

# Ball Milling: A Green Technology for the Preparation and Functionalization of Nanocellulose Derivatives

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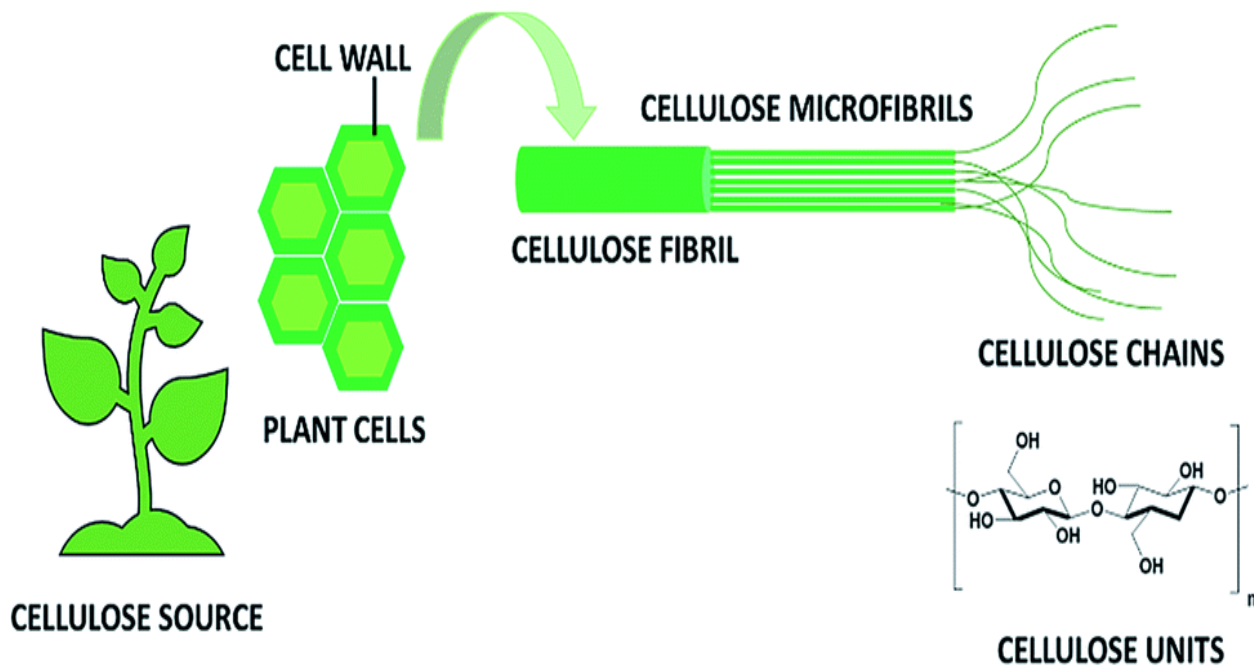
**ABSTRACT:** Ball milling is an easy, fast, and minimum cost technology having a wide range of applications. The manufacturing and chemical optimization of cellulose nanocrystals and nanomaterials is among the most promising uses of this approach to the development of cellulose. Nanotubes are ground into ultrafine powders using the ball milling method. When tiny rigid balls collide in a secret jar mostly during ball milling, localized high pressure is created. Stainless steel, ceramic, as well as flint pebbles are common choices. A ball mill is a tubular grinder for grinding materials like ores, additives, ceramic raw materials, as well as paints. Ball mills rotate along a horizontal axis, partially filled with the substance to be ground and the grinding process. Although many experiments have been conducted, in the form of cellulose nanoparticles, the technique's promise is still to be fully recognized. This paper is an attempt to bring current work into context by emphasizing the importance and promise of this renewable strategy for identifying areas for future growth.

**KEYWORDS:** Amorphous, Cellulose, Nanocrystals, Nanocellulose, Nanocomposites.

## 1. INTRODUCTION

In recent years, there is continuously increasing appreciation of the values of environmentally sustainable chemical product and process design. The idea of sustainability is having a major effect on the chemical industry, which is gradually focused on limiting the use of toxic chemicals and incorporating green synthetic solutions that use natural, organic materials as initial particles. In this respect, cellulose has ignited considerable attention due to a wide variety of uses, involving paper, textiles, surface coating, medical products, implants, and tissue engineering, and many others [1].

The glucose groups in this static homopolysaccharide are linked together through glycosidic bonding. Hydrogen bonds as well as Van der Waals interactions bind the cellulose chains with each other to create primary fibrils, that accumulate as bigger micro as well as nano-fibrils (Figure 1). Depending upon unit cell's dimensions and the chain's directionality, cellulose can occur in a variety of polymorphs. The most popular polymorph of cellulose derivatives is cellulose I, while cellulose II crystalizes during multiple therapies. Micro fibrillated cellulose (MFC) is a term used to classify complexes of cellulose nanofibers, which can be manufactured from raw resources using a mixture of mechanical as well as chemical processes that has both crystalline and amorphous regions. Chemical therapies, along with biological pre-treatments, could help with the elimination of lignin and hemicellulose throughout this process. At relatively low concentrations as 1% wt, In aqueous sources the resulting fibrils may form extremely viscous, entangled channels. Bacteria of various types can also produce strongly crystalline cellulose nanofibers. The fibers are excreted there at air-water interface, and also the plants are grown in soluble nutrient media. Bacterial Nano Celluloses (BNCs) are dimensionally strong and have a strong weight-average molecular mass. The assembly of crystalline rod-like factors have resulted as cellulose nanocrystals is made possible by extracting crystalline regions embedded within cellulose micro-fibrils (CNCs). Acid hydrolysis, that degrades amorphous structure as well as disrupts hydrogen bonds, produces these fragments, that have a distinct shape. CNCs have a lower aperture and are much more crystalline as compared cellulose nanofibers (CNFs). CNFs, CNCs, as well as BNCs are all classified as nanocelluloses, that are cellulosic derivatives or processed materials of a single object on the nanoscale level[2].



**Figure 1: The cellulose fibrils as well as micro-fibrils are shown in this diagram. The assembly of crystalline rod-like units as cellulose nanocrystals is made possible by extracting crystalline regions embedded within cellulose micro-fibril.**

Ball milling is a newer technique for the mechano-chemical extraction of cellulose that avoids the use of organic solvents. Due to its simplicity of use, speed, efficiency, as well as ecologically beneficial nature, in chemistry, this methodology is becoming increasingly prevalent. The implementation of ball milling inside the manufacturing as well as chemical organic compounds of cellulose nanofibers including nanocrystals, as well as recent advances in this area, are discussed in this paper. A number of research papers as well as publications about the usage of ball milling across process engineering, medical applications, as well as biochemical and polymer nanomaterials have previously been published. However, the technique's potential in the area of cellulose nanoparticles is yet to be fully investigated. The goal of this paper is to bring current work into focus by stressing the importance and potential of this renewable, sustainable strategy for defining areas for future growth.

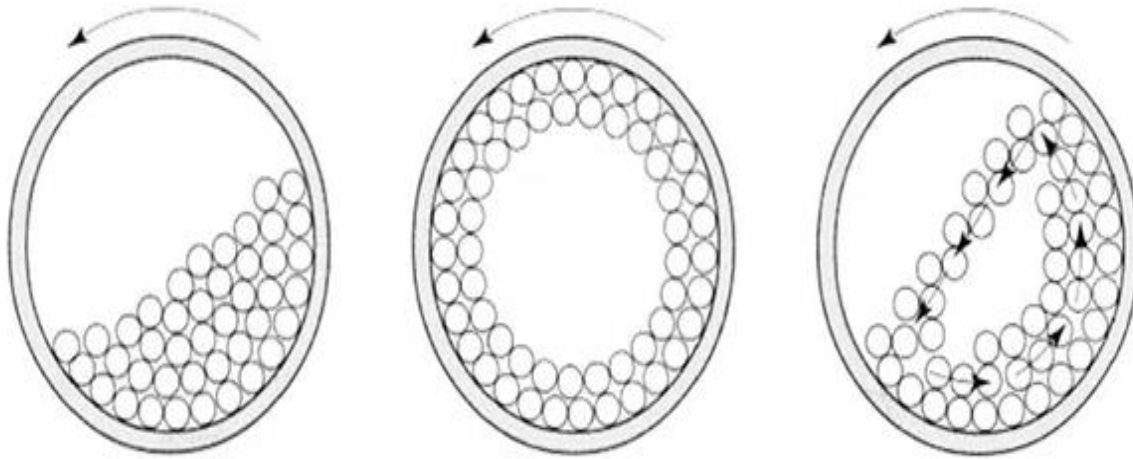
Ball milling is indeed a low-cost, convenient, and easy-to-use green technology with a lot of potential. It could be utilized to manufacture and chemically agglomerate nanocomposites and nanofibers, according to the report. One of the most significant benefits of this approach is that it can be combined with chemical therapies to create ideal materials with minimal effort. However, there are a number of factors to remember that may affect the properties of independent nanocelluloses. In order to distinguish CNCs with the desirable characteristics, process optimization is critical. Isolated nanoparticles' crystallinity, thermal degradation, length, thickness, as well as morphology are all factors that can be affected. It should be remembered, however, the source of the basic starting material might just have a considerable impact on the process' effectiveness and the characteristics of the nanocelluloses obtained, so it should be chosen carefully.

### *1.1 The Fundamentals of Ball Mill:*

A ball mill, often recognized as a tumbling mill or pebble mill, is a milling machine made up of a hollow tube filled with balls which is mounted on a metallic structure that can rotate itself around longitudinal direction. The spheres, that may be of various diameters, take up 30-50 percent of the mill volume and are sized according to the feed and mill scale. Large balls break down coarse feed materials, while smaller balls help in the creation of fine powder by reducing the amount of free space between the balls[3]. Material is ground in ball mills by impact and attrition. The following factors influence the amount of milling in a ball mill:

- The amount of time the commodity spends in the mill container.
- The spheres' amount, height, including density.
- The make-up of the balls.
- The cylinder's rotor speed.
- The feed rate including vessel feed stage.

Ball mills come in a variety of shapes and sizes, and their operating philosophies differ to some extent. The average milling vessel size varies as well, ranging from 0.010 litres for circular ball mills, mixer mills, and acceleration ball mills to many hundred litres for longitudinal rolling ball mills. Figure 2 depicts the proper motion sequence of a ball mill in action.



**Figure 2: The correct cascade of action of a ball mill in operation. There are various kinds of ball mills and their operational principles vary to some degree [Pharmapproach/Ball Mill].**

#### 1.1.1 Uses of Ball Mill in Pharmaceutical:

- Small to moderate ball mills may be used to process drugs to their final form or also to grind concentrations.
- Ores are processed in high-capacity ball mills until medicinal chemicals are processed.

#### 1.1.2 Benefits of Ball Mills:

- Produces a satisfactory powder.
- It can be used fully sealed, it is ideal for milling hazardous materials.
- It has a wide variety of uses.
- It is capable of continuous service.
- Deployed in milling of actual rough constituents.

#### 1.1.3 Drawbacks of Ball Mills:

- Material leakage can occur due to wear and tear, that is greatly exacerbated by the balls and partly caused by the wrapping.
- Machine noise is strong, particularly when the hollow cylinder consists of metal, but it is significantly reduced when rubber is utilized.

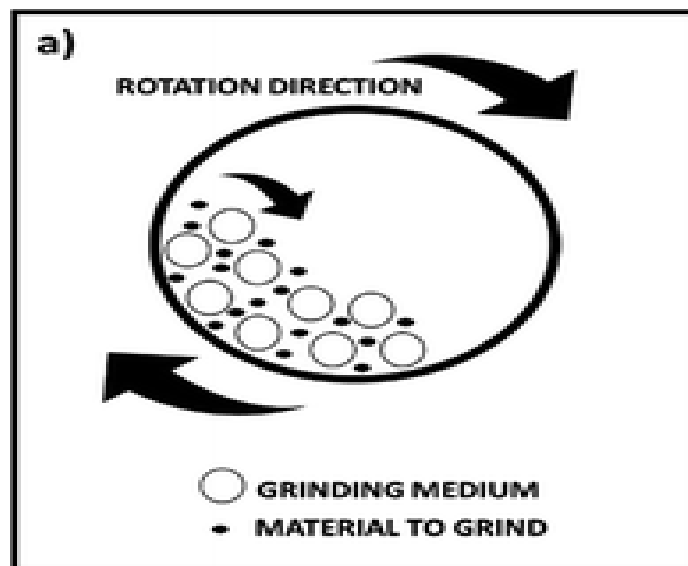
- Duration of milling is comparatively long.
- Difficult to clean the system after it has been used.

## 2. DISCUSSION

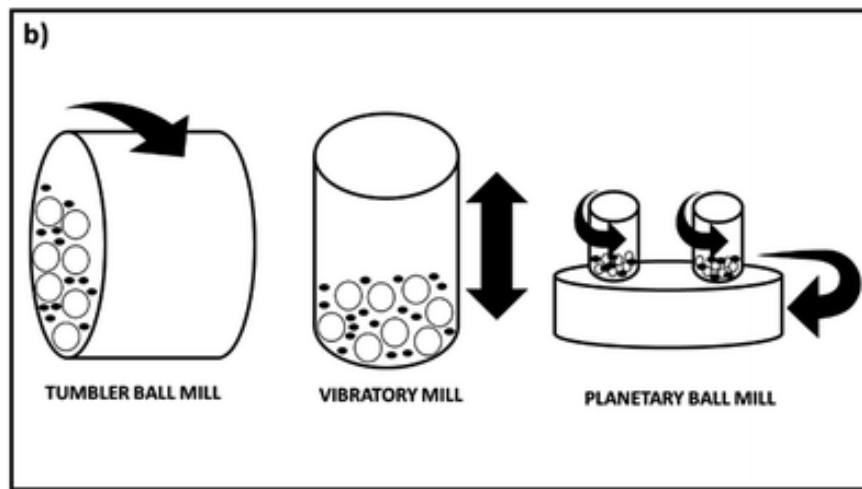
Ball milling is a mechanical process that is commonly used to finely ground powders and mix materials. It has found widespread use in manufacturing all over the world as an environmentally sustainable, cost-effective methodology. Since this study focuses upon on conditions used during manufacturing and cross - The usage of a ball mill to connect nanocellulose items rather than the machinery itself would not explain the various instruments available in manufacturing. Nevertheless, this section gives a broad description of the different forms of machinery. Based on the application, various sorts of ball mills are available. It is usually composed of a hollow spherical tube that rotates on its axis and has been partially filled with metal, stainless steel, plastic, or rubber balls (Figure 3). It is dependent on the energy generated by the balls' impact and attrition and the powder.

Cost-effectiveness, efficiency, simplicity of handling, repeatable performance attributable to resource and speed management, and possible uses an extensive material in a diverse environment are all benefits of this approach. Potential drawbacks include the risk of deterioration, the creation of nanomaterials with odd shapes, and noise. Various models of equipment are accessible reliant on the material that needs to be managed, as detailed in a recent analysis by Gorrasi et al. [4]. They divide ball mills into two classes based on their operating mode i.e., milling can be done in two ways: directly and indirectly. In an example, kinetic energy is transferred specifically to the components through rollers or metallic blades.

The most widely used ball mills throughout the cellulose sector are planetary, tumbler and vibratory mills (Figure 4). It is observed that tumbler mill consists of a barrel that is partly packed with steel balls and rotates around its longitudinal axis. The efficiency of the operation in this type of instrument is largely determined by the mill's diameter. Larger diameters allow for greater fall height and, as a result, more energy transfer. The tank comprising the sample and also the grinding media within vibratory mills is shook back and forth throughout the high oscillation amplitude. The milling medium's mass, vibrational frequency, as well as amplitude all are relevant factors to remember in this case. Finally, in a planetary mill, objects rotate around their own axes while being supported by a revolving disc. Again, the vessel size is an important factor in the process's success because a wider vessel allows for even more kinetic energy thereby stronger effects.



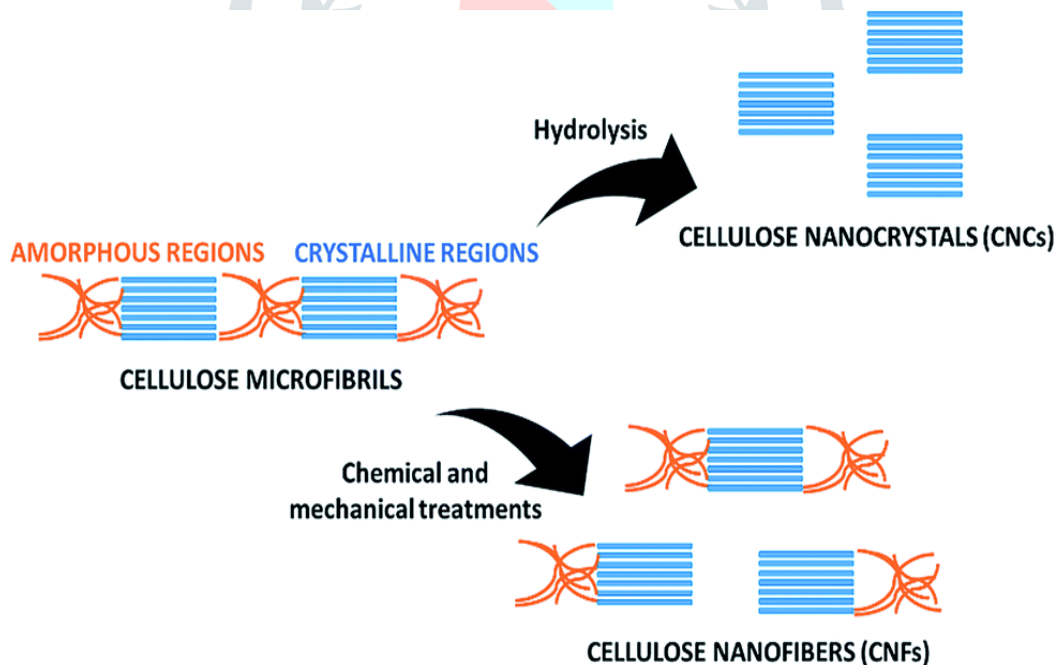
**Figure 3: Pictorial illustration of a ball mill. The efficiency of the operation in this type of instrument is largely determined by the mill's diameter.**



**Figure 4: Various kinds of instruments used. The most widely used ball mills throughout the cellulose sector are planetary, tumbler and vibratory mills.**

### 2.1 Cellulose Nanoparticle Preparation and Chemical Modification:

The processing of CNCs and CNFs is among the most fascinating uses of the ball mill mostly in domain of cellulose (Figure 5). This method has many advantages for obtaining nanocelluloses and cellulose nanocomposites because it is inexpensive, simple to use, and faster. However, to avoid overgrinding of the natural resources, the working conditions must be carefully monitored. This technique could also be used to induce cellulose hydrolysis as well as depolymerization underneath the right circumstances and in combination of chemical or enzymatic treatment.

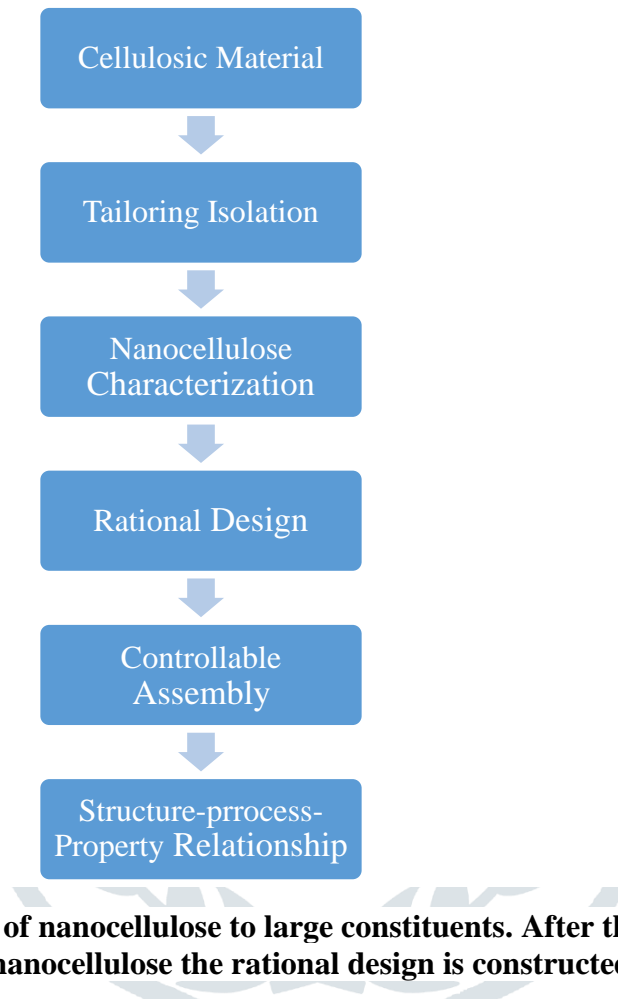


**Figure 5: Production of cellulose nanocrystals from cellulose. To avoid overgrinding of the natural resources, the working conditions must be carefully monitored.**

### 2.2 Cellulose Nanocrystals Processing:

Typically, cellulose nanocrystals are generated by oxidising native cellulose and using chemical techniques that destroys amorphous structure of the cellulose and liberates the crystalline regions. Shearing acts aid in the hastening of this operation. The ball mill is indeed an outstanding method for combining chemical and mechanical activity to produce CNCs since it exerts mechanical forces with in influence of chemical agents. The hydrolysis acid, pre-treatment, as well as milling time and speed should all be recognized since they will affect the crystalline nature and morphology[5].

J. Lu et al. using a mechano-chemical technique and phosphoric acid, a ball mill was used to extract nanocrystals through bamboo content. Then, a Fiber dissociation system was used to pre-treat the pulp. In the presence of phosphoric acid, the extracted material was ball milled at 400 rpm for 1.5-3.5 hours to create a translucent solution. Phosphoric acid has been used as a swirling factor throughout cellulose dissolution within that mechano-chemical process. Several centrifugations and an ultrasonication process at 50 °C for 1-3 hours were used to strip cellulose nanocrystals. The particles ranged 100-200 nm in length as well as 13-30 nm in width and were mostly made up of the cellulose type-II polymorph. Figure 6 shows the processing of nanocellulose to large constituents.



**Figure 6: processing of nanocellulose to large constituents. After the characterization of nanocellulose the rational design is constructed.**

Just after that, using mechano-chemical stimulation in the context of phosphor-tungstic acid, the very same research team developed a new method for removing cellulose nanocrystals through bamboo pulp. Ritual cleansing and ultrasonication were performed following milling for 1.5-2.5 hours. The nanocrystals that resulted had a rod-like shape with a curved flat edge, a length of 200-300 nm, as well as a width of 25-50 nm. The concentration of phosphor-tungstic acid, response time, and milling duration were all significant factors in the process. The yield of distinct CNCs improved with longer reaction times at a steady acid concentration, with optimum conditions occurring until five hours. By increasing phosphor-tungstic acid content from 10% to 15%, the production was also boosted. This made hydrolyzing the cellulose's amorphous structure and removing the nanocrystals far easier.

### 2.3 Functionalization of CNCs:

Ball milling permits for mechanical processing of shear forces to take place within the context of chemical agents. As just a result, this technique could be used to not just to isolate but also agglomerate cellulose nanocrystals. However, since milling length as well as rotation speed have an effect on yield as well as degree of replacement of isolated crystals, it is critical to optimize the process.

In the context of maleic anhydride, J. Tang et al. discovered a solvent-free process for obtaining and chemically altering CNCs [6]. This approach was used on membrane filter cellulose pulp that was mechano-

chemically handled for two hours at 500 rpm. In order to make the chemical reaction more efficient, an ultrasonic reactor protocol was added. The output as well as extent of substitution of the CNCs generated as a result were both affected by the ball mill process. The yield was just 16.3 percent if no ball milling has been used, but increased to 56.1–61.1 percent while milling for 0.5–1 hour. Increasing the processing time for 2 hours destroyed the cellulose crystalline structure unnecessarily, resulting in a 54.7 percent reduction in yield. The degree of substitution values shifted whenever the time of milling augmented to 1-hour and later decreased it was observed that movement period was elevated to 2-hours, showing a similar trend.

## CONCLUSION

Process automation, organic synthesis, as well as the production of nanocomposites have all benefited from ball milling technology. Owing to a lack of testing, the capacity to extract and chemically modify cellulose nanoparticles is still to be completely investigated. Because of their poor solubility in organic compounds, further study into the solubilization of CNCs will be especially important. To date, a very well recognized process is esterification; however, other forms of chemical treatment may be investigated, but they would be constrained by the existence of functional groups. Other reactions may include the cellulosic hydroxyl categories acting as a nucleophile. It is suggested observed that ball milling could be utilized in both hot and cold environments, and it is a green and effective production method. This technique provides an easy and quick way to produce hybrid structures, so further research towards the production of cellulose-based bio-composites will be interesting. As this is a feasible innovation it is anticipated that this research will contribute to a better understanding of its importance and possibilities, as well as identifying areas for future advancement.

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