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Lignocellulosic Properties of Coffee Pulp Waste After Alkaline Hydrogen Peroxide Treatment

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Abstract. The effect of alkaline hydrogen peroxide (AHP) treatment on reducing lignin content in coffee pulp waste (CPW) was investigated to increase the digestibility and accessibility of cellulose during production of valuable products by enzymatic and biological process. Hydrogen peroxide (H₂O₂) at various concentrations (2.5, 5, and 7.5% (w/w of substrate)) was mixed into 10% (w/v) of CPW-NaOH solution at 35 °C for 24 h with pH 11.5. The concentration of lignocellulosic content was investigated. The characteristic of crystallinity index, functional groups, and surface morphology of CPW at before and after the treatment have been observed using XRD, FTIR, and SEM analysis, respectively. The results showed that the highest lignin removal was achieved at the addition of 7.5% H₂O₂ which decreased from 16.85% to 8.5%. The concentration of cellulose and hemicellulose in CPW increased from 53% to 64% and 11% to 24%, respectively. The crystallinity index of AHP-treated CPW has increased from 30.83% to 42.08%. A surface morphological destruction on the CPW was getting worse as along with the increase of H₂O₂ concentration. This would be useful to increase the porosity of biomass to give cellulose accessibility by enzyme for further processes.

1. Introduction

In Indonesia, CPW is reported to have big potential to be converted as valuable products due to its abundant availability with the potential amount of 30-50% of total weight of coffee production by 686 x 10⁶ kg each year [1]. Moreover, it contains a high cellulose compound, about 50-63%, which can be utilized as the feedstock of reducing sugar and its derivative products, such as ethanol, butanol, methane, etc. Its utilization is important because the abundant untreated CPW in the environment will release the xenobiotics, such as caffeine, tannins, and free polyphenols, as major pollutant agent on water and soil that toxic to saprophytic microorganisms which take important biotransformation within the environment. This causes disorderliness in environmental stability [2]. Furthermore, uncontrolled emission of CH₄, N₂O, and CO₂ from the open composting area will increase the negative effect of global warming [3].

Lignin in CPW needs to be removed before a further process to increase the accessibility of cellulose by cellulosic enzyme during the enzymatic or biological process. Therefore, delignification takes an important role to obtain the higher converted product. In this case, chemical treatment using alkaline has been a favored technique for lignin degradation than acid, ammonia, liquid hot water, and pH controlled hot water because it can be applied in lower pressures and temperatures compared to other ones. Alkaline



treatment is generally more effective even if the treatment is carried out at ambient conditions [4]. Recently, AHP treatment, which combine the advantages of sodium hydroxide and hydrogen peroxidase, has been widely applied in reducing lignin of some biomass such as bamboo [5], black liquor residue of poplar wood soda pulp [6], banana pseudostem [7], Douglas fir [8], corncob [9], empty palm fruit bunch [4], rice straw [10] etc. Reference [11] reported that AHP treatment could selectively remove lignin and deconstructs the cell walls which is useful for significant digestibility enhancement of biomass. Besides, hydrogen peroxide is environmental friendly for a cleaner process [12].

Although AHP treatment had been applied for much lignocellulosic feedstock, but not yet for coffee pulp waste. In this present study, the effects of H₂O₂ concentration on lignin and other lignocellulosic contents in CPW after the treatment have been investigated. As well as comparing the change in the characteristic of CPW involve cellulose crystallinity index, its functional groups and surface morphology induced by treatment.

2. Material and Methods

2.1. Materials

Coffee pulp waste was collected from Malang, Indonesia. It was dried under sun radiation for several days until a weight loss of coffee pulp about 50% and milled in a disk mill to pass through a 100-mesh screen. Then, it was dried in the oven at 60 °C until constant weight. The initial lignocellulosic composition of the CPW was observed. It contained 53% (dry basis) of cellulose, 11% of hemicellulose, 16.85% of lignin, 5% of moisture content, and 14.15% of other chemicals.

NaOH and 30% H₂O₂, glacial acetic acid, sodium bicarbonate, and concentrated sulfuric acid were purchased from Merck. Sodium chlorite (NaClO₂) was purchased from Sigma Aldrich. The other chemicals used were of analytical grades.

2.2. Treatment Procedure

Ten grams of coffee pulp waste was introduced into Erlenmeyer flask containing 90 ml of 1% (w/w) NaOH solution that made the solution volume approximately 100 ml. Then, 30% H₂O₂ with the following dosage; 2.5, 5, or 7.5% (w/w of substrate) was added to that flask. The pH of the solution was adjusted to 11.5 using NaOH 6 M. Then, they were placed in an incubator with a rotary shaker at 125 rpm at 35 °C for 24 h. Liquid and solid fraction from the Erlenmeyer flask were drawn at the certain interval of treatment time and separated using a Whatmann filter paper no. 41 on a vacuum filtration. The solid samples were obtained from the solid fraction after washing by distilled water until neutral pH and drying at 60°C in an oven. The treatments were performed in duplicates.

2.3. Analytical Methods

Lignocellulosic content in CPW (before and after treatment) was analyzed. Insoluble lignin was determined by TAPPI T222 om-02 method. Determination of polysaccharides in CPW solid samples was carried out based on the isolation of holocellulose which contains cellulose and hemicellulose using sodium chlorite (NaClO₂), glacial acetic acid and acetate buffer. To determine the cellulose content, the obtained holocellulose was hydrolyzed with dilute hydrochloric acid to remove hemicellulose at boiling temperature using a reflux condenser as described by [13].

Cellulose crystallinity index (CrI) of the samples was scanned using X-ray Powder Diffraction (XRD, PANalytical X'pert Pro) from 5° to 50° of 2θ and calculated by the equation (1) [14]:

$$CrI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100\% \quad (1)$$

where I_{002} is the maximum intensity of the diffraction peak of 002 in 2θ between values of 22-23, and I_{am} is a minimum intensity of the peak between the values of 18-19 [15]. FTIR spectra were recorded to characterize the major functional groups of CPW's samples. Surface morphology of CPW samples was captured using a scanning electron microscope (SEM) after they were coated using Pb-AU. That analysis was applied to the sample at before and after the treatment process.

3. Results and Discussion

3.1. Lignocellulosic Content of CPW after AHP Treatment

Lignin can become a physical barrier and restricting the enzyme access to cellulose due to undertaking non-productive binding with the lignin, which could decrease the efficiency of enzyme performance. [4] have reported that AHP treatment could give a significant reduction in lignin content as compared to the CPW without treatment. According to the results (see Figure 1a), a similar trend of lignin degradation has been achieved in CPW after treatment which decreases along with the higher concentration of H_2O_2 and longer duration time. The different delignification rate was obtained in each concentration and being slower after 6 h and finally, exhibit a significant gap in lignin removal at 24 h of treatment time. As revealed in Figure 1a, the highest lignin removal is successfully achieved at 7.5% H_2O_2 for 24 h, decreasing from 16.85% to 8.5%.

In Figure 1b, the concentration of cellulose and hemicellulose in CPW increase during AHP treatment due to the lignin content reduction in the solid fraction sample. The same result was obtained by [7] who found that the lignin content in treated banana pseudostem using alkaline and peroxide have decreased the lignin content from 17.26% to 7.65% and 7.17%, respectively and increased cellulose content from 60.84 to 75.48 and 74.37%, respectively. In this study, the highest increment of cellulose and hemicellulose content were retrieved from treated CPW using 7.5% H_2O_2 for 24 h which increased from 53% to 64% and 11% to 24%, respectively. The increase in hemicellulose in AHP-treated samples was probably caused by relatively unassociated hemicellulose with lignin and relatively unchanged “macromolecular” structure of the hemicellulose itself [10].

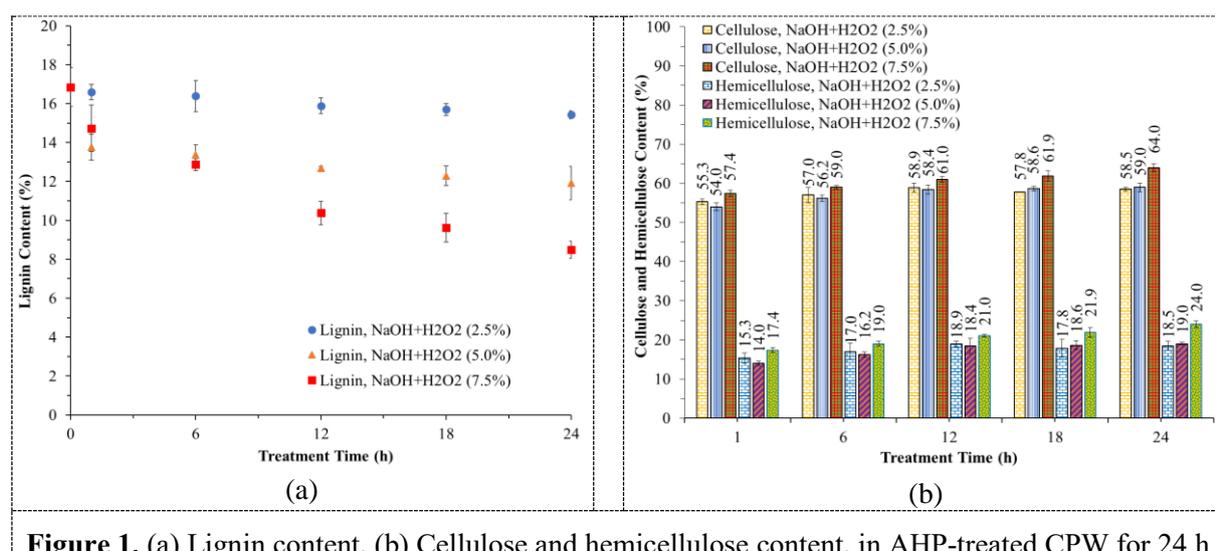


Figure 1. (a) Lignin content, (b) Cellulose and hemicellulose content, in AHP-treated CPW for 24 h

3.2. Characterization of CPW Samples after AHP Treatment

3.2.1. FTIR Analysis of CPW Treated by AHP

The X-ray diffraction of the CPW before and after AHP treatment has been investigated and the crystallinity index was calculated by equation (1), as shown in Table 1.

In Table 1, the crystallinity index value of AHP-treated solid samples is higher than CPW without treatment. AHP-treated samples for 24 h have a significant increase of the CrI from 30.83% to 31-43.68% after treatment. The increase of CrI was mainly due to the removal of amorphous part of lignocellulose which was indicated by weight loss of total solid of CPW after AHP treatment in an average of 4 g per 10 g of initial solid sample. This result was in line with [16] who reported that AHP-treated bamboo has relatively higher crystallinity, due to the dissolution of lignin and in part of hemicellulose. He found that the acid-soluble lignin, organic solvent extractives, and ash were effectively removed by AHP, except the acid-insoluble lignin and holocellulose. Moreover, [9] also

found that the CrI of APH-pretreated corncob was higher than that of the raw material due to the growth in cellulose content in that solid sample.

Table 1. Crystallinity index of CPW without and with treatment by alkaline hydrogen peroxide

Variable	CrI (%)
Untreated CPW	30.83
Treated CPW by NaOH+H ₂ O ₂ 2.5%, 6 h	31.22
Treated CPW by NaOH+H ₂ O ₂ 5.0%, 6 h	36.16
Treated CPW by NaOH+H ₂ O ₂ 7.5%, 6 h	30.95
Treated CPW by NaOH+H ₂ O ₂ 2.5%, 24 h	31.49
Treated CPW by NaOH+H ₂ O ₂ 5.0%, 24 h	43.68
Treated CPW by NaOH+H ₂ O ₂ 7.5%, 24 h	42.08

3.2.2. Surface Morphology of CPW

Figure 2 shows the surface morphology of AHP-treated CPW after 24 h compared to untreated CPW. At glance, there is a significantly different between each other where untreated CPW is looked more compact than others which are destroyed. The destruction on the CPW surface is getting worse as more H₂O₂ concentrations were added. This reveals by Figure 2b which has wrinkles in its surface while Figure 2b and 2c are fully ripped. Theoretically, NaOH and hydrogen peroxide (under proper pH, 11.5-12) do the synergistic activities during the lignin degradation. NaOH breaks the ester bonds cross-linking lignin [4], while hydrogen peroxide destroys the ether bonds between lignin and hemicellulose and decreases the polymerization degree of lignin in the cell wall. That condition leads to the partial dissolution of lignin and increases the porosity of biomass [17]. The increasing of porosity would be useful to give cellulose accessibility by enzyme or chemicals for further processes.

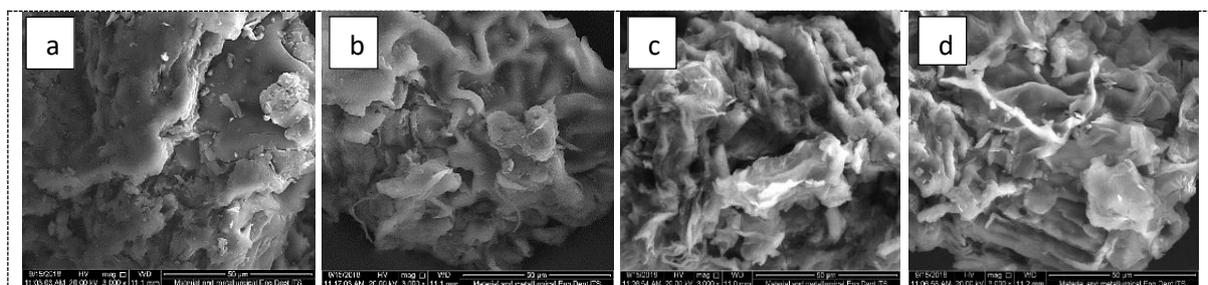


Figure 2. Surface Morphology of CPW, a) without treatment, b) treatment NaOH+H₂O₂ 2.5%, c) treatment NaOH+H₂O₂ 5%, and d) treatment NaOH+H₂O₂ 7.5%.

3.2.3. FTIR Analysis of CPW Treated by AHP

The FT-IR spectra of functional groups in solid CPW before and after treatment using various concentration of H₂O₂ for 6 and 24 h of pretreatment time are shown in Figure 3. The peak at 1025-1027 cm⁻¹ related to methoxy groups. The signal at 1158-1163 and 890-898 cm⁻¹ are the representation of C-O-C stretching at the β-(1-4) glycosidic bounds [18]. The absorption at 1235-1246 cm⁻¹ and 1410-1422 cm⁻¹ indicated the C=C and C=O stretching vibrations and C-H in-plane deformation, respectively. The peaks at 1315 cm⁻¹ are due to symmetric CH₂. The signals at 1515 cm⁻¹ have resulted from the aromatic skeletal vibration from lignin. An aromatic ring vibration is observed at 1615-1624 cm⁻¹. The peak at 1726-1729 cm⁻¹ is relevant to ester group of hemicellulose and lignin. The peaks at 2850 and 2919 cm⁻¹ are from C-H stretching vibrations in lignin. The peaks at 3289-3321 cm⁻¹ are due to the stretching of OH groups, as the representation of phenolic hydroxyl groups [6]. These results show that the AHP

treatment under-investigated conditions could not eliminate most functional groups in the lignin of CPW.

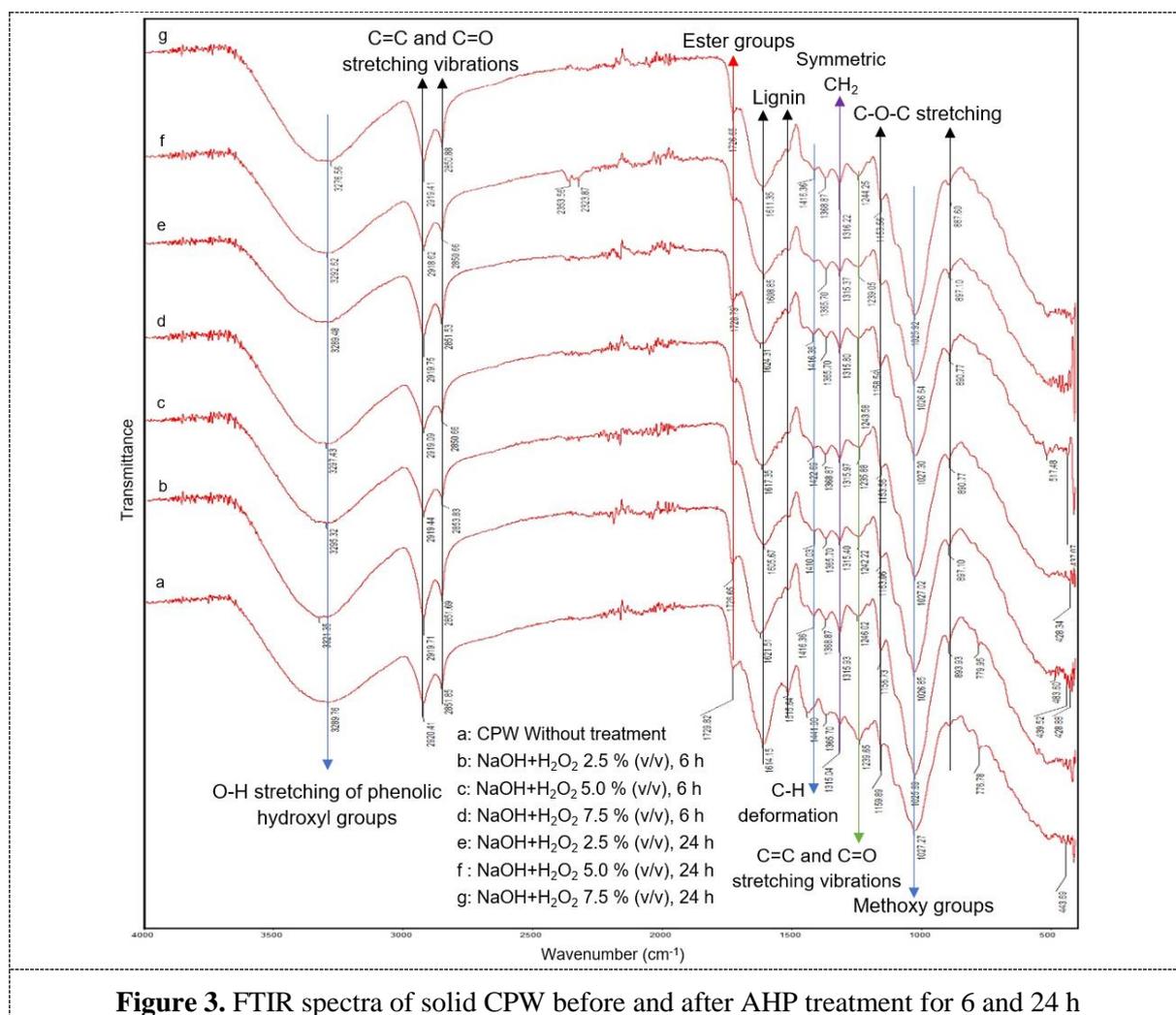


Figure 3. FTIR spectra of solid CPW before and after AHP treatment for 6 and 24 h

4. Conclusion

The effect of AHP treatment on reducing lignin content of coffee pulp waste (CPW) was conducted using the different concentrations of H₂O₂ (2.5, 5, and 7.5% (w/w of substrate)) which was mixed into 10% (w/w) of CPW solution at 35 °C for 24 h. The pH of the solution was 11.5, adjusted by NaOH. After AHP treatment for 24 h, the highest lignin removal is achieved at 7.5% H₂O₂ which decreased from 16.83% to 8.5%. In contrast with lignin removal, the concentration of cellulose and hemicellulose in CPW increased during the treatment. The highest increment of cellulose and hemicellulose content were obtained from treated CPW using 7.5% H₂O₂ for 24 h which increased from 53% to 64% and 11% to 24%, respectively. There was a significant increase in the crystallinity index of treated CPW. FTIR analysis has shown that AHP treatment could not completely eliminate most functional groups in the lignin of CPW. The captured surface morphology by SEM revealed that the destruction on the CPW's surface was getting worse along with more H₂O₂ concentrations addition into the system. This would be useful to increase the porosity of biomass to give cellulose accessibility by enzyme or chemicals for further processes. For further application, hopefully, this study can provide an overview of the process improvement in CPW pretreatment using AHP, especially in reducing the inhibitory content in CPW.

Acknowledgments

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