The use of nanofibrils cellulose of sugarcane bagasse as precursor in synthesizing carbon nanodots by hydrothermal method

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Abstract. Sugarcane bagasse is an organic waste which has been produced in industrial scale. This waste has big potential to be utilized into carbonaceous material, such as carbon dots throughout its carbon contents. However, to synthesize carbon nanodots, temperature and carbon content source have important aspects. Therefore, this study is conducted to synthesize this material, and to investigate the properties of carbon nanodots. Cellulose fibrils were isolated by steam explosion treated within alkaline condition, and the nano-sized material was obtained by homogenizing alpha-cellulose. While the carbon nanodots were synthesized by hydrothermal method involving acidic reagents for 4, 8, and 12 hours. Based on FTIR analysis, the patterns showed similar properties to cellulose regarding on functional groups of O-H, C=O, C-O-C, and amino whereas the amount of cellulose fibrils isolated accounted for almost 30 percent from the raw materials, which show potential value of sugarcane bagasse. Photoluminescence characteristics were performed to determine the carbon nanodots property under UV-Lights, and the results showed that each samples displayed different colours from green to blue. Therefore, carbon nanodots which were successfully synthesized from nanofibrils cellulose were affected by time.

1. Introduction

Sugarcane bagasse is considered as biomass containing organic compounds. Interestingly, the sugarcane bagasse is resulted from sugar companies as the residual waste accounted for 40-50% [1]. The composition of chemical contents within sugarcane bagasse is quite promising because more than half of its composition is cellulose [2]. According to the Ministry of Agriculture of Indonesia, the national total production of sugarcane reached to 33 million ton per year, which shows big opportunities in utilizing this organic waste.

To obtain the cellulose, there must be several treatments. The process of isolation the cellulose is started by removing the lignin and hemicellulose, while the size of the fibers is also important to be removed. Therefore, mechanical treatments could be difficult due to different size of fibers [3]. It has been reported that separation of lignin could be done by implementing steam explosion [4], steam integrated with alkaline condition [5]. The chemicals treatments are used to remove the lignocellulose...
compound, whereas the mechanical treatments are such homogenizer and steam are used to obtain the nanoscale.

Cellulose, an abundant organic polymer, contains organic elements such as carbon, hydrogen, and oxygen. This biomaterial which can be found from plants and vegetables, for instance, banana [6], corncob [7] has been used as precursor in synthesizing carbonic materials. The presence of carbon in cellulose provides unlimited raw materials, so that many carbonaceous materials could be obtained, including carbon nanodots [8]. Given that sugarcane bagasse contains cellulose as its main composition, this organic waste could become alternative precursors.

However, the process of synthesizing carbon nanodots require carbon element in the beginning. In addition to start the synthesizing process, cellulose is treated to be a nano-scale by implementing the mechanical approach. After obtaining the nano-scale materials, sample is heated inside furnace to start the process of carbonization. Then, the carbon element is obtained which will be ready for being synthesized.

In this research, we performed the hydrothermal method in synthesizing the carbon nanodots. This method has been considered as an environmental friendly based on its steps which involve chemical liquids and high temperature [9]. The nanofibrils cellulose samples were characterized by Fourier Transform Infrared (FTIR) to investigate the functional groups, whereas carbon nanodots were tested to observe the fluorescence properties under the UV lights.

2. Methods

2.1 Materials
Sugarcane samples were taken from Kualamadu plantations. The chemicals compounds are sodium hydroxide (NaOH), hydrogen peroxide (H$_2$O$_2$), nitric acid (HNO$_3$), sulphate acid (H$_2$SO$_4$), hydrochloric acid (HCl), acetate acid (CH$_3$COOH), and sodium hypochlorite (NaOCl) were supplied by Merck.

2.2 Methods

2.2.1 Isolation cellulose from sugarcane bagasse
The beginning process was by cutting the sugarcane bagasse into smaller size. The small-size bagasse then was dried to remove the liquid contents. Next, samples were put inside a bucket to be immersed within 2% NaOH for 24 hours, so that the impurities of samples were removed. After 24 hours, samples were washed to cleanse the waste of 2% NaOH. To remove the lignocellulosic compounds, samples were immersed with 12% NaOH which was placed inside autoclave instruments to be ready for steam explosion process, involving 2 hours of time with 130°C. After two hours, samples were cooled gradually to be washed until pH reached 7. The samples collected then were immersed to be bleached with mixing liquid of 17.5% NaOH, 7.4% CH$_3$COOH, and 1.75% NaOCl while being heated within 70°C for two hours. After being bleached, samples were filtered and dried inside an oven with 50°C. Finally, the dried samples were collected to be characterized by FTIR instruments.

2.2.2 Isolation nanofibrils cellulose from cellulose
Dried samples of cellulose were collected, and they were placed inside of beaker glass. 10% HCl were added inside the beaker, while at the same time it was sonicated for 3 hours. To obtain the nano-scale, mechanical treatments were performed by using the Dai Han Homogenizer. Therefore, the sonicated samples were washed with distilled water until pH 7 before being homogenized. The homogenization process was performed in 8000 rpm within 15 minutes. The suspended samples then heated inside an oven for 50°C to be dried. Then, these samples were tested by SEM instrument.

2.2.3 Synthesizing of Carbon nanodots from nanofibrils cellulose as precursors
The hydrothermal process involved the mixing liquids of hydrochloric acid and nitric acid with 1:3 ratio, and carbon elements. The first step was by doing carbonization of nanofibrils cellulose in 550°C. Then, 30 mg of carbon elements that was obtained was placed inside a beaker glass which was immersed with 40 ml of nitric acid, and 10 ml of hydrochloric acid. The samples then were heated within 100°C for 4, 8, and 12 hours inside an oil bath to have uniformly thermal distribution. After
being heated, samples were added with 1M NaOH to reach pH 7. Then they were filtered with filtration membrane 0.22 µm. Samples were then tested under UV Visible.

3. Result and Discussion

3.1 Isolation of nanofibrils cellulose from sugarcane bagasse

Samples in the form of bagasse taken from Kualamadu plantations, which have been soaked in NaOH, and through a series of processes, is obtained. In the isolation phase, α-cellulose is used as much as 50 grams of bagasse and at the end of the process pure α-cellulose was produced about 16 grams (as much as 32% of the initial weight of bagasse). The results of α-cellulose obtained from the study can be seen in following Figure 1.

![Figure 1](image1)

**Figure 1.** (A) The pre-treated sugarcane bagasse, (B) alpha cellulose obtained by alkaline treatments

From the Figure 1, the changes of colours from darker to white showed the removal of lignin and hemicellulose. This alpha cellulose shown by Figure 1 (B) was homogenized by high shear homogenizer with 8000 rpm. Then the samples were morphologically analyzed by using SEM, which is displayed by following Figure 2 of SEM images.

![Figure 2](image2)

**Figure 2.** SEM Images of nanofibrils cellulose (A) with 500x magnification (B) 700x magnification

The SEM images shown by Figure 2 display two different magnifications. In Figure 2 (A), it clearly can be seen that the nanofibrils are illustrated by the form of fibrils, while the Figure 2 (B) shows the exactly the same.

3.2 Carbon nanodots
The samples obtained by using hydrothermal methods show different colours of each samples. The following Figure 3 illustrates the three samples which were synthesized by different temperatures along with the fluorescence images.

![Figure 3](image)

**Figure 3.** Sample obtained by hydrothermal method (a) 4 hours (b) 8 hours (c) 12 hours

The Figure 3 shows that the fluorescence colours are changing from yellowish to blue. This suggests that the different times of hydrothermal process provided different colour characteristics of the samples which have been obtained.

4 Conclusion

The use of nanofibrils as precursor in synthesizing carbon nanodots is effective to be done. From the analysis, it can be obtained that sugarcane bagasse provides almost 30% of nanofibrils cellulose from the raw materials. Based on the fluorescence test under UV lights, the carbon nanodots have been successfully synthesized with fluorescence characterizations of colours are yellow to blue. Interestingly, different time of temperatures affected the different fluorescence of colour of each carbon nanodots samples that were obtained.

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