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ORIGINAL RESEARCH

Isolation and characterization of cellulose from rice husk waste and sawdust with chemical method

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Abstract.Cellulose is the biomass that is most easily found in plants, bacteria, and marine organisms. However, it is not found in pure conditions in nature because always bound to other materials such as lignin, hemicellulose, silica, wax, and ash.Cellulose had been isolated from rice husk waste and sawdust with chemical method through hydrolysis with HCl 2.5 N and bleaching process with $H_2O_2$3%.The yields were 13,45% and 22,75% (w/w)of cellulose from rice husk waste and sawdust, respectively. The chemical treatment caused partial removal of lignin and hemicellulose from raw material showed by FTIR spectrum. Structure and morphology of cellulose from rice husk waste and sawdust were investigated using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD patterns showed cellulose structure converted from amorphous to crystalline form after bleaching process while SEM images showed that the isolated cellulose from rice husk waste had rougher surface than cellulose from sawdust. The SEM micrograph also showed that the isolated cellulose from rice husk was in the form of aggregates.

Keywords: Chemical method, rice husk waste, sawdust, cellulose.

INTRODUCTION

Agricultural wastes such as rice husk and sawdust are not currently fully utilized as source of cellulose especially in Aceh. Rice husks are only used as additives for composting while sawdust is used as a wood substitute fuel. Cellulose is main component in rice husk and sawdust, it's about 25-35% in the rice husk [1,2] while sawdust contain about 33% of cellulose [3] Cellulose is one of the important additives to manufacture of bioplastics [4,5,6,7,8 and 9], food packaging materials [10], pharmaceutical, food, cosmetic and other industries [11]. Cellulose is a natural polymer having a linear structure, crystalline form and not easily to dissolve.

Cellulose has never been found in a pure state in nature, but always associated with other polysaccharides such as lignin, pectin, hemicelluloses, wax, ash and xylan [11]. In order to produce pure cellulose from raw material, several methods such as mechanical method (ultrasonic and high pressure), chemical method (strong acid hydrolysis, organosolv, alkaline solvent, oxidation and ionic liquids) and by biological method (using enzyme) can be applied [12].

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Purification of cellulose by hydrolysis using strong acid such as sulfuric acid, hydrochloric acid and perchloric acid is the most commonly used method [14]. The strong acids easily hydrolyze the amorphous part of the fiber, so it becomes shorter. The strong acids also hydrolyze hemicellulose into xylose and other sugars [15]. In addition, to produce pure cellulose, a *bleaching* stage is required. Oxidizing chemical compounds such as hypochlorite [6] and hydrogen peroxide [15] often used in bleaching process. The bleaching step has a purpose to increase the degradation of lignin and other impurities that have not been lost during the chemical process.

In this research, cellulose isolation was conducted with chemical method using strong acid (HCl 2.5 N) for hydrolysis process and followed by delignification process (*bleaching*) using H_2O_2 3%. Characterization of the isolated cellulose were carried out by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM).

METHODOLOGY

Materials

Rice husk waste and sawdust were collected from Aceh Besar. Hydrochloric acid 2,5N, sodium hydroxide 5% and hydrogen peroxide 3% and other chemicals were analytical grade which were purchased from Sigma –Aldrich Canada Ltd.

Isolation of Cellulose

Cellulose was isolated from sawdust and rice husk waste. Each sample (25 g) were hydrolyzed with 200 ml of HCl 2.5 N at 90ºC for 15 min. The mixture was then filtered at room temperature and washed repeatedly using distilled water until neutral pH was reached. The obtained cellulose was then dried in an oven at 60ºC until a constant weight was obtained. The cellulose powder obtained from rice husks and sawdust were crushed into powder using a ball mill at 300 rpm for 10 hours gradually for every hour. Then the cellulose was bleached by adding H_2O_2 3% solution and heated at 90ºC for 1 hour with stirred. The mixture was filtered and rinsed with distilled water until netral pH was reached. The cellulose was dried at 105ºC until a constant weight reached [3,15].

Characterization of cellulose

Isolated cellulose from rice husk waste and sawdust were characterized by optical microscope,SEM(FEI,Type: Inspect-S50) in SEM Laboratory FMIPA ITB, FT-IR spectrometer (Thermo Fisher Scientific Inc., Whatman, MA) in Instrument Laboratory FMIPA Unsyiah and XRD (step scanning at a target voltage of 40 kV and current of 40μA) in Material Laboratory FMIPA Unsyiah.

RESULTS AND DISCUSSION

Isolation of cellulose from rice husk waste and sawdust.

Isolation of celluloses from husk rice waste and sawdust using chemical method (hydrolysis and bleaching) yielded 13,45 and 22,75% (w/w) of cellulose, respectively. The mechanism of hydrolysis with acid was shown in Figure 1. Hydrolysis with acid could remove amorphous parts of cellulose chain. Hydrolysis with acid caused partial separation of cellulose microfibril, where amorphous parts of cellulose were breaked and leaving crystal form of cellulose [16]. Futhermore, the bleaching process with $H_2O_2$3% aimed to increase the degradation of lignin to obtainedpure cellulose.

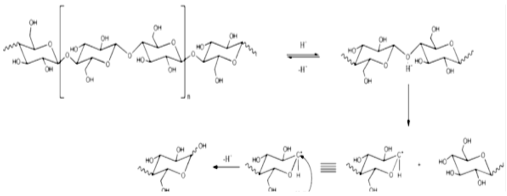


Figure 1. Mechanism of cellulose hydrolysis with acid [12].

In this study, from a total weight of 25 g of samples,the isolation process with chemical method, obtained 3.35g and 5.69 g of isolated cellulose from rice husk and sawdust, or 13.45% and 22.76% (w/w), respectively. This result was lower than other research that yielded about 35% of cellulose from rice husk [1,2] and about 33% of cellulose from sawdust [3]. When compared with the multistage pulping method which has been used to isolate cellulose from sawdust dan rice husk, the results of this chemical method are lower, but simpler and easier to applied.

Characterization of isolated cellulose

X-Ray Diffraction (XRD) analysis was performed to identify the crystallinity of the samples. The typical peaks for cellulose is shown at 2ϴ = 15º - 23º [17,18]. In the study, the structure of cellulose from rice husk and sawdust was measured before and after bleaching (Figure 2). XRD pattern of sawdustt before bleaching process (Figure 2a) showed two broad peaks at 2θ = 15º and 21º. After bleaching, XRD pattern of sawdust exhibited sharper peaks (Figure 2b) than XRD pattern of sawdustt before bleaching process and the similar result was also observed for rice husk waste (Figure 2c).

Cellulose isolated from sawdustt showed sharp peaks at 2θ =16º and 23º and cellulose isolated from rice husk waste exhibited relatively sharp peaks at 2θ = 16º, 21º and 23º. These results

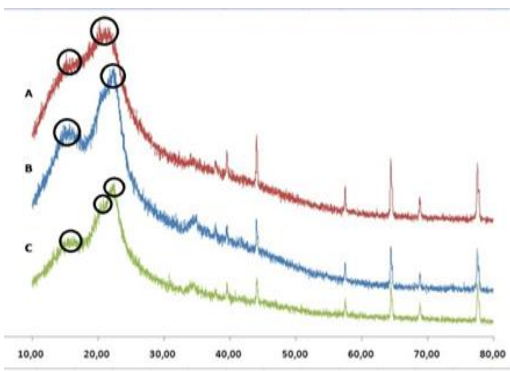


Figure 2. XRD paterns of sawdust before bleaching (a), sawdust (b) and rice husk waste (c) after bleaching.

indicated the change ofcellulose structure from amorphous to crystalline form. It was due to the bleaching process removed amorphous parts of cellulose and amorphous chemical components such as lignin, hemicelluloses and pectin [19].

FTIR spectroscopy was performed to determine the presence of functional groups of the materials. FTIR spectra of cellulose isolated from rice husk waste and sawdust were shown in Figure 3. Figure 3a showed FTIR spectrum of cellulose isolated from rice husk waste. Hydroxyl group of cellulose peak was appear at wavenumber of 3322 cm^{-1}, while $-CH_2$ and C-O vibrations at 2901 and 1029 cm^{-1}. Several absorption bands at wavenumbers 1300-1400 cm^{-1} indicated the presence of -O- which linked with carbon chain in the cellulose [20]. These results showed typical sFTIR spectrum of cellulose. The FTIR spectrum of cellulose isolated from sawdust (Figure 3b) also showed typical cellulose absorption bands, where the absorption bands at wavenumbers 3316, 2930 and 1015 cm^{-1} indicated the presence of OH, CH_2 and C-O functional groups of cellulose in the sample.

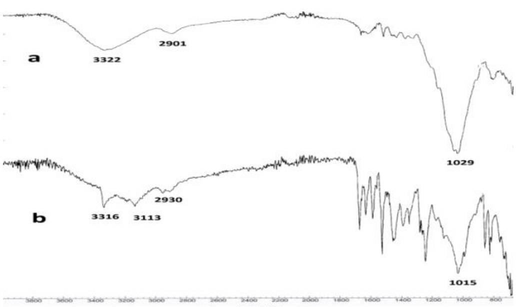


Figure 3. FTIR spectra of cellulose isolated from (a) rice husk waste (a) and (b) sawdust.

The results of isolation of cellulose from rice husk waste and sawdust with chemical treatment were expected to produce pure cellulose. However, FTIR analysis showed the existence of lignin, hemicelluloses and silica that bind with cellulose. The absorption bands were observed at wave number 1100, 1509-1609 and 1700-1740 cm^1. It was probably due to the low concentration of acids used in the hydrolysis process because at low acid concentrations separation between cellulose and hemicelluloses was ineffective [20].

The size of cellulose particle obtained from rice husk waste and sawdust after hydrolysis and bleaching process was determined based on optical microscopy analysis of at magnification 400x. Raw Cellulose usually in the form of fiber (macrophiblri).Hydrolysis and bleaching proses will breakdown of the fibril structur to microfibril. Determination of cellulose particle size after the hydrolysis and bleaching process was carried out with an optical microscope (Figure 4).The average particle size of cellulose isolated from rice husk waste and sawdust were 18,66 µm and 19,65 µm, respectively. The size is obtained from the calculation of the average diameter of the cellulose morphologycal image with the following equation:

$$\text{Average particle size} = \frac{\text{total size per particle}}{\text{average number of particles}}$$

Morphology of the isolated cellulose were performer by SEM photograph at magnification 20.000x and 40.000x as show at Figure 5. Compared with cellulose that isolated from rice husk waste (Figure 5.a), the isolated cellulose from sawdust (Figure 5.b) showed smoother surface. The rought surface maybe caused by some impurities that attached on the surface of the rice husk wastes cellulose. It was due to the high content of silica in rice husk waste. In the other hand silica is difficult to separate from cellulose in rice husk, silica from rice husk can be removed by a combination of alkaline (KOH) treatment followed by precipitation with acid (HCl) [2].

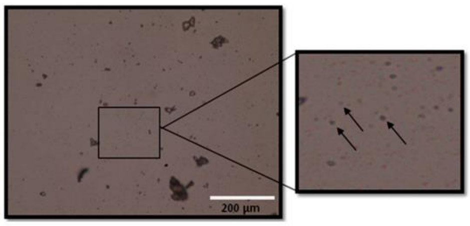
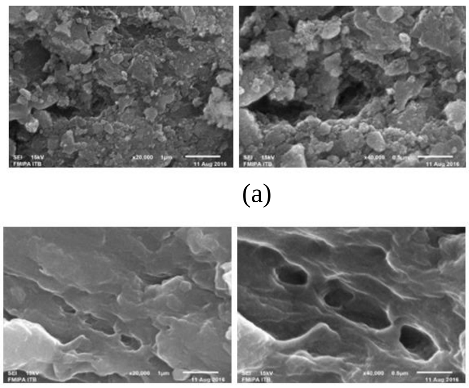


Figure 4. Optical images particel cellulose isolate at magnification 400x.



(a)

(b)

Figure 5. SEM images of cellulose isolated fromrice husk waste (a) and sawdust (b) at magnification 20.000x and 40.000x.

CONCLUSION

Rice husk waste and sawdust can be alternative sources of cellulose. The yield of cellulose from rice husk waste and sawdust were 13.45 and

22.76% (w/w). FTIR spectra confirmed the presence of cellulose in the samples. Chemical treatments (hydrolysis and *bleaching*) process onto rice husk waste and sawdust changed its celluloses structure from amorphous to crystalline form which was identified by the XRD pattern. The result showed that the isolated celluloses were still not pure.

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