Microwave Assisted KOH Activation of Salacca Peel Dericed Activated Carbons as Adsorbents for Methylene Blue Removal from Aqueous Phase

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Abstract. In this study, salacca peel derived activated carbons (SPAC) were prepared by microwave assisted- KOH activation process. In the preparation process, the fixed mass ratio between salacca peel and KOH of 1:2 was used. Next, the effects of activation time (5, 15, 20 and 25 minutes) and microwave power (30, 380 and 700 W) on the characteristics of SPAC were then investigated. The BET surface area of SPAC was about 1491 m²/g for activation time of 25 minutes and microwave power of 700 W. The as-prepared SPAC was then used as adsorbents for methylene blue (MB) removal from aqueous phase. The adsorption data of SPAC were analyzed by Langmuir and Freundlich adsorption isotherms and the best correlation was shown by the Langmuir isotherm with maximum capacity of 327.9 mg/g. The analyses of kinetic data showed that the adsorption of MB on SPAC follow the pseudo-second order kinetic model.

1. Introduction
Activated carbon is one of the most well known carbon materials since it has been widely used in many industrial applications such as purification of liquid and gas, catalyst or (photo) catalyst support, electrodes in supercapacitors or redox batteries and hydrogen storage [1]. Activated carbons have some beneficial characteristics such as high surface area, easy availability and high thermal stability [2].

One of the main problems in commercial production of activated carbons is seeking a low cost, renewable and abundant precursor. There have been many efforts to produce activated carbons from various kinds of biomass [3–5]. Even though biomass has great potencies for activated carbons production, the processing steps are critical [6]. The activation process is the most important part in the production of activated carbon. This process opens or increases porosity on the surface of carbons. In general, activated carbon can be prepared by one of the following two methods of activation which are by physical or chemical activation [7, 8]. Both of them however, consumed much energy and took more than 6 hours to complete [9].

Another new promising technique that can produce equally high quality activated carbon that utilizes relatively less energy in shorter time is by microwave (MW) heating process [10 - 11]. In the MW device, the microwaves supply energy directly to the heated samples. Energy transfer is not by conduction or convection as in conventional heating, but microwave energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction [12]. Microwave heating has been used to prepare activated carbon originated from many types of biomass such as, pineapple peel[13], jackfruit peel [14], mangosteen peel tobacco stem, rice husk,mangosteen peel [15], durian shell [16], orange peel [17], guava peel [18], sugarcane bagasse [19], siris seeds pod [20], rambutan peel [21],...
banana peel [22], Albizia lebbeck seed pods, wheat straw [23], Parkinsonia aculeata wood [24], wood chips [25], almond shell [26] and pine wood [27] precursors.

Although many kinds of biomass precursors have been used to produce activated carbon, the work related to the utilization of salacca peel as precursor using microwave heating process has not been reported elsewhere. Salacca fruit or also known as snake fruit reddish-brown scaly skin is a typical tropical fruit cultivated in Indonesia especially in Bali, Lombok, Maluku and Sulawesi [28-29]. After consumption of the fruit, the peels are usually discarded as waste and until now, there has not been utilized as raw materials for useful products [30]. Our previous works focused on the preparation of SPAC as adsorbent material for removal of methylene blue using conventional heating method [31].

The main objective of this study is to investigate the use of microwave assisted KOH activation process to prepare SPAC. The influences of activation time and microwave power in the preparation process were further investigated. The SPAC was then used as adsorbent for methylene blue (MB) removal from aqueous phase. The adsorption isotherms were used to determine the maximum capacity of MB on SPAC. The adsorption kinetics were studied by the pseudo first and second order model.

2. Experimental

The salacca peel was obtained from the local market in Bandung, Indonesia. The peels were then washed with distilled water, and dried in an oven at 110°C for 24 h to remove the moisture content. The dried salacca peel were crushed and sieved to a uniform particle size (100-200 meshes). The microwave-assisted process was conducted using a modified microwave oven (Electrolux). Mixtures of KOH and salacca peel powder with mass ratio of 2:1 were put in a quartz tube reactor placed in a microwave oven. The activation processes were then subjected to various microwave heating times (5, 15, 20, 25 and 30 minutes) and microwave radiation powers (30, 380 and 700 W) under nitrogen flow. The resulting material was washed repeatedly with hot distilled water until solution pH reached 7.0. The obtained SPAC were dried at 80°C for 24 h and then stored for further analyses.

Characterization in terms of specific surface area, pore volume, and pore diameter of the obtained activated carbons was determined by N₂ adsorption at with surface area and pore size analyzer using the Brunauer-Emmet-Teller (BET) method. The micropore volume was calculated by using t-Plot micropore volume. The pore size distribution was determined by using Barrett–Joyner–Halenda (BJH) model. To study the effect of the initial metal ion concentration, 500 mL of Methylene Blue (MB) at various concentrations (10, 20, 30, 40 and 50 ppm) were mixed with 20 mg of SPAC in the Erlenmeyer flasks at room temperature. These mixtures were kept at room temperature with continuous shaking at 100 rpm. All samples were filtered and analyzed by UV-Vis spectrophotometer.

To investigate the effects of initial pH solution, the initial pH was adjusted by 1 mol/L HCl and NH₄OH with 10 mg of SPAC and 500 mL of MB solutions with initial concentrations of 50 ppm at room temperature. For all the adsorption experiments, they are conducted triplicate and the average values were used for the analysis. The adsorption performances were measured through the adsorption capacity which can be calculated using the following equation:

\[ q_t = \frac{c_0 - c_t}{m} V \]  \hspace{1cm} (1)

where, \( c_0 \) and \( c_t \) (mg/L) are the initial concentration and concentration at time \( t \) of MB, respectively. \( V \) (L) is the total solution volume, and \( m \) (g) is the mass SPAC-adsorbent. The study of adsorption kinetics was conducted at various initial MB concentrations of 10-50 ppm and 5 at room temperature. About 10 mg ASAC was put into Erlenmeyer flasks with 250 mL MB solution; the samples were separated by filtering at different contacting time. The residual concentrations of MB were measured, and adsorption amounts of ASAC were calculated by equation (1).

The experimental data were then analyzed using the pseudo-first-order [32] and second-order kinetic models [33]. The equation of the pseudo first order model is given by:

\[ q_t = q_e(1 - e^{-k_1t}) \]  \hspace{1cm} (2)

where \( q_e \) (mg/g) is the amount of MB adsorbed at equilibrium, \( k_1 \) (min⁻¹) is the pseudo-first-order rate constant, and \( t \) (min) is the contact time.
The form of the pseudo-second-order kinetic model is given by:

\[ q_t = \frac{q^*_2 k_2 t}{1 + q^*_2 k_2 t} \]  

where \( k_2 \) is the pseudo-second-order rate constant (g/mg min).

The capacity of an adsorbent can be represented by its equilibrium adsorption isotherm. The Langmuir and Freundlich adsorption models are commonly used to study the adsorption behavior of materials and the correlation among adsorption parameters. The Langmuir isotherm equation is represented by the following equation:

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

where, \( C_e \) is the equilibrium concentration of (ppm), \( q_e \) is the amount of MB adsorbed (mg/g), \( q_m \) is the maximum adsorption capacity of MB (mg/g), and \( K_L \) is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

The Freundlich isotherm equation is described by the following equation:

\[ q_e = K_F C_e^{1/n} \]  

where \( K_F \) and \( n \) are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity, respectively.

3. Results and discussion
Figure 1 shows the N\(_2\) adsorption desorption profiles of SPAC prepared by Microwave assisted KOH activation method. It can be concluded the profiles follows the Type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification of adsorption isotherms [34]. This is a typical structure of mesoporous material and it is beneficial for adsorption purposes [35].

![Figure 1 Isothermal N\(_2\) Adsorption- Desorption of SPAC prepared by microwave heating and KOH Activation.](image-url)
Table 1 presented the BET surface area of SPAC prepared by microwave heating method at various activation time and microwave power. It can be seen that at short activation time of 5 minutes and all microwave power, the BET surface area of SPAC was lower than 200 m²/g. However, by setting microwave power at 700 W and activation time to 25 minutes, we obtained SPAC with high surface area of 1491.04 m²/g. For the adsorption of methylene blue from aqueous phase, this carbon sample as then used as adsorbents.

| Run | Activation Time (Minutes) | Microwave Power (W) | BET Surface Area (m²/g) |
|-----|--------------------------|---------------------|-------------------------|
| 1   | 0                        | 0                   | 26.42                   |
| 2   | 5                        | 130                 | 54.51                   |
| 3   | 5                        | 230                 | 87.54                   |
| 4   | 5                        | 380                 | 198.43                  |
| 5   | 5                        | 700                 | 114.54                  |
| 6   | 15                       | 700                 | 1302.87                 |
| 7   | 20                       | 700                 | 1056.03                 |
| 8   | 25                       | 700                 | 1491.04                 |
| 9   | 30                       | 700                 | 1325.01                 |

Figure 2 shows the SEM-morphology observation of SPAC prepared by the microwave assisted KOH activation method, it can be seen that the porous structure was found on the surface carbon samples, providing an adequate morphology for MB adsorption.

The adsorption behavior of MB onto SPAC at different pH values is shown in Figure 3. The effect of pH was done by varying the initial pH of MB solutions from 2 to 12. It can be seen that adsorption capacity increased with increasing pH.
Adsorption capacity showed a very significant enhancement at pH of 6-9. This may be related to the protonation of MB in acidic medium, which creates a competition effect between excessive amounts of H⁺ and cationic dye on adsorption sites. Therefore, the surface of SPAC might become negatively charged as the solution pH increases. It can cause the formation of electric double layers which induces a surface polarity change and finally it can enhance adsorption capacity.

Figure 4 shows the profile of adsorption capacity versus contact time as function of initial MB concentration (10-50 ppm). The data were then fitted using the pseudo-first-order and second-order models. Table 2 presents the fitting results for the adsorption kinetics models.
Table 2. Adsorption kinetic parameters

| $C_0$ (ppm) | Pseudo First Order Model | Pseudo Second Order Model |
|------------|--------------------------|---------------------------|
|            | $k_1$ (minute$^{-1}$) | $q_e$ (mg MB/g SPAC) | $R^2$ | $k_2$ (g/mg min$^{-1}$) | $q_e$ (mg MB/g SPAC) | $R^2$ |
| 10         | 0.0578                  | 0.0186                    | 0.533 | 0.2189                  | 0.4588                   | 0.9894 |
| 20         | 0.0602                  | 0.0168                    | 0.81  | 0.2258                  | 0.4655                   | 0.9797 |
| 30         | 0.0726                  | 0.0133                    | 0.719 | 0.2604                  | 0.5189                   | 0.9741 |
| 40         | 0.0888                  | 0.0124                    | 0.6298| 0.3154                  | 0.5745                   | 0.9891 |
| 50         | 0.1049                  | 0.0136                    | 0.6551| 0.3576                  | 0.6105                   | 0.9964 |

The data show that the adsorption of MB onto SPAC was best represented by the pseudo-second-order model. These fitting results implies that the MB-SPAC system followed the pseudo-second-order model and that the overall adsorption process rate was controlled by physisorption at the beginning of adsorption and next is the chemisorption.

The plots of the Langmuir and Freundlich adsorption isotherms models for the adsorption of MB onto SPAC at room temperature according to Eqs. (4) and (5) are shown in Fig 5. The model parameters were calculated from the linearized form of both models, as presented in Table 3. The equilibrium data were best fitted by the Langmuir isotherm model. It showed that the adsorption of MB onto SPAC from aqueous phase occurs via monolayer formation. Furthermore, from Langmuir model, the maximum capacity of MB onto SPAC can be estimated as 375.9 g MB/g SPAC.

Figure 5 Plots of Langmuir and Freundlich models for adsorption of MB onto SPAC (pH 6, 10 mg of SPAC, varying initial concentration of MB from 10 to 50 ppm).
Table 3 Isothermal Adsorption Parameter Models

| Langmuir model | K_L (L/mg) | R^2  | Freundlich model | K_F (mg/g) | n    | R^2  |
|----------------|------------|------|------------------|------------|------|------|
| q_m (mg/g)     | 375.9      | 0.1709 | 0.9816           | 0.0951     | 2.7762 | 0.9011 |

4. Conclusions
This work studied the low cost and renewable adsorbent SPAC that was synthesized by microwave assisted KOH activation method from the salacca peel waste. The activation conditions which gives the highest BET surface area (1491.04 m^2/g) are as follows: a mass ratio (KOH:salacca peel) of 2:1 (w/w), a microwave heating time of 15 min, and a microwave power of 700 W. SPAC was then used as adsorbents for methylene blue (MB) removal from aqueous phase by varying initial pH solution and initial MB concentration. It was found that the adsorption process can be represented by Langmuir adsorption isotherms and the pseudo second order models. The maximum capacity was determined as 375.9 mg/g. Based on the experimental results, it can be said that the microwave assisted activation is an efficient and effective method for preparing SPAC as an excellent adsorbent which can be used for the separation and purification process in the industry.

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