Article

Investigation of Nano structure's morphology extracted from walnut shell using hydrolysis acid and ball milling methods

Zahra Feizi [1], Alireza Shakeri [2] and Abolfazl Ranjbar[1]*

[1] *Department of Desert Studies, Faculty of Natural Resouces and Earth Science, University of Kashan, Iran*

[2] *Faculty of chemistry, University of Kashan; alireza.shakeri@ut.ac.ir*

* Correspondence: aranjbar@kashanu.ac.ir

Abstract: In the current **study nanocellulose was isolated from walnut shell using mechanical and chemical methods. This study highlights the particle size, morphology and these methods' efficiency in nano structure extraction. The difference between morphology and size of the particles (of the both extracted methods) were investigated by field emission scanning electron microscopy (FESEM). Walnut shell is an agro-waste material with source of lignin and cellulose. Ball milling with different times, in the presence and absence of additive and acid hydrolysis were used as mechanical and chemical methods, respectively. The result showed mechanical method is unable to extract nanoparticle and just reshape 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

Population increases and, development and exploitation of 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. Agricultural waste are considerable because of acceptable mechanical properties, environmentally friendly, cheap and availability [1]

Walnut (*Juglans regia* L.) is cultivated mostly in humid regains. Iran is third in walnut production in the world [2]. Walnut outer shell (endocarp) contains cellulose (25.5% wt), hemicellulose (22.2% wt), lignin (52.3% wt) and other substance [3, 4]. 22% of walnut shell are composed of cellulose [4]. endocarp doesn't used and mostly is thrown away due to its hardness.

Cellulose is one of the most abundant and widely used natural polymeric materials in the world [5, 6] 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 [7]. Linear molecules of cellulose are composed of β-1,4-linked anhydro-D-glucose [1, 8] and have a strong tendency to form hydrogen bonds with the adjacent glucose unit [9, 10]. The assembly of these cellulose molecules forms microfibers [11]. Microfibers are composed of two regions, called crystalline and amorphous [12]. Hydrogen bonds in crystalline regions are very strong and cause insolubility in solvents such as water. While the cellulose chains in 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 [13, 14].

Nanomaterials are categorized by geometries into fibrous (NF), layered (NL) and particle (NP) [15]. 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 <

 doi:10.20944/preprints202203.0184.v2

100 nm can be considered a nanoparticle [16]. In the present time, nano structure are widely used in many dosages due to their good solubility, high surface area, less size, better penetrability, low density and high mechanical properties [1] .

Nano structure efficiency depends on the extraction method employed and their sources [17]. Nanoparticles can be synthesized within different time according to plant type and phytochemical concentration [18, 19] 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 [1] and chemical methods such as hydrolysis of acid, periodate, and carboxymethylation. Sulfuric acid hydrolysis is the most widely employed methods for obtaining crystal nano cellulose [6]. In this method, sulfate ions esterify hydroxyl groups of cellulose and nanocellulose dispersed as a stable collied system [20, 21]. 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 [17, 22]. Many unique properties of nanoparticles require not just the particles to be of nano-sized, but also the particles be dispersed without agglomeration [23].

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 [7, 24].

Cellulose nanomaterials have interesting properties such as high mechanical strength, biodegradability, size, shape and low toxicity [7]. 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 [14, 24, 25]. Hydroxyl groups of nanocellulose make prone to chemical reactions [7, 9]and interact with organic compounds and heavy metals [26] and with remove of pollutant act as filtering membrane [27-29].

There are many 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 [23].

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 **affect** on diameter and morphology of synthesized carbon nanotubes, in this way, with increasing temperature, the diameter of the particles increases [30].

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 [31].

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 [12].

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 [22].

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 de-ionized water and finally the 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 nanofibers [32].

Zheng et al., isolated nanocellulose from walnut shell using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation and sulfuric acid hydrolysis. The results exhibited an irregular block structure and rectangular shape from TEMPO and hydrolysis acid method [33].

Ago et al, showed, morphology and cellulose structure affected under ball-milling, due to interaction between solvent and cellulose. Their FTIR observation demonstrated under ball-milling hydrogen bonds formed in the crystalline structure were changed depending on the solvent, therefore, effects on morphology [34].

Lu et al, studied the effects of ball-milling time, reaction temperature and ultrasonication on yield of cellulose nanocrystal via one-pot tandem reactions with 4-dimethylaminopyridine. They investigated yield of nanocellulose product increase with the ball mill time until 2 h and decrease when the ball-milling time is extended to 3 h, because only some of hydroxyl group can acylated [35]

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. All chemical used without any purification. In the whole process, distilled water was used. 4-cape planetary ball mill with argon gas injection manufactured by Amin Asia Fanavar Pars – Iran used. Zirconia balls with diameter 1 mm and rotational speed 1600 rpm used for 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 [33, 36, 37].

- First step: hand griding

For cellulose extracting, 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 [38, 39].

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 produce 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.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 March 2022 doi:10.20944/preprints202203.0184.v2

- Third step: bleaching: this process not only purified cellulose but also reduces the size and enhances the crystallinity and surface area [14, 40].

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). B-WS wight calculated 1 g.

- 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. Next, the solution was placed in a freeze dryer for 24 hours to precipitate the nanoparticles. 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 [14]. Ball mill is a mechanical technique to produce fine particle and consists of balls filled in hallow cylindrical shell that rotate around its axis [41] and act as a top-down technique to form material in smaller scale [42]. 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 the first step, and before milling, walnut shell was dewaxed and dirty removed and then grind handy. Next, 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. The processing was carried out with repeated milling and pausing of 10 min each to avoid overheating 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 as 10-minute ran and 10-minute rest as like as treatment 2.

a)

(**b**)

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

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 31 March 2022 doi:10.20944/preprints202203.0184.v2

Scanning Electron Microscopy

The nano cellulose extracted from walnut shell were observed using a field-emission scanning electron microscope (SEM) JSM-7001F (Jeol Ltd, Japan). Walnut shell powders were coated with a thin gold layer and imaged at an accelerating voltage of 15.0 kV.

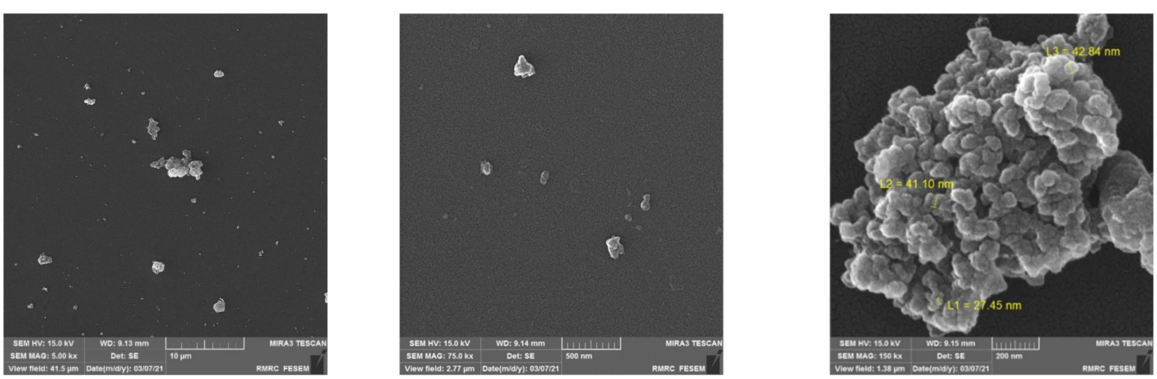
3. Results and discussion

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.

Investigation of acid hydrolysis method

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 to the other researches after hydrolysis acid treatment, most of the impurities remove, the hemicellulose hydrolyze and lignin depolymerize, cellulose structure destroys and finally the particles size decrease [9, 12]. [43] also explained hydrolysis acid decrease size due to converting of cellulose I into various crystalline forms. The size and roughness of nano-cellulose decreased during isolation process due to removal non cellulosic materials. Same outcome demonstrated in review by [1]. As showed in figure 2 (a) cellulose extracted consist of particle of several microns to nano and the mean diameter of spherical nanocrystals was 40± 20 nm. These figures also showed CNCs mostly spherical. This size and shape were in agreement with other studies such as [2, 12]. As show in figure 2(c) particle hardly agglomerated. Agglomeration is a drawback in isolation of nano structure from hard wood pulps as pointed [44]. There are three opinions for agglomeration 1) using freeze dryer 2) 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 3) due to high specific area and strong hydrogen bind between crystallites. A similar outcome was observed by [32] and [12], 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.

One drawback of hydrolysis acid metho is waste water production in washing process in order to pH neutralization. This is a problem pointed by many studies such as [9, 45].



(**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.

 doi:10.20944/preprints202203.0184.v2

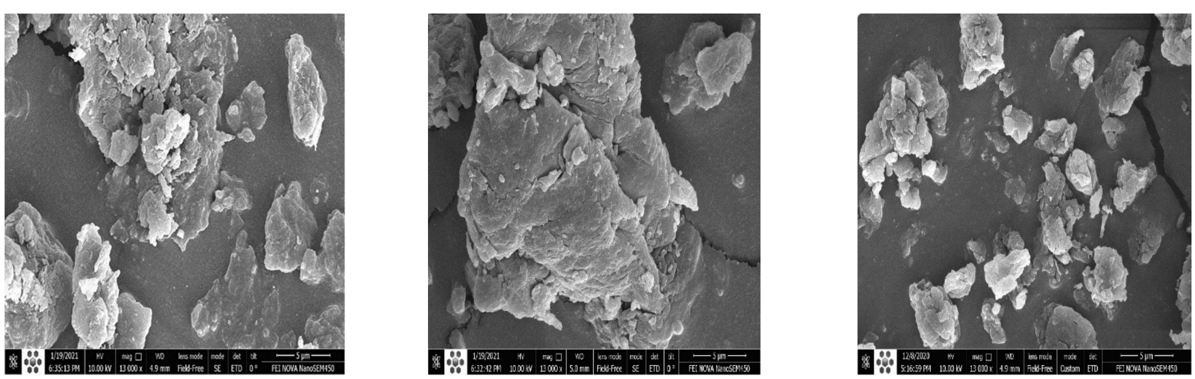
Investigation of ball milling method

The different conditions of ball milling (time, speed and present of solvent) had effect on cellulose structure and morphology[34, 41, 46]. As showed by [1] during fibrillation by mechanical method, nano fiber cellulose tends to agglomeration owing to increasing number of hydrogen bonds and specific surface area. [34] observed that using ball milling globular particles aggregated (5–10 μm diameter) and degree of crystallinity was low.

Microscopic images evident mixture of almost spherical shapes and rough surfaces with not homogenous size. This irregularity illustrates the impurities presence and hydrogen bonding between fibers, as showed by [6]. The use of mechanical techniques is limited due to disadvantages like taking a long time, high energy and water consumption in order to overcome the interfibrillar hydrogen bonds. These challenges were showed in some study such as [14, 32, 47-49]. According to [41] disadvantage of using ball mill including irregular shape of nanomaterial and long milling time. The problem of materials de-crystallization during ball milling also showed by [42]. This irregularity can be obviously showed in figures 2 and 3 compared to 1.

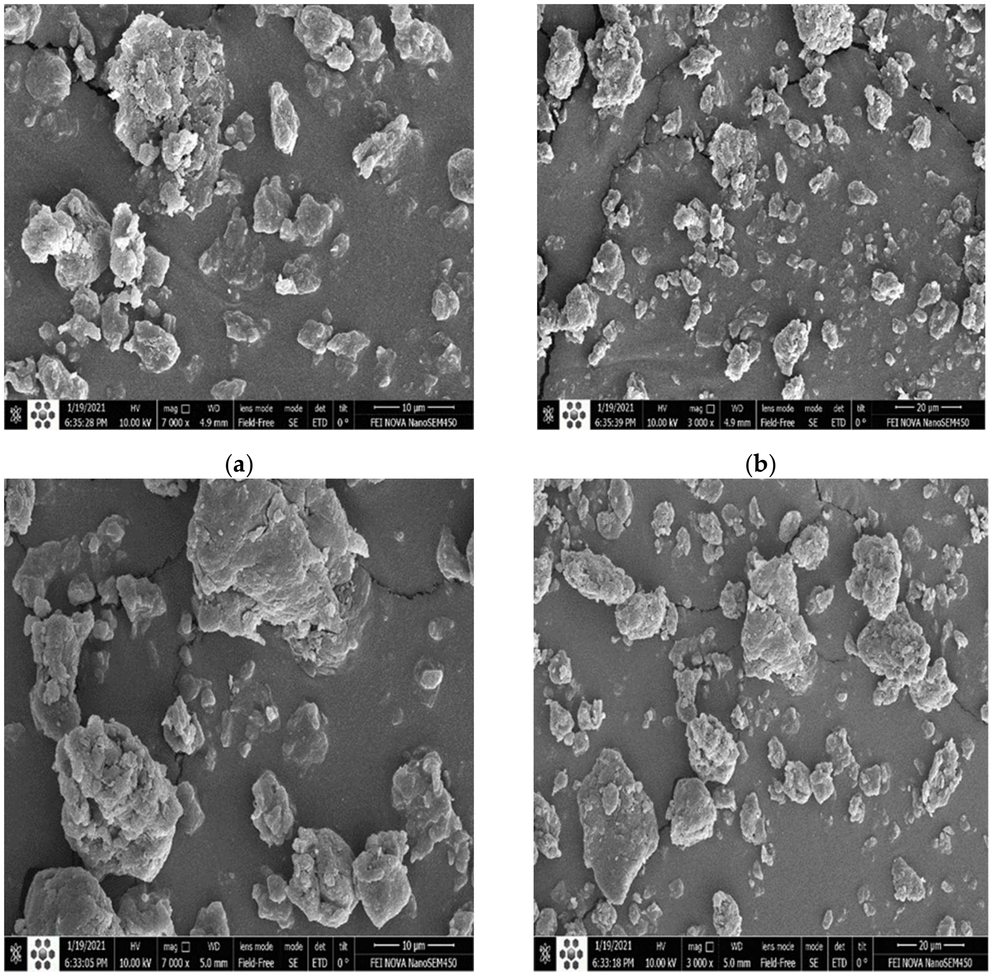
The comparison of FE-SEM images in same magnification with **different ball milling time** as showed in Figure 3, (a, b, c) demonstrate that the ball milling time had a remarkable influence on the diameter and morphology of nano structure, same result was obtained by [46]. With increasing time, the particle 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 [23]. [46] carry outed nanoparticles diameter depended on ball-milling time. They also noted, by selecting an appropriate mall-milling time, nano particles with similar morphology can be prepared.

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 of agglomeration by oleic acid.



(**a**) (**b**) (**c**)

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.



(a) (b) (c) (d)

Figure 2. FE-SEM of nano cellulose extraction by ball milling in same time: (a) 6 hours ball milling with additive in 7000 magnifications; (b) 6 hours ball milling with additive in 3000 magnifications; (c) 6 hours ball milling without additive in 7000 magnifications; (d) 6 hours 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 both methods have some drawbacks in nano cellulose extraction. In environmentally friendly view suggested mechanical method use.

Author Contributions: The chemical method was done in University of Tehran and ball milling was done in industrialization center for applied nanotechnology (ICAN**).**

Funding: This research received no external funding**.**

 doi:10.20944/preprints202203.0184.v2

Abbreviations

WS walnut shell
N-WS walnut shell treated by NaOH
B-WS walnut shell after bleaching
CNC nanocellulose obtained via sulfuric acid hydrolysis

References

1. Rajinipriya, M., et al., *Importance of Agricultural and Industrial Waste in the Field of Nanocellulose and Recent Industrial Developments of Wood Based Nanocellulose: A Review.* ACS Sustainable Chemistry & Engineering, 2018. **6**(3): p. 2807-2828.
2. Hemmati, F., et al., *Synthesis and characterization of cellulose nanocrystals derived from walnut shell agricultural residues.* Int J Biol Macromol, 2018. **120**(Pt A): p. 1216-1224.
3. Pirayesh, H., A. Khazaeian, and T. Tabarsa, *The potential for using walnut (Juglans regia L.) shell as a raw material for wood-based particleboard manufacturing.* Composites Part B: Engineering, 2012. **43**(8): p. 3276-3280.
4. Demirbaş, A., *Relationships between lignin contents and fixed carbon contents of biomass samples.* Energy Conversion and Management, 2003. **44**(9): p. 1481-1486.
5. Sun, X., et al., *Cellulose Nanofibers as a Modifier for Rheology, Curing and Mechanical Performance of Oil Well Cement.* Scientific Reports, 2016. **6**(1): p. 31654.
6. Mahmoud, Y., Z. Safidine, and N. Belhaneche-Bensemra, *Characterization of microcrystalline cellulose extracted from walnut and apricots shells by alkaline treatment.* Journal of the Serbian Chemical Society, 2021. **86**: p. 11-11.
7. Phuong, H.T., et al., *Cellulose Nanomaterials as a Future, Sustainable and Renewable Material.* Crystals, 2022. **12**(1): p. 106.
8. Klemm, D., et al., *Nanocelluloses: a new family of nature-based materials.* Angew Chem Int Ed Engl, 2011. **50**(24): p. 5438-66.
9. Phanthong, P., et al., *Nanocellulose: Extraction and application.* Carbon Resources Conversion, 2018. **1**(1): p. 32-43.
10. Moon, R.J., et al., *Cellulose nanomaterials review: structure, properties and nanocomposites.* Chemical Society Reviews, 2011. **40**(7): p. 3941-3994.
11. Oliveira, F.B.d., et al., *Production of cellulose nanocrystals from sugarcane bagasse fibers and pith.* Industrial Crops and Products, 2016. **93**: p. 48-57.
12. Kasiri, N. and M. Fathi, *Production of cellulose nanocrystals from pistachio shells and their application for stabilizing Pickering emulsions.* International journal of biological macromolecules, 2018. **106**: p. 1023-1031.
13. Wu, Y., *Nanocellulose extraction and surface modification toward active packaging applications*, in *Biological engineering (MU)*. 2017, Missouri-Columbia.
14. Mateo, S., et al., *Nanocellulose from Agricultural Wastes: Products and Applications—A Review.* Processes, 2021. **9**(9): p. 1594.
15. Thostenson, E.T., C. Li, and T.-W. Chou, *Nanocomposites in context.* Composites science and technology, 2005. **65**(3-4): p. 491-516.
16. Kumari, B., *A Review on Nanoparticles: Their Preparation method and applications.* Ind Res J Pharm Sci, 2018. **5**(2): p. 1420.
17. Menon, M.P., R. Selvakumar, and S. Ramakrishna, *Extraction and modification of cellulose nanofibers derived from biomass for environmental application.* RSC advances, 2017. **7**(68): p. 42750-42773.
18. Karimi, P., et al., *Arsenic Removal from Mining Effluents Using Plant-Mediated, Green-Synthesized Iron Nanoparticles.* Processes, 2019. **7**(10): p. 759.
19. Arsiya, F., M.H. Sayadi, and S. Sobhani, *Green synthesis of palladium nanoparticles using Chlorella vulgaris.* Materials Letters, 2017. **186**: p. 113-115.

20. Lu, P. and Y.-L. Hsieh, *Preparation and properties of cellulose nanocrystals: rods, spheres, and network.* Carbohydrate polymers, 2010. **82**(2): p. 329-336.
21. Das, K., et al., *A study of the mechanical, thermal and morphological properties of microcrystalline cellulose particles prepared from cotton slivers using different acid concentrations.* Cellulose, 2009. **16**(5): p. 783-793.
22. Souza, A.G.d., et al., *Cellulose nanostructures obtained from waste paper industry: a comparison of acid and mechanical isolation methods.* Materials Research, 2017. **20**: p. 209-214.
23. Tsuzuki, T. and P.G. McCormick, *Mechanochemical synthesis of nanoparticles.* Journal of Materials Science, 2004. **39**(16): p. 5143-5146.
24. Gupta, G.K. and P. Shukla, *Lignocellulosic Biomass for the Synthesis of Nanocellulose and Its Eco-Friendly Advanced Applications.* Front Chem, 2020. **8**: p. 601256.
25. Abitbol, T., et al., *Nanocellulose, a tiny fiber with huge applications.* Current Opinion in Biotechnology, 2016. **39**: p. 76-88.
26. Wang, S., et al., *Facile fabrication of an effective nanocellulose-based aerogel and removal of methylene blue from aqueous system.* Journal of Water Process Engineering, 2020. **37**: p. 101511.
27. Goncalves, J., et al., *Cellulose nanofibres (CNF) for sulphate resistance in cement based systems.* 2019. **99**: p. 100-111.
28. Tan, H.-F., B.S. Ooi, and C.P. Leo, *Future perspectives of nanocellulose-based membrane for water treatment.* Journal of Water Process Engineering, 2020. **37**: p. 101502.
29. Wertz, J. and I. Schneiders, *Filtration media: Advantages of nanofibre coating technology.* Filtration & Separation, 2009. **46**(4): p. 18-20.
30. Taleshi, F. and A.A. Hosseini, *Evaluation of catalyst ball-milling process on growth and diameter of carbon nanotubes on iron nanoparticles.* International Journal of Nano Dimension, 2013. **3**(4): p. 313-319.
31. Sofla, M.R.K., et al., *A comparison of cellulose nanocrystals and cellulose nanofibres extracted from bagasse using acid and ball milling methods.* Advances in Natural Sciences: Nanoscience and Nanotechnology, 2016. **7**(3): p. 035004.
32. Radakisnin, R., et al., *Structural, morphological and thermal properties of cellulose nanofibers from Napier fiber (Pennisetum purpureum).* Materials, 2020. **13**(18): p. 4125.
33. Zheng, D., et al., *Isolation and Characterization of Nanocellulose with a Novel Shape from Walnut (Juglans Regia L.) Shell Agricultural Waste.* Polymers, 2019. **11**: p. 1130.
34. Ago, M., T. Endo, and K. Okajima, *Effect of Solvent on Morphological and Structural Change of Cellulose under Ball-Milling.* Polymer Journal, 2007. **39**(5): p. 435-441.
35. Lu, Q.-l., et al., *One-pot tandem reactions for the preparation of esterified cellulose nanocrystals with 4-dimethylaminopyridine as a catalyst.* RSC Advances, 2015. **5**(69): p. 56198-56204.
36. Beck-Candanedo, S., M. Roman, and D.G. Gray, *Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions.* Biomacromolecules, 2005. **6**(2): p. 1048-54.
37. Rahimi Kord Solfa, M., et al., *A comparison of cellulose nanocrystals and cellulose nanofibres extracted from bagasse using acid and ball milling methods.* Nat. Sci: Nanosci. Nanotechnol, 2016. **7**.
38. Chen, H., et al., *A review on the pretreatment of lignocellulose for high-value chemicals.* Fuel Processing Technology, 2017. **160**: p. 196-206.
39. Yue, Y., et al., *Cellulose fibers isolated from energycane bagasse using alkaline and sodium chlorite treatments: Structural, chemical and thermal properties.* Industrial Crops and Products, 2015. **76**: p. 355-363.
40. El Achaby, M., et al., *Production of cellulose nanocrystals from vine shoots and their use for the development of nanocomposite materials.* International Journal of Biological Macromolecules, 2018. **117**: p. 592-600.
41. Piras, C.C., S. Fernández-Prieto, and W.M. De Borggraeve, *Ball milling: a green technology for the preparation and functionalisation of nanocellulose derivatives.* Nanoscale Advances, 2019. **1**(3): p. 937-947.

 doi:10.20944/preprints202203.0184.v2

42. Zhang, L., T. Tsuzuki, and X. Wang, *Preparation of cellulose nanofiber from softwood pulp by ball milling.* Cellulose, 2015. **22**.
43. Fink, H.P., D. Hofmann, and B. Philipp, *Some aspects of lateral chain order in cellulosics from X-ray scattering.* Cellulose, 1995. **2**(1): p. 51-70.
44. Stelte, W. and A.R. Sanadi, *Preparation and characterization of cellulose nanofibers from two commercial hardwood and softwood pulps.* Industrial & engineering chemistry research, 2009. **48**(24): p. 11211-11219.
45. Johar, N., I. Ahmad, and A. Dufresne, *Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk.* Industrial Crops and Products, 2012. **37**(1): p. 93-99.
46. Nge, T., S.H. Lee, and T. Endo, *Preparation of nanoscale cellulose materials with different morphologies by mechanical treatments and their characterization.* Cellulose, 2013. **20**.