Synthesis and Characterization of Activated Carbon Derived from Salacca Peel Using ZnCl₂ Hydrothermal Carbonization and Chemical Activation with Microwave Heating

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Abstract. In this paper we describe synthesis and characterization of salacca peel derived activated carbon. The salacca peel was carbonized using hydrothermal carbonization (HTC) at 225°C and 50 bar for 5 h with and without ZnCl₂ as HTC catalyst. The obtained hydrochar was furthermore activated using microwave assisted chemical activation at 700 W for 8 min under inert atmosphere. The ratio between hydrochar and impregnant (ZnCl₂) was varied between 1:2, 1:3, and 1:4. The samples were characterized using methylene blue equilibrium adsorption, Scanning Electron Microscopy (SEM), and Fourier Transform Infra-Red (FTIR) spectroscopy. It was obtained that the presence of catalyst during HTC could increase the methylene blue adsorption capacity (qₑ) and visible pores on the surface. The increase of impregnation ratio gave increase the surface pores and qₑ, with highest qₑ was obtained at impregnation ratio of 1:4. Furthermore, the obtained activated carbon had higher qₑ and oxygen functional groups compared to that of commercial activated carbon, making it suitable for various applications.

1. Introduction

Hydrothermal process is irreversible decomposition of biomass using hot pressurized water. Recently, this process gains its fame due to various advantages, such as green solvent (water) and easily adjusted to obtain valuable liquid, gas, or solid products [1]. Hydrothermal carbonization (HTC) is specifically done to obtain solid, called hydrochar, as the main product. There are some advantages of HTC compared to conventional carbonization, such as lower operating temperature (below 300 °C) and ability to process biomass with high water content [1]. In the context of activated carbon synthesis, according to [2], HTC is an important step that helps pore development in activation process.

Usually HTC needs no catalyst in its process, as the water provide H⁺ ion to hydrolyze the precursor. However, it is known that catalyst could be added to the HTC process to assist some reaction, such as hydrolysis, oxidation, dehydration, acylation, alklylation, etc. during process to obtain specific product (i.e. oil, gas, or char) and properties [3]. Some salts have been used in HTC, namely Na₂SO₄ [4], LiCl [5], CaCl₂, Ca-propionate, Ca-acetate, Ca-formate, Mg-acetate [6], and ZnCl₂ [7]. Combination of ZnCl₂-NaCl [8] and ZnCl₂-urea [9] also have been utilized to develop porosity on carbon during HTC. There are some evidence that ZnCl₂ could act as catalyst in cellulose hydrolysis and glucose decomposition [10], thus resulting in an increase of porosity [8].

Chemical activation with microwave heating was used in this study. Conventional heating depends on temperature gradient that makes long heating period thus resulting in high energy consumption. Microwave heating provides rapid, effective heat transfer, shorter heating period, lower activation
temperature, and simple operation [11, 12]. Moreover, ZnCl$_2$ as impregnant acts as template for microporosity [13], as well as dehydrating agent, inhibiting tar and promoting the reaction to char formation [14].

In this study we utilize salacca peel as precursor to synthesize hydrochar and activated carbon. Salacca is an indigenous plant of Indonesia with large quantity of fruit production annually, namely 900,000 tons in 2018; making huge amount of peel waste is generated [15]. Previously, activated carbon from salacca peel has been utilized as adsorbent [16], Li-ion capacitor’s [17] and Li-S battery’s cathode [18], and Na-ion battery’s anode [19], most of which are using conventional carbonization and activation. A combination of HTC and chemical activation with microwave heating was used to obtain activated carbon. The effect of the presence ZnCl$_2$ catalyst in HTC, and impregnation ratio in chemical activation to the morphology, functional groups, yield, and methylene blue adsorption capacity was investigated and presented in this paper.

2. Methodology

2.1. HTC process
Salacca fruits (*salak pondoh super* or *Salacca zalacca var Gaertner Voss*) were purchased from local markets in Bandung, Indonesia. The peel was separated from its edible parts, and washed repeatedly to remove impurities, and then oven dried for overnight at 110 °C. The dried peel then was crushed and sieved to obtained peel between size of -20+30 standard mesh, which was used as precursor to synthesize hydrochar and activated carbon in this study.

HTC process was done by following the procedure described in [17, 20]. A 5 g of dried salacca peel powder and 1.5 g of ZnCl$_2$ (Merck - p.a) were mixed in 50 mL of distilled water. The mixture was then loaded into a SUS316 subcritical water reactor with volume of 150 mL. The reactor was tightly closed and purged using N$_2$ gas to create inert condition. The pressure in the reactor was adjusted by feeding water into the reactor, using hydraulic hand pump (Sun run, Singapore), under continuous N$_2$ atmosphere for about 15 min. The heater was then turned on to achieve carbonization temperature of 225 °C and pressure of 50 bar. After 5 h, the reactor was cooled down until room temperature, and the obtained hydrochar (Z0) was separated, and oven dried for overnight at 110°C. To study the effect of ZnCl$_2$ during HTC process, the above procedure was repeated without ZnCl$_2$ (C0).

2.2. Chemical activation
The dried hydrochar (C0 or Z0) was impregnated for 24 h using ZnCl$_2$ at various impregnation ratio of hydrochar to ZnCl$_2$ 1:2, 1:3, and 1:4, denoted as Cx or Zx with x is the impregnation ratio and C or Z is the hydrochar without and with catalyst, respectively. The mixture was oven dried at 110 °C for 24 h. The mixture was then put into a quartz reactor and carbonized using modified food microwave oven (Panasonic) at irradiation power of 700 W for 8 min under inert atmosphere. The obtained activated carbon sample was washed using 0.1 M HCl, and repeatedly washed using distilled water until pH neutral was achieved. The sample was oven dried and stored in a desiccator.

2.3. Characterization
The hydrochar and activated carbon samples were characterized using scanning electron microscopy (SEM; JEOL JSM-IT-300) to observe the surface morphology, Fourier Transform Infrared Spectroscopy (FTIR; Prestige 21 Shimadzu Instruments) to analyse the functional groups. Methylene blue adsorption study was done to gain insight on hydrochar and activated carbon samples surface area. As much as 10 mg of sample was shaken overnight in a 250 mL methylene blue solution with initial concentration of 10 mg/L. The equilibrium adsorption capacity (qe; mg methylene blue/ g carbon) was calculated by using Eq 1, where C$_i$ and C$_e$ (mg/L) are initial and final concentration of methylene blue, V (L) is the solution’s volume, and m (g) is the mass of carbon sample. The yield of activated carbon was calculated by following Eq 2.

$$q_e = (C_i - C_e) \times \frac{V}{m}$$  

(1)
\[
\text{\% yield} = \frac{\text{mass of activated carbon (g)}}{\text{mass of hydrochar (g)}} \times 100\% \quad (2)
\]

3. Results and Discussions

3.1. Characterization of hydrochar

The morphology of C0 and Z0 is presented in Fig 1. a-b. It could be observed that more pores were formed on the surface of Z0, compared to C0. This observation is consistent with the \( q_e \) value (Fig 1.c), where Z0 exhibited higher \( q_e \) indicating more porous structure. Similar result was also observed by [9], where the presence of ZnCl\(_2\) during HTC process help hydrolysis and decomposition of cellulose, promote development of porosity, resulting on increase of surface area. This phenomenon also explained lower Z0 yield than C0.

Based the FTIR spectra presented in Fig 1.d, it could be observed that there were some functional groups present in the hydrochar. Both C0 and Z0 samples possessed similar peak in the functional and fingerprint region, indicating similar structure albeit the catalyst in the HTC process. Noticeable peaks presented in the spectra are: broad peak of \(-\text{OH}\) stretching around 3400-3300 cm\(^{-1}\), C-H vibrational stretching at 2951.8 cm\(^{-1}\), 1693.5 cm\(^{-1}\) of C=O stretch, and 1602.85 cm\(^{-1}\) of C=C [21]. Comparing the spectra of C0 and Z0, we could observe that Z0 spectra had lower intensity that C0. It was possible due to the presence of ZnCl\(_2\), which is an acidic catalyst, assists hydrolysis of C-O bond, thus lowering the peak at 1600 cm\(^{-1}\) and 1200-1000 cm\(^{-1}\) [8].

Figure 1. Morphology of C0 (a), and Z0 (b), yield and \( q_e \) (c), and FTIR spectra of C0 and Z0 (d)
3.2. Characterization of activated carbon
As shown in Fig 2.a, an increase of impregnation ratio has increased the $q_e$. It is known that ZnCl$_2$ helps the development of porosity during carbonization [22]. It is known that at impregnation ratio below 2, ZnCl$_2$ gave strong inhibition effect to tar formation and promoted release of volatile gases, resulting in formation of micropores and mesopores [23], thus lowering the activated carbon yield (Fig 2.b). At higher of impregnation ratio, pore widening was more dominant than pore formation, thus creating more visible pores on the surface on activated carbon [24]. This result was in a good agreement with surface morphology, presented in Fig 3. It could be observed for both samples, that more pores were observed on the surface of activated carbon with increase of impregnation ratio. Comparing the effect of catalyst during HTC process, the Z samples generally had higher $q_e$ compared to C samples. We speculate that it was possible due to the initial hydrochar already had more pores in its structure, thus ease the diffusion of ZnCl$_2$ during impregnation process. Both C4 and Z4 samples had higher $q_e$ value compared to that of commercial activated carbon.

![Figure 2. $q_e$ of salacca peel AC compared to commercial AC (a), and salacca peel AC’s yield (b)](image)

![Figure 3. Morphology of C2 (a), C3 (b), C4 (c), Z2 (d), Z3 (e), and Z4 (f) at magnification of 1,000x](image)
The FTIR spectra of C and Z samples are presented in Fig 4.a and b. It could be observed that both activated carbon samples exhibited different peaks in their respective hydrochar in the fingerprint region, indicating transformation of hydrochar to activated carbon during microwave heating activation process [25]. There are some peaks that persisted in the activated carbon, namely –OH (3400-3300 cm\(^{-1}\)) and C=O (1602.8 cm\(^{-1}\)), however at lower intensity compared to the respective hydrochar. It was possible due to decomposition of hydrochar structure to volatile gas (CH\(_4\), CO, CO\(_2\), H\(_2\)O) during activation process [26]. Further comparison of C4, Z4, and commercial activated carbon’s FTIR spectra is presented in Fig 4.c. The activated carbons that were synthesized from hydrochar in this study had higher –OH peak than commercial activated carbon. This results are in a good agreement with previous studies [17, 20]. It was also observed that Z4 had higher intensity of –OH peak than C0. We speculate that the presence of ZnCl\(_2\) during HTC lead more complete conversion of salacca peel to carbon structure, thus most of volatiles are already decomposed during this process, compared to C0. This made Z samples could preserved more functional groups during activation process. Further analysis is needed to confirm this statement.

![Figure 4. FTIR spectra of salacca peel AC carbonized without (a) and with catalyst (b), and comparison of C4 and Z4 with commercial AC](image)

4. Conclusion
We have successfully synthesized activated carbon from salacca peel by using ZnCl\(_2\) catalysed HTC and ZnCl\(_2\) chemical activation with microwave heating. The presence of ZnCl\(_2\) as catalyst during HTC promoted pore development, as observed in the morphology and higher qe, compared to sample without catalyst. Lower intensity of oxygen functional groups’ peak was observed with Z0 sample due to the presence of ZnCl\(_2\) helped the hydrolysis of biomass to gases. The presence of more pores in the Z0 sample helped further pore development in the ZnCl\(_2\) chemical activation with microwave heating.
More pores were observed on the surface of the Z2-4 carbons compared to C2-4 samples as the initially well-developed pores in Z0 might help the impregnant diffusion into the carbon structure. The increase of impregnant in chemical activation resulted on increase of pores observed, and higher qe value indicating higher surface area was obtained. Compared to commercial activated carbon, the activated carbon derived from salacca peel in this study possessed higher qe value and oxygen functional groups, making it more suitable for various applications.

Acknowledgement
This research was funded by the Directorate of Research and Community Service, Directorate General of Research and Development Strengthening, Ministry of Research, Technology, and Higher Education of Indonesia under Research Scheme of Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT) 2017-2019. The authors are thankful for the financial supports.

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