Synthesis and Characterization of Activated Carbon from Sago Waste (*Metroxylon sagu*) with ZnCl$_2$ Activation and HNO$_3$ Modification

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Abstract

Previous researches have shown that activated carbon could be made from various raw materials which contain lignocellulose. The aims of this research were to synthesis and characterize the activated carbon obtained from lignocellulose contained in sago waste. The synthesis was conducted through multiple stages of dehydration, carbonization, silica extraction with NaOH, activation by ZnCl$_2$ 10%, and surface modification using HNO$_3$ 65%, successively. From X-ray fluorescence, it was confirmed that treatment with NaOH removed practically all silica content from the sample with only 1 wt% left. The X-ray diffraction patterns showed that the samples have amorphous structures before the modification and started to form exfoliated graphite crystals, as shown by the peaks at 2θ 30.27° and 35.10°. The significant result was obtained from the series of processes of carbonization, extraction, activation, and modification using 1.5 mL of HNO$_3$ (CEA 1.5), which produced nanoporous particles with regular homogeneous shapes in the range of 200 nm in size as shown by scanning electron images. Finally, the infrared spectra from activated and modified samples confirmed that the oxygen-containing groups had increased.

From the series of processes of carbonization, extraction, activation with ZnCl$_2$, and modification using 1.5 mL of HNO$_3$ of lignocellulose contained in sago waste, it provides the modified-activated carbon samples with XRD pattern (left) for exfoliated graphite crystals. Moreover, SEM image (right) for this sample shows nanoporous particles with regular homogeneous shapes in the range of 200 nm in size.

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Keywords: sago waste, activated carbon, ZnCl$_2$ activation, HNO$_3$ surface modification.

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**Introduction**

Activated carbon has been widely used for the removal of pollutants from gaseous and liquid phases due to its large surface area, microporous structures, high adsorption capacity, and of course low cost. Recently, there has been an increase of interest in the use of activated carbon in some other fields, for instance as an absorbent in separation–purification processes and for electrode materials in energy storage devices such as Electric Double Layer Capacitor (EDLC) or commonly known as supercapacitor [1-5].

Due to the market demand from within Indonesia and overseas, the production of activated carbon in Indonesia has seen accelerated progress. The raw materials for the production of activated carbon had been regularly obtained from plants, animals, and minerals which contain carbon. Previous studies have shown that activated carbon could be made from organic agriculture wastes, such as pumpkin seed shells, cassava peels, coconut shells, bamboo, coffee beans, sunflower seed shells, rice husk, tea leaves, bagasse, etc [3-11]. Some of these raw materials contain similar lignocellulose like that in sago waste. Basically, sago waste (sago lees or sago pith waste), known as sago *hampas* by locals, is a residual extraction of sago starch [12,13]. In the sago waste, lignocellulose material consists of amylose, cellulose, hemicellulose, and lignin, which are rich in carbon substances [14]. Unfortunately, despite the abundance availability, the utilization of sago waste is still limited especially in the Papua region, the largest sago forest and cultivation area in Indonesia.

Sago (*Metroxylon sagu*) is one of the endemic plants in Southeastern Asia which spreads down to the eastern part of Eastern Indonesia. About 50% of sago plants in the world grow in Indonesia and 90% from that total can be found in Papua and Maluku. According to the data from the Department of Research and Development of Forestry of Indonesia published in 2007, the Papua region has 1.200.000 ha sago forests and 14.000 ha sago cultivations. For generations, sago has been one of the local food resources in the coastal area and edge of lake/bog of Papua communities [15-16].

In this study, sago wastes were used as the raw material (owing to its lignocellulose content) for the synthesis and characterization of activated carbon by ZnCl₂ 10% activator and HNO₃ 65% surface modifier. Zinc chloride is one of the most widely used activation agents for preparation of activated carbon due to its large surface area and high porosity leading to high adsorption capacity [3]. According to the study conducted by Ismanto et al, treatment with HNO₃ increased the amount of oxygen-containing groups more than those produced from the use of H₂SO₄ and HCl [4].

**Experimental Section**

**Materials and apparatus**

Sago waste as the raw material was obtained from the traditional production of Sentani people I Maribu Village, Jayapura Regency. Other supporting materials were NaOH 10 M, ZnCl₂ 10% and HNO₃ 65% solution, distilled water, universal test paper, and filter paper. The elemental composition of carbons (before and after extracting) were analyzed by PANalytical Minipal 4 X-ray Fluorescence. The crystallinities of the samples were measured by using PANanalytical E’XPERT PRO X-ray Diffraction. The surface morphologies were investigated by FEI Inspect-S50 Scanning Electron Microscopy (SEM). The SHIMADZU IRPrestige 21 Fourier Transform Infrared (FTIR) Spectroscopy was used to investigate the functional groups contained in the samples.

**Sample preparation**

The samples were prepared according to the procedure described previously by Masdir et al. [11]. The sago waste was repeatedly washed to remove dust and other impurities and then dried naturally under the sunlight for 3 days. This was followed by further drying in an oven for 2 hours at 110°C to reduce the moisture content.

**Carbonization and silica extraction**

20 grams of the dried sago waste was burnt using an electric burner until it became charcoal and was subsequently kept in an oven for an hour at 250°C. After carbonization, the resulting sago waste carbon was ground and sieved to obtain the fine powder of carbon. Silica extraction was performed by mixing the carbon powder with NaOH solution at impregnation ratio of 1:20 (gr mass carbon: ml volume NaOH) and stirred for an hour at 95°C. Then, the result was filtered and washed with distilled water repeatedly until neutral [11].
Activation and surface modification

25 ml ZnCl₂ 10% solution was added to 5 g of the extracted product, which was then boiled for 90 minutes to activate it and filtered. The activated product was then transferred to an oven and heated for an hour at 250°C. After heating, the activated sago waste carbon was washed until neutral and then dried again in the oven at 110°C until reaching a constant weight. The surface modification of the activated carbon was performed with oxidative chemical agents (HNO₃ 65% solution). The activated carbons were mixed with HNO₃ 65% solution at different volume ratios 0.5:1, 1:1; 1:5:1 (volume of chemical agent: the mass of activated carbon), and then stirred at 110°C for 4 hours. The resulting slurry was filtered and washed repeatedly until the pH of the washing solution reaches 6.5, and then dried in the oven at 110°C for 24 hours [4,11]. Thus, the samples were ready to be characterized.

Results and Discussions

As is the normal case with most food ingredients, sago waste has a brown color that is associated with the enzymatic reaction during the dehydration process which alters its color [17]. The dehydration process, which took place an hour in an oven at 100°C, reduced the weight of the sample from 53.2 g down to 26.1 g, which was equivalent to a weight reduction of 50.9%. Table 1 presents the sample codes and the treatments undergone by each of the samples.

![Image](a) ![Image](b) ![Image](c) ![Image](d)

**Figure 1.** The results of synthesis stages: sample preparation (a) fresh sago waste, (b) naturally dehydration, (c) carbonization and (d) carbon powder.

It was found that sago waste contains a significant amount of silica [12], which is also known as silicon dioxide with general formula SiO₂ and belongs to semiconducting material [18]. The aim of silica extraction in this synthesis was to produce a silica-free activated carbon. The process provided an initial structure that stimulated the activated carbon to become purer and more porous [9]. In this work, the silica extraction was conducted by the assistance of the NaOH solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Carbonization</td>
</tr>
<tr>
<td>CE</td>
<td>Carbonization + Extracted</td>
</tr>
<tr>
<td>CEA</td>
<td>Carbonization + Extracted + Activation</td>
</tr>
<tr>
<td>CEA 0.5</td>
<td>CEA + 0.5 ml Modification</td>
</tr>
<tr>
<td>CEA 1</td>
<td>CEA + 1 ml Modification</td>
</tr>
<tr>
<td>CEA 1.5</td>
<td>CEA + 1.5 ml Modification</td>
</tr>
</tbody>
</table>

**Table 1.** Sample codes and description of treatments/process.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Before Extracting (%)</th>
<th>After Extracting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>48</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca</td>
<td>31</td>
<td>65</td>
</tr>
<tr>
<td>P</td>
<td>3.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Mn</td>
<td>3.7</td>
<td>11</td>
</tr>
<tr>
<td>Cu</td>
<td>0.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Zn</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>K</td>
<td>7.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>2.6</td>
<td>11</td>
</tr>
<tr>
<td>Re</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Eu</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Yb</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**Table 2.** Chemical composition of samples before and after silica extraction acquired from X-ray fluorescence.

Table 2 shows that silica extraction was successfully performed, with only 1 wt % of Si left. As discussed earlier, the Si element formed an oxide compound (SiO₂). Therefore, the reaction between SiO₂ and NaOH can occur according to this following reaction:

\[ \text{SiO}_2(s) + 2\text{NaOH} \,(aq) \rightarrow \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{O}(l) \]

The addition of NaOH with stirring bound silica dioxide and converted it to sodium silicate which dissolved in the neutralizing process [11].
Figure 2 shows X-ray diffraction patterns of extracted carbon (CE) and activated carbon (CEA) samples. The qualitative pattern showed that both of them have amorphous structures. Moreover, the diffraction patterns of modified-activated carbon displayed several sharp peaks. Carbon crystals were identified at 30.27° (started from 0.5 ml modification) and 35.10° (seen from 1 ml modification) following Crystallography Open Database (COD 96-901-2232) 5.4% and typical patterns of ZnCl₂ (COD 96-343-3818) 11.1% also HNO₃ 83.4%.

The diffraction patterns of modified-activated carbon samples show that along with the addition of oxidative acid agent, the intensities of identified graphite carbons were pursuing stronger, higher, and sharper indicating the formation of crystalline carbon, while there was some existence of other peaks which dominated in the surface modification patterns. The oxidation with concentrated HNO₃ has a strong effect on decreasing the carbon surface area. This decrease in surface area is related to the destruction of the porous structure caused by the severe oxidation with different volume of nitric acid [19]. Therefore, the crystalline carbon peaks may be due to the severe oxidation. In the stirring process, two possibilities can occur i.e. if a good binding occurs perfectly in the inter-compound it will dissolve together in the washing and neutralizing process, but if partial binding appears it usually comes from weak oxidative agent hence the peaks still identified at X-ray diffraction patterns [5,20]. The presence of typical patterns of ZnCl₂ and HNO₃ suggested that the washing process should be improved.

The FTIR analysis was performed to determine the functional groups in the samples especially the oxygen-containing groups [4]. Figure 4 shows Fourier transform Infrared spectroscopy patterns of the five samples. The activated carbon from sago waste had an addition of oxygen-containing groups along the synthesis stages.
Table 3 reveals the addition of functional groups of carbon surfaces, where several bands were identified, such as -OH, C=O, C=O, and NO3. After the modification, the activated carbon samples showed additional hydroxyl and carbonyl groups. The existence of oxygen-containing groups on the surface of activated carbon can enhance the polarity, which had an effect of increasing the adsorbent ability and effectiveness on the surface area of supercapacitor-based electrodes of activated carbon [22].

Table 3. Peaks of oxygen-containing groups on activated carbon from sago waste

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>CE</th>
<th>CEA 0.5</th>
<th>CEA 1</th>
<th>CEA 1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl Alcohol</td>
<td>3348.42</td>
<td>3304.06</td>
<td>3338.78</td>
<td>350.35</td>
</tr>
<tr>
<td>Alcohol Carboxylic Acid</td>
<td>3267.76</td>
<td>2603.9</td>
<td>2586.54</td>
<td></td>
</tr>
<tr>
<td>Alcohol Carboxyl</td>
<td>1062.8</td>
<td>1070.5</td>
<td>1063.7</td>
<td>1064.7</td>
</tr>
<tr>
<td>Phenol Carboxyl</td>
<td>1361.74</td>
<td>1365.6</td>
<td>1359.81</td>
<td>1361.74</td>
</tr>
<tr>
<td>Carboxylic Acid Quinine</td>
<td>1701.22</td>
<td>1714.72</td>
<td>1714.72</td>
<td>1714.72</td>
</tr>
<tr>
<td>Lacton</td>
<td>1732.08</td>
<td>1732.07</td>
<td>1732.08</td>
<td></td>
</tr>
<tr>
<td>NO3 (Nitro Compound)</td>
<td>1325.1</td>
<td>1323.1</td>
<td>1317.38</td>
<td></td>
</tr>
</tbody>
</table>

Conclusion

Activated carbon from sago waste has been synthesized by ZnCl2 10% activator and HNO3 65% modifier. The extraction treatment was able to remove silica content. Diffraction patterns of extracted carbon and activated carbon were formed amorphous structures while crystal carbons were identified on modified-activated carbons at 2theta 30.27° and 35.1°. The morphology of activated carbon (CEA) showed few microporous, while the significant result of surface morphology has been given obtained from modified 1.5 (CEA 1.5), where it has formed much nanoporous that was regular with homogeneous shapes and sizes, 200 nm. FTIR spectra were performed on the addition of the oxygen-containing group of activated carbon along with synthesis stages that had been accomplished.

Authors’ contribution

Yanti Kiding Allo performed the experiments, analyzed the data and wrote the paper; Sudarmono contributed to refining the papers, and Octilia Togibasa was responsible for all research actions and paper writing.

Conflict of Interest

The authors declare no conflict of interest.

References


