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Preparation of Nano-Cellulose from Industrial Waste by Ultrasonic Device

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Abstract

This research aims at preparing the nano-cellulose in a new way, using technology and raw materials available in the ocean. In this research, waste paper residues isolated from the other wastes (household, industrial, etc.) were completely used. Usually, the initial residues of the waste paper industry will be deposited in the waste. This will cause pollution to the environment. In this way, we will eliminate one of the environmental pollution factors by producing a useful material from these residues, namely, cellulose nano-particles. These substances have a high content of lignocellulosic components that can be converted to the nano-cellulose structures. The acidic decomposition method by 50% sulfuric acid, and the ultrasonic device were used. After cooling and drying, the nano-cellulose was obtained and the diagnosis was made by SEM, AFM, and FT-IR.

Keywords: Nanocellulose, Nanoparticles, Recycling, Paper Lifecycle, Nanocomposites

Introduction

Nanotechnology has become a widely known science which is most commonly used in other fields of science like physics, electronic and engineering since several decades. Recent exploration of nanotechnology in pharmaceutical and biomedical sciences resulted in successful improvement of conventional means of drug delivery system**.** (Bhatia, 2016) Nano-technology is science of technology which is a new and evolving science widely used in recent times. The great development of science and technology that occurred in the second half of the twentieth century not only created new and daring ideas, but also led to the creation of tools that enabled realization of atoms in the materials. Contributed scientific achievements (Figure 1), especially which occurred in the end of the twentieth century was effective in the expansion of nanotechnology. (Szczesna-Antczak et al., 2012)

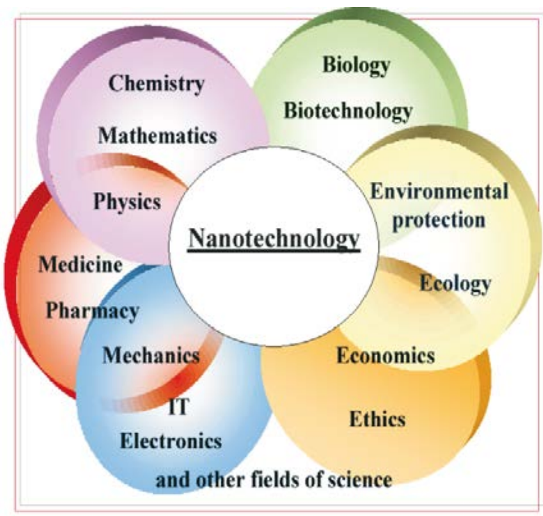

Figure 1. Interdisciplinarity of nanotechnology

Nano-cellulose is a new and widely developed type of cellulose that is found in fibers that can be extracted from trees, plants, some species of bacteria, algae, and some marine organisms. Nano-cellulose is not just one type of material. It is a family of substances, but it is characterized by its different properties. This difference is due to the variation in the preparation method as well as the source from which nano-cellulose was obtained. (Clemons, 2016) The nano-cellulose crystals preparation from the original cellulose have nanostructures with small dimensions. The dimensions of the nano-cellulose crystal are based on the material from which they were started. (Kontturi, 2016) Cellulose is the chemical compound which considered as the most obtainable regenerate polymer that is the most common in nature. (Lee et al., 2009; Wulandari et al., 2016) The structure of cellulose is $[C6H10O5]_{n.}$ At first it was thought the wood was the only source of cellulose, but overtime it was found that other plants such as flax, jute, rice husks, cotton, corn cobs, etc., also some bacteria and sea creatures containe a large quantity of cellulose. Nano-cellulose was discovered around 1950 by the acid hydrolysis of cellulose fibers. (Yousefiandivkolaei, 2016)

The term "recycling" has become a widely used term. "Recycling" is defined as the extraction or separation of useful materials that

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are intended to be recycled for use in other purposes, such as recycling paper for other purposes, for example recycling paper in the cardboard and newspaper industry. (Ortiz, 2005) Almost any type of waste paper can be recycled. However, if the waste paper is in direct contact with the other wastes, it is impossible to take advantage of it and hinders recycling. Therefore, the contaminated paper is not acceptable in this area, for example household waste and health care waste and many more, and also if the waste paper contains materials that are difficult to separate. (Villanueva and Eder, 2011) The paper is used as a consumptive material with a high rate of natural origin. It is derived from raw plant fiber such as trees and other types of perennial plants. These fibers, which are included in the paper industry, are rich in cellulose. The paper residue can be used to extract cellulose and nano-cellulose rather than throwing it as waste, which cause many environmental problems. Moreover, cellulose derived from the remnants of paper can be used in the production of paper; this means that there is sustainability of nature and great economic value could be achieved. (Koplan et al., 2002; Aue, 2003; Smith, 2011*;* Rillen, 2014) Figure 2 shows the flow chart of the paper lifecycle, as presented by the authors of this paper. (Zmak, et al., 2015)

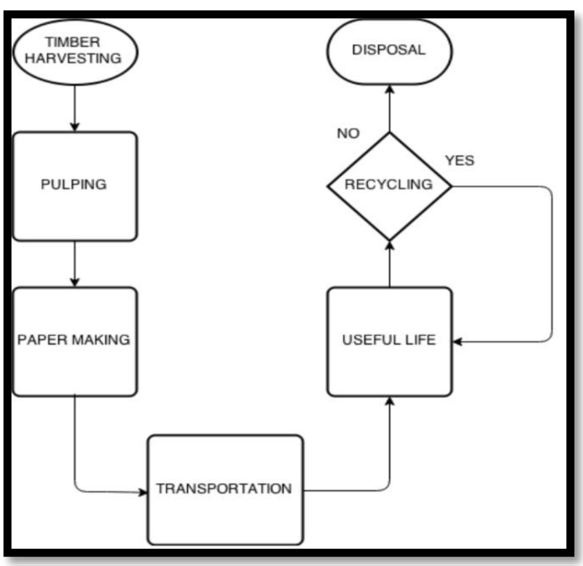


Figure 2: The paper lifecycle

Experimental:

The raw materials are paper residues. In this research, waste paper residues isolated from the rest of the other wastes (household, industrial, etc.) were completely used.

Chemical solution

1. Acetic acid diluted to 90%, mixed with sulfuric acid by 3.5%. The process of acid decomposition of waste paper was done after purification and washing with deionized water for several times.
2. sulfuric acid 50% was used to dissolve existing materials with cellulose.
3. Sodium hydroxide at a concentration of 1% was added to the acid solution until the acidic function reached pH=7. Alkali hydroxide was used to remove the soluble sugars.
4. Sodium hypochlorite was used with a concentration of 4% for the bleaching process and for the removal of most remaining phenols such as lignin and polyphenols.
5. hydrogen peroxide (H_2O_2) with a concentration of 30% was used for bleaching.

Chemical Method:

Extraction of the nano-cellulose from paper residues was done by following steps:

A. Preparation of sample

1. The paper residues were taken, purified and dried, and grinded to became like soft cotton. Then the product was washed with normal water and then with distilled water for several times; then the product was dried.

2. The sulfuric acid was diluted to a concentration of 3.5% and the acetic acid to concentration of 90%. After that 4.0 gm of residues were added to 100 ml of the sulfuric acid (3.5%) and acetic acid (90%), and heated to 80 °C for 1 h with strong stirring. (Souza et al., 2017)

The solution was filtered, and washed with distilled water several times until the smell of acids disappeared. At first the filtration was quick and then became slow and continued for one day. After that the product was dried at 50 °C.

B. Bleaching process:

Bleaching was done by 30% of hydrogen peroxide and 5% of sodium hydroxide. The two solutions were mixed together, and the sample was added to mixture for bleaching. After mixing the solution with paper residues it was heated to 60 °C for 2 h, then filtered and washed with distilled water for several times. After that the product was dried in 70 °C for 3 h.

C. Preparation of nano-cellulose:

The product was added to sulfuric acid at concentration of 50% with strong stirring (Clemons, 2016), then 150 ml of deionized water was added to the final reaction. After that the solution was cooled at 8 °C for 3 h, left at room temperature to separate the components, filtered, and washed with distilled water several times. Then the pH was adjusted to 7 by 1% sodium hydroxide. After that the solution was filtered and collected. The product was added to 100 ml of deionized water, sonicated by Ultra-sonic device for 1 h until it became thick. Then the product was cooled to 8 °C, filtered, kept at 8 °C in plastic tube for 24 h, and dried at 80 °C for 6 h. Then the product was grinded to fine powder; by this way the NC was prepared from paper residues.

Results and Discussion

The nano-cellulose was prepared in a low cost way, namely, acid decomposition, filtration, drying and cooling, and this work was done in a simpler, shorter and lower cost. The present method reduces the use of the chemicals used by using aqueous solutions, and is done with a few concentrations of chemicals. Based on the measurements, good results were obtained:

Fourier transform infrared spectroscopy (FTIR):

FTIR analysis was used to identify the chemical structure of the lignocellulosic components present in the samples. The equipment was a Frontier 94942 (PerkinElmer, Spectrum 65). the spectra were recorded in the range of 400-4000 cm^{-1}. It demonstrates the changes in chemical composition of the fibers. The variations relative to the conversion from macro- to nano-materials are monitored by the changes in the hydroxyl and carboxyl regions. Figure 3 shows the FTIR spectra of the paper residue at 50% concentration of sulfuric acid. The peaks 3340 and 2918 cm^{-1}, which were present in all the samples, were due to hydroxyl group and to aliphatic saturated (C-H) stretching vibrations of cellulose, respectively. The peak at 1640 cm^{-1} is associated with the (O-H) bending vibration. (Oun and Rhim 2016; Johar et al., 2012) Smoothed peaks were observed in the region between 1100 and 1500 cm^{-1}, where it is not possible to attributed signatures for particular vibrations, hence in this region, complex overlap effects may occur. These small peaks could be also from hemicelluloses and proteins which are present in the cellulose fiber walls. (Jiang, Hsieh, 2015) The spectra of all samples are typical of cellulose. The peaks at 1060 and 896 cm^{-1} indicate, according to the literature, the purity of the crystalline band of cellulose, with characteristics of C-O stretching vibration and elongation of cellulose typical pulp β-glycoside bonds, respectively (especially in nano-cellulose spectra). (Chandra et al., 2016)

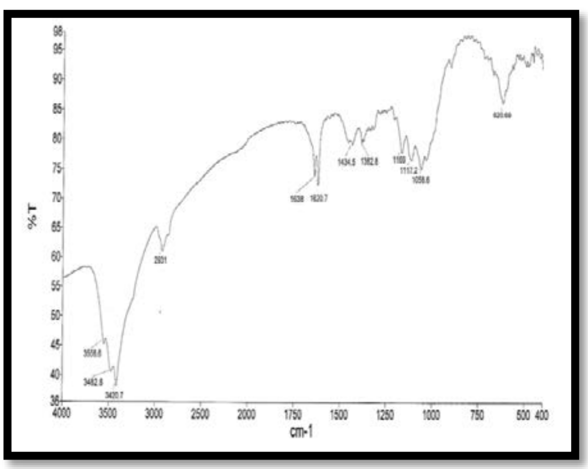


Figure 3: FTIR spectrum of nano-cellulose prepared from paper residues at 50% concentration of sulfuric acid

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) offered important visual information regarding the morphology of cellulose. Figure 4 shows SEM of nano-cellulose prepared from paper residues, and the modification of matrix structure after each treatment step. SEM was utilized to check morphology of the nanoparticles samples. (Dima et al., 2017) Which shows the morphology of the external side after isolation methods. The images show differences in shape of the sample. It showed the existence of organized crystalline regions, but also showed non-amorphous areas. This may indicate that the resulting nanotubes are not stable due to deposition of aggregates in the nanoparticle. sulfuric acid was used to dissolve the non-crystallized region. (Fortunati et al., 2013; Nuruddin et al., 2016; Oliveira et al., 2016).

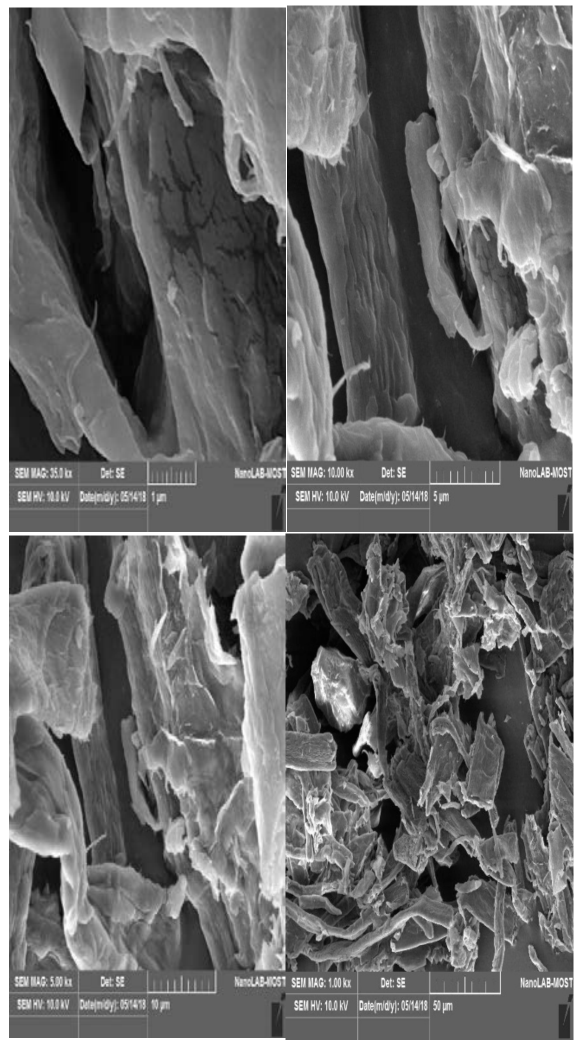
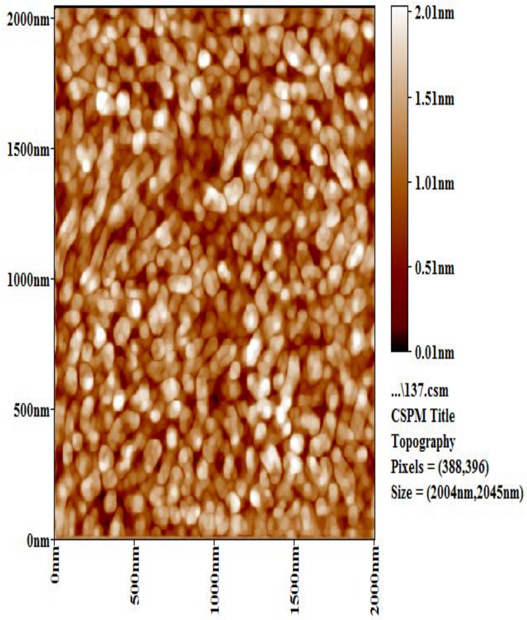


Figure 4: SEM images of NC from paper residues with concentration 50% of sulfuric acid

Atomic force microscope (AFM)

Atomic force microscopy (AFM) was used to know morphological characteristics, particle size and determination of diameter. The average granule size of surfaces nano-cellulose was measured utilizing atomic microscope**.** (Kumar and Rao, 2011) In figure 5 explains images of AFM for NC of residues at concentration 50% of sulfuric acid with size = 2004 nm, 2045 nm, and analytical ability (pixel = 388 nm, 396 nm) Table 1 and figure 6 show the granularity cumulating distribution and average diameter data of NC of paper residues at concentration 50% of sulfuric acid.



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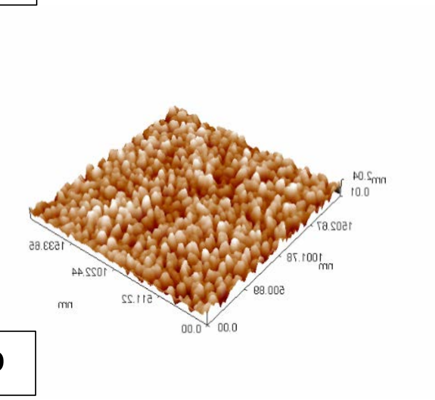

3D

Figure 5: The two-dimensional and three-dimensional AFM image of NC prepared from paper residues at concentration 50% of sulfuric acid, which was sonicated for 60 min.

Table 1: Granularity cumulating distribution and average diameter of NC prepared from paper residues at concentration 50% of sulfuric acid, sonicated for 60 min

Avg. Diameter:78.71 nm								
Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
65.00	12.97	12.97	85.00	13.39	74.90	105.00	4.18	96.23
70.00	14.23	27.20	90.00	6.69	81.59	110.00	0.84	97.07
75.00	17.57	44.77	95.00	5.86	87.45	115.00	2.09	99.16
80.00	16.74	61.51	100.00	4.60	92.05	130.00	0.84	100.00

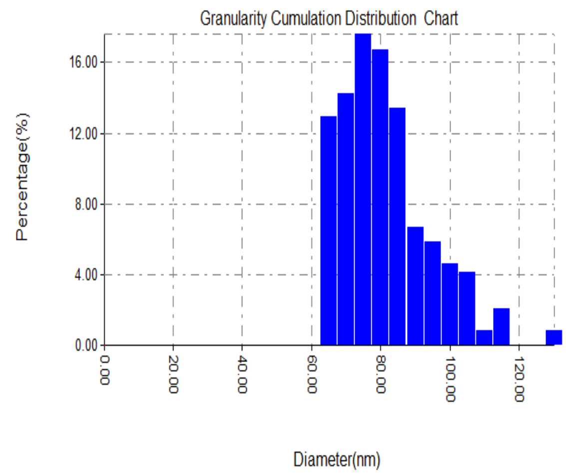

Figure 6: Granularity cumulating distribution of NC prepared from paper residues at concentration 50% of sulfuric acid, sonicated for 60 min

Conclusions

The nano-cellulose was obtained from residues of paper waste isolated by acid hydrolysis using sulfuric acid. Ultrasonic device was used to has be done sonication process of the raw materials and it was obtained a fine powder with good properties that could have been used in other processes and techniques. Fourier transform infrared spectroscopy (FTIR) showed the purity of cellulose by removing lignin and hemicellulose completely, while Atomic Force Microscope (AFM) images showed that the nanocellulose created from rice husks and paper residues is of small nanoparticle and smooth surface and in two dimensions: 2D and 3D. The prepared cellulose nanoparticles can be used in many applications. Therefore, we believe that in the near future, agricultural and industrial wastes containing high cellulose content are very promising sources of low-cost raw materials for nano-cellulose production, as well as other high-value-added biotransformation, thereby minimizing waste, preventing significant damage to the environment, which is eco-friendly.

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