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Extraction of Cellulose Nanoparticles via Modified Thermochemical Processes from Agricultural Wastes

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***Abstract*— Agricultural waste is a critical environmental problem and a major challenge facing environmental pollution. Cellulose extraction from agricultural (wheat straw) wastes is a motivating, sustainable source, and environmentally friendly alternative. In the present investigation, the bleaching process, a thermochemical treatment, was used to treat the agricultural wastes to produce nano-cellulose to reduce its negative environmental effects. The first step of the extraction process begins with removing contaminants, waxes, and other extracts from wheat straw with an alkaline treatment. The second step is the bleaching process with NaClO, followed by treatment with different concentrations of H_2SO_4 and NaOH. All the products were characterized using Scanning X-Ray Diffraction (XRD), Electron Microscope (SEM), and Fourier Transform Infrared (FT-IR). The results showed that cellulose production had an average diameter of 45.06, 56.75, and 30.66 nm when extracted with 40, 50, and 60% H_2SO_4 concentrations. Also, the XRD and FT-IR results confirm the high purity of the produced cellulose nanoparticles (CNPs).**

***Keywords*— Agricultural wastes; Cellulose Nanoparticles (CNPs); wheat straw.**

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I. INTRODUCTION

Agricultural biomass (such as agricultural waste) is a plentiful resource worldwide, considered an alternative source of sustainable materials. Also, it can be used in different applications. The agricultural biomass includes wheat straw, coconut shell, rice husk, and banana pods [1]-[4]. Biomass is one agricultural waste that consists of main materials such as hemicellulose, cellulose, lignin, and ash [2], [5]. Therefore, both the hemicelluloses and cellulose fractions are polymers of sugars. So it is considered a potential source of berserk sugars or other products [6]-[10]. The biomass of lignocellulosic is considered a plentiful and sustainable source due to the production possibility of material besides fuels instead of petroleum products. [11]-[16]. Various methods are used for cellulose extraction from the agricultural biomass, such as the high-pressure process [17], the process of grinding [18], cryo crushing [19], electrospinning and high-intensity ultrasonication process [20], high-speed blending [22], and steam explosion process [21]–[25], and extrusion process [1]-[4]. As a result of the massive challenges of climate change, lignocellulose agriculture waste, sustainable and renewable resources have been considered a likely alternative to cellulose reserves. The environmental problems resulting from fossil fuels will be reduced by increasing using agricultural waste as renewable resources [2], [3]. Many studies have been made in the latest years of crops and agricultural waste [4]. Also, in recent years, cellulose has attracted many researchers' attention because of its various cellulose properties of weightless, biodegradable, biocompatible, and renewable. Although some wheat straw is for energy generation and animal feed, huge quantities of it or rice husk are still burnt [3]-[4]. Previous studies demonstrated that wheat straw contains hemicellulose (17 to 22%), cellulose (25 to 35%), lignin (25 to 30%), and ash (15 to 19%)[4], which are joined together by both intermolecular and intramolecular hydrogen bonds. However, the cellulose polymers are available as a microfibrils structure in nature [6]. Cellulose is a chemical compound considered the most obtainable regenerate polymer that is considered the most common in nature. The structure of cellulose is $C_6H_{10}O_5$ [4]. The effect of various chemicals on the extraction process of cellulose recovery yield of WS was shown in research conducted by Md. Nuruddin et al. [26], where they succeeded in obtaining cellulose from wheat straw by using mixing it with formic acid/peroxyformic acid treatment, following with bleaching and milling process of bleached cellulose. They got a very acceptable ratio in the extraction process; the extracted compounds were about 20.40 % lignin, 9.10 % Cellulose, and 25.02 % of other compounds. In this study, cellulose was isolated from wheat straw using unique processes with a mixture of chemicals materials to produce CNPs with high purity. Moreover, the extraction process of cellulose using several process variables to obtain the most influential factor for producing cellulose with high purity and nanosize such as hydrogen peroxide concentration, and solvent/solid ratio, were studied.

II. Materials and Method

A. Materials

Agricultural waste (wheat straw) collected from the Iraqi farm was used as a raw material to synthesize CNPs products. In addition, other chemicals such as the hydroxide of sodium (NaOH), the acid of hydraulic (HCl), and the acid of sulfuric (H_2SO_4) were imported from the fluke company.

B. Purification and grinding

The distilled water was used to remove the suspended matter, dust, and other contaminants of the agricultural wastes (wheat straw). The process aims to wash these wastes at least three times. After that, the wheat straw was dried under sunlight for 24 hours until the wheat straw became completely dry. Then, the wheat straw is followed with a milling process several times by a mechanical cutting machine; the output of the milling process was passed through sieves of 150 µm to produce wheat straw grinding WSG. Fig. 1 shows the procedure of obtaining CNPs.

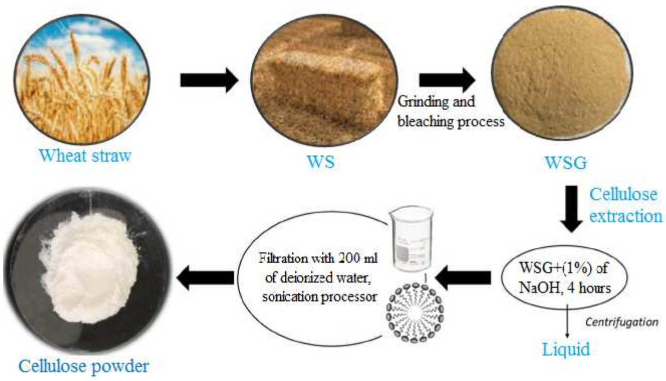


Fig. 1 CNPs preparation steps.

C. Bleaching of the wheat straw (WS)

In the first stage, a 20 g sample of ground WS was added to 200 ml of NaClO at 100ºC for 3 hours under a constant stirring process. Then, the product was filtered by a vacuum pump (VALUE-VE115N) and washed many times with distilled water to make it free of chemicals. The sample was dried at 70ºC for 5 hours to get a fine powder. In the second step, in 250 mL from ($C_2H_4O_3$) acid solution (38% hydrogen peroxide H_2O_2, 50% acetic acid, and 12% distilled water), 20 g of a pre-treatment with the alkaline sample was treated at 70ºC under stirring for 12 hours. The product was filtered under a vacuum, the pH value became 7 after continuous washing with distilled water, and dried in an oven at 70ºC for 12 hours. The bleached wheat straw was labeled as WSB.

D. Preparation of cellulose nanoparticles (CNPs)

The product of the bleaching steps has been hydrolysis in 100 ml of sulfuric acid 45% H_2SO_4 under the stirring process at 35ºC for 5 hours. Then, dilute with deionized water as 150 ml. After that, it was left at room temperature for one day to be cooled down to 10ºC to separate cellulose until the separation was completed. The product was filtered and washed with distilled water many times. Then, it is treated with 1N NaOH until it becomes pH =7. After neutralization, the solution was filtered and collected. Next, 200 ml of deionized water was added to the sample under sonication at 180 min. Finally, the sample was dried at 70ºC for 12 hours, and thus, a perfect powder was obtained. The fine powder was put in a plastic tube; Fig. 2 shows the prepared CNPs.

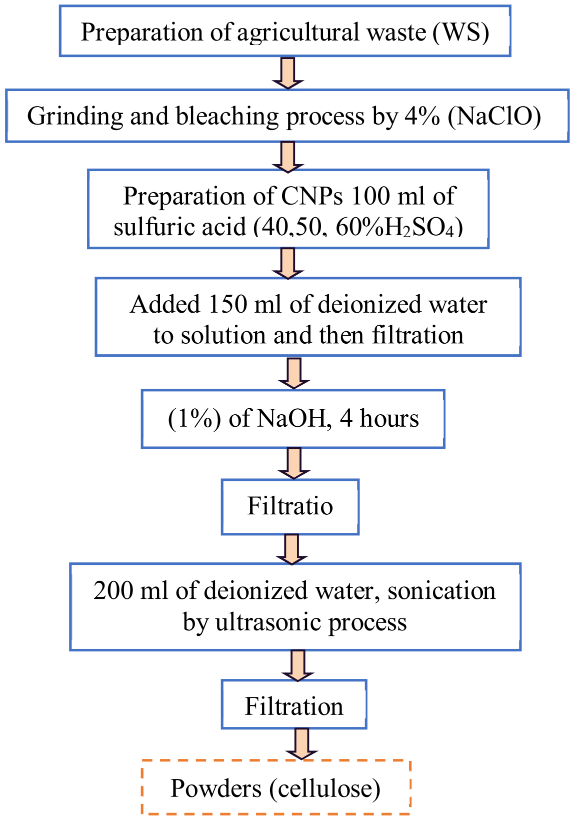
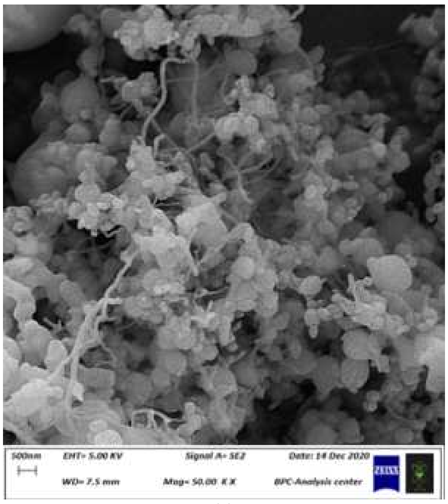


Fig. 2 Extraction steps of CNPs from wheat straw

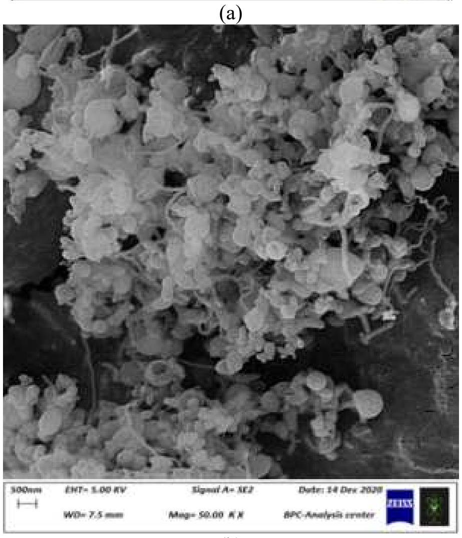
III. Results and Discussion

From the previous studies, the wheat straw's chemical composition is composed of cellulose (38 to 45%), hemicellulose (24 to 28%), lignin (7 to 27%), and ash (3 to 9%) [13]. Factors affecting the concentration of different components varied based on harvesting methods, growing area and season, and testing procedures. The yields of CNPs and residues are shown in Fig. 2. Sulfuric acid concentration had a marked effect on the yield of CNPs. When the sulfuric acid concentration was 60 wt%, the initial cellulose was highly hydrolyzed, resulting in a high CNPs yield.

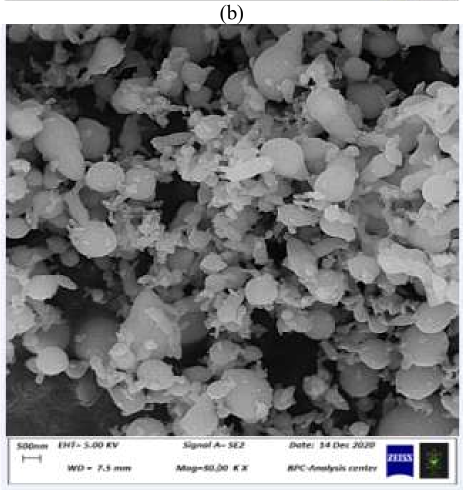
The Field Emission Scanning Electron Microscope (FE-SEM) (Vega3, TESCAN, USA) image of the WS-CNPs powder is given in Fig. 3. The surface morphology of WS-CNPs was analyzed using FE-SEM. Accordingly, it has a disorganized shape with a large agglomeration of particles.



(a)



(b)



(c)

Fig. 3 FE-SEM for CNPs at a) 40%H_2SO_4, b) 50%H_2SO_4, and c) 60%H_2SO_4.

Fig. 4 shows the patterns of X-ray analyses for WS three samples. Cellulose's existence was very obvious as three diffraction peaks in the WS diffraction diagrams in different media. Some peaks were revealed at 16.5° and 22.5° in the WS pattern. Cellulose type and purity of cellulose were confirmed with these peaks. After chemical treatment, the peaks become very clear. The experimental XRD patterns of the final product at 40, 50, 60% H_2SO_4 demonstrate sharp and narrow peaks. This is an indication of the successful extraction process by converting cellulose. Very obvious peaks at around $2\theta = 16.3°$, and 22.6°, can be indexed as (110) and (200) planes represent a typical cellulose structure. Finally, it can be concluded that the formation of CNPs and the degree of CNPs purity are highly affected by the experimental conditions. The results in Fig. 4 show that the highest purity of the extracted CNPs is obtained at 60% H_2SO_4 and followed by 50% H_2SO_4.

The WS-CNPs FTIR spectra (Bruker –Tensor 27/Germany) are shown in Figure (5). The following spectral bands were identified: 3415 cm^{-1}(O-H stretching intramolecular hydrogen bonds for cellulose); 2900 cm^{-1}(C-H stretching), the bands at 1614 cm^{-1} (O-H adsorbed water) indicate that carboxylic acid groups and 1445cm−1(C-H_2 scissoring movement in cellulose) indicate that carboxylate groups exist on the surface. 1160 cm^{-1}(C-O-C stretching vibration).

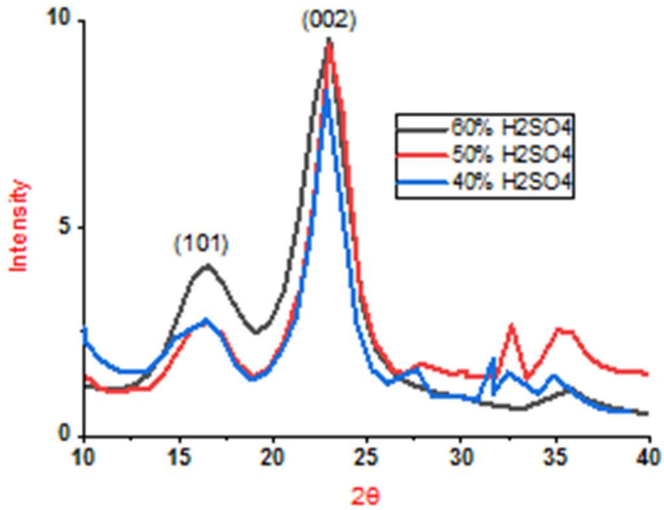


Fig. 4 XRD diffractograms of the extraction CNPs.

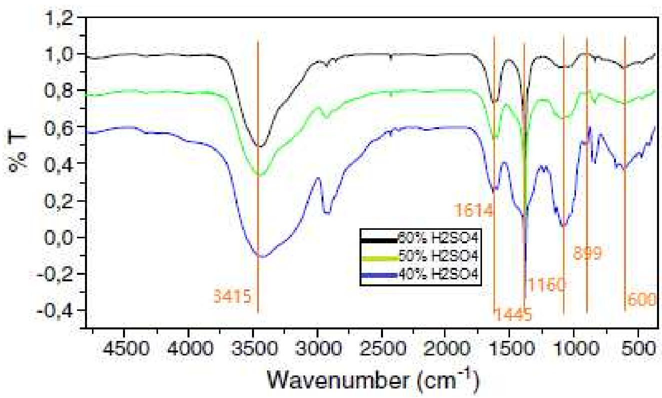
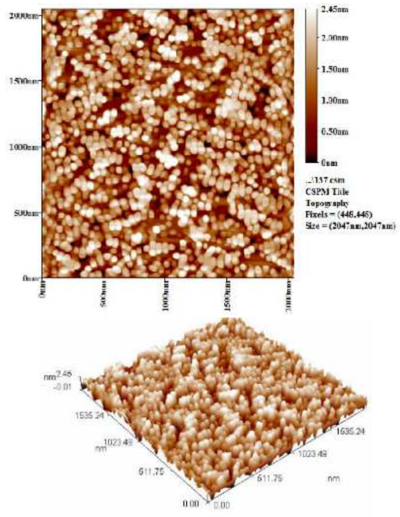
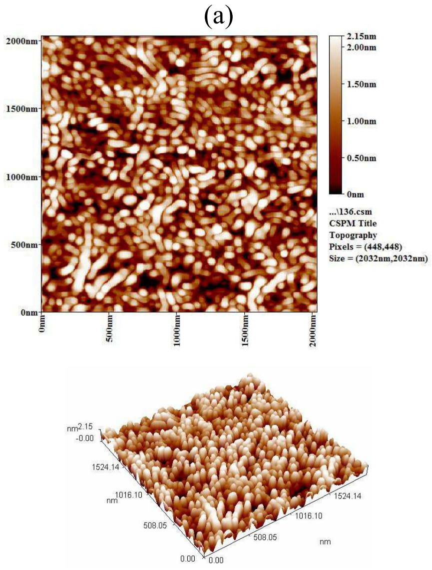


Fig. 5 FT-IR spectrum of cellulose CNPs.

The morphology and diameters of the produced CNPs were strongly affected by the concentration of H_2SO_4 used to extract cellulose. It is studied using AFM (type angstrom, scanning probe microscope, advanced Inc, AA 3000Aº, USA) with (408-406) pixel density, which is visualized particle density, surface, and the topography of cellulose with a high degree of accuracy. Fig. 6a and 6b show the two and three-dimensional surface images of the CNPs extracted at 40 and 50% H_2SO_4. These figures confirm that the CNPs are a tenuous agglomeration. Particle size analysis of the obtained CNPs identifies that the prepared CNPs diameter has an average diameter of 45.06 and 56.75 nm. Also, Fig. 6c shows the particle distribution of CNPs at 60% H_2SO_4. The average particle distribution was 30.66 nm.



(a)



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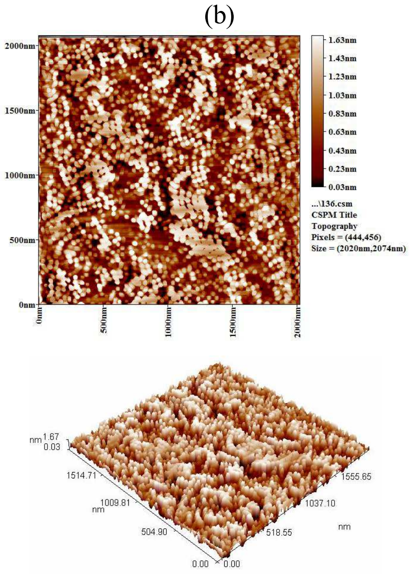

(c)

Fig. 6 AFM image of CNPs extracted of two-dimensional and three-dimensional, prepared from WS at (a) 40, (b) 50, and (c) 60% of sulfuric acid.

IV. CONCLUSION

CNPs were successfully prepared from wheat straw by chemically modified precipitation technique. The use of NaClO in the bleaching process and H_2SO_4 in the preparation of CNPs was proved to be very effective in the digestion of WSA. NaOH treatment followed by peracetic acid bleaching effectively reduced the lignin content in WS. Also, the chemical treatment processes were with affective parameters for producing high purity nano-cellulose with particle sizes 45.06 to 30.66 nm. The cellulose crystallized as interconnected webs of tiny nanoparticles with diameters < 100 nm to several micrometers. From an engineering point of view, the modified production method is economical, flexible non-complicated, and produces high-quality nano-cellulose from agriculture wastes. It is considered an environmentally friendly and sustainable process. However, this process could be used for production on an industrial scale.

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