



## Sodium Hydroxide Treatment for Cellulose Fiber Accessibility from Corncobs under Microwave Assistive

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### Abstract

Corncob is abundantly available lignocellulosic biomass resources obtained from crops harvesting and found to be solid waste accumulation on a field. Less corncob is used as a solid fuel for cooking, and a more significant portion is vanished on the field by burning. Promisingly, corncob contains considerable cellulose as one value-added component potentially utilized as biomaterial or biofuel feedstock. However, the presence of lignin in natural lignocellulosic biomass results in recalcitrant structure and hinders cellulose accessibility. This study aimed to investigate microwave-assisted alkaline treatment to retain cellulose in the solid product while removing other impurities in corncob, especially hemicellulose and lignin. Sodium hydroxide was selected as a chemical with some variations in concentration. The chemical treatment was carried out under 400 W microwave power with various residence times and a 1:10 solid to liquor ratio. The cellulose content upgraded from 26.97% to 71.26% while reducing hemicellulose and lignin from 38.49% to 18.15% and 19.28% to 6.4%, respectively, on chemical treatment using 8% sodium hydroxide concentration for 20 minutes residence time. Scanning electron microscope (SEM) and Fourier transform infrared (FTIR) analysis also confirmed the results. The treated corncob also increased its crystallinity from 30.11% to 52.91%.

Keywords: Alkaline treatment, corncobs, lignocellulosic biomass, microwave-assisted

### 1. Introduction

Lignocellulosic biomass is one potential renewable resource with abundant availability as material feedstocks for chemicals, biodegradable polymers, or fuels. Including the lignocellulosic biomass is agricultural byproducts, one renewable resource that has gained interest since they have not been optimally utilized and spread out in almost all regions in Indonesia. Corncobs, one of the agricultural byproducts, will be interesting to investigate by considering the fact that Indonesia is one of the largest corn producers in the world, providing around 30.69 million tons of annual crops production (FAO, 2020). Approximately 15% of the total corn production to estimate is corncobs (Ashour, et al., 2013), then there will be projected about 4.60 million tons of corncobs potentially available per year in Indonesia. Typically to be used as daily intake in the livestock industry, it has left beds of corncob as solid waste in planting areas. Only a small portion is used as conventional solid fuel, sometimes diminished by burning. The burning of solid biomass may contribute to

the emission of pollutant gases that worsen atmosphere quality. Applying corncobs as a renewable resource might reduce carbon emissions, solve the waste accumulation problem on planting areas, and maintain feedstocks sustainability besides providing more economical feedstocks.

Cellulose is one of the major lignocellulosic components that has played a role in manufacturing industries (Brodin, et al., 2017). Cellulose is a homopolymer of 5000 to 10,000 glucose units that can be seen as a repetition of D-anhydroglucopyranose units through (1,4) glycosidic bonds (Klemm, et al., 2005; Croker and Andrews, 2010). Cellulose constructs rigid microfibrils network due to intra- and intermolecular hydrogen bonds in its molecule structure and combines to constitute fibrils and subsequently form cellulose fibers. Hemicellulose binds cellulose microfibrils by hydrogen bonds and lignin by covalent interaction through ester, ether, and glycosidic linkages. Lignin molecules cover hemicellulose and cellulose and associate with covalent bonds through ester, ether, and glycosidic linkages, and their presence

hinders cellulose accessibility (Mussatto and Dragone, 2016).

Many efforts have been investigated to access cellulose fibers from the recalcitrant structure of biomass through mechanical, physical, chemical, biological treatment, or even by a combination of any others (Chen, et al., 2017; Mankar, et al., 2021). Alkaline treatment is a preferable chemical treatment to obtain cellulose fibers since it enables to retain of more than 95% of cellulose in pretreated solid lignocellulosic biomass (Chen, et al., 2013). Sodium, potassium, calcium, and ammonium hydroxide are environmentally benign and readily available chemicals to be used, can be applied at low concentrations, low temperature and atmospheric pressure, and relatively lower cost than any other chemicals (Menon and Rao, 2012). However, alkaline treatment may take longer to ensure the process completes (Xu and Sun, 2016). Microwave-assisted chemical reactions enhance reaction rates, reduce the reaction time, increase selectivity, and selective heating for polar materials (Loupy, 2006; Li, et al., 2016) due to its thermal and nonthermal effects (de la Hoz, et al., 2005). Microwave processing uses less energy consumption and integrates easily with other biomass treatment technologies (Chen, et al., 2012). Microwave directly interacts through electromagnetic radiation with both lignocellulosic biomass raw material and liquor involved in chemical treatment (Lu, et al., 2013).

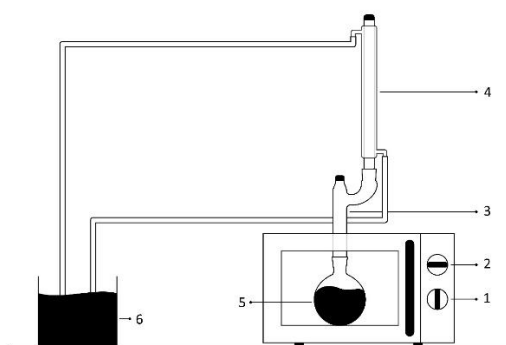
Some works have been publicized in performing microwave-assisted alkaline treatment for agricultural byproducts, particularly corncobs. Li, et al. (2014) isolated cellulose fibers from corncobs using two-steps alkaline and hydrogen peroxide under microwave-assisted. In the study, the solid powder biomass was pretreated with 8% NaOH solution with 1:15 solid to liquor ratio for 3 minutes under 500 W microwave power followed by bleaching with 5% hydrogen peroxide solution for 3 minutes under 500 W microwave power. This experiment resulted in cellulose fiber comprised of 86.18% cellulose, 10.68% hemicellulose, and 2.21% lignin, and 73% relative crystallinity. Winarsih and Siskawardani (2020) applied sodium hydroxide pretreatment with microwave-assisted corncobs for bioethanol production. Using 1:10 solid to liquor ration for 20 min treatment using 0.1 N sodium hydroxide under microwave assistive, cellulose content in the corncobs raised about 40% while hemicellulose and lignin content reduced around 17% and 20%, respectively.

This study conducted microwave-assisted alkaline treatment using sodium hydroxide to enhance cellulose content while removing impurities, especially hemicellulose and lignin, as other main components. Sodium hydroxide concentrations and reaction time were varied. While previous studies did not explain explicitly (Li, et al., 2014; Winarsih and Siskawardani, 2020), these sodium hydroxide treatments were designed to perform around atmospheric conditions. Sodium hydroxide was selected as liquor due to its advantage of being inexpensive and safely used, besides enables to the recovery of hemicellulose and lignin as value-added side products (Ma, et al., 2016; Xu and Sun, 2016).

## 2. Methodology

### 2.1. Materials and equipment

The corncob used a sample is species of BISI-99 and retrieved from Margodadi, Jatiagung, Lampung. The alkaline solution was made by dissolving NaOH crystalline (PA, Merck) into distilled water, and its concentration was varied into 4, 6, and 8% (w/v). Prior to alkaline pretreatment, the corncobs were previously washed using clean water, fragmented to give around 1 to 1.5 cm particle size, and dried at 105°C for 4 hours in a drying oven. The predried sample was then subjected to a dish-mill and passed through a 60 mesh sieve. The ground powder samples under 60 mesh were saved in zip-bag containers and located in a desiccator.



**Figure 1.** Schematic diagram of lignocellulosic biomass pretreatment apparatus (1. Time setter; 2. Power setter; 3. Glass connector; 4. Condenser; 5. Reactor; and 6. Chiller).

The alkaline pretreatment was carried out in an apparatus by combining several units, as shown in Figure 1. The microwave oven (AQUA AEM-S1112S) has 51.2 cm x 40 cm x 34.7 cm dimension, 17 L capacity, and 400 W maximum power output. It can run at 220 –

240 Volt/50 Hz and 2450 MHz frequency. The lignocellulosic sample was put in a 500 mL flat-bottom round boiling flask as a chemical reactor connected by a 50 cm Liebig condenser. This equipment enables the chemical treatment to perform in atmospheric pressure.

## 2.2. Alkaline Treatment

About 10 g corncob powder from under the previous mechanical treatment was mixed with 100 mL NaOH solution and handshake gently for several minutes to ensure the corncob powder was embedded into the solution. The concentrations of NaOH solution used in this treatment were varied to 4, 6, and 8% (w/w). The alkaline treatment was carried out under 400 W, and residence time varied, 10, 15, 20, and 25 minutes. When the sodium hydroxide treatment ended, the treated solid was recovered from the darker suspension through filtration that was previously rinsed several times using distilled water until the pH of the solution was neutralized. The treated solid was then dried in a drying oven at 80°C until the constant weight of the solid was achieved. The dried solid was removed from the drying oven, put in a zip-bag container, and located in a desiccator before being analyzed.

## 2.3. Analysis of lignocellulosic biomass components

The main lignocellulose components, hemicellulose, cellulose, and lignin, from treated corncob were determined according to analysis procedures developed by Datta (Datta, 1981). About 1 g solid sample, defined as  $W_0$  was refluxed for 2 hours by 150 mL distilled water at 100°C. The solid was separated from its filtrate and dried at 60°C for 16 to 18 hours. This dried solid was measured its weight and defined as  $a$ . Sequentially, it was mixed with 0.5 M  $H_2SO_4$  and refluxed for 2 hours at 100°C. Afterward, the dried solid recovered from the suspension after filtration was dried, weighted its mass, and defined as  $b$ . The solid was then mixed with 10 mL of 72% (v/v)  $H_2SO_4$  solution and acclimated for 4 hours. Following this step, water was added to the mixture to give 0.5 M  $H_2SO_4$  solution. The suspension was then refluxed under 100°C for 2 hours, washed and recovered its solid through filtration, and dried. The dried solid was weighed its mass and defined as  $c$ . Finally, this solid was subjected to a furnace, burned at 600°C for 2 hours. The ash that resulted from the combustion was measured its mass and defined as  $d$ . The three main lignocellulosic

components can be calculated as mass ratio from the completed procedures by Equations 1 to 3:

$$\text{Hemicellulose} = \frac{a - b}{W_0} \times 100 \quad (1)$$

$$\text{Cellulose} = \frac{b - c}{W_0} \times 100 \quad (2)$$

$$\text{Lignin} = \frac{c - d}{W_0} \times 100 \quad (3)$$

## 2.4. Fourier transform infrared (FTIR)

FTIR analysis of corncob and alkaline treated corncob was carried out to observe any changes in the structure resulting from the chemical treatment corresponding to the transmittance changes of specific functional groups in cellulose, hemicellulose, and lignin. FTIR analysis was performed using Agilent Cary 630 FTIR Spectrometer recording spectra between 4000-650  $cm^{-1}$ , with a resolution of 16  $cm^{-1}$ , and 32 total scans for each sample.

## 2.5. Scanning electron microscopy

The morphology and microstructure from corncob and alkaline treated corncob was performed using a scanning electron microscope (SEM) Inspect-S50 FEI. The sample was coated by Au-Pd, and the image was taken with 20 kV accelerating voltage.

## 2.6. X-ray diffraction (XRD) analysis

Both corncob and treated corncob samples were determined its crystallinity by XRD diffractometer (PANalytical X'Pert Pro), X'Pert MPD diffractometer type. The diffractometer was performed by Cu radiation and  $K\alpha_1$ .5406 Å, operated at 30 mA and 40 kV to record ( $2\theta$ ) ranging from 5 to 60°. The crystallinity index (CI) of samples were determined using Peak Deconvolution Method (Park, et al., 2010) and calculated by the formula

$$CI = \frac{A_c}{A_c + A_a} \times 100 \quad (4)$$

Where  $A_c$  is integrated of crystalline area and  $A_a$  is integrated of amorphous area.

## 3. Results and Discussion

### 3.1. Chemical compositions of treated corncobs

Corncob samples were prepared by pre-drying and size reduction to give particles under 60 mesh with 7.66% moisture content.

The samples were also determined its major lignocellulosic components, and the results and others from previous works (Li, et al., 2014; Ma, et al., 2016; Winarsih and Siskawardani, 2020) are shown in Table 1. It can be seen that the chemical composition results varied to a certain degree, as is confirmed by literature (Bajpai, 2016).

Figure 2 shows the trends of lignocellulosic components in treated corncobs corresponding to various residence times and sodium hydroxide concentration. It can be seen that the relative percentage of hemicellulose and lignin declined as the residence time increased from 10 to 25 minutes. In addition, the increase of sodium hydroxide concentration used in the chemical treatments, from 4 to 8%, enhanced hemicellulose, and lignin removal. As a result, the relative percentage of cellulose in the treated corncobs increased with the residence time and sodium hydroxide concentration. As shown in Figure 2a, the increased sodium hydroxide concentration from 6 to 8% significantly reduced hemicellulose contents instead of 4% sodium hydroxide. However, the hemicellulose removal using 8% sodium hydroxide was not significant and slightly higher than the treatment using 6% sodium hydroxide solution.

Figure 2b shows the change of cellulose contents in treated corncobs after 10 to 25 minutes of treatment using 4 to 8% sodium hydroxide solution. It can be observed that both the rise of time and concentration of sodium hydroxide enhanced cellulose contents in treated corncobs. However, using 8% sodium hydroxide, the percent of cellulose in treated corncob rose for treatment 10 to 25 minutes, reached the highest cellulose percentage (71.26%), and then fell to 62.60% for 30 minutes treatment. The decrease of cellulose percent for this 30 minutes treatment might result from the dissolution of cellulose into sodium hydroxide solution as described in the literature (Xu and Sun, 2016). Due to the thermal effect of

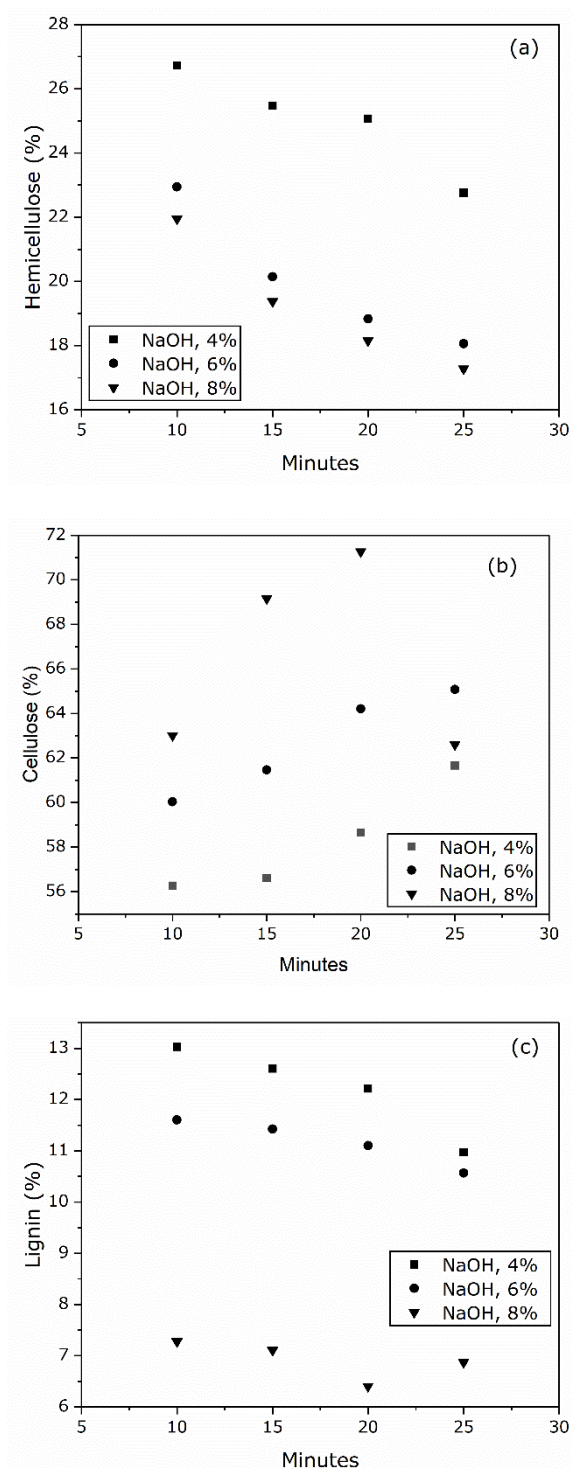
microwave irradiation, the process enables it to run at elevated temperatures.

The effect of microwave-assisted alkaline treatment for lignin reduction in treated corncob for various times and sodium hydroxide concentration is shown in Figure 2c. It can be seen that in every case, the percentage of lignin after treatment decreased with the increase of residence time and liquor concentration. Moreover, using 8% sodium hydroxide, lignin was more significantly removed. However, the lignin removal for this liquor concentration did not differ significantly for the rise of residence time. The lignin percentage for 30 minutes treatment using 8% sodium hydroxide solution was shown higher than for 25 minutes treatment that might be caused by hydrolysis of the amount of cellulose.

The alkaline treatment removes amorphous components in lignocellulosic biomass and is effective for agricultural byproducts treatment owing to its lower lignin content (Xu and Sun, 2016; Chen, et al., 2017). Sodium hydroxide effectively ruptures the ether and ester bonds in the lignin carbohydrate complex structures while breaking the ester and carbon to carbon molecules in lignin molecules (Kim, et al., 2016). The OH<sup>-</sup> ions from sodium hydroxide swollen the microfibrers, cleavage hydrogen linkage between cellulose and hemicellulose, and hydrolysis of ester bonds connected to other polymers constituents (Ma, et al., 2016). As shown in Table 2, microwave-assisted sodium hydroxide treatment for 25 minutes using 8% concentration solution gave the highest percentage of cellulose, namely 71.26%, while reducing hemicellulose and lignin composition to 18.5% and 6.40%, respectively. Using 1.5 N NaOH solution for 30 minutes with a 1:10 solid to liquor ratio, Winarsih et al.; obtained treated corncob with composition 67.68% cellulose, 14.28% hemicellulose, and 8.51% lignin (Winarsih and Siskawardani, 2020).

**Table 1.** Composition of lignocellulosic components in corncob sample and its comparison with previous works.

Components	This works	Li et al.	Ma et al.	Winarsih and Siskawardani
Hemicellulose, %	44.12	42.25	34.3	31.58
Cellulose, %	27.03	40.16	35.3	28.77
Lignin, %	21.54	10.78	15.8	28.97



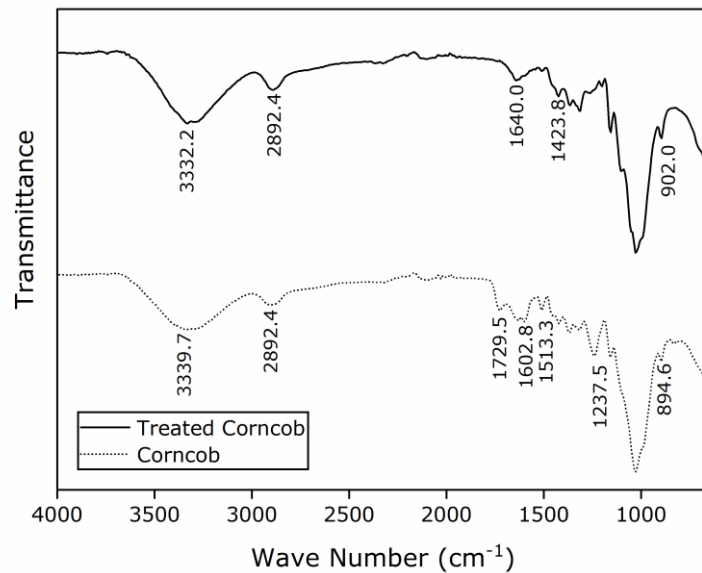
**Figure 2.** The percentage of hemicellulose, cellulose, and lignin in corncob after treatment by various residence time and sodium hydroxide concentration under microwave assistive.

### 3.2. FTIR analysis

The change of corncob chemical compositions was qualitatively measured using FTIR, and the results are shown in Figure 3. The prominent peak at  $3339.7\text{ cm}^{-1}$  from the corncob powder spectrum and  $3332.2\text{ cm}^{-1}$  from the treated corncob spectrum is due to the stretching vibration of O-H (Sun, et al., 2000). The FTIR spectra of both the treated and untreated corncob samples show broad absorption bands between  $3700\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$ , indicating the presence of hydrogen-bonded hydroxyl groups in their structure. The intense peak at  $2892.4\text{ cm}^{-1}$  represents the stretching vibration of saturated C-H in cellulose and hemicellulose (Sun, et al., 2005). The prominent band at  $1640\text{ cm}^{-1}$  is particularly associated with the bending vibration of the absorbed water molecules.

A sharp peak at  $1729.5\text{ cm}^{-1}$  in the corncob powder (untreated) is related to the carbonyl groups stretching, representing the acetyl and uronic ester groups, or the ester linkage of the carboxylic group of acetic, ferulic, and p-coumaric acids, which are the dominant constituents of hemicellulose and lignin (Sun, et al., 2005). The intensity of this peak ( $1729.5\text{ cm}^{-1}$ ) has almost vanished in the treated corncob samples, indicating the breakage ester bond and carboxylic group in hemicellulose and lignin.

Characteristic peaks at  $1602.8\text{ cm}^{-1}$  and  $1513.3\text{ cm}^{-1}$  in the corncob powder can be assigned to this C=C stretching in the aromatic structure (aromatic ring) of lignin structure. These peaks almost disappear in the treated corncob sample owing to partial removal of lignin (Xiao, et al., 2001). The intensity of the peak at  $1237.5\text{ cm}^{-1}$ , representing the absorption of ester, has significantly decreased after microwave-assisted sodium hydroxide treatment. This observation indicates that the hemicellulose has been almost removed during treatment. The peak at  $902.0\text{ cm}^{-1}$  in corncob and  $887.1\text{ cm}^{-1}$  corresponds to the  $\beta$ -linkage in cellulose. The intensity of this peak has increased in the treated corncob sample indicates the increase in the characteristic cellulose structure (Sun, et al., 2000). These results also indicate that the hemicellulose and lignin removal increased cellulose percentage in the treated corncob sample.

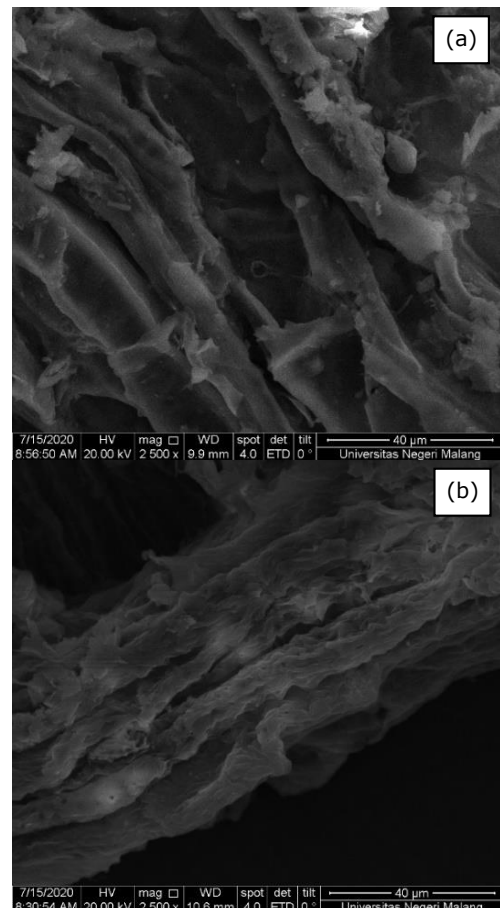


**Figure 3.** FTIR spectrums from corncob and treated corncob using 8% sodium hydroxide solution for 25 minutes.

### 3.3. Morphological analysis

Scanning electron microscopy figures out the change of the morphological surface of samples before and after treatment and the results are shown in Figure 4. Figure 4a shows the surface morphology of corncob powder before treatment, while Figure 4b shows the surface morphology of treated corncob using 8% NaOH solution for 20 minutes treatment under microwave assistive. It can be observed; there is a change in the structure of the corncob before treatment and after treatment (b). Before treatment, the surface morphology of corncob powder still contains noncellulosic components as impurities (Mussatto and Dragone, 2016).

These impurities coverage cellulose fiber and hinder cellulose fiber accessibility. In contrast, Figure 4b illustrates the surface morphology of corncob powder after treatment. Most impurities were successfully removed during this treatment, and cellulose fiber is more clearly shown. The cellulose fiber acquired from this treatment has around 20  $\mu\text{m}$  in diameter or lower, almost similar to previous work (Li, et al., 2014). Nevertheless, the cellulose fiber acquired in this study is still connected, which might be due to the presence of particularly hemicellulose remaining after treatment (see Table 2). It can be seen from Figure 4b that cellulose fiber is agglomerates of microfibrils which has 3 nm in diameter (Li, et al., 2014) that links together.



**Figure 4.** SEM images from corncob (a) and treated corncob using 8% NaOH solution for 20 minutes under microwave assistive.

Sodium hydroxide proceeded saponification reaction of ester bonds found between the inner molecules, enabling to breakage of this connection, consequently creating the pore structures of lignocellulose owing to the diminishing of the connecting bonds (Chen, et al., 2017).

### 3.4. Crystallinity Index

Untreated corncob contains cellulose, hemicellulose, and lignin as its three main constituents. Cellulose fibers mainly comprise crystalline structures surrounded by amorphous hemicellulose and lignin (Li, et al., 2014). The hemicellulose and lignin removal during sodium hydroxide treatment caused a reducing amount of amorphous components and increased the crystallinity of treated lignocellulosic biomass as the rise of cellulose percentage.

Figure 5 shows XRD spectra of both corncob and corncob after 20 minutes of treatment using 8% sodium hydroxide solution. It can be seen that the highest crystalline peak I002 for both samples was found around  $2\theta = 22^\circ$ , while it clearly shows that XRD spectra for treated corncob look sharper, indicating the rise of crystallinity in treated corncob. Quantitative measurement of crystallinity of these samples according to the reference method (Park, et al., 2010) was carried out by curve fitting using the Gaussian function. Individual crystalline peaks were extracted from the spectra, and the crystallinity index (CI) was calculated by dividing the total area of all crystalline peaks by the total area. CI

calculation results according to Equation 4 showed a rise of CI due to microwave-assisted sodium hydroxide treatment of corncob, from 30.11% to 52.97%. The results indicate that the treated corncob still retains amorphous components after 20 minutes of treatment using 8% sodium hydroxide concentration.

The percentage of amorphous components might result from the presence of hemicellulose and lignin in treated corncob, as shown in Table 2. Alkaline treatment reduces the degree of polymerization and crystallinity due to chemical bonds breakage between lignin and carbohydrates and destroying lignin structure (Agu, et al., 2017). Particularly, sodium hydroxide treatment of lignocellulosic biomass is possibly for a complete transformation of cellulose I into cellulose II, which has a shorter chain and lower CI (Xu and Sun, 2016). On the other hand, microwave irradiation assists in depolymerizing cellulose by fragmenting crystalline molecules of cellulose due to thermal effects and the ability of cellulose molecules to absorb microwave irradiation (Hoang, et al., 2021). Using 800 W microwave irradiation for 20 minutes, microcrystalline cellulose pretreatment with water resulted in a CI decrease from 76.04 to 73.34% (Peng, et al., 2014). Therefore, microwave-assisted sodium hydroxide treatment enhances hemicellulose and lignin consumption, resulting in increased treated corncob crystallinity while reducing the crystallinity of cellulose contained.

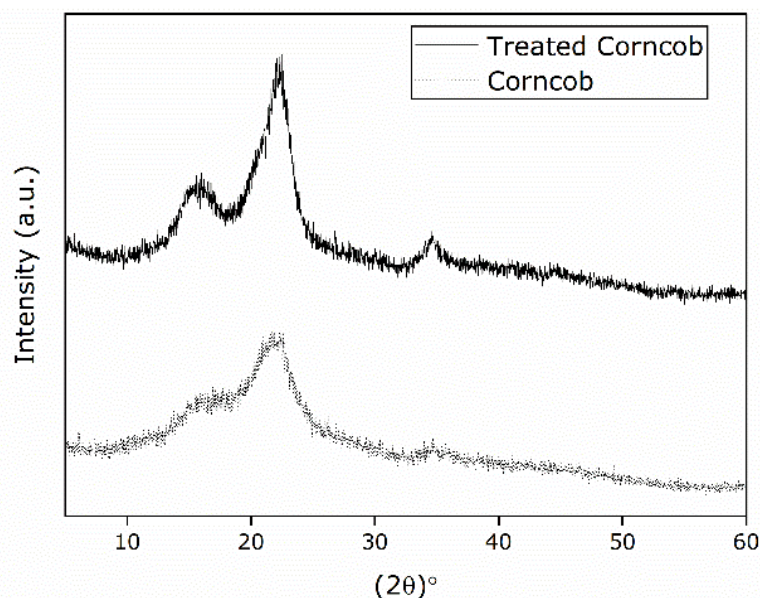


Figure 5. XRD spectra of corncob and treated corncob

**Table 2.** The change of compositions of lignocellulose from corncobs before and after treatment.

Materials	Celulose, %	Hemicellulose, %	Lignin, %	CI, %
Corn cob	26.97	38.50	19.30	30.11
Treated corn cob	71.26	18.15	6.40	52.91

#### 4. Conclusions

The sodium hydroxide treatment assisted by microwave for cellulose fiber extraction from corncobs were successfully removed a significant amount of impurities, mainly hemicellulose and lignin, under various residence times and liquor concentrations. The treated corncob with the highest cellulose percentage was acquired for 20 minutes using 8% sodium hydroxide with 1:10 solid to liquor ratio and 400 W microwave power. Cellulose content results from these operating conditions increase from 26.97 to 71.26%. Consequently, the relative percentage of hemicellulose and lignin decreased from 38.50 to 18.15% and 19.30 to 6.40%, respectively. The processing also increased the CI of treated corncob from 30.11 to 52.91%. Observation from scanning electron microscopy and FTIR has confirmed the success of the processing. However, the result needs further bleaching to enhance brightness while removing hemicellulose and lignin.

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