CELLULOSE NANOFIBRILS - AN ANALYSIS OF THE ISOLATION METHODS

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Abstract: The systematic review utilized the PRISMA protocol to examine various methods of obtaining nanofibrils from plant fibers, aiming for ideal values of width, length, and crystallinity. A total of 13 articles were found, of which 3 were included due to their relevance, showcasing shorter processing times and larger dimensions in the nanofibrils. The studies employed sustainable approaches, such as the use of renewable deep eutectic solvents (DES) and p-toluenesulfonic acid (p-TsOH), followed by high-pressure homogenization and centrifugation. These methods are environmentally friendly and result in high-quality nanofibrils with excellent mechanical properties, making them versatile for various applications. Exploring techniques like ball milling could be a future industrially scalable option, reducing energy consumption while maintaining nanofibril quality.

Keywords: Cellulose nanofibrils; Methods; Width; Length.

NANOFIBRILAS DE CELULOSE - UMA ANÁLISE DOS MÉTODOS DE ISOLAMENTO

Resumo: A revisão sistemática utilizou o protocolo PRISMA para analisar diferentes métodos de obtenção de nanofibrilas a partir de fibras vegetais buscando valores de largura, comprimento e cristalinidade ideais. Foram encontrados 13 artigos, dos quais 3 foram incluídos devido à sua relevância, apresentando tempos de processamento menores e maiores dimensões nas nanofibrilas. Os estudos empregaram abordagens sustentáveis, como o uso de solventes eutéticos profundos renováveis e ácido p-toluenossulfônico, seguidos por homogeneização de alta pressão e centrifugação. Esses métodos são ecologicamente amigáveis e resultaram em nanofibrilas de alta qualidade com excelentes propriedades mecânicas, tornando-as versáteis para várias aplicações. A exploração de técnicas como a moagem de bolas pode ser uma futura opção escalável industrialmente, reduzindo o consumo de energia, mantendo a qualidade das nanofibrilas.

Palavras-chave: Nanofibrilas de celulose; Métodos; Largura; Comprimento.

1. INTRODUCTION

Throughout history, nanotechnology has emerged as a field of exploration and discussion, driven by the vision of physicist Richard Feynman, who in his 1959 lecture "There's Plenty of Room at the Bottom" [1], presented the possibility of manipulating matter at the atomic and molecular scale. This starting point marked the beginning of a journey that quickly expanded and played a central role in various industries and sectors. This exploration came to life in the subsequent years, resulting in the remarkable growth of the global nanotechnology market [2]. In 2022, this market was valued at USD 7.33 billion and is projected to reach approximately USD 114.54 billion by 2030, maintaining an annual growth rate of 41%. Similarly, the nanocellulose market, valued at USD 416.03 million in 2022, has also experienced significant growth, with an annual rate of 18.31%, and is expected to hit the USD 1.597 billion mark by 2030 [3,4].

As exploration advanced, so did research in the field. Over the past 22 years (2000-2022), more than 2.5 million articles have been indexed in the Web of Science, with 230,000 of these articles published in 2022 alone. This represents an annual increase of approximately 12.6% in the quantity of articles related to nanotechnology. However, regarding the number of patents published, according to the European Patent Office (EPO), while there has been a rising trend, this curve began to decline from 2019, with 2018 marking the highest number of patents published at a total of 12,690 [3,4,5]. Research in this area extends beyond mass production; it also involves the exploration of renewable raw materials, such as cellulose derived from plant fibers. These fibers, classified as lignocellulosic due to their components including hemicellulose, lignin, organic extracts, and pectins, serve as the foundation to produce nanocellulosic materials. These materials, such as cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC), have promising potential for several applications in terms of nanotechnology [6,7].

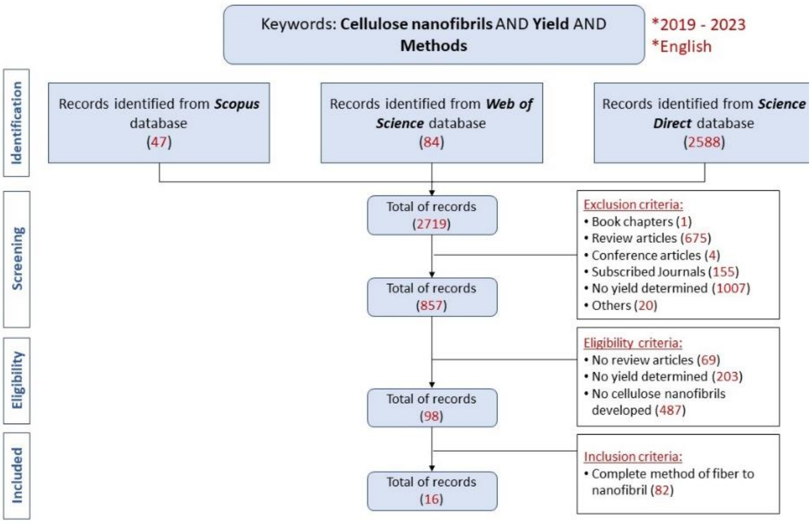
In the CNF production process, a series of steps are undertaken, ranging from purification and mechanical pre-treatment to the actual defibrillation process. This process, which can be both chemical and mechanical, allows for the adjustment of properties such as crystallinity, morphology, and surface chemistry, making nanocellulosic materials highly adaptable to their intended purposes. The dimensions of nanofibrils are considered critical in this context, as the relationship between their length and width directly influences their mechanical properties and performance in various applications. To obtain accurate information about these parameters, microscopy techniques such as Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) are often employed, providing direct measurements and detailed insights [8,9,10].

Consequently, the objective of this study is to examine articles presenting quantitative values of width or length of produced nanofibrils, contributing to the validation of extraction methods' efficiency and deeper comprehension of the mechanical, chemical, and thermal properties of these materials. These insights are crucial not only for academia but also for assessing the industrial scalability viability of these promising nanomaterials.

2. METHODOLOGY

The methodology of this article aimed to construct a systematic review, based on the PRISMA method [11], including studies that carried out the extraction process of nanofibrils from renewable, residual, or non-residual plant sources using chemical and/or mechanical methods. The goal was to identify studies that, when validated, resulted in appropriate values for the length, or width of cellulose nanofibrils, therefore, characterization methods to validate this parameter should also be included in the selected studies. The searched databases and the keywords used are presented in Figure 1, where the Boolean operator 'AND' was applied between the keywords in the article filtering process. It is valid to emphasize that the same search method was applied to all selected databases. However, it is known that each database has its own characteristics and ways of indexing and presenting information, differing, for example, in their article inclusion policies, publication agreements, and search and indexing algorithms. This justifies the discrepancy in the results of the initial filtering process.

Figure 1: Summary methodology for searching articles for each database based on the PRISMA protocol.



After the screening/exclusion step, eligibility was performed with the assistance of ASReview software [12], which utilizes artificial intelligence methods to rank the articles based on their relevance, according to an initial indication from the user. The final inclusion was performed with the complete reading of the 49 selected articles, considering the method of extracting the natural fiber up to the nanofibrils isolation, excluding studies that started the process with bleached fiber pulp, skipping process steps. Finally, 13 studies were finally selected, where the best results regarding the quality of the obtained nanofibril are discussed in the next section.

3. RESULTS AND DISCUSSION

The dimensions of a nanofibril play a significant role in determining its properties and surface interactions. Nanomaterials that have high width, such as cellulose nanofibrils (CNFs), have unique characteristics due to their elongated shape and large surface area. The high proportion of CNF, typically ranging from 4 to 20 nm in diameter (or width) and 500 to 2000 nm in length, contributes to their excellent mechanical and thermal properties [10,13].

The elongated structure of CNFs allows for efficient charge transfer and reinforcement in composite materials, resulting in higher mechanical strength and stiffness. Moreover, the specific surface area (482 m²/g) of these nanomaterials provides a high number of reactive sites, enabling strong interactions with other materials and facilitating the formation of hydrogen bonds, electrostatic forces, and Van der Waals interactions that can influence the rheological behavior and gelation properties of nanofibril suspensions [14].

In Table 1, the selected final articles are presented. Excellent mechanical properties are the main investigated requirement in the studies, and the parameters that also influence this property are the width, length and crystallinity of the nanofibrils.

The selected articles provide information about the extraction method, the used fiber, and the results of the defined parameters. The second column related to the "extraction method" follows the logical reference line: pre-treatment → delignification → refining → defibrillation, presenting the approach adopted in place of these terms.

Table 1: Relevant information about the selected articles via PRISMA protocol.

Ref.	Extraction/Isolation method	Source	Width (nm)	Length (nm)	Crystallinity (%)
15	Hydrothermal digestion → Acid hydrolysis → Microfluidization	Eucalyptus Wood	8	700	75,0
16	Recyclable p-Toluenesulfonic acid (p-TsOH) → Centrifugation → Homogenization/Sonication	Poplar sawdust	22,5	-	62,3
17	Acid hydrolysis → Ball milling/ Centrifugation/Freeze-drying	Sisal	12,3	-	-
18	Kraft pulping → Bleaching → TEMPO-mediated oxidation / Dialysis → Liquefaction	*Rattan manaus* rod (wicker)	18,5	-	66,5
19	Grinding/Sieving → Deep eutectic solvent synthesis → Centrifugation → Homogenization	Corn cob	15	-	-
20	Sieving → Deep eutectic solvent synthesis → Centrifugation → Homogenization	Bamboo dust	8,8	-	62,9
21	Washing/Drying/Grinding/Sieving → Ball milling + NaOH → Centrifugation → Dialysis	Pineapple peel	42,8	1782	69,6
22	Milling → Alkaline treatment → TEMPO-mediated oxidation → Agitation	Sugar cane bagasse	7,5	350	-
23	Milling/Sieving → Alkaline treatment with NaOH → Supermasscoloider/Sonication	Jute	31	-	68,0
24	Washing/Drying/Grinding → Extraction removal → Alkalization → Bleaching → Mechanical agitation → TEMPO-mediated oxidation → High-pressure Nano-homogenizer	*Ampelodesmos mauritanicus*	5,6	108,9	68,0
25	Cutting/Drying → Alkaline pulping/Disk refiner/Centrifugation → NaClO2 + CH_3COOH → Supermasscoloider	Peach palm	2	270	31,5
26	Maceration → Delignification → Bleaching → Disintegration separation → PFI milling	Sunflower stalks	15	60,4	83

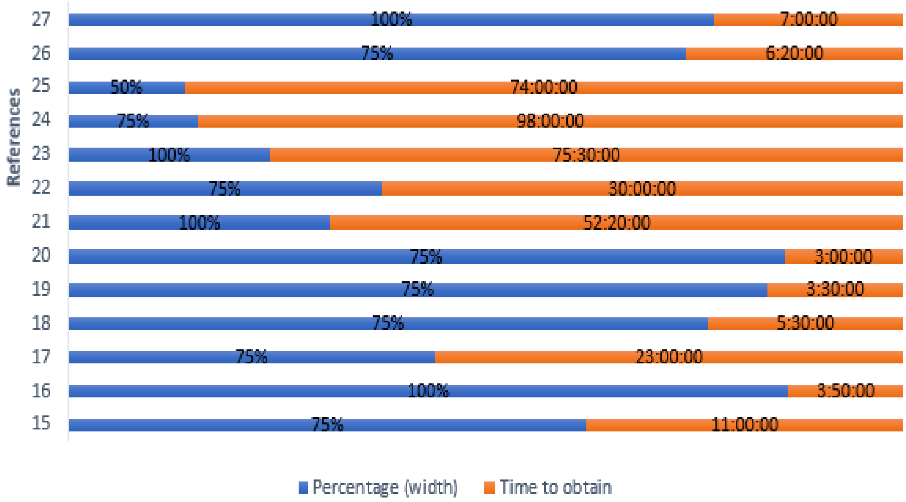
	→ Mechanical homogenizer → Supermasscoloider				
27	Alkalization → Bleaching → Liquefaction → Microfluidization	Cassava pulp	20	-	61

A high aspect ratio implies that the fibrils are more elongated compared to their width, leading to a greater crystalline orientation along their longitudinal axis, with a surface area than their volume. This facilitates the nucleation and growth of crystals on their surface, resulting in higher crystallinity in the nanofibrils. All selected articles showed satisfactory crystallinity indices, except for the study by Franco et al (2020) [25], which subjected the peach palm fiber to delignification with acidic solvents whose hydrogen ions can interact with the hydroxyl groups of cellulose, promoting the breaking of intermolecular hydrogen bonds, affecting its crystalline organization and consequently reducing its crystallinity [28].

The processing time is a fundamental parameter in the production of CNFs and plays a crucial role in their viability and industrial application, directly impacting several important factors such as process optimization, scalability, comparative analysis, process improvements, and economic feasibility [29].

Figure 2 below provides graphical information about the relationship between nanofibril width and its total extraction time. The value, in percentage, was calculated based on the ideal range (between 4 and 20 nm), according to the literature [10], assigning a maximum score to nanofibrils with a larger width. A larger wi tends to increase the cross-sectional area of the fiber, which can lead to higher load-bearing capacity and resistance to deformation. The grading and, consequently, the percentage were calculated as follows: 50% for values <4nm, 75% for values between 4 and 20nm, and 100% for values >20nm. Considering that the larger the width, the better the mechanical properties will be, consequently, it fits the parameter more effectively, meeting it at 100%. For example, in reference [21], a nanofibril had a width of 42nm (above 20nm = 100%). However, in reference [25], the nanomaterial had only a 2nm width, below the range between 4 - 20nm, meeting only 50% of the requirement. Despite having a smaller cross-sectional area, it might not fulfill the mechanical property criterion, but it could meet other properties depending on the final application of the nanofibril.

Figure 2: Relationship between width and time to obtain.



The advantage of using deep eutectic solvents (DES) combined with mechanical fibrillation to obtain nanofibrils lies in the unique properties of DES and their ability to facilitate the fibrillation process. DES is a class of green solvents that have gained attention in various fields due to their superior properties. They are easy to prepare, readily available at low cost, biodegradable, and recyclable. They exhibit high thermal stability, low volatility, adjustable polarity, and have a lower melting point compared to their individual precursor components, making them effective in breaking down cellulose fibers. The studies by Ren et al. (2023) [19] and Xu et al. (2023) [20] obtained cellulose nanofibrils from different plant sources (corn cobs and bamboo powder, respectively) by using deep eutectic solvents combined with mechanical fibrillation (centrifugation followed by homogenization). The prior grinding of both fibers facilitated the chemical accessibility of the solvent to their structure, enabling the dissolution and defibrillation of the fibers, thus improving the efficiency of the nanofibril production process. The use of centrifugation and homogenization brought significant advantages, including purification, control of fibril size, uniform dispersion, improved reproducibility, and overall process efficiency. Short and closely spaced production times can be observed in the graph for these two discussed studies, primarily due to the use of DES, which accelerates the production process due to its efficient dissolution of various materials. Additionally, the diameters of the obtained nanofibrils met 75% of the equivalent score within the defined range (15nm for nanofibrils from corn cobs and 8.8nm for those from bamboo powder), positively affecting the mechanical properties of the fibrils [30].

In the study by Liu et al. (2023) [16], cellulose nanofibrils derived from poplar wood sawdust were isolated through treatment with recyclable p-toluenesulfonic acid (p-TsOH) followed by high-pressure homogenization. In this more sustainable approach, p-TsOH is used as a catalyst to hydrolyze cellulose fibers into nanofibrils, offering advantages such as the recyclability of the catalyst, high yield, and control over the dimensions of the resulting CNFs. Essentially, this treatment breaks down cellulose fibers into nanofibrils that can be further processed mechanically, with high-pressure homogenization selected in this study to assist in further refining the CNFs, improving properties such as surface area and dispersibility. The width of the obtained nanofibrils was approximately 22.5 nm with a processing time of 3 hours and 50 minutes.

Obtaining cellulose nanofibrils through synthesis methods using recyclable and environmentally friendly approaches, such as DES and p-TsOH, presents significant advantages. These approaches are sustainable, utilizing compounds derived from renewable sources and minimizing environmental impact. Additionally, they produce high-quality CNFs with excellent mechanical properties and a high aspect ratio, making them ideal for various applications. However, despite the widely applied mechanical methods of centrifugation and homogenization used in the studies, there are some disadvantages, such as high energy consumption, increasing operational costs, and negative environmental impacts. Another concern is the negative effects on the integrity of the nanofibrils, as significant mechanical forces and stresses can lead to breakage or damage to their structures, resulting in a loss of mechanical or structural properties of the nanomaterial, affecting their desired characteristics [31].

4. CONCLUSION

Methods for obtaining nanofibrils using solvents like DES and p-TsOH followed by homogenization and centrifugation are environmentally friendly and sustainable approaches. They employ solvents derived from renewable sources and can be recycled, thereby reducing environmental impact. These methods produce high-quality nanofibrils with excellent mechanical properties, making them versatile for various applications. However, the cost and complexity of the required equipment can be a challenge, as well as the high energy consumption during high-pressure homogenization and the control of nanofibril integrity, which can be affected by mechanical forces during the process. A possible approach for future studies is to replace homogenization and centrifugation methods with ball milling, which consumes less energy and is more easily scalable for industrial applications in terms of equipment. Finally, it is important to emphasize the need for conducting experimental studies and optimizing milling conditions to ensure the quality and uniformity of the obtained nanofibrils.

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