EXTRACTION, CHARACTERIZATION AND COLORATION OF NANOCRYSTALLINE CELLULOSE FROM CORN COB

BY

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NIGERIA

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DECLARATION

I hereby declare that this thesis titled “Extraction, characterization and coloration of nanocrystalline cellulose from corn cob” has been carried out by me in the Department of Textile Science and Technology. No part of this thesis was previously presented for another degree or diploma at this or any other institution. All information from other sources has been duly acknowledged by means of references.

_____ _____

YUSUF SALEH MAIGARI DATE

CERTIFICATION

This thesis titled "EXTRACTION, CHARACTERIZATION AND COLORATION OF NANOCRYSTALLINE CELLULOSE FROM CORN COB" by YUSUF MAIGARI SALEH meets the regulation governing the award of the Master of Science in Colour Chemistry and Technology of Ahmadu Bello University Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

I dedicated this piece of work to my mother, HauwaAdamu.

ABSTRACT

Nanocrystalline cellulose (NCC) was extracted from corn cob using Acid hydrolysis. Pre-treatments applied to the corn cob before the acid hydrolysis include: grinding to provide more surface area for hydrolysis and subsequent processes, caustic soda treatment (scouring) to remove lignin and other unwanted materials and bleaching to remove the inherent natural yellowing in plant materials. The extracted NCC was characterized using SEM, PSA, FT-IR, XRD and TGA. Other properties investigated are density and swelling index. The extracted NCC was then dyed (alongside fabrics as control) with disperse, reactive, direct and acid dyes. The exhaustion of each of the dyes was investigatedand fixation of the reactive dye also studied. Colour fastness of the dyed NCC to washing, chlorinated water and light were then investigated. The FT-IR results showed that there is successful removal of lignin and hemielluloses. The X-ray diffraction analysis shows successful increase in crystallinity from corn cob (crystallinity index 67.65%) to NCC (crystallinity index 78.90%). The thermogravimetric analysis shows that thermal stability of polymers is directly related to number of units fused together. It also shows that the present of impurities increase thermal stabilities. Satisfactory exhaustions were obtained with both dyes. This shows that, NCC can be dyed with any of the three classes of dyes used. However, the colour fastness results show that the choice of dye depends on the end use of the NCC to be dyed.

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CHAPTER ONE

1.0 INTRODUCTION

Cellulose is the most abundant natural biopolymer on earth, which is renewable, biodegradable, as well as non-toxic. It is a carbohydrate polymer made up of repeating β-D-glucose units. It consists of both amorphous and crystalline regions (Coffey *et al.*, 1995; Lima and Borsali, 2004).

The repeating unit of cellulose is cellobiose. Hydroxyl groups present in cellulose macromolecules are involved in a number of intra- and intermolecular hydrogen bonds, which result in various ordered crystalline arrangements. Four different crystalline allomorphs have been identified by their characteristic X-ray diffraction (XRD) patterns and solid-state ^{13}C nuclear magnetic resonance (NMR) spectra: celluloses I, II, III and IV. Cellulose I is the most abundant form found in nature. Cellulose II can be prepared by two distinct routes: mercerization (alkali treatment) and regeneration (solubilisation and subsequent recrystallization). Celluloses III_I and III_{II} can be formed from celluloses I and II, respectively, by treatment with liquid ammonia, and the reaction is reversible (Hayashi *et al.*, 1975). Celluloses IV_I and IV_{II} can be obtained by heating celluloses III_I and III_{II}, respectively (Gardinerand Sarko, 1985).

Cellulose, being the main building block of plant, is available in large quantities in the agricultural products and their wastes. These agricultural wastes are produced all over Nigeria and their disposal is a problem as every part of the country has its own dominant crops and therefore different agricultural wastes to deal with. An estimate of agricultural

wastes produced in Nigeria in 2004 was made independently by two researchers(Osaghae, 2009 and Jekanyinfa and Scolz, 2007).

Table 1.1:Crop residue generation in Nigeria.

Crop residue	**Total amount (Metric tonnes)**
Cassava	29,000,000
Yam	22,000,000
Millet	11,000,000
Maize	3,500,000
Rice	1,800,000
Potato	600,000
Cowpea	4,050,000
Groundnut	6,000,000
Oil palm	400,000
Sugar cane	300,000
Sweet potato	1,000,000
Cocoyam	1,500,000
Coffee	400,000
Cashew	300,000
Plantain	9,450,000
Sorghum	1,500,000

Although other methods of controlling these crop residues are being employed in the various locations where they are produced, the conversion of these materials into useful

productsis a recent development. These include the conversion of biomass into biofuel (mainly bioethanol) and extraction of cellulose (refined cellulose, microcrystalline cellulose and nanocrystalline cellulose).

Nanocrystalline cellulose (NCC) is a kind of renewablenatural resource. It is typically rod-shaped monocrystalline cellulose with tens to hundreds of nanometers in length and 1 – 100 nm in diameter (Ruiz *et al.*, 2000).

Nanocrystalline cellulose (NCC) is an emerging renewable nano material that holds promise in many different applications, such as foods, pharmaceuticals, personal care, etc. Its properties and many potential forms allow many uses which, in addition to the afore mentioned, are iridescent magnetic films, improved construction products, biocomposite for bone replacement, paint additives, reinforced composites, recyclable interior and structural components for the transportation industry (Coffey *et al.*, 1995; Lima and Borsali, 2004).

In this work, NCC will be produced using acid hydrolysis of corn cob powder. Other processes that can be applied to manufacture NCC are enzymolysis and chlorine oxidation degradation. Although these other processes have been attempted and each has its own peculiar effects on the resulting NCC, theacid hydrolysisis a well-known process used to dissolve the amorphous regions of cellulose effectively (Bai*et al.*, 2009).

1.1 STATEMENT OF RESEARCH PROBLEM

Although research works have been reported on various aspects of NCC and its modification, there is still scanty literature on its colouration. Also, there is need to identify which class of dye will best suit its colouration process.

1.2 JUSTIFICATION OF STUDY

Corn cob represents a large portion of our agricultural wastes, especially in northern region of the country where maize is one of the largely produced grains from subsistence farming. As a result, various research outlets have tried devising means of reducing this waste into useful products. This research has its significance reflected both in economic and environmental management of these wastes.

1.3 AIM AND OBJECTIVES

AIM

To extract, characterize and colour NCC from corn cob (waste to wealth).

OBJECTIVES

To characterize the extracted NCC using FTIR, SEM, PSA, TGA and XRD analysis.

To colour the produced NCC using reactive, disperse and direct dyes.

To identify the most suitable dye class for the extracted NCC.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 CELLULOSE

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundreds to many thousands of β linked D-glucose units. The "ideal" cellulose is a linear polymer composed of individual anhydroglucose units (also called glucopyranose units) linked at the 1 and 4 positions through glucosidic bonds with the *beta* configurations (http://en.wikipedia.org/wiki/Cellulose).

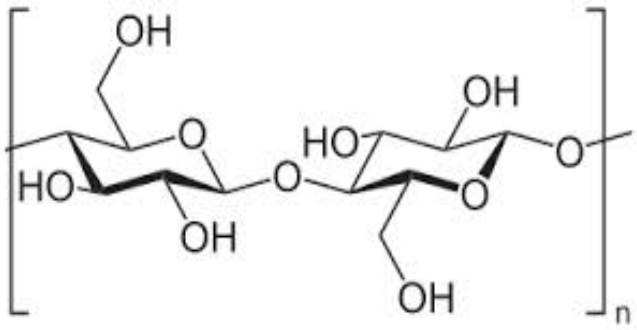


Figure 1: structure of cellulose

2.1.1BriefHistory of Cellulose

Cellulose was discovered in 1838 by the French chemist Anselme Payen, who isolated it from plant matter and determined its chemical formula. Cellulose was used to produce the first successful thermoplastic polymer, 'celluloid', by Hyatt Manufacturing Company in 1870. Production of Rayon (artificial silk) from cellulose began in the 1890s and 'cellophane' was invented in 1912. HermannStaudinger determined the polymeric structure of cellulose in 1920. The compound was first chemically synthesized (without the use of

any biologically derived enzymes) in 1992, by Kobayashi and Shoda (http://en.wikipedia.org/wiki/Cellulose).

2.1.2Occurance of Cellulose

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all the vegetable matter in the world. It is present in a wide variety of living species including plants, animals and some bacteria (Lima and Borsali, 2004). It is the main constituents of the cell wall of the higher plants, having received its name for this reason. Its existence in the lower orders of the vegetable kingdom has been disputed, but there is good evidence that it does occur in many of the lower species.

2.1.3 Sources of Cellulose

The main source of cellulose is the occurrenceof this polysaccharide in different types of plants often combined with other biopolymers. Of great scientific importance is access to cellulose using enzymatic and chemical methods, respectively, developed during the last decade. Cellulose sources can be categorized into two, natural and synthetic sources:

2.1.3.1 Natural sources

The primary occurrence of cellulose is theexisting lignocellulosic material in forests, with wood as the most important source. Other cellulose-containing materials include agriculture residues, water plants, grasses, and other plant substances. Besides cellulose, they contain hemicelluloses, lignin, and a comparably small amount of extractives (Hon, 1996). Commercial cellulose production concentrates on harvested sources such as wood or on naturally highly pure sources such as cotton (Table 2, adopted from Hon, 1996).

Table 2.1:Chemical composition of some typical cellulose-containing materials.

S/N	Source	Composition (%)			
		Cellulose	Hemicellulose	Lignin	Extract
1	Corn cobs	45	35	15	5
2	Corn stalk	35	25	35	5
3	Wheat straw	30	50	15	5
4	Cotton	95	2	1	0.4
5	Bagasse	40	30	20	10
6	Jute	71	14	13	2
7	Kenaf	36	21	18	2
8	Ramie	76	17	1	6
9	Hardwood	43 – 47	25 – 35	16 – 24	2 – 8
10	Softwood	40 – 44	25 – 29	25 – 31	1 – 5

2.1.3.2 Synthetic sources

The chemosynthesis of functionalized cellulose by ring-opening polymerization of 3,6-di-O-benzyl-d-glucopyranose 1,2,4-orthopivalate (Pandey*et al.*, 2008) or by stepwise reactions of selectively protected d-glucose e.g., 1-allyl-2,6-di-O-acetyl-3-benzyl-4-O-(p-methoxybenzyl)-d-glucopyranoside (Nishimura *et al.*, 1993) has been experimentally realized.

Up to now, complete deprotection of the polymers may yield cellulose with a rather low DP in the range from 9 to 55, dependent upon the applied protecting groups. The non-biosynthetic preparation of cellulose of a molecular weight of 6300 g $mol^{-1}$was described involving an enzymatic polymerization using d-cellobiosyl fluoride as a substrate for purified cellulase, in a mixture of acetonitrile and acetate buffer at pH 5 (Kobayashi *et*

al.,1991). Whether the cellulose I or cellulose II polymorph is formed depends on the solvent composition and the purity of the cellulose (Lee *et al.*, 1994). This approach has interesting potential for the control of molecular weight and disparity of the cellulose formed.

2.1.4Crystallinity of Cellulose

Cellulose and its various derivatives were among the first polymers for which phase transitions in the solid and the semi-solid state were studied. Many concepts and ideas presented here were gradually developed by experimental data collected with cellulosic materials, and this approach still represents an important branch in cellulose research. The fine structure of the crystalline domains in cellulose is relatively well known, but the proper characterization of the amorphous and glassy areas is still in a rather preliminary state.As compared with other polymers, cellulose shows a distinct tendency for crystallisation, probably caused by the relative stiffness of the glucosidic chains and the hydrogen-bonding capacity of its frequent hydroxyl groups. The flat shape of the ring and the spatial distribution of the hydroxyl groups appear to favour the formation of ribbon-shaped laterally ordered sheets which exhibit threefold anisotropy as far as bonding strength is concerned (Hermans and Weidinger, 1949).

Along the macromolecules, in the direction of the *b*-axis of the crystalline domains, the coherence is affected by covalent 1,4-glucosidic bonds between carbon and oxygen atoms, which have a dissociation energy of about 80 kcal. Perpendicular to the chains, in the planes of the anhydroglucose rings and in the direction of the *a*-axis of the lattice, the hydrogen bonds between the hydroxylgroups and the ring oxygen atoms are responsible for the coherence; they have average bond strength of about 5 kcal. and, perpendicular to the

chains and to the plane of the anhydroglucose rings and parallel to the *c*-axisof the lattice, the only existing attraction is due to van der Waals forces between the anhydroglucose rings and their substituents which was estimated to be about 2-3 kcal/mol. This system of bonding can be considered as a reasonable starting point for the explanation of the crystalline tendency of cellulose. It leads to the existence of elongated thin sheets with high lateral order, which in turns seems to explain, in a satisfactory way, the observed macroscopic mechanical and flow properties of cellulose fibres and films in the dry and swollen state (Emil *et al.*, 1954).

A parameter termed the crystallinity index (CI) has been used to describe the relative amount of crystalline material in cellulose. The traditional two-phase cellulose model describes cellulose chains as containing both crystalline (ordered) and amorphous (less ordered) regions. The CI of celluloses have been measured using several different techniques including XRD, solid-state ^{13}C NMR, infrared (IR) spectroscopy and Raman spectroscopy. There have also been several methods used for calculating CI from the raw spectrographic data, particularly for XRD. Methods using Fourier transform FT-IR spectroscopy determines CI by measuring relative peak heights or areas (Akerholm*et al.*, 2004). The determination of CI using FT-IR spectroscopy is the simplest method, but gives only relative values, because the spectrum always contains contributions from both crystalline and amorphous regions. In many studies, the CI calculated from an FT-IR spectrum is compared with those from XRD and/or NMR measurements. Raman spectroscopy has also been employed to determine CI (Schenzel*et al.*, 2005). The CI of cellulose has been used for more than five decades to interpret changes in cellulose structure after physicochemical and biological treatments. However, it has been found that

the CI varies significantly, depending on the choice of measurement method.In recent times, the determination of crystallinity using XRD is the most frequent practice. In using XRD data to determine crystallinity, there are three popular approaches(Sunkyu*et al.,* 2010);

a. **Peak height Approach:** This method, developed by Segal and co-workers (Segal *et al.,* 1962), examined the changes in XRD spectra during decrystallization of cotton cellulose by chemical and mechanical methods. The proposed method was for the empirical measurements to allow rapid comparison of cellulose samples. CI was calculated from the ratio of the height of the 002 peak (I_{002}) and the height of the minimum (I_{AM}) between the 002 and the 101 peaks.
b. **The XRD Peak Deconvolution Method:** This method requires software to separate amorphous and crystalline contributions to the diffraction spectrum using a curve-fitting process. For the curve fitting, a few assumptions have to be made, such as the shape and number of peaks. Gaussian (Hult*et al.,* 2003 andTeeäär*et al.,* 1987), Lorentzian (He*et al.,* 2008) and Voigt (Garvey *et al.,* 2005) functions are commonly used for deconvolution of XRD spectra. Five crystalline peaks (101, 10ī, 021, 002 and 040) have been separated in many cases (Garvey*et al.,* 2005 &Hult*et al.,* 2003), but four crystalline peaks (101, 10ī, 002 and 040) have been assumed in other studies (He*et al.,* 2008).
c. **The XRD amorphous subtraction Method:** the basis for this method has been outlined by Ruland in 1961, who determined crystallinity by subtracting the amorphous contribution from diffraction spectra using an amorphous standard. The challenge is to select an amorphous standard that is similar to the amorphous

component in the sample. Various materials have been used as an amorphous standard, such as ball-milled cellulose, regenerated cellulose, and xylan or lignin powder. A scale factor is applied to the spectrum of the amorphous material so that after subtraction of the amorphous spectrum from the original spectrum, no part of the residual spectrum contains a negative signal.

2.1.5 Other Components of the Cellulose Cell-wall

2.1.5.1 Lignin

Although lignin, like cellulose, has given rise to a special field in organic chemistry, the literature of which has grown tremendously during the past twenty-five years, the close association of lignin with cellulose warrants discussion in treatise on the latter. Unlike cellulose, lignin has never been found alone in nature but is always associated with carbohydrates. The origin of lignin is still unknown, although there has been much speculation as to the possibility of its being derived from carbohydrates (Emil *et al.,* 1954).

In straw and other annual plants, lignin seems to be mainly on the surface of the fibre and in a less highly condensed state, since it can be removed much more readily than from wood. Lignin therefore may be defined as the part of wood and straw that remains as an insoluble product when such lignified materials, after removal of the tannis, resins, and other extractives, are treated with strong mineral acids. Lignin differs from cellulose in that it has high content of methoxyl groups which are attached to the aromatic rings of the lignin molecule (Emil *et al.,* 1954).

Lignin is a constituent of the cell walls of almost all dry land plant cell walls. It is the second most abundant natural polymer in the world, surpassed only by cellulose. Of all the polymers found in plant cell walls, lignin is the only one that is not composed of carbohydrate (sugar) monomers.Lignin is unique in that it is the only large-scale biomass source of an aromatic functionality. It is composed of up to three different phenyl propane monomers, shown in figure 2, depending on the species. Coniferyl alcohol occurs in all species and is the dominant monomer in conifers (softwoods). Deciduous (hardwood) species contain up to 40% syringyl alcohol units while grasses and agricultural crops may also contain coumaryl alcohol units (http://www.lignoworks.ca/content/what-lignin).

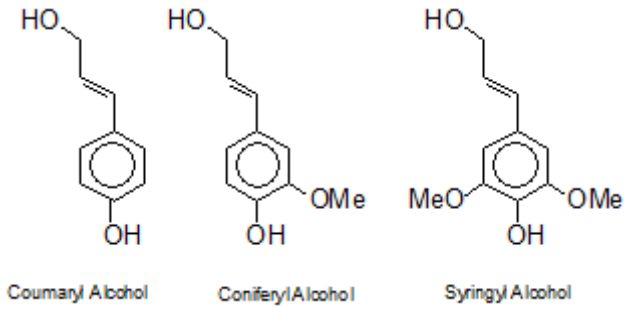


Figure 2: the three phenyl propane monomers in lignin

2.1.5.2 Hemicellulose

Hemicelluloses, on the other hand, are a large group of polysaccharides found in the primary and secondary cell walls constituting the second most abundant polysaccharide in nature. They are classically defined as alkali soluble material after removal of peptic substances, and have a much lower degree of polymerization (100–200 U) compared with that of cellulose (10,000–14,000). The principle sugar components are d-xylose, d-mannose, d-glucose, d-galactose, l-arabinose, dglucuronicacid, 4-Omethyl- d-glucuronic

acid (MeGlcA), d-galacturonic acid, and to a lesser extent, l-rhamnose, l-fucose, and various O-methylated sugars (Xiao et al. 2001). Hemicelluoses could be classified into four groups (Spiridon2008):

Xylans (b-1,4-linked D-xylose units)

Mannans (b-1,4-linked D-mannose units)

Arabinans (a-1,5-linked L-arabinose units)

Galactans (b-1,3-linked D-galactose units)

The distinction between cellulose and hemicellulose was made first by Schulze on the basis of solubility of the latter in dilute alkalis. It was his belief, however, that the hemicelluloses were closely related to cellulose both chemically and functionally, hence the similarity in nomenclature (Emil *et al.,* 1954).

2.2 NANOCRYSTALLINE CELLULOSE (NCC)

The term 'Nanocellulose' generally refers to cellulosic materials having at least one dimension in the nanometre range (Abdul Khalil *et al.,* 2014). They are characterized by increased crystallinity, high aspect ratio, developed specific surface, improved dispersion ability, biodegradability, and stability to aggressive medium, increased temperatures and proteolytic enzymes (Ioelovich, 2004).

Native cellulose contains both amorphous and crystalline regions. The amorphous region is of lower density than the crystalline region. So, when this cellulose is subjected to harsh acid treatment, the amorphous region breaks up, releasing the individual crystallites (Peng*et al.,* 2011).

2.2.1 Extraction of Nanocrystalline Cellulose

The extraction of nanocrystalline cellulose is based on the hydrolysis of the amorphous regions of the cellulose raw-material. This is best achieved by Acid hydrolysis. Although other processes such as enzymolysis and chlorine oxidation degradation have been attempted and each process has its own peculiar effects on the resulting NCC, acid hydrolysisis a well-known process used to dissolve the amorphous regions of cellulose effectively (Bai*et al.*, 2009).

Before hydrolysis, the raw material to be used e.g. paper pulp, wood pulp, bagasse, corn cob, rice husk, straw etc. will be subjected to a pre-treatment process to remove natural impurities. Thispre-treatment is often achieved by using desired concentration of caustic soda solution at a particular temperature for a certain period of time. Other reagents e.g. peroxyformic acid, hydrochloric acid etc. were also reported tohave given successful pre-treatment. After hydrolysis, the product is further disintegrated using mechanical isolation process e.g. high pressure homogenization, high intensity ultrasonication, microfluidization, grinding or cryocrushing; with each process having a different effect on the final product (Abdul Khalil *et al.,* 2014).

2.2.2 Drying of Nanocrystalline Cellulose

The nanocrystalline cellulose is produced in form of suspension and thus the powder can be obtained after drying.A comparison of these processes was made by Peng*et al.*, (2012) and summarized in table 2.2.

Table 2.2:Drying methods for nanocrystalline cellulose

Drying method	**Particle Size**	**Advantages**	**Disadvanntages**
Freeze-drying	Micro to millimetre length or width, nano size thickness	Keep one dimension in nano size, well established method	High cost, agglomeration
Super critical drying	Nano size fibrous NCC	Keep one dimension in nano size	High cost, complicated method using solvent replacement, impractical scale up
Spray drying	D [n, 0.9] = 7.48 µm	Low cost, controllable size, continuous and scalable	Agglomeration, range of particle size from nano - micron
Oven drying	Hundreds of Microns – millimetres	Wellestablished process in the industry	Generate bulk materials, loose nano dimension

Due to the existence of NCC particles as biological materials, the temperature at which drying is carried out is also very important if the inherent properties of the material are to be preserved. For this reason, special drying processes are employed. Drying of individual and well dispersed NCC is an important challenge for its application. It is worth mentioning here that often irreversible agglomeration happens during drying, which affects the dimension of the NCC particles and hence the unique properties that are related to their size (Beck *et al.*, 2012).

2.2.3Modification of Nanocrystalline Cellulose

The most serious issues that need to be solved are the incompatible nature and difficult dispersion of cellulose in polymer matrix (Heux*et al.*, 2000) as well as poor interfacial adhesion between cellulosic fibres as polar materials with non-polar medium like polymeric materials. One approach to overcome these problems is surface modification of the cellulosic material or the matrix (Akil*et al.*, 2011). Because of a natural advantage of an abundance of hydroxyl groups at the surface of NCC, different chemical modifications have been attempted, including esterification, etherification, oxidation, silylation, polymer grafting, etc. Non-covalent surface modification, including the use of adsorbing surfactants and polymer coating, has also been studied (Habib*et al.*, 2010).

The chemical functionalization has been mainly conducted to:

1. Introduce stable negative or positive electrostatic charges on the surface of NCC to obtain better dispersion (e.gNCC obtained after sulfuric acid hydrolysis introduces labile sulfate moieties that are readily removed under mild alkaline conditions) and
2. Change the surface energy characteristics of NCC to improve compatibility, especially when used in conjunction with nonpolar or hydrophobic matrices in nanocomposites.

The main challenge for the chemical functionalization of NCC is to conduct the process in such a way that it only changes its surface, while preserving the original morphology to avoid any polymorphic conversion and to maintain the integrity of the crystal (Habib*et al.*, 2010).

2.2.3.1 Formation of ionic groups

Carboxymethylation, oxidation and sulfonation are three routes to introduce ionic groups on the surface of cellulose.

Carboxymethylation - The surfaces of cellulosic fibres can be modified by carboxymethylation process. This process makes the surfaces negatively charged, promotes formation of stable suspension from carboxymethylated fibres and increases the breakup of lignocellulosic fibres to nano size (Hubbe*et al.,* 2008). Carboxymethylation involves two reaction stages: mercerization and esterification. These reactions are commercially carried out in water-alcohol mixtures, usually as a slurry process at 10% pulp concentration.

Oxidation – 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation is a kind of pre-treatment that facilitates isolation of nanofibres. This method selectively introduces carboxyl (acidic) groups at the C_6 of the glucose unit. In TEMPO oxidation process, an additional catalyst (NaBr) and primary oxidant (NaClO) are applied at pH9-11. (Saito *et al.,* 2009).

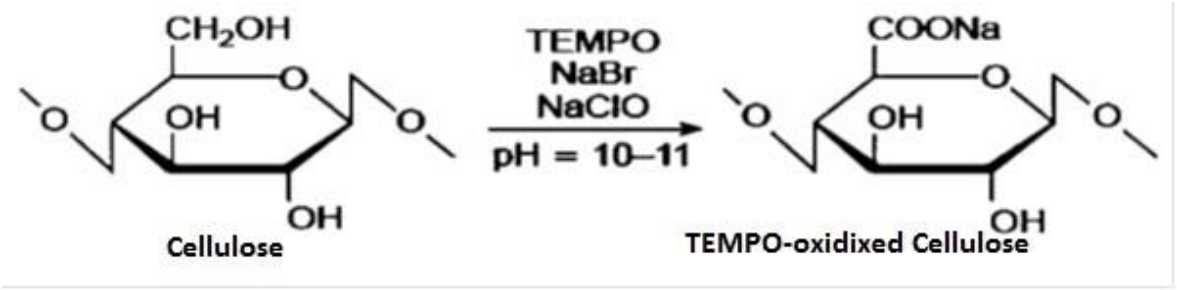


Figure 3:TEMPO oxidation of cellulose (Isogai and Kato, 1998)

Sulfonation–sulfonation is considered as a way to induce anionic charge on the surface of nanofibrillated cellulose. The key point of this process is that oxidative sulfonation prevents the production of halogenated wastes and is called green procedure.

Liimatainen*et al* (2013) applied periodate and bisulfite and achieved sulfonation. They showed that only 0.18mmol/g of sulphated groups were needed to enable nanofibrillation (Abdul Khalil *et al.*, 2014).

2.2.3.2 Generation of hydrophobic surfaces

Modifying the surface of NCC for making it more hydrophobic is a suitable method to reduce agglomeration (especially in polymer matrix) of these materials which have been stated earlier. Reactions to change the surface ofcellulose from hydrophilic to hydrophobic includes: acetylation, isocyanation and silylation (Abdul Khalil *et al.*, 2014).

Acetylation - One practical approach to make the surface of NFC more hydrophobic is the formation of ester groups (Ifuku et al., 2007). Acetylation of cellulosic fibres is an effective method in this regard.The principle of acetylation is the reaction of OH groups of cellulose with acetyl groups which cause plasticization of lignocellulosicfibres.

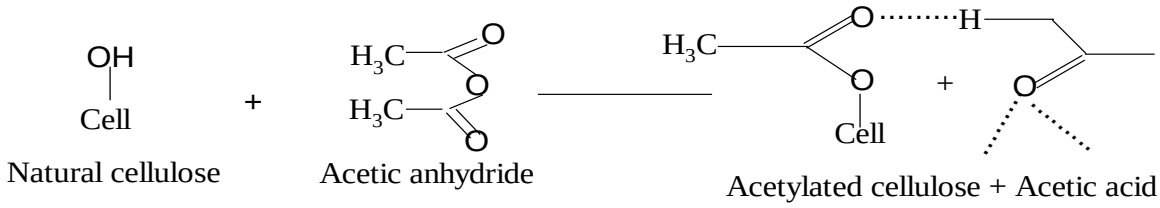


Figure 4: Acetylation of cellulose

Isocynation - Since isocyanate can generate covalent bonds with surface hydroxyl groups, it can be an alternative material for hydrophobic surface generation (Hubbe*et al.*, 2008).

Silylation - Silane based surface modification is a popular way to change the surface of fibers from hydrophilic to hydrophobic. In the absence of water, even at elevated temperature, no reaction happens between Si–OR and OH groups of cellulose, whereas Si–OR reacts with lignin's phenolic OH. Addition of moisture initiates a reaction between

silanol groups and OH groups of cellulose at high temperature Surface silylation of NCC from bleached softwood pulp using chlorodimethylisopropylsilane was investigated by Andresen *et al.* (2006). They noted that the degree of surface substitution was around 0.6–1 which indicated that silylated NCC could be dispersed in a polar solvent(Hubbe*et al.*, 2008).

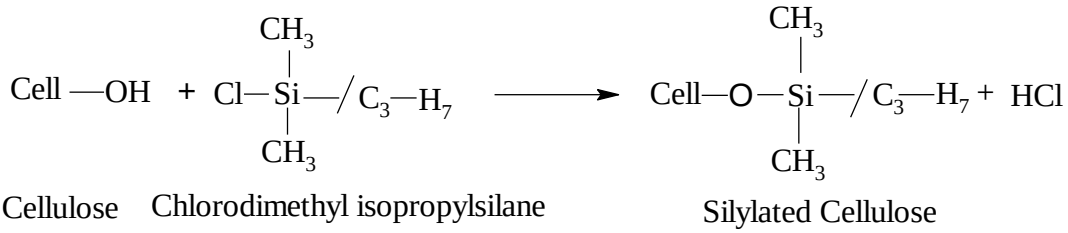


Figure 5:schematic reaction route between cellulose and chlorodimethylisopropylsilane and cellulose (Gousśe*et al.,* 2004).

2.2.4 Applicationsof Nanocrystalline Cellulose

Nanocrystalline cellulose is anew class of cellulose material that can find wide application in various technical areas, biotechnology and medicine (Ioelovich, 2012).It finds wide variety of applications in many fields due to its high Young's modulus and unique tensile strength (Ruiz *et al.*, 2000), distinctive optical properties and high surface area (Bai*et al.*, 2009), biodegradabilityand environmentally friendly.

According to the Finnish Centre for Nanocellulosic Technologies Finland, NCC holds a lot of promises and potential applications which include:

Advanced building materials

Recyclable structural and interior components of transport industry

Novel bioplastics

Fibre-reinforced composites

Switchable optical films

Biocomposites for bone-repair

Additive for paints, pigments and inks

Cosmetic products

Iridescent or magnetic films, etc.

2.3 Textile Dyes

Any coloured compound is not a Dye or Dyestuff. A dye is a coloured organic compound that absorbs light strongly in the visible region and can firmly attach to the fibre by virtue of chemical and physical bonding between group of the dye and group on the fibre. To be of commercial importance a dye should be fast to light, rubbing and water (Iqbal, 2008).

For a compound to be regarded a dye, it must fulfil the following conditions (Chatwal, 2009):

(i) It must be soluble in water or must form a stable and good dispersion in water. Alternatively, it must be soluble in the medium other than water. However, it is to be rememberedthat the pick-up of the dye from the medium should be good.

(ii) It must have a stable colour.

(iii) It must have an attractive colour i.e., it should not undergo structural changes readily.

(iv) It must have affinity for the fibre and must be substantive.

(v) It must possess acceptable level of colour fastness.

Dyes are classified according to structure or according to method of application. Classes according to method of application are: direct, reactive, disperse, acid, basic, mordant and vat dyes. In this work however, only direct, reactive and disperse dyes will be discussed.

2.3.1 Direct dyes

These contain acidic or basic groups and combine with polar groups in the fibre. Such dyes colour a fabric directly when the fibre is immersed in a hot aqueous solution of the dye. Direct dyes are used to dye wool and silk. Two examples of this class are Naphthol Yellow *S* and Martius Yellow. Both compounds are acids and combine with the free amino groups present in wool and silk fibres. Synthetic polyamide fibres (*Nylon*) can also be dyed by this method. Direct dyes are also used in the non-textile field, in particular for dyeing paper and leather. Direct dyes are classified into three classes: class A, class B and class C direct dyes (Iqbal, 2008).

Chemically, nearly all direct dyes are azo compounds containing sulphonic acid groups to impart aqueous solubility, the dyes themselves being the sodium salts of these aromatic sulphonic acids. The main setback of direct dyes is their rather low fastness to wet treatments and sometimes also to light (Nkeonye, 1987. However, this poor fastness can be reduced by applying an after-treatment process. An example of direct dye is C.I Direct Red 118:

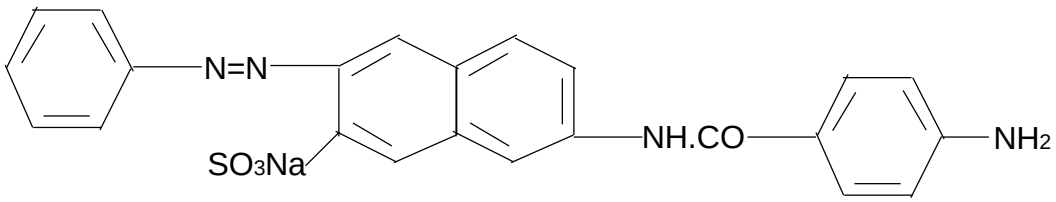


Figure 6: C.I Direct Red 118

2.3.2 Reactive dyes

A reactive dye, according to a useful definition by Rys and Zollinger, is a coloured compound which has a suitable group capable of forming a covalent bond between a carbon atom of a hydroxy, an amino or a mercapto group respectively of the substrate. They point out that this definition excludes mordant dyes and 1: 1 chromium azo dye complexes, which are used in dyeing protein fibres, may form covalent bonds between metal ion and nucleophilic groups of the fibre (Iqbal, 2008).

Reactive dyes generally give dyeings of very good to excellent fastness to washing on cellulosic materials. Light fastness is, on the average, only moderate. The main application of reactive dyes is in cellulosic fibre dyeing, though some ranges are now manufactured specifically for use on wool and nylon (Nkeonye, 1987). An example of a reactive dye is given below:

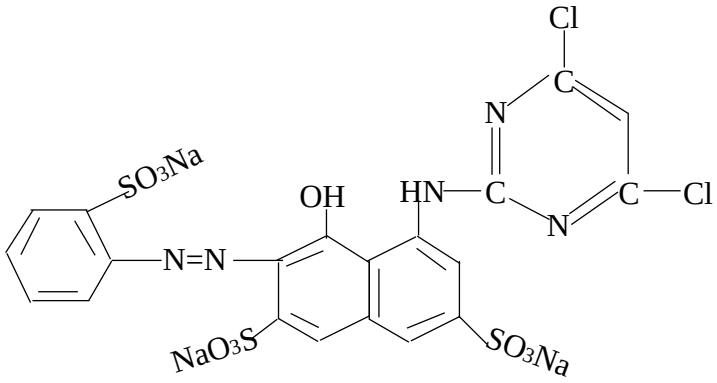


Figure 7: Procion Red MX-2B

2.3.3 Disperse dyes

These are non-ionic, water insoluble class of dyes. The name 'disperse' was derived from the fact that they are only sparingly soluble in water. When pure, they are crystalline compounds of comparatively low molecular weight (240 – 350). Disperse dyes are the most important class of dyes for the colouration of cellulose acetate and polyester, and are also of importance in the dyeing of other hydrophobic fibres such as nylon, acrylics and polypropylene (Nkeonye, 1987). They are characterized by good all round fastness properties. An example of a disperse dye is C.I Disperse Red 1

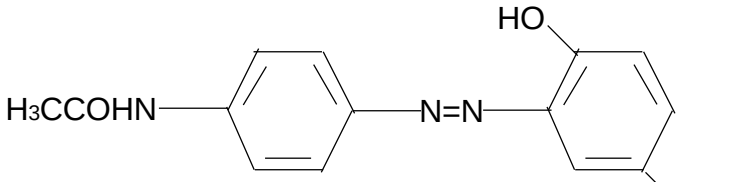


Figure 8: C.I Disperse Red 1

2.4 Textile Dyeing

Textile dyeing is defined as the overall colouring of fibres, yarns or fabrics in one uniform shed usually by immersing in a dyebath. The most common process of textile dyeing is the Exhaustion method. When a textile material is dyed by the conventional exhaustion method (gradual heating of the dyebath followed by a dwell time at the top temperature), the dyeing circle can be considered to involve three stages: transportation of the dye through the bulk solution of the dyebath to the surface of the fibre, adsorption of dye molecules on the surface of the fibre and diffusion of the dye molecule from the surface to the interior of the fibre (Nkeonye, 1987).

2.4.1 Forces responsible for dye-fibre attraction

In the dyeing process, the dye is required to transfer from water to the fibre. If the dyed material is to have satisfactory fastness, the dye must remain in the fibre and not migrate back into water on subsequent laundering. For this to be possible, an interaction must occur between the dye and the fibre. The nature and extent of this interaction affect the strength of attachment between dye and fibre. The forces responsible for this attachment are (Nkeonye, 1987):

(i) **Ionic forces:** these are mutual attractions between acidic groups in the dyes and basic groups in the fibre (or vice versa) which result in the formation of a salt between the fibre and the dye. The dyeing of wool or nylon with an acid dyestuff provides a typical example; the amino groups in the fibre forming ionic or salt linkages with the sulphonic acid groups present in the dye.

(ii) **Van der Waals' forces:** these nonpolar forces, first recognised by Van der Waals in 1873, arise out of the natural tendency of atoms and molecules to attract each other when they approach sufficiently closely. The strength of attraction here is proportional to the area of possible contact. They appear to be particularly effective when the dye and the fibre have certain special characteristics, e.g. when both are long and flat as in the case of direct dyes and cellulose.

(iii) **Hydrogen bonding:** this results from the ability of a covalently bound hydrogen atom to accept a lone pair of electrons from an electron donor atom. Typical donor groups in dyes and fibres include $–NH_2$ and –OH, while the –H atoms of groupings such as –NH–CO– and –O–H can serve as acceptors.

(iv) **Covalent bonding:** in this type of bonding, each of the two participating atoms contributes one electron to the common linkage and the two electrons are those shared to unite the atoms with bond of high energy. The only class of dyes which is attached to fibres by covalent bond is the reactive dyes. During dyeing, the reactive group in these dyes reacts with suitable groupings in the substrate, such as –OH groups in cellulose and the $–NH_2$ groups in wool and nylon.

(v) **Retention by insolubilisation:** the reason for the high wash fastness on cotton of such dyes as vat, azoic, sulphur and ingrain is the water-insoluble nature of the dye formed inside the fibre after dyeing. Since the dye inside the dyed material is water-insoluble, it does not dissolve into the water on washing.

(vi) **Retention by solid solution:** dyes devoid of ionic groups do not dissolve to any appreciable extent in water. Such dyes because of their hydrophobic nature dissolve in hydrophobic fibres (like dissolves like) such as polyester or nylon to form a solid solution of the dye in the polymer. Disperse dyes are of this type.

2.5 Review ofNanocrytalline Cellulose

Habibi*et al.* (2010) reviewed the chemistry, self-assembly and applications of Nanocrystallinecellolose. It was reported in this work that acid hydrolysis is the main process of NCC isolation. Nanocrystalline cellulose is often referred to as microcrystals, whiskers, nanocrystals, nanoparticles or nanofibers. The work reported different dimensions (length and width) of NCC extracted from different sources. Surface modification is possible in NCC because of the natural abundance of hydroxyl groups on the surface. Esterification,etherification, oxidation, silylation, polymer graftinghave all been reported.Noncovalent surface modification, including the use of

adsorbing surfactants and polymer coating, has been also studied. Self-organization phenomenon was revealed by theappearance of “fingerprint” patterns obtained from suspensions observed by polarized optical microscopy, indicative of a chiral-nematic ordering.

Peng*et al.* (2011) discussed the chemistry and application of NCC. Chemical modifications such as Tempo-mediated oxidation, esterification, fluorescent labelling, silylation, polymer grafting and surface cationization have all been reported. Appications and processings such as Drug delivery, nanocomposite films, extrusion and impregnation, electrospinning, casting evaporation were all discussed.

Ioelovich (2012) investigated the optimal conditions for the isolation of NCC. The experiment showed that isolation of NCC is carried out in narrow interval of the acid concentration: from 50 to about 61 wt. %. If concentration of sulphuric acid is less than 50 wt. % then micro-scale particles are isolated. On the other hand, if concentration of sulphuric acid is higher than 63 wt. % the cellulose completely dissolves, and as a result instead of nanocrystalline, the amorphous particles are formed with decreased yield. He therefore proposed the optimal conditions for the isolation of NCC to be: concentration of sulfuric acid 57-60 wt. %, acid to cellulose ratio 8-10, temperature 45-55ºC, time 40-60 min. These optimal conditions in combination with the high-power disintegration permit obtaining the rod-like nanocrystalline cellulose particles (150 – 200 × 10 – 20nm) with the increased yield (70 – 75%).

Yu *et al.* (2012) prepared and characterize NCC from Bamboo pulp. Effects of acid concentration and hydrolysis time were investigated. When the temperature was 50ºC, the concentration of the sulphuric acid was 48 wt% and the reaction time was 30 mins, a high

quality NCC was obtained; under these conditions, the length of the NCC fibres ranged from 200 – 500 nm, the diameter was less than 20 nm, the yield was 15.67% and the crystallinity was 71.98%.

Chen *et al.* (2012) prepared NCC by controlled enzymolysis from pre-treated cotton fibres. The pre-treated cotton fibres were hydrolysed by Cellulase (*Trichodermavride*G). The experimental results proved that the pre-treated cotton fibres could be hydrolysed by *Trichoderma*cellulose to prepare a nanosized strip (10 – 40 nm × 70 – 280 nm) and grainy (6 – 20 nm) crystalline cellulose in which the different morphologies resulted from the different manners of pretreatment. The highest yield obtained was 32.4%. crystallinity obtained from XRD analysis is 78.1%.

Lu and Hsieh (2012) extracted and characterize NCC from rice straw. Two different samples (CNC30 and CNC45) were extracted where CNC30 denotes NCC extracted by 30 minutes hydrolysis and CNC45 NCC extracted by 45 minutes hydrolysis at the same temperature and concentration of sulphuric acid. Characterizations carried out include FTIR, XRD, BET SEM, TEM and AFM. Crystallinity indexes obtained were 86.0% and 91.2% for CNC30 and CNC45 respectively. CNC30 were wider (30.7 nmwide, 5.95 nm thick) and longer (270 nm long) than CNC45 (11.2 nm wide, 5.06 thick and 117 nm long). Surface areas recorded from BET were8.922 m^2/g and 27.625 $m^2/g$for CNC30 and CNC45, respectively.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

Corn cob

Sodium Hydroxide (NaOH)

Sulphuric Acid (H_2SO_4)

Sodium bicarbonate (Na_2CO_3)

Sodium hypochlorite (NaOCl)

Acetone

Hexane

Ethanol

Dispersing agent

Soap solution (5g/l)

Dyes (Reactive, Direct, and Disperse)

3.2 Equipment

Centrifuge

Sonicator (W220F)

Rotary evaporator

Pycnometer

Particle size Analyser (Mal1084260zetasizer v. 1.7)

FTIR (Shimadzu FTIR-8400S)

SEM (PhenomWorld)

XRD (Empyrean diffractometre DY674)

TGA (PerkinElmer TGA 4000)

3.3 Methods

3.3.1 Collection of raw material

The dry Corn Cob was collected from a farm at Maidile, Kumbotso Local Government Area of Kano State. This was then washed, dried and ground into smaller particles to increase surface area for reaction.



Plate I:(a) Corn cob (b) Corn cob Powder

3.3.2 Purification and removal of lignocellulosic materials

Purification was carried out by treating the corn cob powder in a solution of 4% caustic soda (NaOH) for two hours at 75ºC. The lignin and other impurities were dissolved during this treatment and decanted off. This was followed by washing with distilled water, rinsed and dried. The alkali treatment was repeated for the second time then finally rinsed and dried.

3.3.3 Extraction

Hydrolysis was carried out using concentrated sulphuric acid (64%) at material to liquor ratio of 1:15 for 60 minutes at 55ºC with constant stirring. The hydrolysis was stopped by pouring content of the beaker into a tenfold of water with stirring and then allowed to settle for 6 hours. The clear top was decanted and the content washed with more distilled water by centrifugation at high speed (2000 rpm) for 5 minutes. It was then washed with a solution of sodium bicarbonate (5%) to neutralise any residual acid and finally rinsed with water.Bleaching was then carried out using 5% hydrogen peroxide (H_2O_2) solutionin a bath containing 2% sodium silicate, 2% sodium hydroxide, at 70ºC, material to liquor ratio 1:15 for one hour. It was allowed to cool, the water decanted and then rinsed with fresh distilled water. The bleaching was repeated three times to achieve satisfactory results.

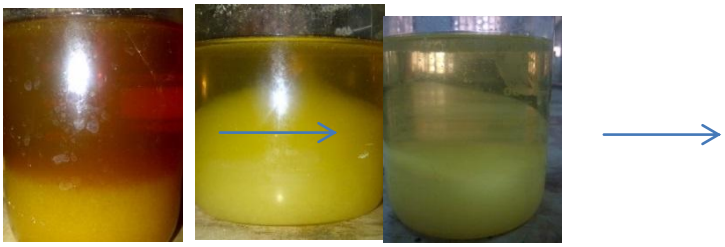


Plate II:Bleaching Sequence of NCC

The bleached cellulose was then diluted with distilled water to about 2 – 3% solid concentration and then disintegrated using ultrasonication at 20 kHz for 20 minutes. This process gives a dispersion of the NCC.

The NCC suspension was then evaporated in a vacuum to a solid concentration of 10 – 15%, washed with absolute ethanol, acetone and hexane in this order.



Plate III: NCC lump prior to drying and grinding.

This was then dried at 50ºC to a constant weight. Finally, the NCC powder was obtained after grinding using pistil and mortar.Acid Hydrolysis method reported by Ioelovich, 2012) was adopted.

3.3.4 Characterisation

3.3.4.1 Scanning Electron Microscope

The dried corn cob and NCC powders were mounted on aluminium stubs with conductive carbon tape and sputtered with gold under vacuum at 20mA for 2 minutes. The samples were then imaged.

3.3.4.2 Fourier-transformed Infrared Spectroscopy

The dried NCC powder was embedded in KBr pellets and was analysed by using SHIMADZU (Model 8400S) FT-IR spectrophotometer. The spectra were recorded in the absorption band range of 4000 – 400cm^{-1}.

3.3.4.3 X-ray Diffraction Analysis

The powdered samples were poured into a sample holder with a groove. The sample was made well levelled inside the groove and remaining powder outside scrapped off. The sample was then covered with a cover glass and loaded into the X-ray generating chamber. The glass doors were then covered and x-rays generated whereas the diffractogram was plotted on a monitor.

The crystallinity index was calculated using the peak height method with the formula:

$$crystallinity\ Index\ (CI) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \text{----------} \quad (1)$$

Where; I_{002} and I_{am} are the intensities of the crystalline peak and amorphous valley, respectively.

3.3.4.4 Thermogravimetric Analysis

This analysis records the weight of sample in dynamic conditions between 30°C and 850°C at a constant heating rate 10°C mn^{-1} under an inert atmosphere of Nitrogen gas at 20ml/min and 3.1 bar. 5mg to 33mg masses of the samples were analysed. The experimental results were achieved using a TGA7 Perkin Elmer. The sample was placed in a little cup made of aluminium hanging from a microbalance. The variation of the mass of the sample allows

drawing the TG (variation of the mass in function of the temperature) and TGD (derivative of loss of mass versus the time) thermograms. The combination of these two thermograms gives a clear indication of number of stages of the thermal degradation

3.3.4.5 Swelling test

The swelling capacity of the NCC powder was estimated as described by Iwuagwu and Okoli (1992). 3g of the NCC powder was placed in a measuring cylinder, 20ml of water was added into the cylinder and the volume of the NCC was then recorded as V_i. This was allowed for one hour and the volume of the NCC was again observed and recorded. The volume was observed and recorded at an hour interval until there was a constant volume V_f. The swelling index wasthen calculated as follows:

$$Swelling\ Index = \frac{V_f - V_i}{V_f} \times 100 \text{ ---------- (2)}$$

3.3.4.6 Density determination

The density of the NCC sample was determined using pycnometry. The water was used as the pycnometre liquid. The weight of pycnometre filled with water was measured and represented as M_1. Weight of sample was measured and represented as M_2. Weight of pycnometre filled with water + sample measured and recorded as M_3. The density of the NCC sample (P_p) was then calculated using the relation;

$$P_p = P_w \times \frac{M_2}{M_1 + M_2 - M_3} \text{ ---------- (3)}$$

Where: P_p and P_w are densities of NCC powder and water respectively. M_1, M_2 and M_3 are as described above.

3.3.4.7 Particle size analysis

Particle size analysis was carried out using Malvern particle size analyser (MAL1084260). The powdered NCC was dispersed in water (viscosity = 0.8872) at 25ºC inside a disposable sizing cuvette and run for 60 seconds where particle size distribution graph was plotted.

3.3.5 Dyeing

The NCC produced was dyed with reactive dye (Procion Violet H-3R), direct dye (Solophenyl Yellow PFL) and disperse dye (ForonYellow S.E 2GL)to determine which of the dyes best suits the material. Fabric samples were dyed at the same condition alongside the powder to serve as control.

The stock solution used for each of the dye was 1%, percentage shade 3%, and the material to liquor ratio is 1:20. The calculation of the dye bath volume was carried using:

$$\frac{weight\ of\ NCC\ powder \times percentage\ shade}{concentration\ of\ stock\ solution} \quad \text{---------- (4)}$$

3.3.5.1 Dyeing with Direct dye

The dye was added in a well-dissolved condition to the dye bath containing a wetting agent. Common salt (20% owf) was then added. 0.5 g of the sample (NCC in one bath and cotton fabric in another) was then added into the dye bath at 40ºC. The temperature of the bath was raised to the boil over a period of 30 minutes and dyeing was continued at this temperature for 60 minutes. Thereafter, the samples were then rinsed with distilled water and dried(Nkeonye, 1987). The direct dye used was solophenyl yellow PFL which is a bright yellow dye with the chemical structure:

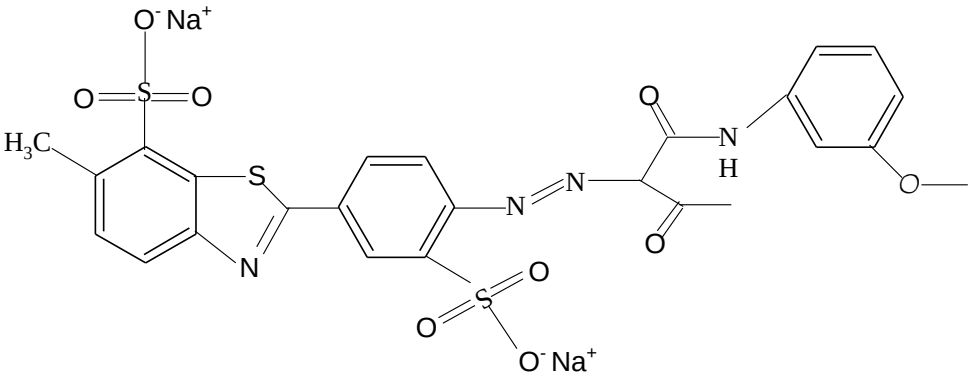


Figure 9**:** Solophenyl Yellow PFL

3.3.5.2 Dyeing with Reactive dye

0.5g of thesamples (NCC powder and cotton fabric) were introduced into a neutral dye bath at 30ºC, equilibrated over a period of 20 minutes, common salt (20% o.w.f) was then added and dyeing was continued for 20 minutes. 0.3% caustic soda (NaOH) was added at this juncture to effect fixation and dyeing was continued for another 20 minutes at 60ºC after which the samples were rinsed and dried (Nkeonye, 1987).The dyed samples were then soaped at boil for 30 minutes, rinsed with distilled water and dried. The reactive dye used is Procion Violet H-3R

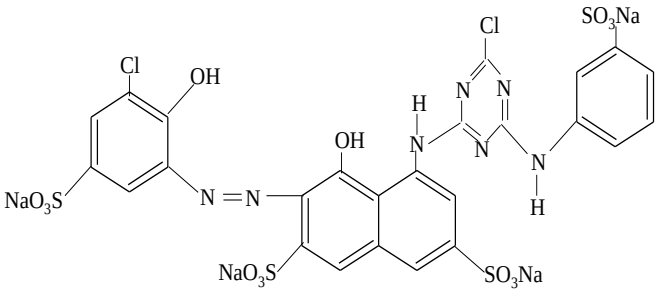


Figure 10:Procion Violet H-3R

3.3.5.3 Dyeing with Disperse dye

High temperature method of disperse dyeing was adopted. 0.5 g each of the NCC powder and fabric were introduced into separatedyebathscontaining 5 g/l soap solution(dispersing agent) at 60ºC. The temperature was raised to the boil and dyeing was continued for 90 minutes. The dyed samples were soaped, rinsed with distilled water and dried. The disperse dye used was Foron Yellow S.E – 2GL with the chemical structure:

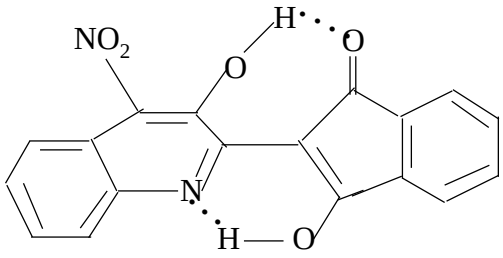


Figure 11:Foron Yellow S.E 2GL

3.3.6 Determination of Percentage Exhaustion

The percentage exhaustion of each of the dyes used was determined by measuring the optical densities of dye solutions before and after dyeing. In the case of the disperse dye, optical densities were obtained by taking 3 ml of the prepared dyebath into a beaker, the water was then allowed to evaporate and 2 ml of absolute ethanol added, stirred well and then the optical density measured as OD_1. After dyeing, 3 ml of the used dye liquor was measured into a beaker and the water allowed to evaporate, 2 ml of absolute ethanol was then added into the beaker and stirred, the optical density was then measured as OD_2. These values where then used in the formula:

$$Exhaustion\ (\%) = \frac{OD_1 - OD_2}{OD_1} \times 100\% \text{ ---------- (5)}$$

Where: OD_1 is optical density of dye solution before dyeing

OD_2 is optical density of the dye solution after dyeing.

3.3.7 Determination of Percentage Fixation

The percentage fixation is the amount of the total dye in dye bath that has been retained by the material being dyed. It is express as a percentage and was calculated using the formula

$$Fixation\ (\%) = \frac{OD_1 - OD_2 - OD_3}{OD_1 - OD_2} \times 100\% \text{ ---------- (6)}$$

Where: OD_1 and OD_2remain optical densities before and after dyeing, respectively, and

OD_3 is the optical density after soaping.

3.3.8Colour Fastness Tests

After dyeing, the dyed NCC powder and fabrics (dyed alongside as control) were subjected to colour fastness tests to investigate how well the dyed powder can withstand certain agencies. It is worth mentioning here that the fastness tests were only conducted in relation to the end use of the NCC. Thus, Fastness to Washing, light and chlorinated water were conducted.

3.3.8.1 Washing fastness (ISO test No. 1)

The samples were introduced into the wash bath containing 5g/l soap solution at 40ºC using liquor ratio of 50:1. Washing was carried out for 30 minutes after which the NCC

was filtered, rinsed and dried. The grey scale was then used to access change in colour in comparison with the untreated sample.

3.3.8.2 Light fastness (ISO B01: 1978)

The dyed samples (NCC powder and fabrics) were exposed facing due south, sloping at an angle from the horizontal. The samples were covered with glass and provision was made for ventilation. Together with the samples, eight blue card standards were exposed with the samples and the blue card standardspartly covered with an opaque cardboard paper. Exposure was terminated when the contrast between the exposed and unexposed parts of the samples was equal to grade 3 on the Grey Scale for assessing change in colour (Nkeonye, 1987).

3.3.8.3 Fastness to chlorinated water (ISO 105 – E03)

This test was intended to access the resistance of coloured NCC to concentrations of active chlorine such as used in the treatment of water for swimming baths. The NCC was introduced into a still container containing a solution of sodium hypochlorite (20mg/l active chlorine) at a pH of 8. The container was closed and agitated for 1 hour in the dark at 27 ± 2ºC (room temperature). The specimen was filtered, rinsed and dried after which change in colour was accessed using the grey scale for accessing change in colour (Nkeonye, 1990).

CHAPTER FOUR

4.0 RESULTS

4.1Yield Analysis

The yield of the hydrolysis process was determined using the formula

$$percentage\ yield = \frac{dry\ weight\ of\ NCC}{dry\ weight\ of\ purified\ cob\ powder} \times 100\% \text{ ---------- (7)}$$

The percentage yield was calculated from three hydrolysis processes, the average was used as the overall yield. The table below shows the result of the yield analysis:

TABLE 4.1: Yield of nanocrystalline cellulose Extraction

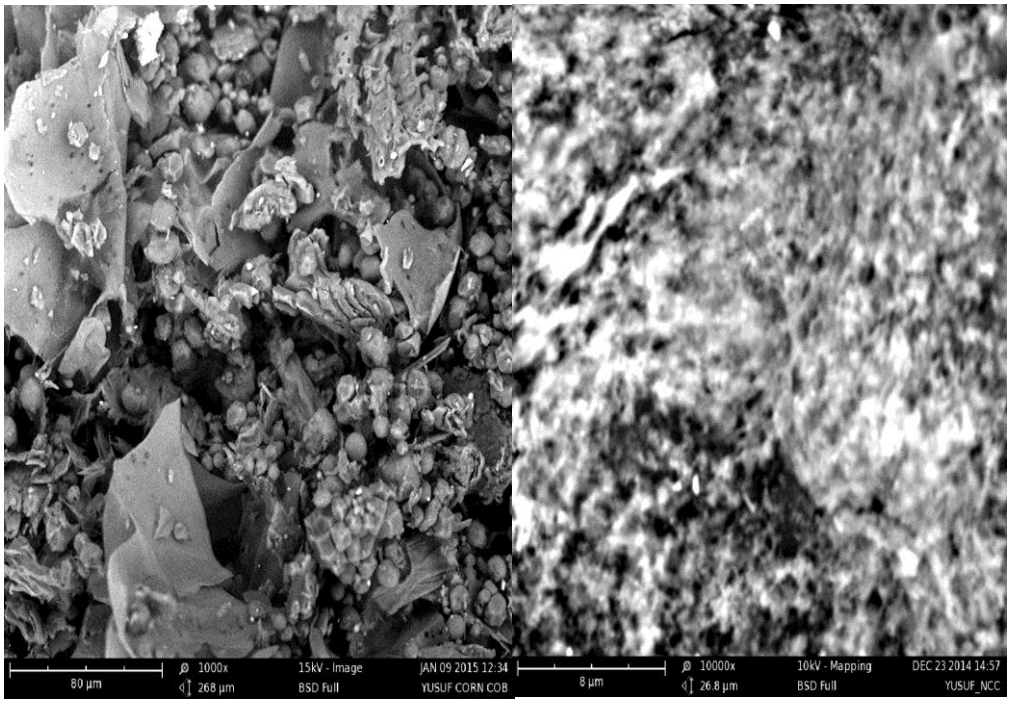
S/N	Weight of purified cob powder (g)	Weight of NCC powder (g)	Yield (%)
1	9.90	3.11	31.41
2	20.00	5.85	29.25
3	20.00	6.06	30.30

$$Average\ yield\ (\%) = \frac{31.41 + 29.25\ + 30.30}{3}$$

$$= 30.32\%$$

4.2 Scanning Electron Micrograph Results

The SEM images of both the corn cob and NCC samples at a magnification of ×1000 are shown in plate IV.



(a) (b)

Plate IV: SEM images of; (a) Corn cob (b) NCC

4.3Fourier-Transformed Infrared Interpretation

The graphs of the IR absorption of both the corn cob and NCC are shown in figure 12 below;

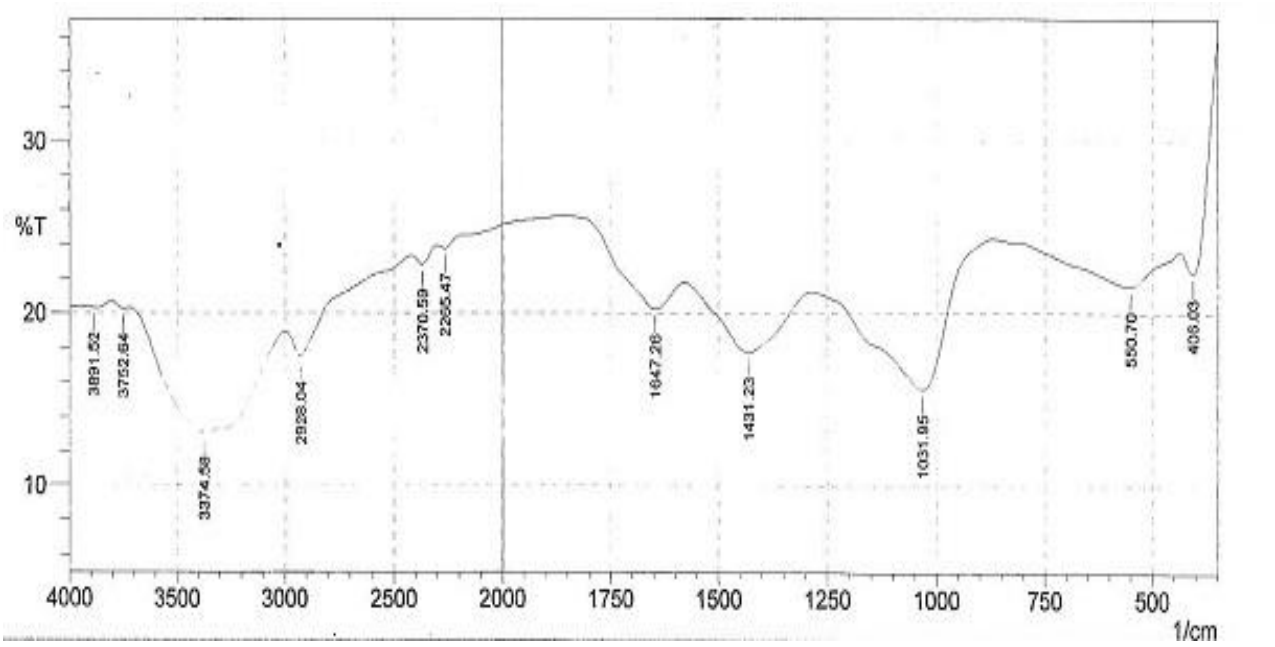


Figure 12a:FTIR graph of Corn Cob powder

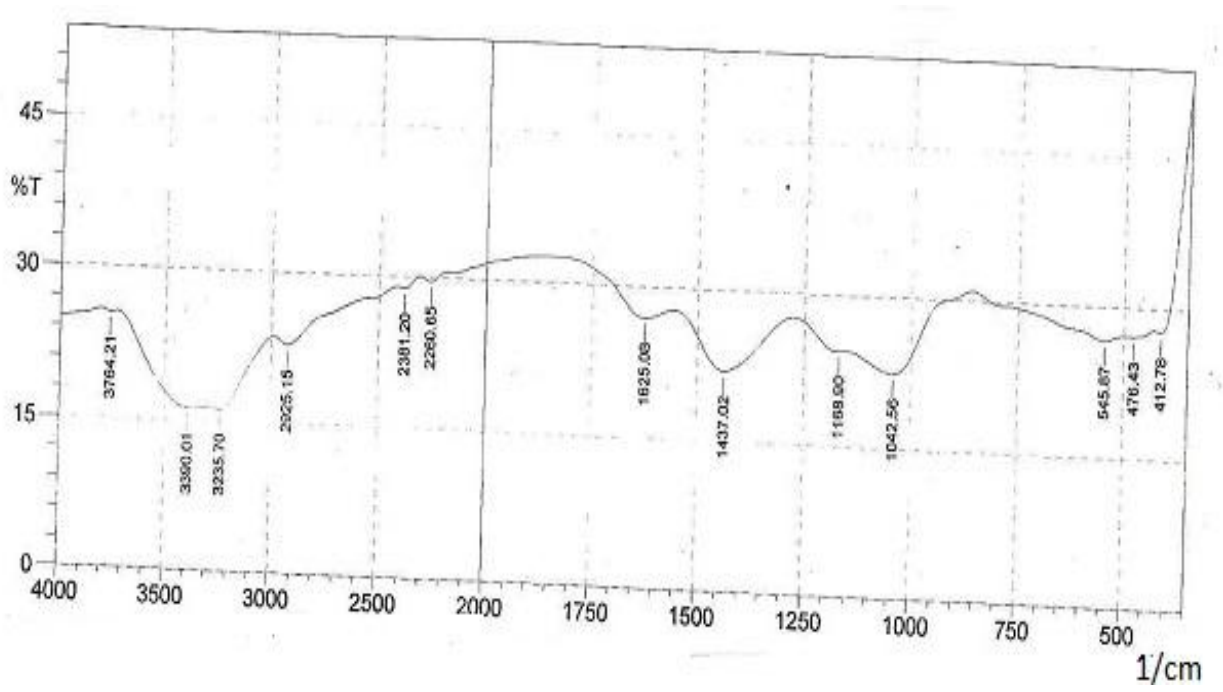


Figure 12b:FTIR graph of NCC powder

4.4 X-Ray Diffraction Results

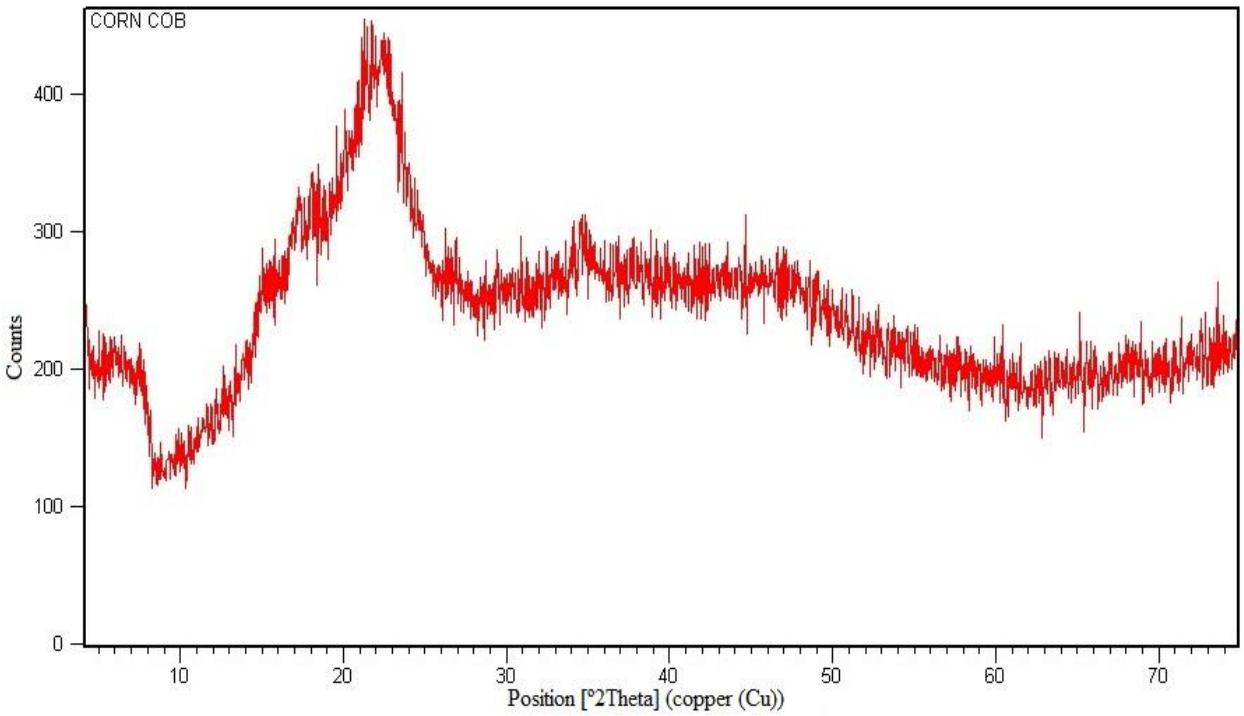


Figure 13a: Diffractogram of Corn Cob powder

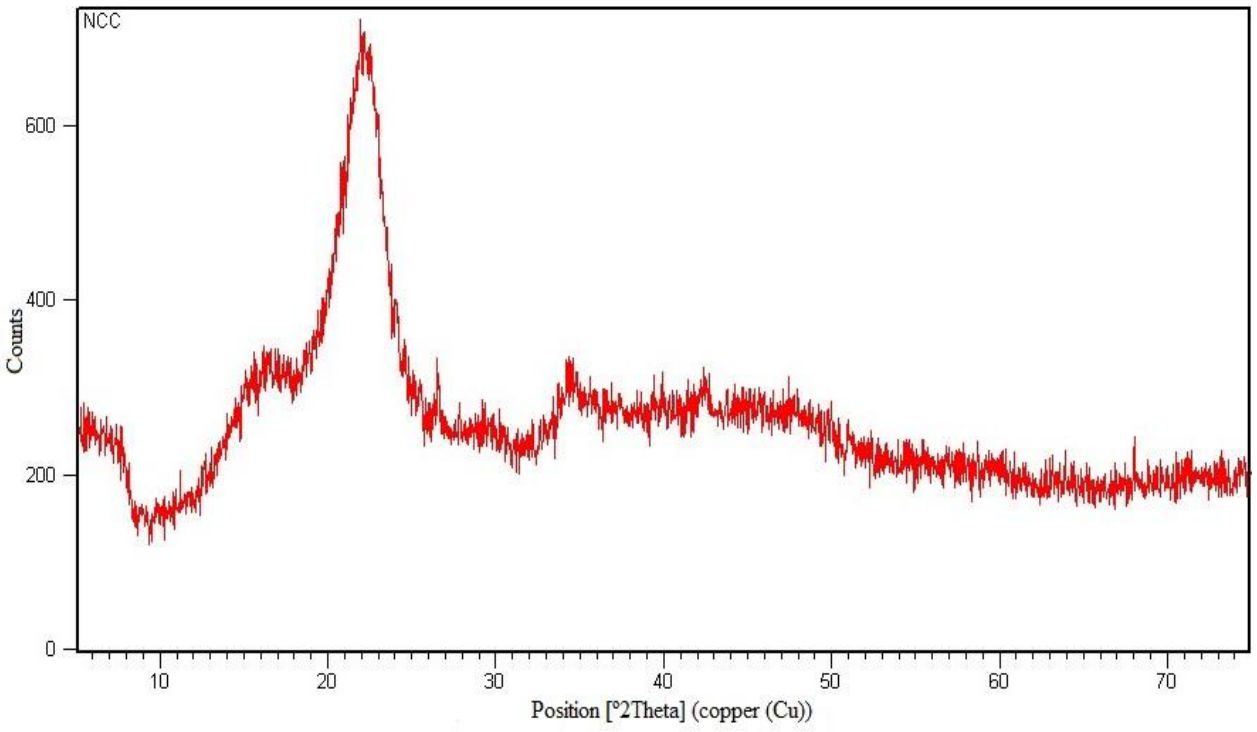


Figure 13b: Diffractogram of NCC powder

The crystallinity of both corn cob and NCC was determined from the diffractograms shown in Figure 13(a) and (b) above. The crystallinity index was determined using the peak high method using the formula in 3.2.4.3.

I_{002} and I_{am} were found from the diffractograms in Figures 13a and 13b to be 675.5 and 142.5 for NCC and 421.4 and 136.3 for corn cob, respectively. Thus, the crystallinity index (C.I) of the corn cob was calculated as follows:

$$C.Icc = \frac{421.4 - 136.3}{421.4} \times 100$$

$$= \frac{285.1}{421.4} \times 100$$

$$= 0.676 \times 100 = 67.6\%$$

Likewise, the crystallinity index of the NCC was calculated:

$$crystallinity\ index\ of\ NCC\ (C.I) = \frac{675.5 - 142.5}{675.5} \times 100$$

$$= \frac{533.0}{675.5} \times 100$$

$$= 0.7890\ \times 100$$

$$= 78.9\%$$

4.5 Thermogravimetry Results

Figure 14 below shows the respective TGA and DTG thermograms of both corn cob and NCC, respectively.

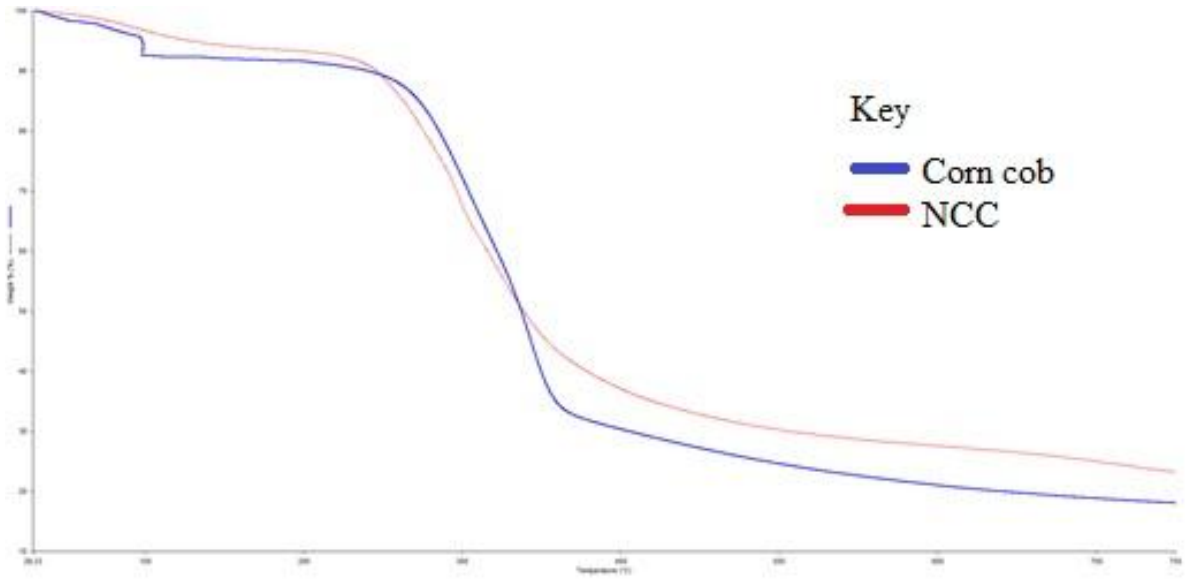


Figure 14a:TGA of Corn Cob and NCC.

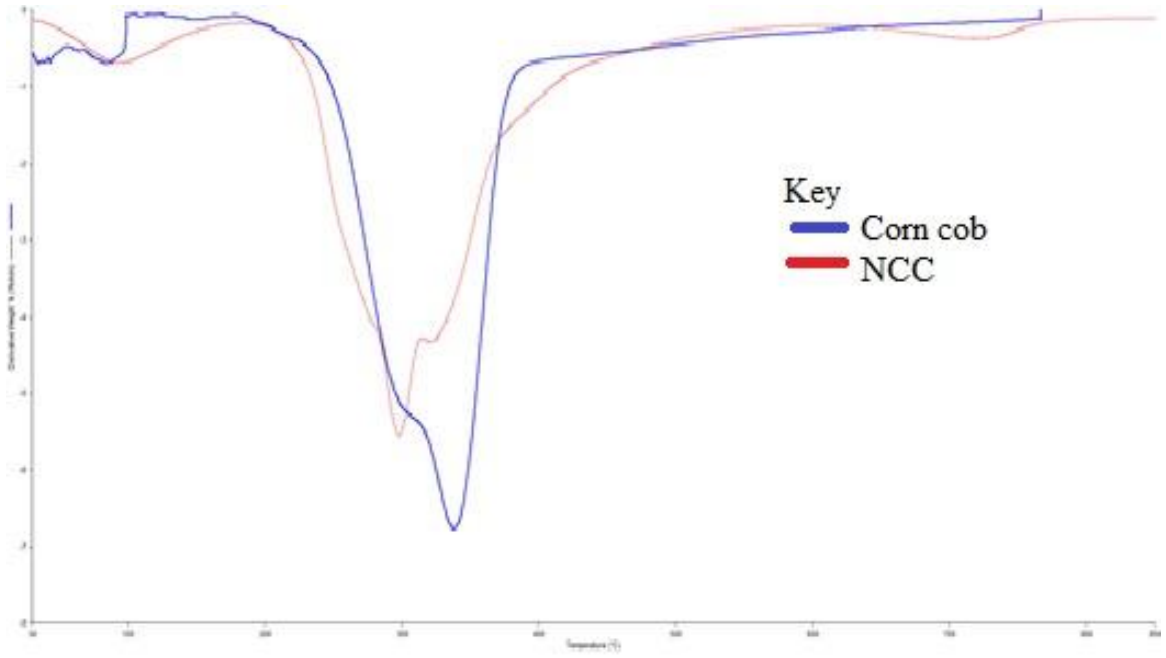


Figure 14b: DTG thermograms of Corn Cob and NCC

The following information was obtained from the two graphs using the Delta Y software.

Table 4.2:Thermal parameters from thethermograms

S/N	Property	NCC	Corn Cob
1	Moisture Content (%)	5.771	7.495
2	Perc. Degradation (%)	70.432	71.187
3	Peak temperature (°C)	298.94	339.77
4	T_{50} (°C)	336.99	336.89
5	Ash Content (%)	1.148	2.599
6	Degradation Temp. range (°C)	184.76 – 755.62	195.84 – 620.88
7	Onset	X= 251.93°C	X= 279.98 °C
		Y = 92.402%	Y = 89.82%

4.6 Swelling Test Result

The swelling index was determined usingthe formula in Equation 2 above. Thus:

$$swelling\ index = \frac{7.5 - 6.0}{7.5} \times 100\%$$

$$= 20\%.$$

4.7 Density Test results

Using the formula in section 3.2.4.6, the density of the NCC powder was calculated with M_1, M_2 and M_3, measured as 185.03g, 2.34g and 185.36g, respectively. Density of water (Pw)= 0.9975g/ml. Thus,

$$P_p = P_w \times \frac{M_2}{M_1 + M_2 - M_3}$$

$$= 0.9975 \times \frac{2.34}{185.03 + 2.34 - 185.36}$$

$$= 0.9975 \times \frac{2.34}{2.01}$$

$$= 0.9975 \times 1.1641$$

$$= 1.1612\ g/ml$$

Equally, the density of corn cob powder was also determined and calculated as above the value obtained been 1.1600g/ml.

4.8 Particle Size Analysis result

The graph below gives the particle size distribution of the NCC. It is important to note here that; the graph gives distribution based on a single dimension (in this case, length).

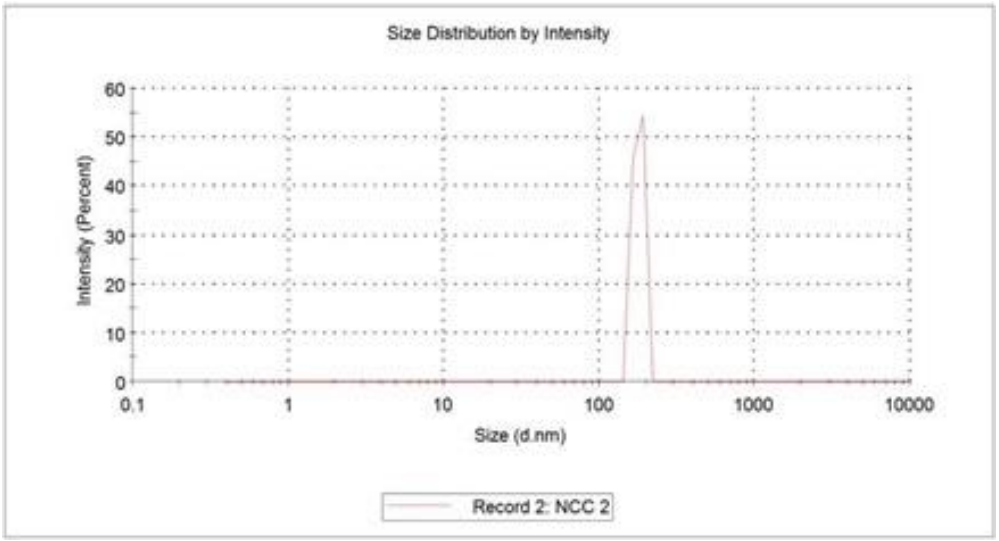


Figure 15:Particle Size Distribution

4.9Percentage Exhaustion and Fixation of Dyes

The percentage fixation of the reactive dye on NCC and fabric were calculated as 64.79% and 76.36%, respectively. Percentages of exhaustions were calculated for each of the dyes. The results are shown below:

TABLE 4.3: Dye exhaustion on NCC and fabrics

S/N	Dyes	NCC Powder			Fabric		
		OD_1 (mg/l)	OD_2(mg/l)	Exhaustion (%)	OD_1 (mg/l)	OD_2(mg/l)	Exhaustion (%)
1.	Foron Yellow S.E-2GL	1.33	0.62	53.38	1.33	0.58	56.39
2.	Procion Violet H-3R	1.56	0.50	67.94	1.56	0.52	66.66
3.	Solophenyl Yellow	1.42	0.66	53.52	1.42	0.71	50.00

4.10Colour Fastness Results

The results for the colour fastness to washing, light and chlorinated water are as follows

TABLE 4.4: Colour fastness ratings of dyed NCC and control fabrics

S/N	Dyes	NCC Powder			Fabric		
		Wash fastness	Light fastness	Chlorinated water	Wash fastness	Light fastness	Chlorinated water
1.	Foron Yellow S.E-2GL	3 – 4	6	2	4	6 – 7	2
2.	Procion Violet H-3R	3	6	2	3	6	2
3.	Solophenyl Yellow PFL	2	5	3	2	5	2 - 3

CHAPTER FIVE

5.0 DISCUSSION

5.1 Yield Analysis

30% yield was obtained using the sulphuric acid hydrolysis. This yield is close to the yield obtained through enzymolysis by Chen *et al.*,(2012). According to them, the NaOH pre-treatment swells the cellulose more thereby making it more susceptible to hydrolysis which is confirmed by comparing the yield obtained with untreated cotton fibres (14%) to that of NaOH pre-treated fibres (32%). During the hydrolysis, considerable amount of the raw cellulose is lost as more amorphous regions were dissolved, this leads to the increased yield obtained as there is lesser content of unreacted fibres compared to that which remained in the NaOH untreated sample.

5.2 Scanning Electron Microscopy

The scanning electron microscope images shown in plate IV(a) and (b) show a clear difference between the two samples.The corn cob image (a) shows a rough surface of different sizes and orientation of particles. This can be attributed to the fact that the corn cob powder contains all the components that give plant cell its rigidity and therefore rough appearance. After pre-treatment and subsequent hydrolysis, increased homogeneity and lustre was observed (image b). These effects are due to the chemical treatment the corn cob underwent. The hemicelluloses, lignin and pectins were successfully removed and the SEM image thus represents appearance of nanocrystalline cellulose. The two images show successful modification of the rough corn cob.

5.3 Fourier-transformed Infrared Spectroscopy

The FT-IR spectra give us useful information on functional groups present in the sample. However, not all the peaks in the spectra can be assigned functional groups as some of these peaks arose from impurities that might have got into the sample during preparation and handling. Subsequently, only key characteristic peaks are considered.

The two spectra shown in figure 12(a) and (b) above are similar with little shift in position of certain peaks and also change in intensity. This suggests an unaltered chemistry of the starting material.

In both spectra, peaks were observed around 1031 – 1042 cm^{-1}, 1431 – 1437 cm^{-1}, 1625 – 1647cm^{-1}, 2925 – 2928 cm^{-1} and around 3374 – 3390 cm^{-1} corresponding to C – O stretching vibration of primary alcohols and phenols, CH_2 bending vibration (deformation), free O – H stretching vibration of absorbed water, C – H stretching vibration and hydrogen bonded O – H stretching vibration, respectively. There is however, one peak of interest that appears to be absent in the NCC spectra; the peak at around 1558cm^{-1}. This peak is assign to aromatic C = C stretching vibration of remaining lignin (Qui and Chen, 2008). The absent of this peak in the NCC spectra confirmed the removal of lignin from the corn cob.

Another band of interest is the band around 1430 – 1440 cm^{-1}. This is called "the crystallinity band". Increase in intensity of this band means increase in crystallinity of the sample. In the corn cob spectra, this band appeared at exactly 1431.23cm^{-1} with intensity of 3.749(appendix I) whereas in the NCC spectra, it appeared at exactly 1437.23cm^{-1} with intensity of 5.7072 (appendix II). This increase in intensity showed us successful increase in crystallinity as we go from corn cob to NCC.

5.4 X-ray Diffraction Analysis

The XRD patterns shown in Figures 13(a) and (b) have distinctive differences. The characteristic peak at the 002 plane ($2\theta = 22^{o}$) is associated with crystallinity. It can be seen from the two diffractograms which shows that this peak (002) is very broad in corn cob than in NCC. The broadening of the peak is attributed to increased amorphousity as the corn cob contains all the amorphous regions predominated by lignin and hemicelluloses. It is generally accepted that in the cellulose community that peak broadening is due to amorphous cellulose. After hydrolysis, the characteristic peak at the 002 plane showed increased sharpness and intensity. This is an evidence that hydrolysis (destruction of the amorphous regions) took place.

The crystallinity index of the corn cob as calculated here is less than that of the NCC calculated (CC = 67.65% and NCC = 78.90%). This is because the corn cob contains both crystalline and amorphous regions. After hydrolysis, more amorphous regions were destroyed leaving much more crystalline regions and thus increased crystallinity.

The crystallinity index obtained here for the NCC is very close to that obtained by chen*et al.,* 2012 through enzymolysis (78.1%). Because of the complexity of the cellulose structure, some amorphous regions still exist between the crystalline regions and so the crystallinity of NCC cannot reach 100% (chen*et al.,* 2012).

5.5 Thermogravimetric Analysis

The degradation of the corn cob begins at around 196^{o}C while that of the NCC starts around 185^{o}C. The decrease in degradation temperature from corn cob to NCC can be attributed to the fact that the raw corn cob contains more of inherent organic matter and

other constituents together with the cellulose, as it does not undergo any purification. This heterogeneous nature of the corn cob causes its degradation to commence at slightly higher temperature. The NCC obtained on the other hand, contains more of cellulose only and thus earlier degradation observed. Although pyrolysis in corn cob started at slightly higher temperature, it can be seen from the DTG thermogram that the degradation temperature range is narrower than that of NCC. This is probably due to the non-homogeneity of the cob, as the other inherent components contribute to more amorphousity, the degradation once started tends to be rapid. This indicates that; increase in crystallinity favours steady pyrolysis.

The onset temperatures from the diffractograms are 251.93 ºC and 279.98ºC for NCC and corn cob, respectively. This suggests that; the corn cob is slightly more thermally stable than the NCC. The corn cob contains more polymer chains fused together from cellulose, hemicelluloses and even lignocelluloses. After hydrolysis, there is a significant reduction in the fused unit length as most of these lignocellulose and hemicelluloses are washed off. This suggests that as the units in a chain increases the thermal stability of the molecule increases, a fact well accepted in polymer chemistry for all types of polymers (Priyanka and Anjani, 2014).

5.6 Swelling Test

The swelling index obtained is low indicating that: NCC have a very low swelling capacity. This is true because the NCC is much more compacted and since the amorphous regions were hydrolysed this leaves little or no spaces for water retention which will subsequently lead to swelling.

5.7 Density Test

There was only a slight increase in density from the corn cob to NCC. This can be explained on the basis of the concept of density itself. Density of any material is inversely proportional to the volume it occupied at a constant mass. The corn cob will occupy higher molecular volume because of the high level of amorphousity and thus less dense. On the other hand, NCC is made up of more compact structure and occupies less volume and therefore appears denser than the corn cob. We can say here that: Density can be directly proportional to crystallinity.

5.8 Particle Size Distribution

The particle size distribution analyser gives us average particle size in one dimension (diameter). From the distribution graph above, the mean length of the NCC particles was found to be 178nm. However, this may be different from particle size analysis where a different approach has been employed.

5.9 Percentage Exhaustion and Fixation

From table 4.3 above, the reactive dye (Procion Violet H-3R) has the best exhaustion, followed by the direct dye (Solophenyl Yellow) and the Disperse dye (Foron Yellow S.E 2GL). The high exhaustion of the Reactive dye is as expected because, although the material is highly crystalline, it is still purely cellulose and therefore possess good affinity for reactive dyes. The dyeing of NCC with reactive dye is achieved through covalent bonding between the dye reactive group and the OH groups of the NCC.

The exhaustion of the disperse dye is also reasonably good and resulted from the hydrophobic forces existing between the highly hydrophobic fibres and the hydrophobic dye molecule. However, the dyeing method used also has influence on the exhaustion of the dye, which means an even better exhaustion is possible when carrier dyeing is used. The small molecular size of disperse dyes is also an additional advantage to the dyeing of crystalline materials.

The dye retention of NCC when with direct dyes is achieved mostly through van der Waals forces of attraction and hydrogen bonding between the dye molecules and the NCC. Direct dyes are known to have high affinity for cellulose.

5.10 Colour Fastness

Washing

From table 4.4, we can see that NCC sample dyed with direct dye (Solophenyl Yellow PFL) shows poor fastness to washing (rating of 2). This is typical of direct dyes. However, poor fastness to washing in direct dyed material is often reduced using after treatment process like treatment with cationic fixing agents, formaldehyde, metallic and diazonium salts (Nkeonye, 1990).

The reactive dyed NCC shows better fastness to washing with rating of 3. This fairly good fastness can be attributed to the covalent bond that exists between the dye reactive groups and the cellulose. The covalent bond is thought to be a very strong attraction and therefore difficult to be broken by ordinary washing.

The disperse dyed NCC shows the best washing fastness among the three. This can simply be attributed to the compactness of the NCC and once the disperse dye molecules find their way in, they become locked in and very difficult to come off.

Light

From table 4.4 also, reactive and disperse dyed NCC have very close rating in light fastness. Light fastness is affected by a number of factors e.g. the intensity and spectral composition of the light used for exposure, the spectral properties of the dyed fibre, the nature of bond between the dye and the fibre, the dye concentration in the fibre, the dye reactivity, the state of the dye in the fibre and physical and chemical constitution of the fibre (Thiagarajan and Nalankilli, 2010). That is to say, the close fastness of the two to dyes can be better understood if those factors have been critically looked into. However, disperse dyes are known to have slightly better light fastness than reactive dyes.

The direct dyed NCC shows lesser fastness rating than the two dyes. Also, direct dyes are known to have moderate to good fastness to light.

Chlorinated water

The Disperse and reactive dyed NCC show poor fastness to chlorinated water. This is because the chlorine has bleaching effect on the dyes. However, the direct dyed NCC shows excellent fastness to chlorinated water. This is because the decolouration effect of the chlorine is on the bond between the fibre and the dye and not on the dye molecule itself. This was confirmed by treating each of the dyes solution with sodium hypochlorite (20mg/l available chlorine) in the absence of light. After 60 minutes, coloured solutions

remained unchanged; confirming that the bleaching effect was not directly on the dye molecules.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECCOMENDATIONS

6.1 Summary

Nanocrystalline cellulose was successfully extracted from corn cob using acid hydrolysis process. The extracted NCC was characterized using FT-IR, SEM, XRD, TGA and PSA. Other tests conducted were Pycnometry (density test) and swelling test. The extracted NCC was then dyed using disperse, reactive and direct dyes. The percentage exhaustions were calculated and the dyed NCC was subjected to fastness tests.

It was found out that the chemical treatment carried out on the corn cob improve the surface properties of the cellulose which also help interaction between the cellulose and other molecules. The FT-IR analysis confirmed that no damage was done to the functional groups of the original cellulose and also shows the successful removal of lignin and related compounds. It was evident that the hydrolysis process increases the crystallinity of the material. This was confirmed by the increase in intensity of the crystallinity peak ($1437.23cm^{-1}$).

The XRD analysis showed that the hydrolysis process increases the crystallinity of cellulose and it was also derived from this analysis that 100% crystallinity is difficult to obtain due to complexity of natural cellulose.

The TGA analysis showed that the refined NCChas lower thermal stability than the natural cellulose but with wider degradation temperature range. This also suggests that; the longer the fused unit chains, the better the thermal stability.

The dyeing of the NCC showed that: Disperse dyes are better dyes for the colouration of NCC, followed by reactive dyes and then direct dyes in this order. However, the fastness tests conducted showed that any of the three dyes can be used to colour NCC depending on the targeted end use application. After treatments processes may be applied where necessary.

6.2 Conclusion

Based on the research carried out it can be concluded that:

Lignin, present in lignocellulosic materials can be successfully removed by caustic soda treatment at appropriate conditions. The acid hydrolysis is an efficient process of extraction of nanocrystalline cellulose. Moreover, more ordered, crystalline regions of cellulose are resistance to sulphuric acid attack at 50 - 60ºC. After comparison with similar works on extraction, the crystallinity index for NCC ranges between 70 – 90%. The crystallinity hardly exceeds this range due to the complex nature of cellulose. Thermal degradation of NCC starts around 185ºC. The thermal stability is proportional to the chain length of the polymer.The dual nature (hydrophilic and highly crystalline) of NCC makes it dyeable with both hydrophilic (reactive and direct) and hydrophobic (disperse) dyes. However, the colour fastness results show that the choice of a particular class of dye depends on the end use of the NCC being dyed.

6.3 Recommendations

At the end of the research, the following recommendations were made.

1. Application of other classes of dyes should be investigated including disperse-reactive dyes should be investigated.
2. More forest and agricultural residues should be used for NCC extraction.
3. Other important material properties should be investigated to widened application areas for NCC.
4. More projects aimed at solving environmental problems and depending on locally available raw materials should be embarked on.

REFERENCES

Abdul Khalil H.P.S., Davoudpour Y., Nazrul Islam M.D., Mustapha A., Sudesh K., Dungani R. and jawaid M. (2014). Production and Modification of Nanofibrillated Cellulose UsingVarious Mechanical Processes: a review. *Carbohydrate polymers,* 99: 649 – 665.

Akerholm M, Hinterstoisser B. and Salmen L. (2004). Characterization of the Crystalline Structures of Cellulose using Static and Dynamic FT-IR Spectroscopy.*Carbohydrate Residues,* 339: 569 – 578.

Akil, H. M., Omar M. F., Mazuki A. A. M., Safiee S., Ishak Z. A. M. and Abu Bakar A. (2011). Kenaf Fibre Reinforced Composites: A review. *Material and Design*, 32: 4107–4121.

Bai, W., Holbery J. and Li K. (2009). A Technique for Production of Nanocrystalline Cellulose with a Narrow Size Distribution.*Cellulose* 16: 455 – 465.

Beck S., Bouchard J. and Berry R. (2012).Dispersibility in Water of Dried Nanocrystalline Cellulose.*Biomacromolecules,* 13: 1486–1494.

*Cellulose.*Retrieved June 11, 2015, from http://en.wikipedia.org/wiki/Cellulose.

Chatwal G. R. (2009). *Synthetic Dyes*. Himalaya Publishing House, Mumbai, p.1.1

Chen, W., Yu H., Liu Y., Hai Y., Zhang M., and Chen P. (2011). Isolation and Characterization of Cellulose Nanofibres from Four Plant Cellulose Fibres Using a Chemical-Ultrasonic Process.*Cellulose,* 18: 433–442.

Chen X., Deng X., Shen W. and Jiang L. (2012). Controlled Enzymolysis Preparation of Nanocrystalline Cellulose from pretreated Cotton Fibres.*Bioresources* 7(3): 4237 – 4248.

Coffey D.G, Bell D.A. and Henderson A. (1995).*Food Polysaccharides and their Applications*.In: Stephen A.M, (Ed) *Cellulose and cellulose derivatives*. Marcel Dekker,New York, p124.

Emil O., Harold M. S. and Mildred W. G. (Eds.). (1954). *Cellulose and Cellulose Derivatives*.Intersciencepublishersinc., New York.

Gardiner E.S., Sarko A. (1985). Parking Analysis of Carbohydrates and Polysaccharides 16:The Crystal Structures of Cellulose IV_I and Cellulose IV_{II}. *Canadian Journal of Chemistry*, 63:173 – 180.

Garvey C.J., Parker I.H., Simon G.P. (2005). On the Interpretation of X-ray Diffraction Powder Patterns in Terms of the Nanostructure of Cellulose I Fibres**.** *Macromolecular Chemistry and Physics*, 206:1568-1575.

Gousse C., Chanzy H., Cerrada M.I and Fleury E. (2004). Surface Silylation of Cellulose Microfibrils: Preparation and Rheological Properties. *Polymer*, 45: 1569 – 1575.

Habib Y., Lucian A. L. and Orlando J. R. (2010). Cellulose Nanocrystals: Chemistry, Self-Assembly and Applications.*Chemical Review*, 110: 3479 – 3500.

Hayashi J., Sufoka A., Ohkita J, Watanabe S (1975). Confirmation of existence of cellulose III(I), III(II), IV(I) and IV(II) by X-ray method. *Journal of polymer science*, 13: 23-27.

Hermans P.H. and Weidinger, A. (1949). X-ray Studies on theCrystallinity of cellulose. *Journal of Polymer Science*, 4:135-144.

He J, Cui S, Wang S.Y (2008).Preparation and Crystalline Analysis of High-Grade BambooDissolving Pulp for Cellulose Acetate**.***Journal of Applied Polymer Science*, 107:1029 –1038.

Heux L., Chauve G. and Bonini C. (2000).Nonflocculating and Chiral-Nematic Self-Ordering of Cellulose Microcrystals Suspensions in Nonpolar Solvents.*Langmuir*, 16: 8210–8212.

Hon D.N-S (1996) Functional polymers: a new dimensional creativity in lignocellulosic chemistry. In: Hon D.N-S (Ed),*Chemical modification of lignocellulosic materials.* Dekker,New York, pp. 1–10.

Hubbe M. A., Rojas O. J., Lucia L. A. and Sain M. (2008). Cellulosic Nanocomposites: A Review.*Journal of Bioresources*, 3: 929–980.

Hult L.E, Iversen T. and Sugiyama J. (2003).Characterization of the Supramolecular Structure of Cellulose in Wood Pulp Fibres**.***Cellulose,* 10:103-110.

Ifuku S., Nogi M., Abe K., Handa K., Nakatsubo F. and Yano H. (2007). Surface Modification of Bacterial Cellulose Nanofibers for Property Enhancement of Optically Transparent Composites: Dependence on Acetyl-group DS. *Biomacromolecules*, 8: 1973–1978.

Ioelovich M. (2012). Optimal Conditions for Isolation of Nanocrystalline Cellulose Particles.*Nanoscience and Nanotechnology*, 2(2): 2 – 13.

Iqbal M. (2008). *Textile Dyes*. Rehbar Publishers, Karachi, Pakistan, pp. 63 – 65.

Iwuagwu M.A and Okoli P.C. (1992). The disintegrant properties of pregelatinized cassava

andwhite yam starches. *World Journal of Pharmacy and Pharmacology*, 9: 49-53.

Jakayinfa S.O. and Scolz V. (2007).*Assessment of Availability and Cost of Energetically Usable Crop Residues in Nigeria*.(Conference on International Agricultural Research forDevelopment, University of Kassel-Witzenhausen and University of Gottingen).

Kobayashi S., Kashiwa K., ShimadaJ., Kawasaki T. and Shoda S. (1992). Enzymatic Polymerization: The First in Vitro Synthesis of Cellulose viaNonbiosynthetic Path Catalysed by Cellulase.*MakromolekulareChemie. Macromolecular symposia*, 54-55(1): 509 – 518.

Liimatainen H., Visanko M., Sirvio J., Hormi J. and Niinimaki J.D. (2013).Sulfonated Cellulose Nanofibrils Obtained from Wood Pulp through RegioselectiveOxidativeBisulfite Pre-Treatment. *Cellulose*, 20(2): 741–749.

Lima M. M., and Borsali R. D. (2004). Rodlike Cellulose Microcrystals: Structure, properties and applications. *Macromolecular Rapid Communication*, 25: 771 – 787.

Nisizawa K. (1973). Mode of Action of Cellulose.*Journal of Fermentation Technology*, 51: 267 – 304.

Nkeonye P.O., (1987). *Fundamental Principles of Textile Dyeing, Printing and Finishing*.

Ahmadu Bello University Press Ltd.,Zaria,Nigeria. pp. 27, 34-36, 57-98, 176, 267-279.

*Occurance, Chemical Structure and Function.*Retrieved June 11, 2015, from http://www.lignoworks.ca/content/what-lignin.

Osaghae O. J. (2009). *Potential Biomass Based Electricity Generation in a Rural Community in Nigeria*.(Masters Thesis, Department of Applied Physics and Mechanical Engineering,Division of Energy Engineering, Lulea University of Technology, Sweden).

Pandey A., Mathew G.M., Sukumaran R.K. andSinghania, R.R. (2008). Progress in Research onFungal Cellulases for Lignocellulose Degradation.*Journal of Scientific and IndustrialResearch*, 67: 898-907.

Peng B.L., Dhar N., Lui H.L. and Tam K.C (2011). Chemistry and Applications of Nanocrystalline and its Derivatives: A Nanotechnology Perspective. *Canadian Journal of Chemical Engineering*, 9999: 1-16.

Peng Y., Gardner D. J. and Han Y. (2012). Drying Cellulose Nanofibrils: In Search of a SuitableMethod.*Cellulose*, 19: 91–102.

Ping L., You-Lo H., (2012). Preparation and Characterization of Cellulose Nanocrystal fromRice Straw. *Carbohydrate Polymers*, 87: 564 – 573.

Priyanka R. S. and Anjani .J. S. (2014). Thermal Stability of Cellulose and their Nanoparticles:Effects of Incremental Increases in Carbonyl and Aldehydes Groups. *Carbohydrate Polymers*, 114: 339 – 343.

Qui W.H. and Chen H.Z. (2008). FTIR Spectra Analysis of the Reactivity of lignin Modified with Laccase.*Spectroscopy and Spectral Analysis* 28: 1501 – 1505.

Ruiz M. M., Cavaille J. Y., Dufresne A., Gerard J.F. and Graillat C. (2000). Processing and Characterization of New Thermoset Nanocomposites Based on Cellulose Whiskers. *Composite Interfaces* 7(2): 117 – 131.

Saito T., Hirota M., Tamura N., Kimura S., Fukuzumi H. and Heux L. (2009). Individualization of Nano-sized Plant Cellulose Fibrils by Direct Surface Carboxylation Using TEMPOCatalyst under Neutral Conditions.*Biomacromolecules* 10: 1992–1996.

Schenzel K, Fischer S, and Brendler E. (2005). New Method for Determining the Degree of Cellulose I Crystallinity by Means of FT-Raman Spectroscopy. *Cellulose*, 12: 223-231.

Segal L, Creely J.J, Martin A.E Jr and Comrad CM (1962). An Empirical Method for Estimatingthe Degree of Crystallinity of Natural Cellulose Using the X-ray Diffractometre.*Textile Research Journal*, 29: 786 – 794.

Spiridon I. and Popa V.I (2008). Hemicelluloses: Major Sources, Properties and Applications. In: Belgacem M.N. and Gandini A. (Eds), *Monomers, Polymers and Composites from Renewable resources*. Elsevier, Amsterdam, pp. 289 – 304.

Sunkyu P., John O. B., Michael E. H., Philip A. P. and David K. J. (2010). Cellulose Crystallinity Index: Measurement Techniques and their Impact on Interpreting Cellulose Performance. *Biotechnology for Biofuels*, 3:10.

Teeaar R, Serimaa R. and Paakkarl T. (1987).Crystallinity of Cellulose as Determined by CP/MAS NMR and XRD Methods**.***Polymer Bulletin*, 17: 231-237.

Thiagarajan P. and Nalankilli G. (2010). A Review of Light fastness of Reactive and Other Classes of Dyes on Cotton Material.*Colourage*, 57: 47.

Xiao B., Sun X.F. and Sun R.C. (2001). Chemical, Structural, and Thermal Characterizations of Alkali-solubleLignins and Hemicelluloses from Maize Stems, Rye Straw and Rice Straw.*Polymer Degradation and Stabilility* 74(2): 307–319.

Yu M., Yang R., Huang L., Cao X., Yang F. andLui D. (2012). Preparation and Characterization of Bamboo Nanocrystalline Cellulose.*Bioresources*, 7(2): 1802-1812.

APPENDICES

Appendix I

FTIR absorption peaks of corn cob with intensities

No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	406.03	22.343	5.785	438.82	349.13	53.024	4.992
2	550.7	21.585	2.259	870.89	438.82	276.249	8.421
3	1031.95	15.621	7.525	1285.6	870.89	295.032	28.32
4	1431.23	17.757	3.749	1577.82	1285.6	207.231	12.182
5	1647.26	20.223	2.617	1824.72	1577.82	160.748	5.88
6	2265.47	23.758	0.364	2303.08	2185.42	72.765	0.318
7	1558.54	22.81	0.768	2421.71	2303.08	75.16	0.814
8	2928.04	17.504	1.97	2999.41	2421.71	394.166	2.7
9	3374.58	13.127	6.511	3711.17	2999.41	577.122	73.232
10	3752.64	20.231	0.046	3799.89	3747.81	35.956	0.034
11	3691.52	20.287	0.003	3899.23	3890.55	6.01	0

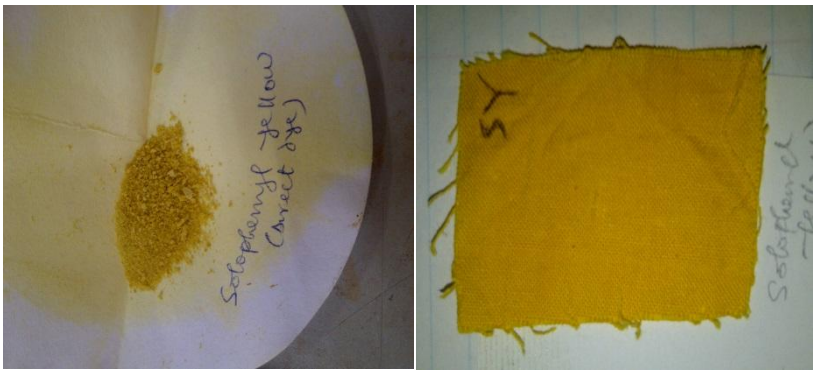
Appendix II

FTIR absorption peaks of NCC with intensities

No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
							1/cm
1	412.78	27.6759	5.1442	429.18	349.13	37.5737	3.9967
2	476.43	27.1698	0.0149	477.4	429.18	27.091	0.0765
3	545.87	26.6394	1.0611	860.28	498.62	197.063	2.84
4	1042.56	22.464	4.4528	1149.61	860.28	169.8555	7.9516
5	1168.9	24.4803	0.511	1274.99	1149.61	73.9399	0.5984
6	1437.02	22.0212	5.7027	1557.57	1274.99	171.2712	13.7471
7	1625.08	26.8809	2.0878	1843.04	1557.57	150.4805	1.7777
8	2260.65	29.5591	0.7671	2311.76	2179.63	68.9999	0.6361
9	2381.2	28.8208	0.5549	2417.85	2311.76	56.5952	0.427
10	2925.15	22.7398	1.4792	2988.8	2417.85	334.4033	1.9198
11	3235.7	16.1504	1.632	3295.49	2988.8	220.5954	3.9659
12	3390.01	16.1864	2.1825	3730.45	3295.49	312.6065	12.879
13	3764.21	25.4291	0.0463	3800.86	3758.42	25.1623	0.0266

Appendix III

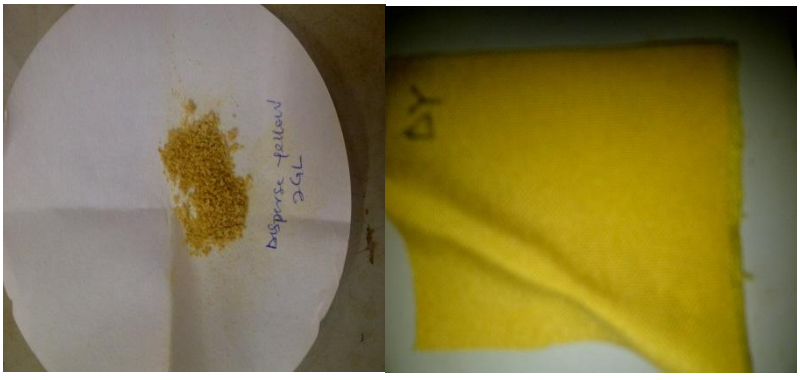
Dyed NCC and fabrics



Solophenyl Yellow NFL dyeings



Procion Violet dyeings



Foron Yellow S.E 2GL dyeings