



# PREPARATION AND CHARACTERIZATION OF CELLULOSE NANOFIBERS FROM AGRICULTURAL WASTE

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**Abstract**— Cellulose is considered to be the most suitable precursor for eco-friendly and renewable materials due to its green nature and inexhaustibility. Nano cellulose can be extracted from low value, India rich agro residual (Bamboo, Neem and Pinewood) with high strength biopolymers. The new cellulose-based nanofibers were obtained by the size reduction process of native cellulose fibres of soft wood pulp by TEMPO-mediated oxidation. TEMPO oxidation is an efficient, faster and better control method of selective conversion of primary alcoholic hydroxyl groups to aldehydes, ketones and carboxyl groups under mild conditions. This regioselective oxidation can be achieved with sodium hypochlorite and catalytic amounts of 2,2,6,6 -tetramethylpiperidine-1-oxyl radical (TEMPO) and sodium bromide under aqueous conditions at pH 10 and ambient conditions. Significant amounts of carboxylate groups are selectively formed on each cellulose fibril surface by TEMPO-mediated oxidation. After TEMPO oxidation carboxylate groups were confirmed by FTIR spectroscopy and quantified titre metrically. The morphology of the fibres was studied by Scanning electron microscope Analysis (SEM). This SEM analysis of the cellulose nanofibers revealed that the diameter is 500nm for Bamboo, 10µm for Neem and 10µm for Pine wood.

**Keywords:** Cellulose nanofibers, TEMPO oxidation, Characterization, Bamboo wood, Neem wood and Pinewood

## I. INTRODUCTION

Cellulose is a first agro-polymer in the biosphere and most common organic compound on the planet. Cellulose possesses many functional properties such as strength, stiffness and toughness. Cellulose is found in the cell walls of plant and bacterial cells. Cellulose is composed of long chains of glucose molecules. The primary commercial source for cellulose is wood, which is essentially a network of cellulose

nanofibers has a hierarchical structure with hemicelluloses and held together by a matrix of lignin of another natural polymer which is easily degraded and removed. Hardwood fibers are generally shorter than softwood fibers. In average, fibers from hardwood are 1mm whereas the length of soft wood fibers ranges from 3-8mm. Nanotechnology researchers are interested in it because these are biodegradable, highly-crystalline cellulose nanofibers, abundantly present in natural plant bodies, have unique properties and sizes different from synthetic nanofibers. Natural fibres come from renewable animal or plant sources but they usually lack the high-performance characteristics of many synthetic fibers. This may change, as the new field of bio-based nano materials promises to deliver eco-friendly, high-performance bio-fiber materials that can replace some of the synthetic materials. Natural fibers provides many advantages including low cost good specific mechanical properties, low density reduced tool wear and biodegradability.[1] Svagan et al., prepared bio foams based cellulose nanofibers from wood pulp [2] nano scale celluloses are intensively used for potential applications such as biomedicine,[3-4] biomaterials engineering,[5-9] membranes,[10-14] and polymer nano composites[15-25] efficient catalysts, electro optical films, microelectronic, gas-barrier films,[26] cosmetics,[27],nanofibers-reinforced composites,[28] flame-resistant materials and other high-tech and high performance materials.

TEMPO oxidations the only method to obtained long and individualized cellulose nano fibrils. The oxidation system is conducted in environmentally-benign conditions and the surface modification reduces energy consumption in mechanical disintegration process. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) is a highly stable nitroxyl radical which is used extensively in the selective oxidation of primary alcohols to corresponding aldehydes and carboxylic acids [29-31]. TEMPO and its analogues are water-soluble, commercially available and stable nitroxyl radicals. Catalytic oxidation using TEMPO has opened a new field of



efficient and selective conversion chemistry of alcoholic hydroxyl groups to aldehydes, ketones and carboxyl groups under mild conditions. Many related studies have been extensively carried out in the last two decades, and have been reviewed in detail.[32-33] Particularly, de Nooy et al., first applied TEMPO-mediated oxidation to water soluble polysaccharides such as starch, amylopectin and pullulan for regioselective conversion of C6 primary hydroxyls to carboxylate groups.[34] In this system, catalytic amounts of TEMPO and NaBr were dissolved in polysaccharide solutions at pH 10–11, and oxidation was started by the addition of NaOCl solution as a primary oxidant. The efficient conversion of primary hydroxyl groups to carboxylates via aldehydes is hypothesized to proceed according to the mechanism. [35-36] Various TEMPO-mediated oxidation reactions of mono-, oligo- and polysaccharides for regioselective conversion of primary hydroxyls to carboxylate groups have been reported. [37-38] The schematic diagram of TEMPO oxidation was shown in scheme 1.

Scheme1: TEMPO-mediated oxidation of primary alcohols to carboxyl groups. [35-36]

The main objective of this paper is preparation of high quality cellulose nanofibers from India rich agro residual (Bamboo, Neem and Pinewood) by using TEMPO-mediated oxidation. We are believing that the TEMPO oxidised cellulose nanofibril having a remarkable advantages in the terms of extremely small diameter and bio-productivity together with eco-friendly preparation process. Our synthesized nanofibers are having a 500nm-10µm length with huge number of carboxylic functional groups. We are strongly believe that these functionalised cellulose nanofibers will act as a nano fillers for metals and metal oxides and the obtained composites will show a better performance for energy and environmental applications.

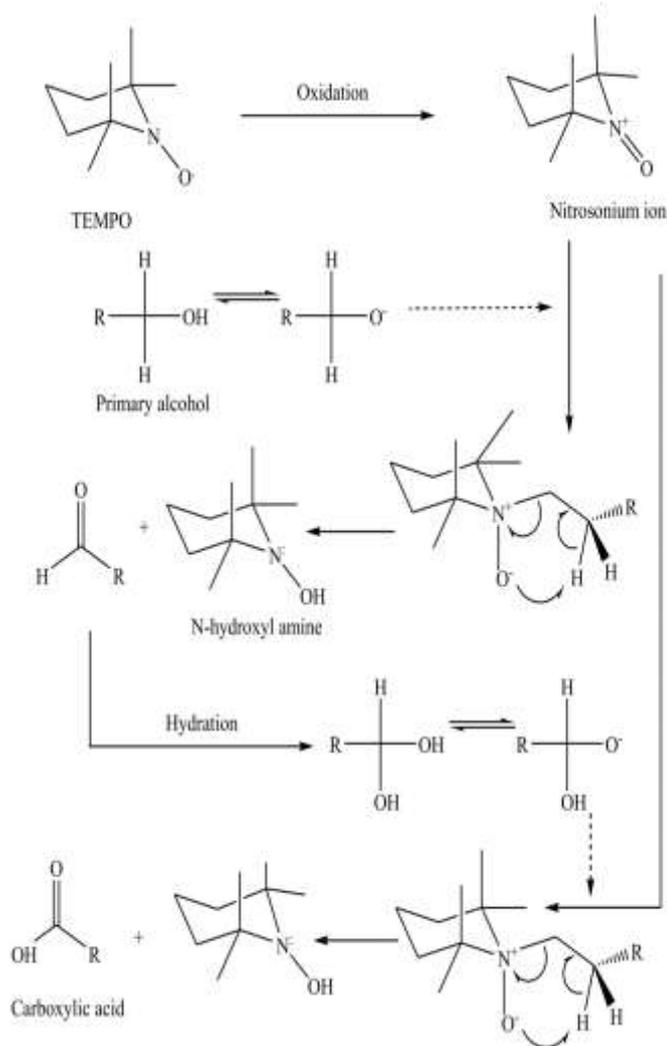
## II. EXPERIMENTAL

### A. Method and Materials

TEMPO, Sodium chlorite ( $\text{NaClO}_2$ ), sodium bromide ( $\text{NaBr}$ ), sodium hypochlorite ( $\text{NaOCl}$ ) solution, Ethanol, Toluene, Methanol, Acetic acid, and other chemicals were purchased from Sigma-Aldrich.

### B. Preparation of cellulose nanofibers

Wood based nano cellulose is extracted from wood pulp was conducted in a soxhlet extractor. Each wood waste (Bamboo, Neem and Pine wood) was prewashed with distilled water followed with ethanol. The authenticated samples were air dried, grinded and sieved into fine particles. About 10 g of authenticated wood sample were packed into soxhlet apparatus for extracting the wax from wood pulp by 1:1 toluene, ethanol at 180 °C. De-waxed wood waste will performed a chemical pre-treatment approach involving chlorites bleaching (delignification) according to the Wise method. Corresponding experimental representation with digital images was shown in Figure 1. For this purpose take 10 g. of De-waxed wood waste and dispersed in 100 mL of distilled water. To this added 1g of  $\text{NaClO}_2$  and 2 mL acetic acid and maintained continuous stirring at 70 °C. After one hour again added 1g of  $\text{NaClO}_2$  and 2mL acetic acid and maintained same experimental conditions. This delignification treatment was repeated four times with fresh chemicals. Thus obtained wood holocellulose was thoroughly washed with water and kept in the wet state. During the delignification process, the lignin is oxidized with the acid chlorite solution appeared a bright yellow colour, finally the cellulose has returned to the white colour.



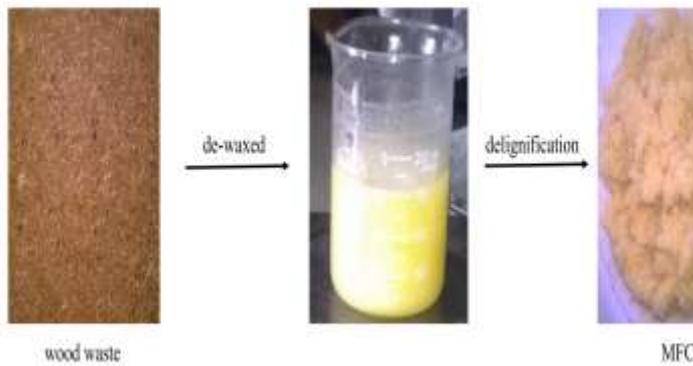


Figure 1. Digital images of preparation of micro fibrillated cellulose from wood waste.

### C. TEMPO mediated oxidation

Cellulose nanofibers were prepared through TEMPO oxidation and mechanical disintegration. Holocellulose (0.648 g, 4 mmol) were dispersed in distilled water (60 mL) with a mechanical stirring. TEMPO (10 mg, 0.065 mmol), NaBr (0.21 g, 2 mmol), and NaOCl (1.76 M, 0.5mL, 0.88 mmol) were stirred in 10 mL of water until complete dissolution. This solution was then added to the holo cellulose suspension, which was mechanically stirred at room temperature. The pH 10 was maintained by adding 0.1M NaOH solution until no more variation in pH was observed, indicating that the reaction was finished. A total of 5 ml of methanol was then added to destroy the residual NaOCl and the pH adjusted to 7 with 0.5 M HCl. Thus-obtained TEMPO oxidized wood holo cellulose nano-fibers with sodium carboxylate groups (TOCNF-COONa) were washed thoroughly with deionized water, centrifuged and stored in the wet state. Fibrillation of TEMPO-oxidized holo cellulose into TEMPO-oxidized nano cellulose will accomplished by ultra-sonication (Al Cano model PS-10A) of oxidized pulp suspension. Corresponding digital images was shown in Figure 2.

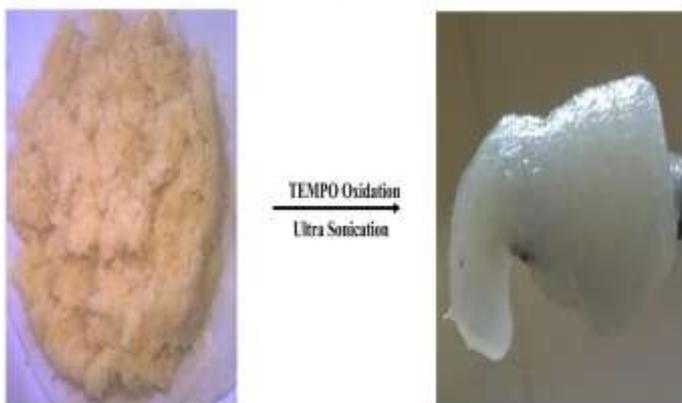


Figure 2: Digital images of preparation of TEMPO oxidized nano cellulose fibers from Micro fibrillated cellulose

### D. Quantification of COOH groups in TEMPO oxidized cellulose nanofibers:

The carboxyl content of the fibers was determined using acid base titration method. The cellulose should be obtained in the acidic form by replacement of its cations by hydrogen ions by the treatment of cellulose samples (0.5g) with 0.01M HCl for 1 h, followed by washing with distilled water. After that 50 ml of distilled water and 30ml of 0.25 M of Calcium-acetate solution were added to the fibers suspension. After standing during 2 h with frequent shaking, to facilitate completion of the interchange, 30 ml portions of the suspension were titrated with 0.01 M sodium hydroxide, using phenolphthalein indicator. The carboxyl contents are calculated as follows

$$\text{Amount of COOH} = \frac{80}{30} \frac{0.01MV(\text{NaOH})}{m(1 - \frac{w}{100})} \text{ mmol}$$

Where 0.01 M is concentration of NaOH, V is Volume (ml) of NaOH solution used for titration, m is weight of treated fibers (g) and w is moisture content (%).

### E. Determination of moisture sorption

Moisture sorption of oxidized cellulose fibers was determined according to standards (ASTM D 2654-76, 1976). Fibers were exposed to standard atmosphere for 24 h. Moisture sorption was calculated as weight percentage of absolute dry material.

## III. RESULTS AND DISCUSSION:

The proposed mechanism of TEMPO-mediated oxidation assumes that the actual oxidation of the substrate is effected by a nitrosonium ion, which is derived from the TEMPO radical by the primary oxidant. During the reaction, the nitrosonium ion is reduced to a hydroxylamine molecule, which subsequently reacts with one molecule of nitrosonium ion (in alkaline medium) to regenerate 2 molecules of TEMPO radical and water. Most TEMPO-mediated oxidation of cellulose is carried out in aqueous media at alkaline P<sup>H</sup>. A TEMPO/NaOCl/NaBr system is often used whereby the degree of cellulose oxidation is determined by the amount of NaOCl added. Systematic diagram of TEMPO oxidation of cellulose was shown in Figure 3.

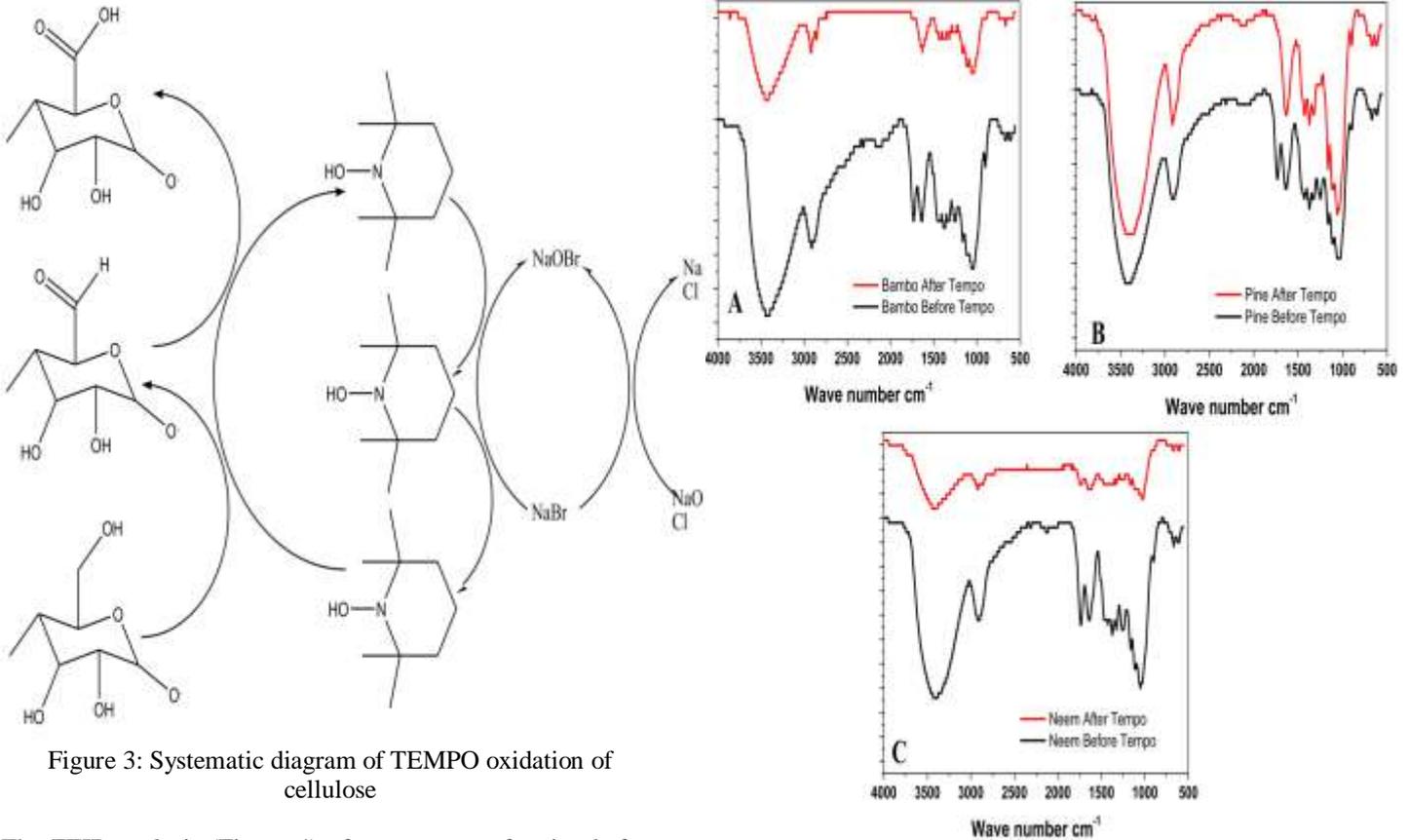


Figure 3: Systematic diagram of TEMPO oxidation of cellulose

The FTIR analysis (Figure 4) of non-aqueous fraction before oxidation with Tempo shows a broad peak of Primary alcohol OH range from 3740-3850  $cm^{-1}$  for cellulose nanofibers prepared from Bamboo, Pine and Neem, respectively. After oxidation with TEMPO a peak range from 1730-1740  $cm^{-1}$  is due to  $-COOH$  stretch along with broadened peak of  $-OH$  range from 3415-3425  $cm^{-1}$  confirms formation of  $-COOH$  group in Bamboo, Pine and Neem celluloses, respectively.

Figure 4: IR graphs of cellulose fibers before and after TEMPO oxidation of a) Bamboo b) Pine c) Neem

The morphology of the fibers can be studied by using scanning electron microscopy (SEM) are shown in Figure 5. SEM observations of highly oxidized celluloses have indicated individual cellulose fibrils that is nanofibers. The fibrillation process was greatly affected by micro and nanostructures of Bamboo and Pine, Neem fibers, though ultra-sonication is a strong treatment for break the structures of fibers. Finally fibrillation will affect the chemical process and final product. According to SEM images Bamboo has shown better nanofibrils with length of 500nm by comparison of Pine and Neem woods.

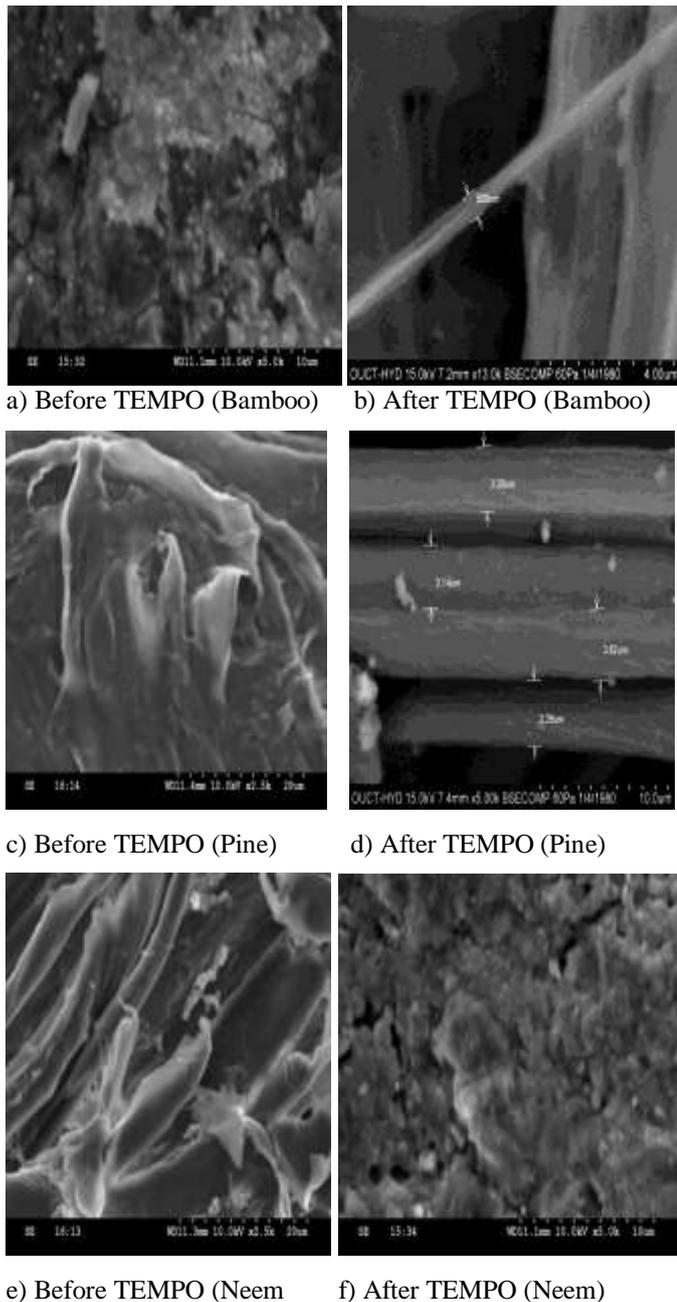


Figure 5: SEM images of cellulose fibers a) Before TEMPO (Bamboo) b) After TEMPO (Bamboo) c) Before TEMPO (Pine) d) After TEMPO (Pine) e) Before TEMPO (Neem) f) After TEMPO (Neem)

**A. Determination of carboxyl groups in the TEMPO-oxidized cellulose fibers:** The amount of COOH groups in cellulose nanofibers of Pine is 4.41mmol/g, Neem is 3.88mmol/g and Bamboo is 4.07mmol/g. The amount of carboxyl content is more in Pine when compared to Neem and Bamboo wood wastes.

**B. Determination of moisture sorption:** The moisture sorption of Pine is 1.61%, Neem is 18.425% and Bamboo is 26.185%. Moisture sorption is less in Pine when compared to Neem and Bamboo wood wastes.

#### IV. CONCLUSION

Cellulose nanofibers were isolated from a variety of natural fibers by chemical treatments. The objective of this paper is to preparation of TEMPO oxidized nanofibers of Bamboo, Pine and Neem woods with length ranging from 500nm-10 $\mu$ m. Development of cellulose nanofibers relatively cheap, biodegradable cellulose and biodegradable-renew-able polymers is particularly attractive from an environmental point of view. We believe that the prepared functionalized cellulose fibers is a good template for metals and catalysts for different applications in energy, environmental and bio applications.

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