Cellulose extraction from sugar palm (*Arenga pinnata*) fibre by alkaline and peroxide treatments

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Abstract. Cellulose is a versatile polymer which can be extracted from various agricultural waste. Sugar palm (*Arenga pinnata*) fibre (SPF) is one of potential cellulose source. The cellulose extraction from SPF was conducted by alkaline treatment with sodium hydroxide (NaOH) solution (10%) and peroxide treatments with hydrogen peroxide (H₂O₂) solution (5, 10, 15%). The alkaline treatment was supposed to remove most of hemicellulose and some of lignin. The following peroxide treatment aimed to remove remaining lignin. The results of each step were analyzed its composition, visual appearances, colour and morphological aspect. The results showed that increasing of H₂O₂ solution concentration not only tends to increase cellulose content and whiteness but also reduce the diameter size of fibre which indicates the removal of impurities (hemicellulose and lignin) from the fibre. In conclusion, cellulose was successfully extracted from SPF by alkaline treatment followed by peroxide treatments which the best result was in condition of 15% H₂O₂ solution concentration.

1. Introduction

One of biopolymers most found and produced by nature is cellulose with an estimated production of around 5 million tons per year [1]. It is a versatile polymer which has widely use in various fields. In order to maximize its utilization, cellulose could be modified into cellulose esters, cellulose ethers and regenerated cellulose [2]. Furthermore cellulose based material could be utilized into fibres, films, membranes, bioplastics and composites [3].

Mostly, cellulose is obtained from lignocellulosic material by removing other constituents, mainly lignin and hemicellulose. Wood (hardwood, softwood) and non-wood (cotton linter, agricultural residue) are two main sources of lignocellulosic material [4]. Due to deforestation issue, non-wood biomass could become attractive sources of cellulose since they have high cellulose content. In addition to sugar palm fiber, sugarcane (*Saccharum officinarum*) bagasse, oil palm (*Elaeis guineensis*) empty fruit bunch and rice (*Oryza sativa*) straw are few examples as non-wood biomass that have been studied to produce cellulose [5].

One of exciting agricultural waste material is sugar palm (*Arenga pinnata*) fibre (SPF). As side product of sugar palm process production, SPF has excellence properties according to their high durability and resistance to sea water [6]. Moreover, SPF has high content (>40%) of cellulose [7] which
make it appealing material for cellulose source. Previous studies have been focusing on utilizing SPF into cellulose based products such as micro [8-9] and nanocellulose [7,10]. To produce these products, SPF has to be converted into pure cellulose, which mainly involving 2 stage processes, alkaline treatment and bleaching. Unfortunately, a common bleaching process still involves chlorine-based chemical i.e. natrium chlorite (NaClO₂) as bleaching agent. In spite of its cheapness and effectiveness as bleaching agent [11], chlorine bleaching has famous with its toxic waste [12]. Thus, alternative environmentally bleaching agent is inevitably needed.

Oxygen based bleaching agents are evidently potential alternative environmentally bleaching agents [13]. One of them is hydrogen peroxide (H₂O₂) which famous of its environmentally friendly and strong oxidizing ability [13-14]. In most cases, alkaline-hydrogen peroxide condition is chosen to accelerate bleaching process [13-17]. This bleaching method was in SPF processing into cellulose, therefore this research focus on the effects of hydrogen peroxide treatment in extracting cellulose from SPF. The bleaching method used hydrogen peroxide and sodium hydroxide well known that they do not produce harmful waste and more environmentally friendly. The bleached fibres have higher degree of brightness compared to the results of bleaching fibers in previous studies.

2. Materials and methods

2.1. Materials
Sugar palm fibre (SPF) was obtained from sugar palm starch factory in Klaten, Central Java, Indonesia. The SPF was washed with tap water to remove debris and other impurities, followed by sun drying. The chemicals, i.e. cellulose (Sigma-Aldrich), acetone (technical grade), hydrogen peroxide H₂O₂ 30% solution (Merck), sulfuric acid H₂SO₄ 95-97% (Merck), sodium hydroxide NaOH (Merck) and distilled water were used as received without further purification.

2.2. Cellulose extraction
Two stages extraction with acetone and water were conducted in order to prepare extractive free SPF sample [18]. Alkaline pretreatment with 10% w/w NaOH solution was conducted at temperature of 150°C for 2 h. The last stage was bleaching process with H₂O₂ solution. Selected H₂O₂ concentration were 5, 10 and 15% at adjusted pH 9-10, temperature of 60°C and reaction time 90 minutes. The obtained sugar palm cellulose (SPC) was filtered and washed with distilled water followed by oven drying at temperature of 60°C. Plastic bag was used to keep the SPC at room temperature for further used.

2.3. Compositional analysis
Analysis method by Chesson-Datta [19] was used to determine percentage of hemicellulose, cellulose, lignin and ash. The sample was refluxed using 150 mL of 1 N H₂SO₄ solution for 2 hours at 100°C to quantify the hemicellulose content. Subsequently, the sample was macerated for 4 hours in 10 mL of 72% H₂SO₄ solution at room temperature then added with 150 mL of 1 N H₂SO₄ solution and refluxed for 2 hours at 100°C in order to measure cellulose content. Burning of samples in muffle furnace has been carried out to measure the ash content [20]. The lignin content was measured as the different between sample before and after burned. The compositional percentage was stated in extractive free sample basis.

2.4. Surface morphological analysis
Analysis using scanning electron microscope (SEM) Hitachi SU3500 at 550x magnification was done to analyzed surface morphology of the SPC. The analysis was carried out at voltage accelerate of 5kV. Samples were coated with gold using ion sputtering MC1000 before analyzed.
2.5. Colour measurement

Colour determination of sample was conducted with Colour reader Konica Minolta CR-20 CIE method. The L, a and b parameter value were measured. The colour difference (ΔE*) between sample and cellulose standard was calculated using Equation 1 [21] below.

\[
\Delta E^* = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}
\]

Where \( \Delta L = L^*_{\text{sample}} - L^*_{\text{standard}} \), \( \Delta a = a^*_{\text{sample}} - a^*_{\text{standard}} \) and \( \Delta b = b^*_{\text{sample}} - b^*_{\text{standard}} \).

2.6 Statistical Analysis

Statistical analysis was conducted using CoStat software.

3. Results and discussions

3.1 Chemical compounds analysis of sugar palm fibre

Table 1 is shown the result of the sugar palm fibres (SPF) chemical compounds analysis at different stages of treatment. The cellulose content of raw SPF was 50.68±2.37%. This result was in line with previous study conducted by Ilyas et al. (2018) which cellulose content of raw SPF is more than 40% [7]. After treating the SPF with 10% NaOH solution for 2 hours, the cellulose content was increased to 78.17±0.88%. NaOH is a strong base chemical which able to remove hemicellulose and lignin under certain condition [22-23] thus in this condition the lignin and hemicellulose was decreased. Furthermore alkali-treated SPF (SPF-A) was bleached with \( \text{H}_2\text{O}_2 \) solution in alkaline condition in order to remove remaining impurities.

| Treatments            | Hemicellulose (%) | Cellulose (%) | Lignin (%) | Residual Ash (%) |
|-----------------------|-------------------|---------------|------------|------------------|
| Raw (SPF-R)           | 35.00±1.08        | 50.68±2.37    | 13.45±1.33 | 0.87±0.05        |
| Alkali Treated (SPF-A)| 11.97±0.56        | 78.17±0.88    | 9.70±1.45  | 0.16±0.02        |
| \( \text{H}_2\text{O}_2 \) 5% (SPF-05) | 11.60±1.63<sup>a</sup> | 82.88±0.51<sup>b</sup> | 5.34±1.36<sup>a</sup> | 0.18±0.05<sup>a</sup> |
| \( \text{H}_2\text{O}_2 \) 10% (SPF-10) | 10.22±0.48<sup>a</sup> | 84.51±1.83<sup>ab</sup> | 5.10±2.31<sup>a</sup> | 0.16±0.02<sup>a</sup> |
| \( \text{H}_2\text{O}_2 \) 15% (SPF-15) | 9.95±0.87<sup>a</sup> | 86.99±1.98<sup>a</sup> | 2.90±1.38<sup>a</sup> | 0.15±0.05<sup>a</sup> |

The analysis was conducted in triplicate. The values are as mean ± standard deviation. Different letters in the same column indicate significant differences (p < 0.05).

Table 1 also shows the significant effect of \( \text{H}_2\text{O}_2 \) solution concentration on cellulose content. The increasing of \( \text{H}_2\text{O}_2 \) solution concentration tends to increase cellulose content, which highest cellulose content was found in treatment with 15% \( \text{H}_2\text{O}_2 \) solution (86.99±1.98%). The increasing of cellulose content was caused by the partial elimination of hemicellulose and lignin. This phenomenon was marked by decreasing of hemicellulose and lignin content along with increasing of \( \text{H}_2\text{O}_2 \) solution concentration. This result is consistent with the research conducted by Coniwanti et al. (2015) that the greater the concentration of hydrogen peroxide used, the less lignin content in the product [24], therefore increasing cellulose content.

3.2 Visual appearances and morphological analysis

The effects of SPF bleaching with \( \text{H}_2\text{O}_2 \) solution could be observed not only from its compositional changing but also from its physical and morphological appearances. The changing of physical appearances can be seen using the bare eyes. From Figure 1 it is clearly shown that discoloration of SPF occurs at different stages of treatment. The color of the SPF changed from dark brown (Figure 1a) to dark grey after alkali treatment (Figure 1a), and became white after bleaching treatment (Figure 1c, d, e).
Besides of the physical appearance, the color determination of the sample is conducted with the Konica Minolta CR-20 CIE Color reader. Table 2 shows the comparison of color measurements between standard cellulose and cellulose from bleaching treatment using H$_2$O$_2$ solutions with concentration of 5%, 10%, and 15%. The lightness of the pulp can be seen with the parameters L *, a *, and b * which can be read directly on the instrument. L which shows the lightness value, the greater the% L, the higher the sample lightness. a * is a value that indicates the level of greenness and redness of the pulp. The more positive the a * value is, the more the pulp is red and conversely the more negative the value of a *, the more green the pulp is analyzed. b *, which is the value that shows the yellowness and bluish level of the pulp. The more yellow pulp colour well marked with the more positive the value of b *. Meanwhile, the more negative the value of b * indicated the more blue pulp colour of samples [25].

![Figure 1. Photographs of (a) raw sugar palm fibres, (b) alkali-treated fibres, (c) bleached fibres by H$_2$O$_2$ 5% (SPF-05), (d) bleached fibres by H$_2$O$_2$ 10% (SPF-10), (e) bleached fibres by H$_2$O$_2$ 15% (SPF-15)](image)

**Table 2. Colour measurement of raw and treated SPF**

| Treatments            | L      | a      | b      | ∆E    |
|-----------------------|--------|--------|--------|-------|
| H$_2$O$_2$ 5% (SPF-05)| 81.6±0.1$^c$ | 0.9±0.3$^a$ | 7.9±0.8$^a$ | 12.1±0.2$^a$ |
| H$_2$O$_2$ 10% (SPF-10)| 84.4±0.2$^b$ | 0.3±0.1$^b$ | 7.0±0.2$^b$ | 9.1±0.2$^b$ |
| H$_2$O$_2$ 15% (SPF-15)| 85.6±0.4$^b$ | 0.1±0.1$^b$ | 6.6±0.1$^b$ | 7.9±0.1$^c$ |
| Cellulose Standard    | 93.2±0.0 | -0.2±0.0 | 4.8±0.1 | -     |

The analysis was conducted in triplicate. The values are as mean ± standard deviation. Different letters in the same column indicate significant differences (p < 0.05).
The concentration of H$_2$O$_2$ solution affects the values of L, a and b. Table 2 shows that cellulose standard has high L value of 93.2 ± 0.0% and L value of bleached SPF increased as increasing of H$_2$O$_2$ concentration. The L value of SPF-15 is closer to L value of standard cellulose than L value of SPF-05 and SPF-10. Meanwhile the increasing of H$_2$O$_2$ concentration tend to decrease a and b value. Based on the result known that it is suitable with the research conducted by Jayanudin et al. (2010) that the increase in peroxide concentration will increase L value and decrease a and b value [25].

The total change (ΔE) in L, a and b is a parameter used to measure colour changes. The greater ΔE, the greater change in L, a, b and this indicates greater colour different between bleached SPF and cellulose standard. The results show that H$_2$O$_2$ concentration has significant effect on ΔE value. The increasing of H$_2$O$_2$ concentration tends to decrease ΔE value which means the sample condition is closer to cellulose standard. This phenomenon was caused by the reducing of impurities (lignin, hemicellulose) in the SPF as H$_2$O$_2$ concentration increase.

![SEM micrographs 550x magnification of (a) raw sugar palm fibres, (b) alkali-treated fibres, (c) bleached fibres by H$_2$O$_2$ 5% (SPF-05), (d) bleached fibres by H$_2$O$_2$ 10% (SPF-10), (e) bleached fibres by H$_2$O$_2$ 15% (SPF-15).](image)

**Figure 2.** SEM micrographs 550x magnification of (a) raw sugar palm fibres, (b) alkali-treated fibres, (c) bleached fibres by H$_2$O$_2$ 5% (SPF-05), (d) bleached fibres by H$_2$O$_2$ 10% (SPF-10), (e) bleached fibres by H$_2$O$_2$ 15% (SPF-15).

The bleaching and alkali treatments not only cause changes in chemical composition of SPF but also affect the structure of the fibres surfaces. SEM pictures of SPF at various conditions were taken to investigate the alteration of SPF diameter after treatment. Initially the raw SPF has diameter more than 100 µm which then reduced to size of tens µm followed by less than 10 µm size after bleaching. This occurrence was caused by the removal of lignin and hemicellulose through the process of alkali treatment and bleaching treatment. This results were in line with previous study by Ilyas et al. (2018) that the removal of lignin and hemicellulose caused size reduction in SPF diameter [7].

4. Conclusion
Cellulose was successfully extracted from sugar palm fibre (SPF) by alkaline and peroxide treatments. The alkaline treatment was able to remove most of hemicellulose and some of lignin. Following treatment with various concentration of hydrogen peroxide (H2O2) solution was significantly
increasing cellulose content. The results shows that cellulose content is getting higher with increasing concentrations of H$_2$O$_2$. The higher of H$_2$O$_2$ solution concentration also increase the lightness degree of sample. From morphological aspect, the alkaline and peroxide treatment were able to reduce the diameter size of fibre which indicate the removal of impurities (hemicellulose and lignin) from fibre.

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