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Isolation and Characterization of Nanocellulose Structure from Waste Newspaper

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ABSTRACT

Nanocellulose, a kind of biomaterial in nanoscale size particle that have big potential performs in a many fields and application. Aim of this study was to extract and characterize the nanocellulose from waste newspaper as an approached of environmental friendly source material. In addition, it gives low cost in extracting nanocellulose process. First part of this study reports on the extraction and characterization of cellulose from waste newspaper by bleaching and alkaline treatment. Then, sulphuric acid hydrolysis employed to isolate nanocellulose by varying several parameters such as acid concentration, reaction time and reaction temperature. The best condition for isolation of nanocellulose with the nanocellulose yield of 45% is using 45 wt.% of acid sulphuric at temperature of 40 °C in 20 minutes. The structural analysis was performed using Fourier transform infrared spectroscopy (FTIR) which confirmed the effectiveness of removing of non-cellulosic components after the treatment. Scanning electron microscopy (SEM) was used to analyse the morphology of the nanocellulose that revealed the refinement of surface after the acid hydrolysis method.

Keywords:
Nanocellulose, acid hydrolysis, waste newspaper

1. Introduction

Cellulose is the main components of lignocellulosic existed in plant's cell wall. It comes along with hemicellulose, lignin, pectin, wax and others components with 25-50% lies in plants. Hemicellulose which is a mixture of carbohydrates also called by it scientific name, amorphous polysaccharide [1]. There are complex chains of phenyl propane that used as a connector to produce exact morphology in cell wall of plants. As the plants make its own food, through photosynthesis process, some of it used as fuel and some of its will be stored which is known as starch. Some of the food generated will form a structure that bind together as cell wall called as

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lignocellulose. These three components (cellulose, hemicellulose and lignin), catch intense attraction to researchers in order to obtain the maximum ability of the material to human life.

Nanocellulose, a nano structure of cellulose, also a natural nanomaterial that able to contribute in various of field to obtain the unique and super-strong material properties for variety different end product. Nanocellulose is described as the products or extracts from native cellulose that found in plants, animals, and bacteria composed of the nanoscaled structure material. Generally, nanocellulose can be categorized into three main types, (1) cellulose nanocrystals (CNC), with other designations such as nanocrystalline cellulose, cellulose (nano) whiskers, rod-like cellulose microcrystals; (2) cellulose nanofibrils (CNF), with the synonyms of nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC), cellulose nanofibers; and (3) bacterial cellulose (BC), also referred to as microbial cellulose [3]. Although all types are similar in chemical composition, they are different in term of morphology, particle size, crystallinity, and some properties due to the difference of sources and extraction methods [4,5].

Isolation of nanocellulose was prepared from variety of cellulose fiber gain interest in world of research along with advance of nanotechnology. Most of them use natural resource of raw material which is more reliable in this era. Apart of that, nanofibres proposed in such a wide used. For instance, in electronics, nanofibres are used to prepare a flexible circuit, optical application and flexible solar panel [1]. Nanocellulose has distinctive characteristics such as good mechanical strength, crystallinity, good possibility for chemical modification, biocompatibility, high specific surface area, biodegradability, high aspect ratio, beneficial rheological, lightweight, exceptional oxygen permeation and water-vapour transmission resistance, oil grease barrier, aqueous liquid barrier, optical characteristics and inexpensive in cost [6,7].

Recently, nanocelluloses have been extensively used in nanocomposite materials, surface modified materials, and transparent paper with special functions due to its excellent mechanical properties and biodegradable as well as high thermal properties with lightweight and transparency [8,9,10]. To date, nanocellulose has been used as the filler in polymer matrix due to the high strength of polymer reinforced with cellulose can bear high capacity to hold water. So these researches mainly aimed to take maximum benefits of this unique balance of properties of fibre consist in plant for composite application [2]. Remarkably, nanocomposite materials can be applied in many fields in our daily life. The windmill blade with high strength structure, lightweight armor, flexible batteries, and others have been made from nanocellulose [11,12]. Other applications of nanocellulose in the medical field such as drug delivery into target cells, implant of soft tissue, blood vessel replacements and so on are also investigated in recent years [6,13]. Other than that, nanocellulose can be also applied in other fields. For examples, it can be used as the thickener in cosmetics, the texturing agent in food, filler of special textiles, biodegradable package, CO^2 adsorbent, and oil recovery.

The main extraction methods to attained nanocellulose are categorized to three techniques which are acid hydrolysis, enzymatic hydrolysis and mechanical process. Commonly, acid hydrolysis is used for the extraction of nanocellulose from cellulosic materials. Due to the combination of ordered and disordered regions in cellulose chains, the disordered regions can be easily hydrolyzed by acid and the ordered parts are left as the remaining [4,5]. Sulfuric acid is the acid mostly used for acid hydrolysis. It can not only strongly isolate nanocrystalline cellulose, but also make the nanocellulose dispersed as a stable colloid system due to the esterification of hydroxyl group by sulfate ions [14,15]. The important parameters which affect the properties of obtained nanocellulose are reaction time, temperature, and acid concentration [5,16].

Even though nanocellulose has various outstanding properties and high availability in nature, the extraction of nanocellulose from lignocellulosic biomass or cellulosic materials is still a main challenge. Due to the strong aggregation of lignin, hemicelluloses, and other materials in plant cell wall, the biomass pre-treatment is an essential step for removing all non-cellulosic materials. However, such a pre-treatment always includes complex steps, takes a long time, and consumes toxic chemicals and generates wastewater. Furthermore, the general methods for the nanocellulose extraction from cellulosic materials contain drawbacks that consumed the high amount of acid waste water generation for the acid hydrolysis, high energy consumption for mechanical process, and long reaction time for enzymatic hydrolysis [17].

2. Experimental

2.1 Materials

Chemicals used in this this study were sodium hydroxide (NaOH), sodium chlorite ($NaClO_2$), sulphuric acid (H_2SO_4), and distilled water. Raw material used is waste newspaper that were collected from Kampus Uniciti Alam, Sungai Chuchuh.

2.2 Extraction of Cellulose from Waste Office Paper

In this study, cellulose was extracted from waste newspaper (WNP). WNP was cut into small pieces and partially dried under the sun [18]. The pieces of WNP then placed in stagnant water for three days and the water was periodically changed. Then, WNP was dried under the sun and ground using mill. Grounded paper was then treated with 4% of NaOH at 125 °C for about 2 hours. Then, the paper was treated with bleaching treatment using 1.7 w/v % of $NaClO_2$ at pH of 4.5 and 125 °C for 4 hours. The ratio of the waste newspaper to liquor was 5:100 (g/ml) [18]. Each step was repeated several times and distilled water was used to wash the sample.

2.2 Preparation of Nanocellulose via Acid Hydrolysis

Nanocellulose prepared via acid hydrolysis method. The chemicals involved in this part was sulphuric acid (H_2SO_4) with the range of 20-60 wt. %. Samples was treated with sulphuric acid with initial temperature of 30 ^oC and steady whirled. The hydrolysis time was 1 hour and the acid ratio of 1: 2. After that, the blended compound washed with distilled water and lastly proceed with centrifugation. Suspended obtained from centrifugation was washed with distilled water to get the constant pH value is obtained from suspended sample [19].

2.3 Characterization of Extracted Cellulose and Nanocellulose from Waste Newspaper

2.3.1 Functional Group Analysis

The functional group of the untreated waste newspaper and the extracted cellulose were analysed using Fourier Transform Infrared spectroscopy (FTIR). The functional group analysis was carried on a Perkin-Elmer spectrophotometer (spectrum GX) in the range 4000-500cm^{-1} with a scanning resolution of 8cm^{-1}.

2.3.2 Surface Morphology Analysis

The surface morphology of nanocellulose was analyzed by scanning electron microscopy (SEM). Samples were sputter-coated with gold and images are taken at average voltage 5kV.

3. Results and Discussion

3.1 Extraction of Cellulose from Waste Newspaper

The components composition of fiber affected by the extraction process. By using sodium hydroxide, alkalization processes able to extract and hydrolyse hemicellulose, silica, ash and soluble salt of the waste newspaper. Another stage is bleaching, a process of removing lignin components. This stage affected the result a lot because it exposed under a condition of low pH and high temperature. The untreated waste newspaper and the extracted cellulose by chemical treatment showed the different composition and structure. Based on the previous study, the cellulose content of the *mengkuang* leaves was increased and petosans, lignin and hemicellulose content were decreased after treat with the sodium hydroxide [18].

Generally, this result shows the successful extraction of cellulose from waste newspaper due to the removal of hemicellulose and lignin from waste newspaper chemical treatment. It was clearly observed that the hemicellulose and lignin have been removed after chemical treatment. FT-IR spectra of the WNP and extracted cellulose are shown in Figure 1 (a) and Figure 1 (b) respectively.

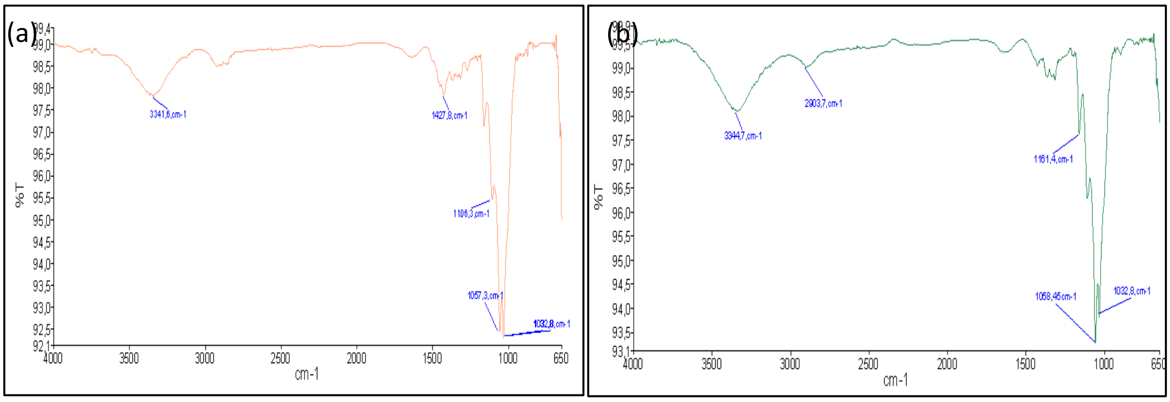

Fig. 1. FTIR spectra of (a) waste newspaper (WNP) and (b) extracted cellulose

Figure 1(a) shows the presence of a band at 2900 cm^{-1} to 3341 cm^{-1} attributed to O-H group that particularly represented as the pure waste newspaper cellulose. Next band is appeared at 1427 cm^{-1} that indicates C=C of aromatic stretching in plane or ring in lignin. The range between 1057 cm^{-1} to 1105 cm^{-1} indicates the presence of the C-O stretching that shows the presence of carbohydrate [18]. The peak at 1730 cm^{-1} represent the C=O stretching which indicates that the presence of pectin, hemicellulose and lignin [21].

Based on the FTIR analysis of extracted cellulose in Figure 1(b), peak at 3347 cm^{-1} shows the O-H bond that represented as the WNP cellulose. After the treatment, the band that shows the pectin, hemicellulose and lignin (1734 cm^{-1}) is shifted. Band that appeared after the treatment is at 1556 cm^{-1} which indicates the lignin associated with vibration of aromatic skeleton (C=C) showed the removing of lignin at band 1427 cm^{-1} (from untreated).

3.2 Isolation of Nanocellulose via Acid Hydrolysis

Nanocellulose was isolated from cellulose by using acid hydrolysis method. Several parameters were varied such as acid concentration, reaction time and reaction temperature in order to study the effect of hydrolysis conditions on nanocellulose yield. The nanocellulose was characterized by using Scanning Electron Microscope (SEM).

3.2.1 Effect of Acid Concentration on Nanocellulose Yield

The concentration of sulphuric acid was varied from 40-60 wt% wt with the hydrolysis time and reaction temperature were kept constant at 20 minute and 40 ^{o}C respectively. Figure 2 illustrates the effect of sulphuric acid concentration on the nanocellulose yield.

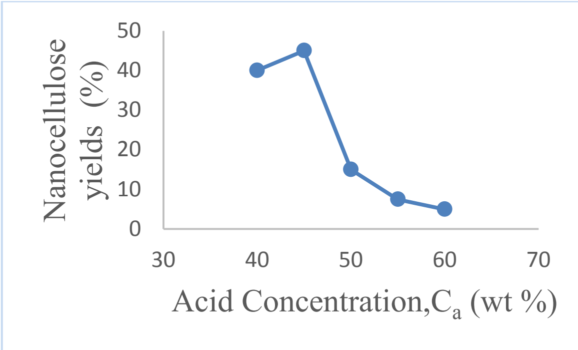

Fig. 2. Effect of sulphuric acid concentration on the yield of nanocellulose

As shown in Figure 2, initially, as the acid concentration increased up to 45 wt% the nanocellulose yield could reach the maximum performance. As the acid concentration further increased, the nanocellulose yield was greatly decreased. Loelovich [5] stated that solubility of the initial sample elevated continuously under room temperature with the concentration in range 50-60 % of H_2SO_4 [5]. Regarding to previous study, it stated that the ideal concentration to prepare nanocellulose is in the range of 57-60 wt. % but it is still depending on the material used. The increasing of the acid concentration might cause lost a lot of sample and sample would burn.

3.2.1 Effect of Reaction Time on Nanocellulose Yield

Reaction time used in this study are 10-60 minutes. The best condition from the acid concentration was kept constant at 45 wt % with temperature of 40 ^{o}C. Nanocellulose yield decreased as the reaction time increased. The graph of the nanocellulose yields response on reaction time is shown in Figure 3.

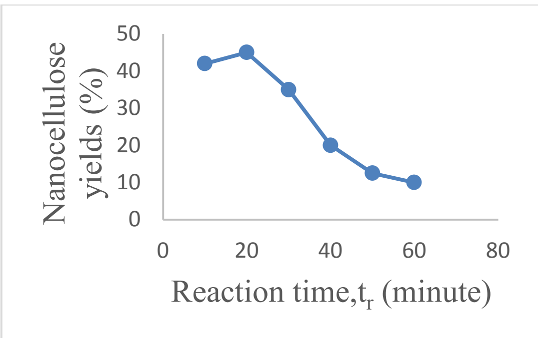

Fig. 3. Effect of reaction time on the yield of nanocellulose

Based on the graph, as the time increased, the nanocellulose yields decreased. Reaction time at 10 minutes and 20 minutes shows the increment with highest nanocellulose yield obtained. But, the yield became lower after 20 minutes and above. Previous study on nanocellulose extraction from *Xanthoceras Sorbifolia* husks, stated that acid solutions permeate into the extracted cellulose and lead to the split of glycosidic bond of sample [21].

3.2.1 Effect of Reaction Temperature on Nanocellulose Yield

The nanocellulose yield was evaluated by varying the reaction temperature in the range of 30-50 °C while the other parameters like acid concentration and reaction time were fixed at 45 wt% and 20 minutes respectively.

Based on the graph displayed in Figure 4, the optimum nanocellulose yield can be obtained at 40 °C of reaction temperature. The yields kept increasing as the reaction temperature increased from 30 °C to 40 °C and reach the maximum yield that is 47.5% at temperature of 40 °C. The graph shows decrement after 40 °C due to lots of sample consumed during experiment ran. As the temperature increased over 50 °C, the higher possibility of the sample to burn or lost. Sulphuric acid used with higher temperature lead to direct heat that cause a rapid burn [20].

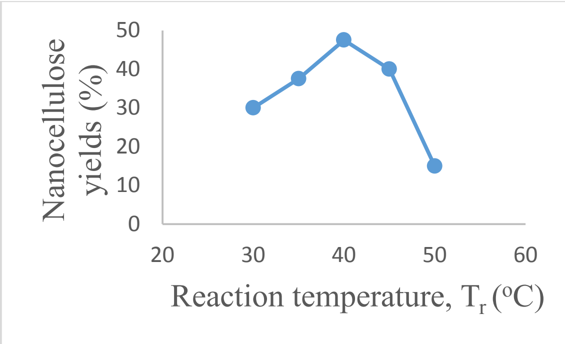

Fig. 4. Effect of reaction temperature on the yield of nanocellulose

3.3 Characterization of Nanocellulose

The characterization of nanocellulose used scanning electron microscopy (SEM). Scanning electron microscopy was used in order to study the surface morphology of nanocellulose. The surface rough-ness shown in the image indicates the removal of the cementing materials.

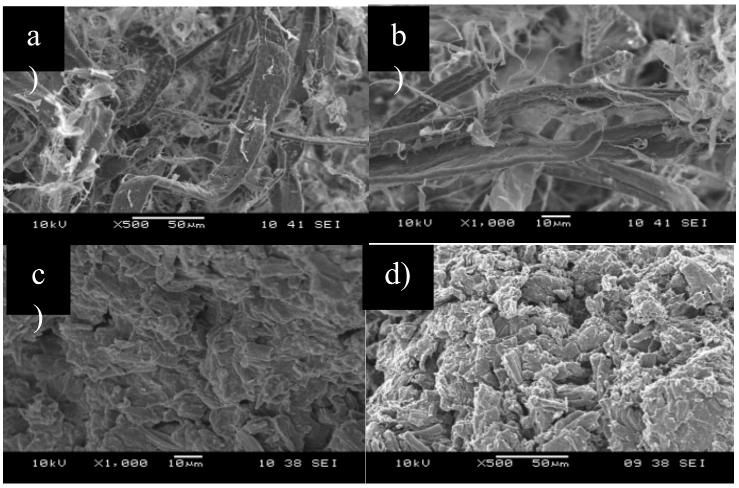

Fig. 5. SEM image of cellulose (a-b) and nanocellulose (c-d) samples

Furthermore, the mechanical grinding increases the surface area and facilitates the ease of access acid into the interior part of the fibre. This contributes the effective defibrillation which is clearly demonstrated in the Figure 5 (c-d) the diameter is reduced from the cellulose in Figure 5 (a-b). From the SEM image of nanocellulose, it clearly seems to have refinement of the fibrillar structure associated with further reduction in its diameter.

4. Conclusion

The successful isolation of cellulose nanofibrils from WNP gives an opportunity for the effective utilization of a waste product that would otherwise would pollute the environment and faces the additional hazard of toxic inks, dyes and polymers that could be potentially carcinogenic when incinerated. The FTIR spectra showed that the chemical treatments was successfully removed the hemicellulose, lignin, pectin and other non-cellulosic material. The optimum nanocellulose yield was obtained with condition of 45 wt% of acid concentration, 20 minutes of reaction time and 40 ^{o}C of reaction temperature.

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