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Abstract. Cellulose is the greatest abundant and renewable biopolymer resources in world, it has been widely used in many industrial applications because of its favorable characteristics. Various cellulose resources, especially those obtained from local resources and agriculture waste, are being exploited to reduce the impact of environmental damage. This study presents an environmental friendly methods to produce cellulose from local plant, *Eleocharis dulcis*. *E. dulcis* is an aquatics plant belonging to the Cyperaceae family, mainly abundant in swampy area in South Kalimantan, Indonesia. In this study, α-cellulose were isolated from *E. dulcis* as a new renewable industrial resources. The sample was dewaxed using ethanol-toluene, then the free extractive sample was bleached using $NaClO_2$ to produce holocellulose. The influence of type of alkali (NaOH and KOH) and concentration (15%; 17.5% and 20%) on the properties of α-cellulose was investigated. The Total Crystallinity Index (CrI), Lateral Order Index (LOI), Hydrogen Bond Intensity (HBI) and whiteness of α-cellulose were analysis using FTIR and CIELab color system, respectively.

Keywords : cellulose, holocellulose, *Eleocharis dulcis*, FTIR, total crystallinity index

1. Introduction

Cellulose materials such as from various wood, grass, and agriculture waste [1-3] have developed as potential bioresources for bioenergy and bioproducts. Cellulose is a linear biopolymer consisting of (1,4-β-D) anhydroglucopyranose units, which is abundance, renewable, and eco-friendly materials [4, 5]. It has excellent properties, such as low density, hydrophilicity, and reinforcing ability, being an cooperative modification and used in many applications, such as in textiles, pulp and paper, food, pharmaceutical, and cosmetics products, composites, polymers and others [4].

Eleocharis dulcis, belonging to the family of Cyperaceae, is originally from South-East Asia and has distributed to Japan, China, Taiwan, Madagascar, West Africa, and the Pacific [1-3] Islands. It is an aquatic plant and considered a dominant weed in swampy areas, irrigations canals, black water rivers, and ex-coal mining lake. *E. dulcis* can grow rapidly in acidic (pH 3-6) water and low nutrients. Its commonly knows as “purun tikus” and have been used for variety traditional handicraft and

ruminant feed. *E. dulcis* is very inexpensive and abundant in South Kalimantan, Indonesia. According to previous research [2], purun tikus consists of about 40% cellulose, which can be isolated and used for various useful functional materials. However, research and literature on the utilization of *E. dulcis* are very limited to date.

Although cellulose production by delignification and isolation process has been carried out for a hundred years, research on the production of cellulose continues to increase and interest to explore. Many technologies for cellulose isolation or bleaching process have been studied, such as using alkaline, hydrogen peroxide, and hypochlorite. The choice of the isolation process is a key factor and related to the quantity and quality of cellulose and also to avoid the alterations of the cellulose structure. Alkaline hydrolysis with NaOH being the most common isolation process. The properties of cellulose are dependent on the type of alkali, alkali concentration, temperature, and the hydrolysis time [6].

In this study, we focused on new material cellulose exploration from wetland and improving cellulose characteristics using a low-cost and environmentally friendly process. The main aim of this research was to evaluate the effect of the cellulose isolation methods on the characteristic of *E. dulcis* cellulose using alkaline (NaOH and KOH) in various concentration.

2. Methods

2.1. Samples Preparation

Eleocharis dulcis was collected from Bati-bati, Tanah Laut district, South Kalimantan, Indonesia. The *E. dulcis* were cut, dried, and grounded using kitchen blender and then sieved through 60 mesh and stored in containers at ambient temperature before use.

2.2. Soxhlet Apparatus

Air-dried *E. dulcis* powdered stems were extracted with a mixture of 95% ethanol and toluene (1: 2, v/v) for 6 hours using a Soxhlet extractor. The objective of this step is to eliminate extractives and waxes in the sample. The sample was then kept at room temperature for 24 h to remove the residual solvents.

2.3. Holocellulose Isolation

The holocellulose (5 g) was isolated by the following procedures: free extracted of *E. dulcis* and distilled water (300 mL) were put in a 1000 mL Erlenmeyer flask. The CH_3COOH (0.4 mL) and $NaClO_2$ (2 g) were added to the flask, and the flask was heated at 70°C in a water bath. $NaClO_2$ and CH_3COOH were added to the flask at every hour during 4-hour reaction. The mixture was then filtered through a 1G3 glass filter, and the residue was washed with 1000 mL distilled water and with 100 mL acetone. The residue (holocellulose) was air-dried in a fume hood for one day and then dried in the oven at 105 ± 3°C overnight.

2.4. Isolation of α-cellulose

The amount of α-cellulose was determined using holocellulose from the previous sections. Holocellulose (0.5 g) and a 12.5 mL various alkaline aqueous solution (NaOH (m/v): 15%; 17.5%; and 20% and KOH: 15%; 17.5% and 20%) were added to a 30 mL beaker, the sample was left still for 4 minutes, and then homogenized by a glass stick for 5 minutes. After 21 minutes, 12.5 mL distilled water was added to the suspension and then left still for 5 minutes. The content in a beaker was filtered through a 1G1 glass filter within 5 minutes. Then, the residue was washed with 20 mL of 10% CH_3COOH and left still for 5 minutes. After that, the residue was washed with 500 mL distilled water and then dried in the oven at 105 ± 3°C overnight. The yield of α-cellulose was determined gravimetrically.

2.5. Degree of Whiteness Measurement

Degree of the whiteness of holocellulose and α-cellulose was measured using a colorimeter (CR-400, Konica Minolta, Japan). The CIELab color system value (L^*, a^*, b^*) was used to estimate the whiteness degree, where L^* is lightness, a^* is the redness and b^* is the yellowness. The L^* value

varies between 0-100 (black to white). The value of +*a** (positive) describe a red shift, the value of -a* (negative) describe a green shift, the values of +b* (positive) describe a yellow shift, and the values of -*b** (negative) describe the blue shift.

2.6. *Fourier Transform Infrared Spectroscopy Analysis*

Fourier transform infrared (FTIR) spectra of holocellulose and α-cellulose was presented on a Shimadzu FTIR-8201 PC spectrometer using KBr disks in the wavenumber range between 4000 and 400 cm^{-1}. The typical bands spectra of the holocellulose and α-cellulose samples were recognized with the support of the literature. The infrared spectra also were used for estimation of the Lateral Order Index (LOI, A_{1427}/A_{894}), Total Crystallinity Index (TCl, A_{1373}/A_{2900}) and Hydrogen Bond Intensity (HBI, A_{3400}/A_{1319}) [7-10].

3. Result and Discussion

3.1. Extraction of α-cellulose from holocellulose

The cellulose from various lignocellulose materials was commonly obtained by bleaching process and alkali treatment. Thus, in this study, alkali treatment using NaOH and KOH were used to produce pure α-cellulose from *E. dulcis* holocellulose. Figure 1 shows the photograph of *E. dulcis* holocellulose and α-cellulose using various alkali aqueous solutions. After the alkali hydrolysis process, the color of holocellulose was changed from yellowish brown to white. The color change of holocellulose and α-cellulose was due to the removal of non-cellulosic materials such as residual lignin and hemicellulose after alkali hydrolysis.

Figure 1. Photograph of holocellulose and α-cellulose from *E. dulcis*

The yield of the alkali hydrolysis process is the percentage of comparison between the weight of α-cellulose and holocellulose on an oven-dry basis. The results showed that no significant effect between the yield of α-cellulose and type of hydrolysis agent and concentration (Table 2). The highest yield of 50.5% was obtained from the use of NaOH 15% solution (m/v) as a hydrolysis agent. The yield of α-cellulose decreased with increasing concentration of NaOH. However, the increasing concentration of KOH did not effect the yield of α-cellulose.

The results showed that the interaction between the type of hydrolysis agent and concentration on the color or whiteness degree of the α-cellulose (Table 2). According to the data in Table 2, the whiteness of α-cellulose higher than holocellulose. The whiteness degree in the α-cellulose is influenced by the content of non-cellulosic materials such as lignin and hemicellulose. The smaller content of lignin in the α-cellulose, the higher whiteness degree [6]. Additionally, the use of KOH and NaOH showed that the whiteness degree of α-cellulose produced was significantly different. Hydrolysis process using KOH solution produces higher whiteness degree (higher L* value;

brightness) than NaOH solution. However, the interaction between concentration NaOH and KOH had no significant effect on the whiteness degree.

Table 1. Summary yield of α-cellulose from *E. dulcis* holocellulose. Percentage data based on weight of oven-dried holocellulose

Sample	Concentration (%, m/v)	Yield (%)
Cell NaOH	15	50.5
Cell NaOH	17.5	50.2
Cell NaOH	20	50.0
Cell KOH	15	50.0
Cell KOH	17.5	48.4
Cell KOH	20	50.2

Table 2. The CIELab system value of *E. dulcis* holocellulose and α-cellulose

Sample	L*	a*	b*
Holocellulose	79.6 ± 0.82	7.2 ± 0.02	19.0 ± 0.12
Cell NaOH 15	83.6 ± 0.26	3.6 ± 0.18	11.9 ± 0.33
Cell NaOH 17.5	82.5 ± 0.44	3.6 ± 0.08	12.2 ± 0.99
Cell NaOH 20	83.5 ± 0.83	3.6 ± 0.08	11.9 ± 0.15
Cell KOH 15	85.0 ± 0.17	3.6 ± 0.6	10.8 ± 0.05
Cell KOH 17.5	86.4 ± 0.04	3.8 ± 0.06	11.5 ± 0.20
Cell KOH 20	85.3 ± 0.37	3.8 ± 0.07	12.2 ± 0.39

3.2. FTIR Analysis

The Fourier transform infrared (FTIR) spectra can be used to evaluate chemical components of lignocellulose and confirm their chemical structure. Figure 2 showed the FTIR spectra of holocellulosa and α-cellulose from *E. dulcis* with various alkali solution as a hydrolysis agent to remove non-cellulosic materials. Holocellulose contains hemicellulose and cellulose that form an amorphous part around cellulose part. Hemicellulose is softer than cellulose. The fingerprints of the functional group obtained for holocellulose and α-cellulose is showed in Tabel 3.

In the spectra, the peak at 3400 cm^{-1} is characteristic of the O–H stretching frequency of the O-H group and assigned to the adsorbed water. The peak at 2924 cm^{-1} is associated to C–H stretching frequency in the methyl and methylene groups of cellulose. The peak at 1735 cm^{-1} is due to C=O stretching frequency in carboxylic groups (C–O stretching frequency of the acetyl groups or the ester linkage of carboxylic groups of hemicelluloses part). The peak at 1635 cm^{-1} is corresponded to absorbed water and peak at 1424 cm^{-1} corresponds to CH or OH bending frequency in cellulose and hemicelluloses [4]. The peak at 1373 and 1319 cm^{-1} are recognized to C–H deformation vibration frequency and O–H vibration frequency in celluloses. The peak at 984 cm^{-1} is due to C-H deformation vibration glucose ring stretching of β-glycosidic linkage of cellulose and hemicellulose. By comparing the spectra of holocellulose and α-cellulose, the peak at 1249 and 1735 cm^{-1}, which are assigned to the guaiacyl in the lignin and the characteristic feature of carbonyl groups of hemicellulose, is absent in α-cellulose spectra. Based on the result, the extraction of α-cellulose from *E. dulcis* holocellulose was effectively accomplished.

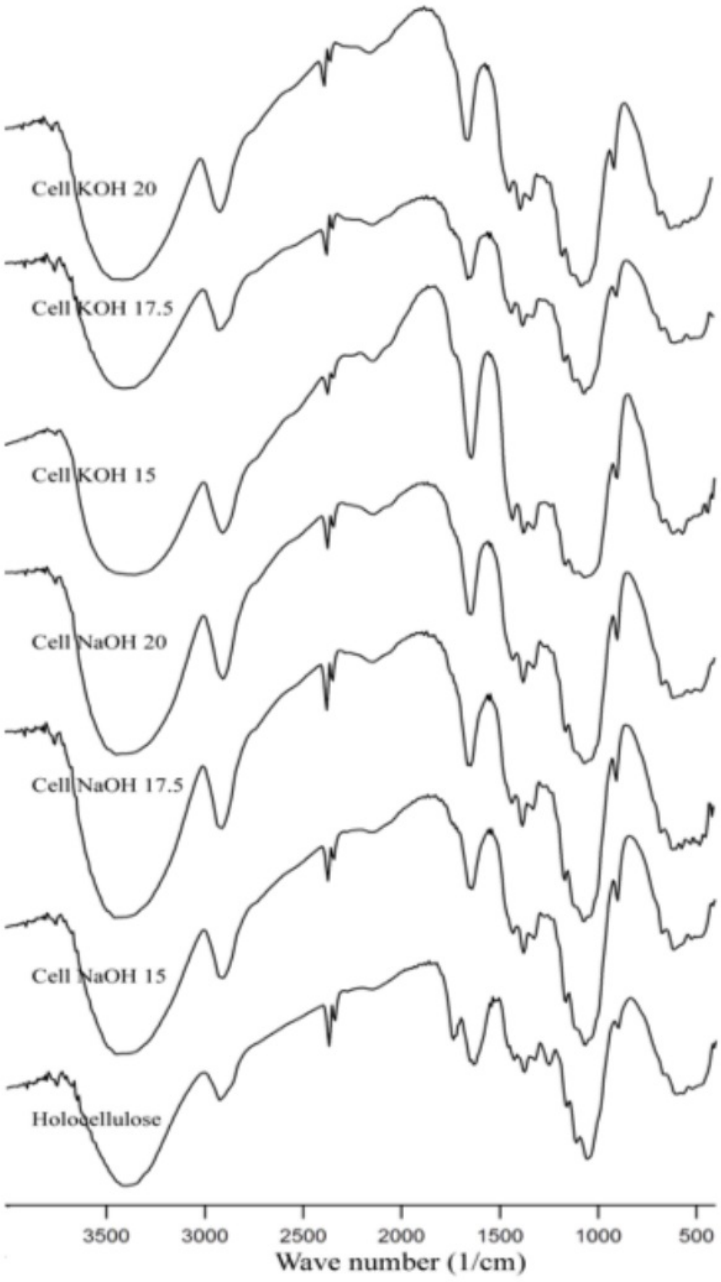

Figure 2. FTIR spectra of *E. dulcis* holocellulose and α-cellulose

Table 3. Summary of the FTIR spectra of *E. dulcis* holocellulose and α-cellulose

Wavenumber (cm^{-1})		Functional Group	Assignment
Holocellulose	**Cellulose**		
894	894	C-H deformation; glucose ring stretching	β-glycosidic linkage of cellulose and hemicellulose
1056	1056	C-O stretching	cellulose and hemicellulose
1249	-	C-O stretching	guaiacyl in the lignin
1319	1319	O-H bending vibration	cellulose
1373	1373	C-H deformation vibration	cellulose
1427	1427	CH_2 bending vibration	cellulose
1635	1635	O-H group stretching	absorption of water
1735	-	C=O stretching	carbonyl groups of hemicellulose
2924	2900	C-H stretching	methylene and methyl group of cellulose
3402	3400	O-H stretching	hydroxyl in cellulose (hydrogen-bonded)

3.3. Crystallinity of Cellulose

The crystallinity index was estimated using a simple method based on spectra FTIR. The peak at around 1427 cm^{-1} and 894 cm^{-1} are correlated with the amount of the crystalline cellulose part and non-crystalline (amorphous) cellulose part, respectively [8]. *Lateral Order Index* (LOI) is corresponded to the total degree of the ordered structure in cellulose [8]. *Total Crystallinity Index* (TCI) is corresponded to the structure of cellulose I and cellulose II [8]. The hydrogen bond intensity (HBI) of cellulose is correlated to the crystal unit and the degree of intermolecular regularity interaction and considering the chain mobility and bond distance of molecule[12]. LOI, TCI, and HBI values were determined as the ratio between peak at 1427 and 894, 1373 and 2900, and 3400 and 1319 cm^{-1}, respectively [7-9, 11, 13-14]. The infrared-based crystallinity data and hydrogen bond intensity of *E. dulcis* holocellulose and α-cellulose are presented in Table 4.

Table 4 showed that the low LOI, TCl and HBI value of holocellulose, suggesting the low degree of crystallinity of cellulose, a more non-ordered cellulose structure, and a more non-regular intermolecular crystal system. The LOI values of cellulose fluctuate with an increase in concentration of NaOH and KOH solution. However, the TCl values of cellulose increase with an increase in a solution concentration of NaOH, and KOH. The LOI value indicates that KOH 15% solution can remove amorphous cellulose selectively and produce the highest LOI value. The TCl and HBI reached the highest values at the hydrolysis process using NaOH 20% and KOH 15%. Based on the data of LOI, TCI, and HBI, it is suggested that, the optimum concentration of alkali solution for hydrolysis holocellulose between NaOH and KOH is different.

Table 4. Infrared crystallinity data and hydrogen bond intensity of *E. dulcis* holocellulose and α-cellulose

Sample	LOI	TCl	HBI
	A_{1427}/A_{894}	A_{1373}/A_{2900}	A_{3400}/A_{1319}
Holocellulose	1.07	0.94	1.38
Cell NaOH 15	1.09	0.93	1.44
Cell NaOH 17.5	1.06	0.99	1.44
Cell NaOH 20	1.07	1.01	1.54
Cell KOH 15	1.18	1.00	1.53
Cell KOH 17.5	1.05	0.99	1.26
Cell KOH 20	1.07	0.99	1.37

4. Conclusion

Eleocharis dulcis is an abundant, low-cost, and renewable source of cellulose, which largely abundant in swampy area in South Kalimantan, Indonesia. The type of alkali and concentration of solution for α-cellulose isolation from *E. dulcis*'s holocellulose was not affected the yield, color, lateral order index, total crystallinity index, and hydrogen bond intensity. Isolation of cellulose from this source using a lower concentration of alkali solution could be alternative for environment-friendly process. Cellulose from *E. dulcis* has the potential to be applied in various industries such as paper making, food, pharmaceutical, and composites.

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References

[1] Istikowati W T, Aiso H, Sunardi, Sutiya B, Ishiguri F, Ohshima J, Iizuka K, and Yokota S 2016 *J. Wood Chem. Technol*. **36** 250-258
[2] Sunardi, Febriani N M, and Junaidi A B 2017 *AIP Conference Proceeding* **1868** 020008
[3] Sunardi, Tanabe J, Ishiguri F, Ohshima J, Iizuka K, and Yokota S 2016 *Int. Biodeter. Biodegrad*. **110** 108-112
[4] Naduparambath S and Purushothaman E 2016 *Cellulose* **23**1803-1812
[5] Teixeira E T, Bondancia T J, Teodoro K B R, Corrêa A C, Marconcini J M, and Mattoso L H C 2011 *Ind. Crops Prod*. **33** 63-66
[6] Arnata I W, Suprihatin F F, Fahma F, Richana N, and Sunarti T C 2019 *Orient.J. Chem*. **35** 8-19
[7] Nada A M A, Kamel S, and El-Sakhawy M 2000 *Polym. Degrad. Stab*. **70** 347-355
[8] Nelson M L and O'Connor R T 1964 *J. App. Polym. Sci*. **8** 1311-24.
[9] Sunardi, Istikowati W T, Ishiguri F, and Yokota S 2018 *AIP Conference Proceedings* **2026** 020024.
[10] Bolhuis G K and Armstrong A A 2006 *Pharm. Dev. Technol*. **11** 111-124
[11] Corgié S C, Smith HM, and Walker L P 2011 *Biotechnol. Bioeng*. **108** 1509-1520
[12] Oh S Y, Yoo D I, Shin Y, and Seo G 2005 *Carbohydr. Res*. **340** 417-28
[13] Carrillo F, Colom X, Sunol J J, and Saurina J 2004 *Eur Polym J*. **40** 2229-2234
[14] Poletto M, Zattera A J, and Santana R 2014 *J. Appl. Polym. Sci*. **126** 336-343

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