, two isotherm models including Langmuir and Freundlich were analyzed. Langmuir isotherm model is based on the assumption of monolayer adsorption with a homogeneous adsorbent surface. In this sense, adsorption sites on the adsorbent surface are assumed to be identical. The linear form of the Langmuir equation is described in Eq. (2) [13].

\[ \frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{1}{q_m} C_e \]  

where \( q_m \) is the maximum adsorption capacity (mg/g) and \( k_L \) (L/mg) is Langmuir constant related to the affinity of the binding site. In contrast to the Langmuir model, the Freundlich model is an empirical equation based on the assumption of a heterogeneous adsorbent surface with a random distribution of adsorption heat over the adsorbent surface. The linear form of the Freundlich equation is described in Eq. (3) [13].

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]
where $K_F$ (L/g) is the Freundlich constant indicated the adsorption capacity while $1/n$ is a model parameter involving adsorption intensity. The value of isotherm parameters can be calculated from the slope and intercept of the graphed line in Figure 4. It shows that adsorption data be best fitted to the Freundlich isotherm model due to the value of $R^2$ for the Freundlich isotherm was closer to unity ($R^2=0.965$). It implied that the MAC surface was known to be highly heterogeneous with the value of $K_F$ and $n$ was 45.91 and 1.092, respectively.

**Figure 4.** (a) Langmuir and (b) Freundlich isotherm plot for the malachite green adsorption by MAC

### 4. Conclusion

This study has demonstrated the suitability of kepok banana peel activated carbon prepared by microwave heating for malachite green adsorption. The optimum adsorption of the malachite green occurred at pH 10 for 180 min. Adsorption data be best fitted to the Freundlich isotherm model.

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