Comparation of hydrolysis acid and ball milling methods in extraction Nano structure from walnut shell

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Abstract: This study compared the properties of nano structure extraction from walnut shell using mechanical and chemical methods. Walnut shell is an agro- waste with source of lignin and cellulose. Mechanical method including using ball mill with different time and in present of additive and without additives and for chemical method hydrolysis acid were used.   This study highlights the particle size and morphology and efficiency these methods in nano structure extraction. The result showed mechanical method is unable to extract nanoparticle and just re-shape the walnut shell. Milling time were also found important in morphology of fiber extracted. FE-SEM images represented that structure mean diameter of using ball mill was 1± 5 μm while hydrolysis acid method extract nano particle with mean diameter of 40± 20 nm.

Keywords: walnut shell, nano structure, ball milling, hydrolysis acid

1. Introduction

Increasing of population and using agricultural by product has resulted in the increasing of agricultural waste and environmental concerns. Recent studies are focused on making this agro-waste as recyclable or biodegradable products in different field.

Walnut is cultivated mostly in humid regain of Iran. Iran is third in walnut production in the world [1]. Walnut shell because of hardness don't used and mostly is thrown away. This material is an attractive source of cellulose and lignin.

Cellulose is one of the most abundant and widely used natural polymeric materials in the world [2] and often contains a mixture of various impurities such as lignin, pectin, hemicellulose, fat and protein. The natural properties of cellulose structure such as shape, length and diameter as well as their efficiency depend on the source and method of extraction [3]. Cellulose molecules are linear and have a strong tendency to form hydrogen bonds. The assembly of these cellulose molecules forms microfibers. Microfibers are composed of two regions: regular (crystalline) and irregular (amorphous) [4]. Hydrogen bonds in crystalline regions are very strong and cause insolubility in solvents such as water. While the cellulose chains of the amorphous part are longer apart and are more available for hydrogen bonding and they are easily hydrolyzed by mineral acids and the crystalline part is separated from each other [5, 6].

Nanomaterials are categorized by geometries into fibrous (NF), layered (NL) and particle (NP) [7]. Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of < 100 nm can be considered a nanoparticle [8]. In the present time nano structure are widely used in many dosages from due to their good solubility, high surface area, less size and better penetrability.

Nanoparticle classified according to sizes as fine (particles are sized between 100 and 2500 nanometers) and ultrafine (particles cover a range between 1 and 100 nanometers). Nanoparticles are also sized between 1 and 100 nano meters similar to the ultrafine particles [8].

Nano structure efficiency depends on the extraction method employed and their sources [9] . Nanoparticles can be synthesized within different time according to plant type and phytochemical concentration [10, 11] and by using the various technics such as mechanical and chemical methods. Mechanical methods such as high-pressure homogenization (HPH), micro fluidization, ball milling, cryocrushing, high-intensity ultrasonication and chemical methods such as hydrolysis acid, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), periodate, and carboxymethylation. In mechanical methods hydrogen bonds and cell wall structure break down by shear forces but nano structure extraction by hydrolysis acid result by destroying of amorphous area of cellulose fibers [9, 12]. Many unique properties of nanoparticles require not just the particles to be of nano-sized, but also the particles be dispersed without agglomeration [13].

Nanocellulose is a unique nano structure derived from ordinary biomass and it is an environmentally friendly compound. various efforts have been prepared to use nanocellulose due to its tremendous functionality i.e., greater surface area, low in cost, biotic possessions, lower density, low toxicity, and significant mechanical properties [3, 14].

Cellulose nanomaterials have interesting properties such as high mechanical strength, biodegradability, size, shape and low toxicity [3]. Cellulose contains hydroxyl groups that make prone to chemical reactions [3, 15]. Nanocellulose materials are used in the production of bio-components, antimicrobial barrier or coating materials in the food industry, pharmaceutical sectors, production of nanocomposite materials and environmentally utilization such as soil stabilization and dust control [6, 14, 16]. Hydroxyl groups of nanocellulose interact with organic compounds and heavy metals [17] and with remove of pollutant act as filtering membrane [18-20].

There are many different studies about nano structure extraction using hydrolysis acid and ball milling such as Tsuzuki and McCormick, reviewed mechanochemical synthesis of nanoparticles. Their review showed in order to produce nano particle it is necessary to avoid combustion during ball milling, reduce volume fraction between particles and control ball milling time and grinding media size [13].

Taleshi and Hosseini, evaluated crystal process of ball-milling on growth and diameter of carbon nanotube on iron nanoparticles. The results showed that using ball milling method can **effects** on diameter and morphology of synthesized carbon nanotubes at 925 C, in this way, with increasing temperature, the diameter of the particles increases [21].

Rahimi Kord Sofla, compared properties of cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) extracted from sugarcane bagasse respectively using hydrolysis acid and ball mill. The result showed CNC was needle- like and CNF was rope- like in structure and mean diameter of CNC was 148 nm while CNF had a median size 240 ± 12 nm and 10 μm [22].

Kasiri and Fathi, studied isolation and characterization of cellulose nanocrystals (CNC) from pistachio shell using hydrolysis acid and their application to stabilize Pickering emulsion. FE-SEM images represented both rod-like and spherical shapes of CNC and TEM image showed particles with mean diameter of 68.8 ±20.7 nm [4].

Souza et al, compared compositional, thermal, morphological and dimensional properties of cellulose nanostructure obtained through chemical and mechanical isolation processes. The result showed their average size for chemical method was smaller than mechanical method and the CNS agglomeration by chemical isolation was smaller than mechanical [12].

Radakisnin et al, investigated the isolation and utilization of cellulose nanofibers (CNF) from Napier fiber (Pennisetum purpureum) via ball-milling assisted by acid hydrolysis. First ground fibers treated with hydrolysis acid sulfuric and after chemical treatment milling was done using zirconia balls with a diameter of 15 mm for 180 min in deionized water and finally resulting suspension was sonicated. Ultrasonication was done in an ice-bath to prevent heat-up where de sulfation can occur due to the presence of sulfate groups on the fibers. FE-SEM results displayed a compact structure of the nanofiber

network, due to the freeze-drying effect that resulted in the agglomeration of the nano-fibers [23].

This study compared nano structure obtained from two methods of hydrolysis acid and ball milling. The difference between morphology and size was studied using field emission scanning electron microscopy (FESEM).

2. Materials and Methods

Walnut was obtained from Damavand city in Iran. For extraction nano cellulose by chemical method sulfuric acid (0/95-0/98 wt%), sodium chlorite and sodium hydroxide purchased from Sigma-Aldrich and used without further purification. The chemical method was done in University of Tehran and ball milling was done in industrialization center for applied nanotechnology (ICAN). Zirconia balls with diameter 1 mm and rotational speed 1600 rpm used as dry ball milling.

Nano cellulose extraction using hydrolysis acid sulfuric

In order to extract of nano cellulose using chemical method we used hydrolysis acid method according to [24, 25]. Acid hydrolysis is the most widely employed methods for obtaining crystal nano cellulose [6].

• First step: hand griding

For extracting cellulose, firstly the walnut shell washed to remove any impurity and dirty, then it ground and milled and passed through a 60-mesh sieve. The product was called WS.

• Second step (Alkaline treatment): hemicellulose removing due to breakage of connections between intermolecular α- and β-aryl ether of hemicellulose and lignin [26, 27].

Firstly, sodium hydroxide aqueous solution of 2% (w/v) prepared. 2g WS mixed with 20ml NaOH (2% wt) for 4 h at 100 °C under mechanical stirring. The alkali treatment conducted 4 times and after each treatment, the fibers filtered and washed with distilled water to remove the alkali components. Finally, they were dried at 50 °C for 24 h in an air-circulating oven. The weight product was 1.4 g and called N-WS.

• Third step: bleaching: this process not only purified cellulose but also reduces the size and enhances the crystallinity and surface area [6, 28].

In this step firstly buffer solution was prepared with a mixture made of 2.7 g of NaOH and 7.5 ml of glacial acetic acid, diluted to 100 ml of distilled water. 1.4 g N-WS fibers then were bleached with 14g mixture made of equal parts of (v:v) sodium chlorite (1.7% $NaClO_2$ in water) and buffer solution. The bleaching treatment was performed at 80 °C for 6 h under constant agitation and was repeated twice. The bleached fibers were washed several times with distilled water for reaching neutral pH and then dried at 50 °C for 24 h in an air-circulating oven (B-WS).

• Forth step: nano particle extraction

1 g B-WS added to 8.75 ml sulfuric acid (64%) under constant stirring at 45 °C for 1 h. Finely, to stop reaction distilled water was added and centrifuged at 10000 rpm for 15 minutes. The product was then washed with distilled water until it reached a neutral pH. The dialyzed solution was placed in a freeze dryer for 24 hours to precipitate the nano-particles. The by product called CNC.

Nano structure extraction using ball milling at different time

In order to extract cellulose nanofiber, it is necessary to subject cellulosic fiber to mechanical treatment [6]. Ball mill consists of balls filled in hallow cylindrical shell that rotate around its axis [29] and act as a top- down technique to form material in smaller scale [30]. In this study ball milling method in different condition (time and chemical modifier) used to extract nanofiber from walnut shells.

Treatment 1: ball milling for 2 hours

In first step, and before milling, walnut shell was dewaxed and dirty removed and then grind handy. After that WS was sent to crystallography lab of Tehran university. Ball mill was done for 2 hours.

Treatment 2: ball milling without additive

After first step, WS was sent to ICAN lab. Ball mill was done for 6 hours at 400 rpm as 10-minute ran and 10-minute rest. The aim of rest time was avoiding of increasing temperature and particles collecting.

Treatment 3: ball milling with additive

In this treatment in order to create friction between article and clogging prevention additive was added. The additive used was oleic acid according to the lab experiences. Oleic acid equally added to WS and then ball mill was done for 6 hours at 400 rpm as10-minute ran and 10-minute rest as like as treatment 2.

a)   (b)

Figure 1. nano extraction of walnut shell (a) using ball milling; (b) grinding handy

3. Results and discussion

The morphology of nano crystal cellulose studied by microscopic technics. In order to compare different method and their application in nano structure extraction FE-SEM was used.

Figure 2, shows FE-SEM images of CNC extracted by hydrolysis acid method at 41.5 μm scale (a), 2.77 μm scale (b) and 1.38 μm scale (c). according the other researches after hydrolysis acid treatment, most of impurities remove, the hemicellulose hydrolyze and lignin depolymerize, cellulose structure destroys and finally the particles size decrease [4, 15]. [31] also explained hydrolysis acid decrease size due to converting of cellulose I into various crystalline forms. Theis figures showed CNCs mostly spherical. Cellulose extracted consist of particle of several microns to nano and the mean diameter of spherical nanocrystals was 40± 20 nm. This size and shape were in agreement with other studies such as [1, 4]. As show in figure (c) particle hardly agglomerated. clogging is a drawback in isolation of nano structure from hard wood pulps as pointed [32]. There are three opinions for this drawback the first opinion is using freeze dryer and second is ultrasonication was do not in an ice-bath to prevent heat-up where de-sulfation can occur due to the presence of sulfate groups on the fibers and the third is due to high specific area and strong

hydrogen bind between crystallites. A similar outcome was observed by [23] and [4], their result showed the extraction of CNC from microcrystalline cellulose using acid hydrolysis assisted by ultrasonication degraded the impurities and decreased the diameter of the CNC, breaking them down into nano-sized particles and using freeze dryer effect on particles agglomeration.

(a)   (b)   (c)
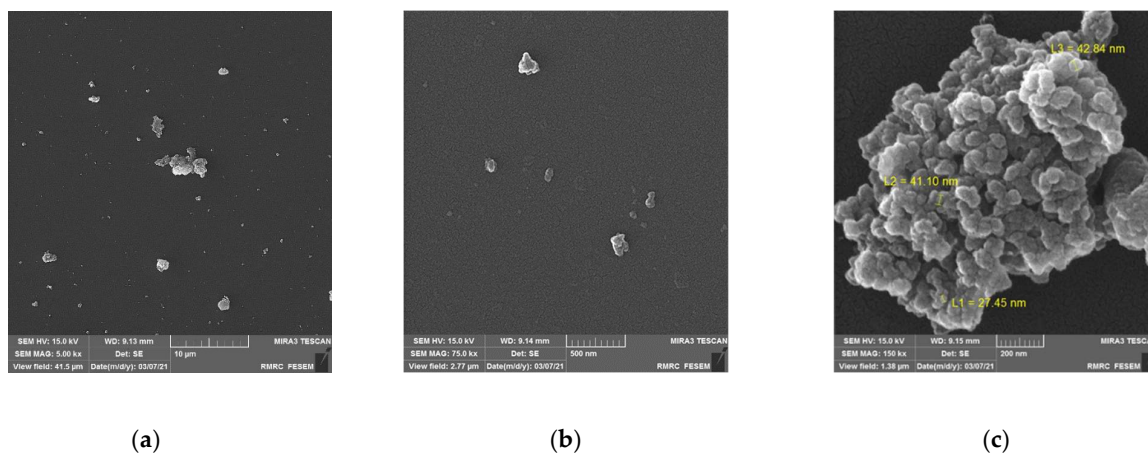
Figure 2. FE-SEM of nano cellulose extraction by hydrolysis acid: (**a**) in view field 41.5 μm; (**b**) in view field 2.77 μm; (**b**) in view field 1.38 μm

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The different conditions of ball milling (time, speed and present of solvent) had effect on agglomeration and morphology as showed by [33, 34]. The comparison of FE-SEM images in same magnification with different ball milling time as showed in Figure 3, (a,b,c) demonstrate that the ball milling time had a remarkable influence on the diameter and morphology of nano structure, same result was obtained by [35]. with increasing time, the particle size increase it can demonstrate this theory that high time of ball milling led to micron- sized particles due to high temperature and finally agglomeration enhance. This is a result that pointed by [13].

The comparation images FE-SEM for same time ball milling in present and absent oleic acid for two magnifications showed particles in present oleic acid become smaller than without it (Figure 4). It could be due to the prevention agglomeration by oleic acid. Oleic acid act as chemical modifier and improve the efficiency of chemical reaction. [36] applied maleic anhydride as chemical modifier and same result was observed.

The use of mechanical techniques is limited due to disadvantages like high energy and water consumption in order to overcome the interfibrillar hydrogen bonds and clogging and chemical methods take a long time and produce waste water in each section. These challenges were showed in some study such as [6, 23, 37-39]. According to [29] disadvantage of using ball mill including irregular shape of nanomaterial and lang milling time. The problem of materials de-crystallization during ball milling also showed by [30]. this irregularity can be obviously showed in figures 2 and 3 compared to 1.
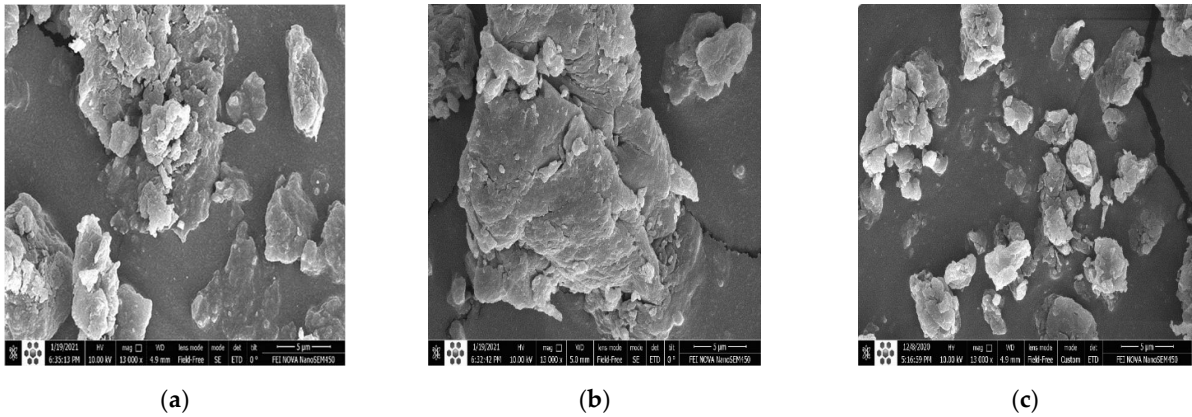
Figure 2. FE-SEM of nano cellulose extraction by ball milling in different conditions: (**a**) 6 hours ball milling with additive; (**b**) 6 hours ball milling without additive; (**b**) 2 hours ball milling.
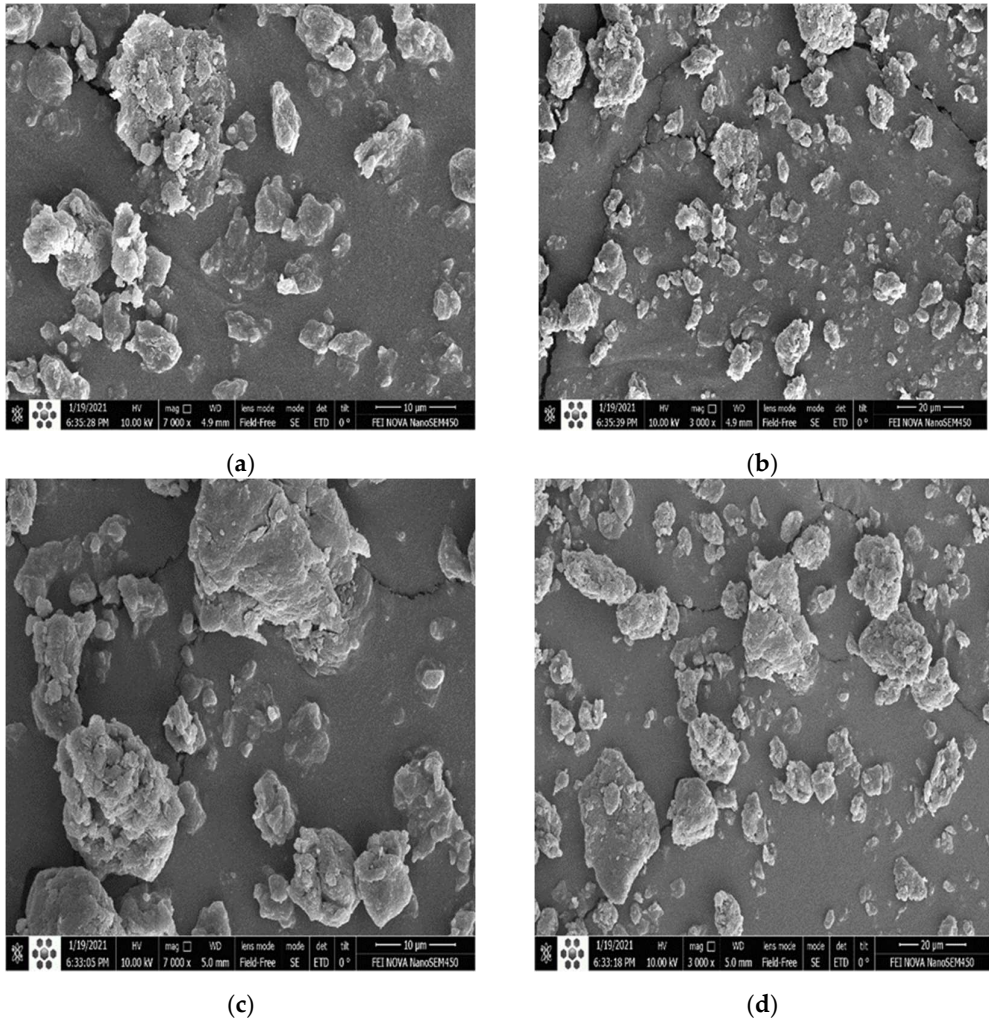
Figure 2. FE-SEM of nano cellulose extraction by ball milling in same time: (**a**) 6 ball milling with additive in 7000 magnification; (**b**) 6 ball milling with additive in 3000 magnifications; (**c**)

6 ball milling without additive in 7000 magnifications; (**d**) 6 ball milling without additive in 3000 magnifications

4. Conclusions

In this study, nanocellulose was isolated from walnut shell via sulfuric acid hydrolysis and mechanical process to obtain distinct morphologies and surface properties. Hydrolysis acid sulfuric destroyed amorphous structure and produced CNCs. While ball milling breaks down the hydrogen bound inter particle and deformed them and create small particles. Fe-SEM image showed different morphologies, with both samples displaying a tendency to agglomerate. The average CNS sizes varied with the method: 40± 20 nm for CNS-chemical samples and 1± 5 μm for WS-mechanical samples.

Generally, this study showed in order to extracting nano structure, a combination of mechanical, and chemical treatment under appropriate condition results in better yield than adopting a single treatment option.

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