Synthesis and characterization of activated carbon derived from rubberwood sawdust by using KOH/KMnO₄ as multiple function activation agents

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Abstract This research is focused on the effects of impregnation ratios using KOH/KMnO₄ as multiple function activation agents on microporous of activated carbon. Rubberwood sawdust, the waste from wood processing industry, was used as a raw material in synthesis of activated carbon by chemical activation. The rubberwood sawdust was carbonized at 400 °C for 1 hour under an inert atmosphere to produce char. Chars were impregnated with different proportions of KOH and KMnO₄. Impregnation time for each mixture proportion (Char: KOH: KMnO₄) was 24 hours before activation for 3 hours at 800 °C. The surface area, pore volume, micropore volume, pore size distribution, porous structure, and adsorption isotherm were examined and considered as the properties of activated carbon. The results showed that the activated carbon with an impregnation ratio of 10:10.5, 10:30.0, and 10:30.5 have the surface area 750.89 m²/g, 1574.39 m²/g, and 1346.10 m²/g, respectively. The pore volume and micropore volume were in the range between 0.3289-0.6405 cm³/g and 0.1920-0.3533 cm³/g. The average pore sizes were 1.75 nm, 1.63 nm, and 1.65 nm, respectively. These synthesized activated carbons were characterized as type I isotherm and microporous solids.

1. Introduction
Activated carbon is a carbonaceous material containing a pore structure with a high specific surface area and pore size distribution [1]. According to it has large surface area and high pore volume, it can be used in many applications such as an outstanding adsorbent [2] and an electrode material for supercapacitor [3]. To prepare the activated carbon, the raw material is carbonized at a temperature between 200°C to 400°C to eliminate volatile compounds and tar and produce char [4]. After that, the activation process is applied. This activation can be divided into two methods. The first method is physical activation, carried out at a high temperature range of 700-1100 °C by using CO₂, steam, or a mixture of these gases. However, activated carbon obtained from this method has a low surface area. The second method is chemical activation involved the use of chemical agent to impregnate and carbonize raw material at a temperature range of 300°C to 800°C under an inert atmosphere. Therefore, chemical activation has benefits over physical activation, such as lower activation temperature, higher yield of activated carbon,
and higher surface area. A widely chemical agent including the acidic group; sulfuric acid (\text{H}_2\text{SO}_4), phosphoric acid (\text{H}_3\text{PO}_4)\text{,}\) potassium hydroxide (\text{KOH}), sodium hydroxide (\text{NaOH})\text{,}\) and the metallic salt; zinc chloride (\text{ZnCl}_2)\text{ are used as a dehydrating agent in chemical activation. Many researches shown that the alkaline group generate more micropore surface area than acidic group (2,10). Therefore, among the alkaline group, KOH is the most effectively used for chemical activation since It can produce micropores, it can easily use for various applications.

Biomass is an attractive raw material to produce activated carbon because it contains high cellulose, hemicellulose, and lignin \text{(11).} The elemental compositions of biomass are carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and slightly sulphur (S). \text{Many studied related to the chemical activation of selected biomass are summarized in table 1. All activated carbons using KOH as a chemical activation agent are carried out at a temperature of 800 °C. Because the activation temperature greater than 800 °C has not shown a significant increase in the surface area (13). Impregnation ratio is an essential parameter for chemical activation. It also affects active carbon porosity. The activated carbon impregnated at the ratio of 1:3 has a higher surface area. In Thailand, Rubberwood is a high potential biomass. However, a little number of researches using rubberwood sawdust as a raw material for physical activation (14) or chemical activation with ZnCl\textsubscript{2} presented in table 1, without studied the effect of KOH to the characteristic of activated carbon derived from this raw material.

Activated carbon can be used as an electrode material for electrostatic double layer capacitors (EDLCs). To improve the electrochemical properties of activated carbon, surface functional groups or metal oxide can be used. Manganese monoxide (\text{MnO}) has higher specific capacitance \text{(1,350 \text{ F/g}) compared with manganese oxides (15,16). However, It has low conductivity and cycle stability. Therefore, MnO was used as an additive to improve the specific capacitance of electrode materials. Potassium permanganate (KMnO\textsubscript{4}) and KOH also have similar activation mechanisms that generate micropores (17). KMnO\textsubscript{4} was decomposed into K\textsubscript{2}O, MnO, and O\textsubscript{2} at an activation temperature of 750 °C, and MnO was added to activated carbon (18). Moreover, KMnO\textsubscript{4} is low cost, environment friendly, and water-soluble. Thus, KMnO\textsubscript{4} is useful to improve the specific capacitance of activated carbon.

In this research, the activated carbon derived from rubberwood sawdust by using KOH and KMnO\textsubscript{4} as a chemical activation agent at the activation temperature of 800 °C were characterized. Surface area \text((S\textsubscript{A}),\) average pore diameter \text((D\textsubscript{p}),\) total pore volume \text((V\textsubscript{Total}),\) pore size distribution, micropore fraction \text((M\textsubscript{F})\), and surface morphology were determined. In addition, the effect of KMnO\textsubscript{4} on porosity textural properties were discussed.

| Materials                     | Activation condition | Surface Characteristic | Ref |
|-------------------------------|----------------------|------------------------|-----|
|                               | Agent | Ratio | Temp \(^\circ\text{C}\) | \(S\text{BET}\)\textsuperscript{a} | \(V\text{Total}\)\textsuperscript{b} | \(V\text{Mic}\)\textsuperscript{c} | \(D\text{p}\)\textsuperscript{d} |     |
| Polyalthia longifolia seed    | KOH   | 1:2   | 600-900             | 226.26- | 0.129- | 0.046- | 1.03- |  13 |
|                               |       |       |                     | 664.45- | 0.276- | 0.234- | 3.09- |     |
| Bambusa vulgaris striata      | KOH   | 1:3   | 800                 | 980.00- | 0.559- | -     | 2.28- |  19 |
| Oleaster fruit                | KOH   | 1:3   | 800                 | 1621.00- | 0.924- | 0.506- | -     |  20 |
| Corncob                       | KOH   | 1:3   | 800                 | 800.00- | 0.340- | -     | -     |  21 |
| Rubberwood sawdust            | ZnCl\textsubscript{2} | 1:1.5 | 500                 | 1,301.00- | - | 0.540- | 1.77- |  22 |

\textsuperscript{a}BET surface area.
b Total pore volume.
c Micropore volume.
d Average pore diameter.

2. Experimental Methods

2.1. The precursor and characteristics
Rubberwood sawdust collected from Southern Biomass Fuel Company, Songkhla province, Thailand, was used as the precursor. The particle sizes of sawdust are around 0.2-1 mm. The rubberwood sawdust was cleaned and dried at 105 °C for 24 hours. Then, it was collected into a sample bag and kept in a dehumidifying box. The thermogravimetric analyzer, model TGA 701, LECO, USA (based on ASTM D7582-15) from the office of Scientific Instrument and Testing, Prince of Songkla University, Thailand was used to examined the proximate analysis of the raw material, carbonized char, and activated carbons. The characteristics are presented in Table 3.

2.2. Activated carbon preparation
The activated carbon was prepared from the Rubberwood sawdust (RS) by a two-step process. The first step was carbonization process. Rubberwood sawdust was dried and placed in a 4-inch diameter tube to produce char. This reactor was loaded into the tube furnace and heated up to 400 °C at a heating rate of 6 °C/min and maintained for 1 hour, and cooled down in the furnace for 12 hours. The second step, the chemical activation process. Using KOH and KMnO₄ as the activating agents. The mixture of char (10 g), KOH (10 g, 30 g), and KMnO₄ (0 g, 5 g) was stirred manually. The well-mixed samples were left for 24 hours and then loaded into the electric tube furnace and heated up to 800 °C for 3 hours. Nitrogen gas was introduced at 500 cm³/min to create inert atmosphere during the carbonization and activation process. The activated carbon derived from rubberwood sawdust was soaked with 0.1 Molar Hydrochloric acid (HCL) for 3 hours in room temperature and washed with distilled water until the pH 7 was reached to remove impurities in activated carbon. Finally, the sample was dried in an oven at 105 °C for 24 hours, collected into a sample zip-lock bag, and kept in a silica gel box to prevent moisture absorption. The activated carbon samples were labeled as 10:10:5 (Char: KOH: KMnO₄), 10:30:0, and 10:30:5. The schematic preparation of activated carbon was shown in figure 1.

![Figure 1. The schematic preparation of activated carbon.](image-url)
2.3. **Textural characterization**

The textural properties of activated carbons such as surface area ($S_A$), total pore volume ($V_{total}$), micropore volume ($V_{Mic}$), average pore diameter ($D_p$), pore size distribution, micropore fraction ($M_F$), and adsorption isotherm were analyzed by using the high throughput surface area and porosity analyzer, Micromeritics (ASAP2460) from the office of Scientific Instrument and Testing, Prince of Songkla University, Thailand. Field Emission Scanning Electron Microscope (FESEM) images were used to examine the morphological properties of activated carbon by Merlin compact, ZEISS Microscopy, Jena, Germany from the Center for Scientific and Technological Equipment, Walailak University, Thailand.

### 3. Results and Discussions

3.1. **The yield of rubberwood sawdust char and activated carbon**

The rubberwood sawdust char and activated carbon yield and activated carbon were presented in figure 2. The yield of char was considered as equation (1) and equation (2), respectively. The yield of rubberwood sawdust char was around 32.85% by weight, and the yield of activated carbons was ranged between 15.10-18.96% by weight. The lowest yield of activated carbon occurred at proportion 10:30:0 (Char: KOH: KMnO$_4$) chemically reaction at 800 °C. At 10:30:5 proportion obtained the highest yield by 18.96%. The yield of 10:10:5 was 17.37%. The trend of the mixtures with KMnO$_4$ have higher yield than the mixture without KMnO$_4$. Therefore, the trend of activated carbon yield was similar in the case of activation by using KOH. Nuilerd et al. [23] revealed that activated carbon yield decreased by increasing of impregnation ratio.

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\text{The yield of char} \ (\% \text{wt}) = \frac{\text{Weight of char}}{\text{Weight of Raw material}} \times 100
\]  \hspace{1cm} (1)

\[
\text{The yield of activated carbon} \ (\% \text{wt}) = \frac{\text{Weight of Activated carbon}}{\text{Weight of Raw material}} \times 100
\]  \hspace{1cm} (2)
Figure 2. The yield of rubberwood sawdust char and activated carbon.

Table 2. Proximate analysis of rubberwood sawdust, char, and activated carbon.

| Samples            | Proximate contents (wt%) |
|--------------------|--------------------------|
|                    | Fixed carbon | Moisture | Volatile | Ash     |
| Rubberwood sawdust | 15.67         | 7.47     | 73.93    | 2.93    |
| Char               | 59.26         | 5.26     | 30.13    | 5.35    |
| AC (10:30:0)       | 76.91         | 4.95     | 12.95    | 5.19    |

3.2. Proximate analysis

Proximate analysis of rubberwood sawdust, char, and activated carbon are showed in Table 2. It is shown that the fixed carbon increased significantly after the carbonization and activation process. Fixed carbon increased from 15.67% to 59.26% and 76.91%, respectively. The raw material contains high volatile, high moisture, and ash content as 73.93%, 7.47%, and 2.93% by weight. The result showed that after the carbonization process, char has lower volatile and moisture but higher ash content as 30.13%, 5.26%, and 5.35%, respectively. The activated carbon with mixing proportion of 10:30:0 (Char: KOH: KMnO₄) and at activation temperatures of 800 °C has the lowest volatile, the lowest moisture, and ash content as 12.95%, 4.95%, and 5.19%.
3.3. Textural properties
Adsorption isotherm of activated carbons was shown in figure 3. The activated carbon with ratios 10:10.5, 10:30:0, and 10:30.5 have similar adsorption isotherm trends. In this study, the adsorption isotherm was obtained at a relative pressure between 0.01 to 0.99 P/Po. All samples were characterized as Type I isotherm. According to the IUPAC classification of adsorption isotherm, the type I isotherm implies the activated carbon as microporous solids and gas molecules adsorb as a monolayer [24]. The surface area (SA), total pore volume (VTotal), micropore volume (Vmic), and average pore diameter (Dp) of activated carbons were shown in Table 3. The surface area of activated carbons with ratios 10:10.5, 10:30:0, and 10:30.5 were 750.89, 1,574.39, and 1,346.10 m²/g, respectively. Kim et al. [18] reported that using KOH/KMnO4 as the activation agent decreased the surface area (SA) because KMnO4 decomposed to K₂O, MnO, and O₂, then MnO was formed into activated carbon and blocked the pores of activated carbon. The addition, KMnO4 decreased surface area around 14.48% by comparing between ratios 10:30:0 and 10:30.5. The decreases in surface area of 10:30.5 can be traced to detecting Mn (4.0 wt%) composition by EDX analysis in figure 7 (b). The total pore volume and micropore volume were in the range of 0.3289-0.6405 cm³/g, and 0.1920-0.3533 cm³/g. The ratio 10:30.0 without KMnO4 also has higher total pore volume and micropore volume than ratio 10:30.5. The micropore fraction of ratios 10:10.5, ratio 10:30.0, and ratio 10:30.5 were 58.37%, 55.15%, 59.19%, respectively. Thus, KMnO4 did not show significant effect in micropore fractions [17,18]. The average pore diameters of ratios 10:10.5, ratio 10:30.0, and ratio 10:30.5 were 1.75 nm, 1.63 nm, and 1.65 nm. These results indicated that the pore sizes of all activated carbons are micropores. The activated carbon pores were presented on the FESEM image, as shown in figure 6 (a)- (d).

| Samples | SBET a (m²/g) | Vtotal b (cm³/g) | Vmic c (cm³/g) | Dp d (nm) | Mf e (%) |
|---------|---------------|------------------|----------------|----------|----------|
| Char    | 0.56          | 0.0004           | 0.0003         | 187.63   |          |
| 10:10.5 | 750.89        | 0.3289           | 0.1920         | 1.75     | 58.37    |
| 10:30.0 | 1,574.39      | 0.6405           | 0.3533         | 1.63     | 55.15    |
| 10:30.5 | 1,346.10      | 0.5543           | 0.3281         | 1.65     | 59.19    |

a BET surface area.
b Total pore volume.
c Micropore volume.
d Average pore diameter.
e Micropore fraction.
3.4. Pore size distribution
Figure 4 presents the activated carbon pore size distribution range between 0.10 nm at ratios 10:10:5, 10:30:0, and 10:30:5. As the result of pore size distribution curves, it can be observed in two different pore size regions; micropores region (pores diameter less than 2 nm) and mesopores region (pores diameter between 2-50 nm). Ratios 10:10:5, 10:30:0, and 10:30:5 were comprised pores with the highest diameter around 1.26 nm with a maximum pore volume of 0.1792 cm$^3$/g/nm, 1.26 nm with a maximum pore volume of 0.3461 cm$^3$/g/nm, and 1.26 nm with a maximum pore volume of 0.2679 cm$^3$/g/nm respectively. The pore size distribution curves, activated carbon ratio 10:10:5 has distribution between 1.26-3.69 nm, ratio 10:30:0 has distribution between 1.18-2.73 nm, and ratio 10:30:0 has distribution between 1.18-4.00 nm, respectively.
3.5. *Cumulative pore size distribution*

The cumulative pore volume of activated carbons is presented in figure 5. The micropores volume at less than 2 nm of pore width indicates the same sharply increases pattern for ratios 10:10:5, 10:30:0, and 10:30:5 of activated carbons. Micropore volume between a range of mesopore regions (2-50 nm) remains constant for all samples. As the result shown activated carbon ratios 10:10:5, 10:30:0, and 10:30:5 have micropore volume 0.2364 cm$^3$/g, 0.4980 cm$^3$/g, and 0.4246 cm$^3$/g at pores width range less than 2 nm.
3.6. Field Emission Scanning Electron Microscope analysis (FESEM) and EDX analysis
The images of rubberwood sawdust char, ratio 10:10:5, ratio 10:30:0, and ratio 10:30:5 are shown in figure 6, (a)-(d), respectively. The Field Emission Scanning Electron Microscope (FESEM) was used to observe the textural surface of activated carbons with 500x magnification. Char are macroporous (>50 nm) structures undeveloped into mesopore or micropore range. Therefore macropores are unnecessary for the process of adsorption compared with mesopore and micropore structure. Ratio 10:10:5 has less porous structure than 10:30:0, and 10:30:5, but all of those were micropores (<2 nm), which is related to average pore diameter, as explained in table 3. Thus, chemical activation by using KOH/KMnO₄ as a multiple function activation agent can produce activated carbon with a well-formed porous structure from rubberwood sawdust char to increase its adsorption capability. Figure 7 (a) and (b) represented the Energy-dispersive X-ray spectroscopy (EDX) of activated carbon ratio 10:30:0 and ratio 10:30:5, which verified the presence of elemental composition of C, O, Ca, and Mg. However, in the ratio 10:30:5 detected, another significant elemental composition was Mn (4.0 wt%).

![Figure 6.FESEM images with 500x magnificent of the samples, (a) Char, (b) ratio 10:10:5, (c) ratio 10:30:0, and (d) ratio 10:30:5.](image-url)
Figure 7. EDX analysis of activated carbons, (a) ratio 10:10.5, and (b) ratio 10:30.5.

4. Conclusions
In this study, the rubberwood sawdust char with low surface area, pore volume, and large pore size can improve its properties after the chemical activation process. The yield of product with a ratio of 10:30.5 has the highest value of 18.96% by weight. Activated carbon without KMnO₄ (ratio 10:30.0) contains the highest surface area, total pore volume, and micropore volume by 1.574.39 m²/g, 0.6405 cm³/g, and 0.3533 cm³/g, respectively. The ratio 10:30.5 has lower surface area (14.48%), total pore volume, and micropore volume than the ratio 10:30.0. MnO introduced into activated carbon, was blocked the pores of activated carbon, thus decreasing the surface area. The micropore fraction of activated carbon was around 55.15.59.19%. Adding KMnO₄ has not significant effect in micropore fractions. The average pore diameters at ratios 10:10.5, 10:30.0, and 10:30.5 were 1.75 nm, 1.63 nm, and 1.65 nm, which were in a range of micropores size. The adsorption isotherm can be characterized as type I isotherm that can be implied that the activated carbon was microporous solid. FESEM images of the product exposed the development of pore and porous structure from rubberwood sawdust char. Thus, the micropore of rubberwood sawdust char can be generated by using KOH/KMnO₄ as an activation agent. Furthermore, the properties of activated carbon derived from rubberwood sawdust are suitable to be used as electrode material in supercapacitor application, and the next study will prove the effectiveness of KMnO₄ on the specific capacitance.

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