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WEALTH FROM WASTE: A REVIEW OF NANOCRYSTALLINE CELLULOSE ISOLATION FROM AGRICULTURAL WASTES.

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ABSTRACT

Nanocrystalline (NCC) cellulose is a renewable natural resource obtained from cellulose-based materials. It is typically rod-shaped monocrystalline cellulose with tens to hundreds of nanometers in length and 1 – 100nm in diameter. Nigeria is blessed with an abundance of different sources of cellulose, more especially our agricultural waste. Although there are various ways of getting rid of these wastes, production of NCC is a very profitable alternative. This paper will discuss the different methods employed by researchers towards the production of NCC, likely limitations of these methods, properties of NCC and its applications in the modern world. This is, with the hope that our researchers take into consideration the exploration of this topic from the well-documented areas to the grey areas.

Keywords: *Nanocrystalline Cellulose, Hydrolysis, Agricultural Waste, modification, lignocellulose, polymer, nanocomposites.*

Introduction:

Agricultural wastes are defined as the residues from the growing and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products and crops. They are comprised of animal waste (manure, animal carcasses), crop waste (corn stalks, sugarcane bagasse, etc.), hazardous and toxic wastes (pesticides, insecticides and herbicides) and food processing waste (Obi et al, 2016). However, agricultural waste we will be referring to here is the crop waste (corn stalks, corn cobs, bagasse, rice and wheat straws etc.) which contains much cellulose.

Recently, there has being a massive come back into the agricultural sector, owing to the government's call towards diversifying Nigeria's economy; as it solely depends on oil and gas. This results in multiplication of agricultural activities all over the country and subsequently, production of much more agricultural wastes than before. There is therefore an increasing need to tackle these wastes in a more profitable way. Some of the various waste utilization includes anaerobic digestion, pyrolysis, direct combustion etc. the production of nanocrystalline cellulose is relatively a recent development.

Cellulose is an important polysaccharide consisting of a linear chain of several hundreds to thousands of β-linked D-glucose units. It is an important component of the plant cell wall. Cellulose is the main building block of plant materials; contributing about 45%, 35%, 30% and 40% by composition of corn cob, corn stalk, wheat straw and bagasse respectively (Hon, 1996).

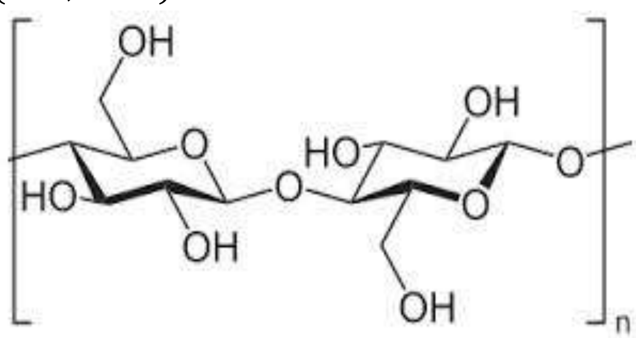

Figure 1: structure of cellulose
(https://en.mwikipedia.org/wiki/Cellulose)

NANOCRYSTALLINE CELLULOSE (NCC)

The term nanocellulose generally refers to cellulosic materials having at least one dimension in the nanometre range (Abdul Khalil, 2014). They are characterized by increased crystallinity than ordinary cellulose materials. They are called nanocrystalline cellulose (NCC), cellulose nanocrystals (CNC) or nanofibrillated cellulose (NFC).

Nanocrystalline cellulose (NCC) is a renewable natural resource obtained from cellulose-based materials. It is typically rod-shaped monocrystalline cellulose with tens to hundreds of nanometers in length and one to hundred nanometre in diameter (Ruiz et al., 2000).

Nanocrystalline cellulose (NCC) has attracted attention of many research individuals and companies, with Canada the leading producers in recent years. This is due to the many prospects and promises NCC holds apparently through its exceptional properties: low thermal expansion, strengthening effect, biodegradability, mechanical and optical properties among others.

Production of NCC

The production or isolation of NCC from the bulk of the cellulose-based raw materials consists of four major steps: the pretreatment of the raw material, hydrolysis, disintegration and; drying.

Pretreatment of the raw material

The raw material is usually subjected to a pretreatment process which is aimed at purifying the cellulose material to remove natural impurities and also, to prepare it for better hydrolysis. The pretreatment conditions depend on the source of cellulose in use, as some sources contain more of cellulose than lignin and hemicellulose and vice versa. The pretreatment involves the following steps:

- The raw material is washed 3-4 times with warm water to remove dirt and aqueous soluble substances, followed by prolonged (about 1 week) air drying (Ping and You-Lo, 2012).
- The dry raw material may then be grinded into powder to increase the surface area for better performance.
- The raw material powder is then treated with 2 – 3 wt% caustic soda solution for 2 hours at around 60 – 80^{0}C. This treatment will disrupt the Lignin structure and, would also breakdown the linkages between Carbohydrate and Lignin (Abdul Khalil, 2014).

Isolation of NCC

The isolation/extraction of NCC is based on hydrolysis. The hydrolysis breaks down the cellulose bulk and released the more organized cellulose. The NCC is obtained after mechanical treatment and the more amorphous cellulose washed off.

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Three different hydrolysis processes are frequent in literature: acid hydrolysis, enzymolysis and chlorine degradation oxidation (Bai et al., 2009).

1. Acid hydrolysis: the acid hydrolysis of cellulose involves the protonation of glucosidic oxygen or cyclic oxygen followed by the water-induced dissociation of glucosidic linkages. This process gives two shorter chain fragments (individual crystallites), preserving the basic nature of the polymer chain, and also involves the esterification (sulphonation) of the hydroxyl groups (-OH) of the polymer chain. At the end of the acid hydrolysis, the mixture undergoes series of separation and washing/rinsing steps, followed by dialysis against deionized or distilled water to remove residual acid and neutralized salts (Kumar and Negi, 2015).

Acid hydrolysis is achieved by treating the pretreated raw material in a bath containing 60 - 67% mineral acid (mostly but not necessarily sulphuric acid) at a temperature between 40 - 70^{0}C for a period of 30 mins – 2 hrs, with continues stirring. The concentration of the acid, the treatment time and temperature; all depend on the material in use and the acid.

2. Enzymolysis: because of the complex nature of cellulose materials, they cannot be satisfactorily hydrolysed using a single enzyme. Therefore, a set of cellulases will give a better result. However, Chen et al., (2012) used *Trichoderma vride G* to prepare NCC. The highest yield in their work was 32.4%. The enzymes help in restrictive hydrolysis of several elements or selective hydrolysis of specified components in the cellulosic fibres (Janardhnan and Sain, 2006). The use of enzymes is a controlled hydrolysis, and results depend on the extent of treatment and pretreatment as well.
3. Chlorine Oxidation Degradation: this method is based on the oxidizing power of chlorine. The source of chlorine could be chlorine dioxide (ClO_2), chlorate (ClO_3^-), chlorite (ClO_2^-), hypochlorous acid (HOCl) or elemental chlorine. Pretreatment is essential as that is where the Lignin and most of the hemicellulose is removed.

Hypochlorous acid (HOCl) was found to attack cellulose in low or absence of Lignin causing oxidation and degradation. The oxidation cotton cellulose by hypochlorite was studied by few researchers in the 60s. The extent of oxidation was found to be pH dependent. According to these studies, the oxidation of cellulose by hypochlorite was most effective around pH 7 (Zhou et al., 2008).

Besides the oxidation of cellulose by hypochlorite, oxidation by aqueous chlorine solution at pH 1–7 has been studied. Under these conditions, chlorine is in equilibrium with hypochlorous acid (known also as chlorine hydrolysis) as shown in the equation below (Zhou et al., 2008):

$$Cl_2 + 2H_2O \leftrightarrow HOCl + H_3O^+ + Cl^-$$

Drying of NCC

Drying of individual and well-dispersed NCC should be approach bearing in mind the preservation of the actual state of the particles. This is because, often agglomeration of the individual nano particles occurs and this will temper with the end use properties of the material; as these properties depends directly or indirectly on the size and sometimes strength of the NCC particles. Irreversible agglomeration of cellulosic suspensions during drying is known as hornification (Eyholzer et al., 2010). This leads to generation of hydrogen bonds, thus making re-dispersion of the NCC difficult.

Different researchers tried different drying methods each with its own impact on the final NCC product. However, Abdul Khalil et al, (2014) compare these different drying techniques as below:

Drying method	Particle size after drying	Advantages	Disadvantages
Freeze drying (FD)	Micron to millimeter length or width, nano size thickness	Keep one dimension in nano size, well established method	High cost, agglomeration
supercritical drying (SCD)	Nano size fibrous NFC	Keep dimension in nano size	High cost, complicated method using solvent replacement
Spray drying (SD)	D [n, 0.9]=7.48μm	Low cost, controllable size, continues and scalable	Agglomeration, range of particle size from nano to micron

Oven drying (OD)	Hundreds of microns to millimeter	Well established process in industry	Generate bulk materials, loose nano dimension

Table 1: drying methods of NCC (Abdul Khalil et al, 2014)

Characterisation of NCC

After the NCC have been extracted and dried, the sample is then characterized based on the targeted properties of the sample. Below are some of the important properties that are investigated:

1. **Crystallinity:** this is the degree of structural order in a solid sample. The degree of crystallinity is usually given as a percentage of the orderly (crystalline) region in the sample. A number of techniques can be used to determine the crystallinity of a given sample. Some of these techniques are X-ray diffraction analysis (XRD), Differential scanning calorimetry (DSC), Solution calorimetry etc.
2. **Particle size:** this usually refers to the average diameter in microns of individual particles. In NCC, both the length and diameter of the particles are important. Particle size can be obtained or measured using particle size analyzer, Scanning electron microscope (SEM), Transmission electron microscope (TEM) etc.
3. **Functional groups:** functional groups dictate a sample's chemical properties and therefore, their determination is very important in both organic and inorganic samples. In NCC, functional groups are investigated to determine and /or confirmed their presence especially when chemical modification is carried out. One of the most commonly used technique is the Fourier transformed infrared spectroscopy (FTIR).
4. **Thermal properties:** here, thermal stability is the most important parameter. However, thermal conductivity can also be investigated depending on the targeted end use. Thermogravimetric analysis (TGA) and Differential Scanning Calorimety (DSC) are the two most commonly used techniques in the determination of thermal stability of NCC.
5. **Density:** the determination of the density is a little difficult and not always accurate because it depends on two separate parametres – mass and volume of the sample. However, the determination of density can be achieved using different methods, notably the use of pycnometre and hydrometer.

Modification of NCC

Being a highly crystalline material, NCC comes with the problem of compatibility in some applications and thus, requires one chemical modification or the other to suit a particular end use. A lot of researches were carried out by different researchers on the modification of NCC. The modifications were possible mainly due to the hydroxyl groups (-OH) the NCC still possesses. Some of the modifications reported in literature are shown in the table below:

Table 2: Chemical modifications of NCC

Type of modification	Modification agent	Reference
Acetylation	Alkyenyl succinic anhydride	Yuan et al., 2006
TEMPO-media oxidation	2,2,6,6-tetramethylpiperidine-1-oxyl	Habibi et al., 2006
Silylation	Series of Alkyldimethylchlorosilanes	Gousśe et al., 2004
Carboxymethylation	Sodium chloroacetate	Hubbe et al., 2008
Sulfonation	Periodate and bisulfite	Liimatainen et al., 2013
Isocyanation	N-octadecyl isocyanate	Siqueira et al., 2009
Cationisation	Grafting Epoxypropyltrimethylammonium chloride (EPTMAC)	Hasani et al., 2008

Colouration of NCC

Colour as an aesthetic property is often as important as other properties, especially in materials. Originally, NCC when prepared appears white and therefore, might not give the aesthetic required in some fancy applications. There were not many literatures on the colouration of NCC. However, Bukhari et. al., (2015) successfully applied three (3) different classes of dyes to NCC; Reactive, Direct and Disperse dyes. The exhaustion and colour fastness studies showed that NCC can be dyed using any of the three classes mentioned. The choice of these three dyes was guided by the nature of NCC:

1. Being originally cellulose and possesses the hydroxyl (-OH) groups, it was successfully dyed with Direct and Reactive dyes (conventional dyes used on cellulosic fibres)

2. Being highly crystalline in nature and somewhat hydrophobic, it was successfully dyed with hydrophobic (disperse) dyes.

Applications of NCC

NCC has a lot of properties that makes it a potential hotcake in the fields of science and technology. Some of these properties are: high crystallinity, high Young's modulus, unique tensile strength, distinctive optical properties, high surface area and biodegradability. According to the Finnish Centre for Nanocellulosic Technologies Finland, NCC potential applications include: advanced building materials, novel bioplastics, recyclable structural and interior components of transport industry, switchable optical films, fibre-reinforced composites, additive for paints, inks, cosmetics, magnetic films etc. however, the two most important areas of application are discussed below:

Reinforcement in Nanocomposite

The major application of NCC is in the reinforcement of polymeric matrix in composites and nanocomposite materials. Important nanocomposite materials such as superabsorbents and nanocomposite films are some of the application. The nanocrystalline cellulose can be incorporated using different methods depending on the end-use requirement.

Biomedical application

NCC is called the eye of biomaterials, and is highly applicable to the biomedical industry; including drug delivery systems, scaffolds for tissue engineering, skin replacement for burns and wounds, stent coverings and bone reconstruction, gum and dura mater reconstruction and blood vessel growth (https://nanografi.com/blog/cellulose-nancrystal-and-its-applications).
Recently, a comprehensive assessment involving toxicity tests with rainbow trout hepatocytes and nine aquatic species were conducted by a team of Canadian researchers. From the initial ecotoxicological characterization of NCC, no serious environmental concerns were observed. However, further testing will be necessary, such as the evaluation on the fate, potential NCC uptake and exposure studies, so that a detailed risk assessment of NCC can be determined (Peng et. al, 2011).

Conclusion and Recommendations

Conclusion

Nanocrystalline cellulose being an organic material with such outstanding properties holds promises in the future of science and engineering. More

importantly, the economically friendly nature of cellulose (being the most abundant natural resource) will contribute towards the production of low cost but efficient products, since it can be extracted from the abundant agricultural wastes and biomass around us. Furthermore, this will help a lot in the control of environmental pollution caused by these wastes.
This paper reviewed several works carried out by researchers in the areas of extraction, modification and application of Nanocrystalline cellulose. The aim of the review is to further draw the attention of researchers especially in Nigeria to dive more into the extraction and utilization of NCC for sustainable development in terms of economy, science and technology.

Recommendations

Looking at Nanocrystalline cellulose applications and potentials, the following recommendations were made:

1. African researchers should descend fully on the isolation and application of nanocrsytalline cellulose from agricultural wastes since the region is blessed with abundance of agricultural activities and hence waste.
2. Ministries of science and technology, Agricultural and forestry agencies as well as related companies should provide funding for researchers in this area as it will go a long way in improving the sustainable development of our economy.

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