Production of Cellulose Nanofibrils from Agro-Industrial Residues: Systematic Review and Experimental Design via Glycerol Swelling and Extrusion

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Abstract: This study presents the systematic review and analysis of scientific articles on cellulose nanofibril (CNF) production from vegetable fibers, with a focus on environmentally friendly methods. The research followed the PRISMA protocol, selecting works that addressed complete extraction processes starting from vegetal fibers and reporting parameters such as length-to-diameter ratio (L/D), crystallinity, and yield of CNFs. Based on the bibliographic findings, a process flowchart and an experimental design were developed for CNF extraction from peach palm sheath, combining glycerol swelling, single-screw extrusion, and dilute acid hydrolysis (0.4–0.6% H_2SO_4). The choice of this route was based on its potential to promote controlled mechanical shear after glycerol plasticization, facilitating the opening of the cell wall and selective removal of amorphous regions while preserving crystallinity. The proposed methodology, supported by literature evidence, offers a technically feasible and sustainable approach for the valorization of agro-industrial residues, with potential for scaling up to pilot and industrial levels.
Keywords: Cellulose nanofibrils. Glycerol swelling. Single-screw extrusion. PRISMA protocol. Agro-industrial residues.

1. INTRODUCTION

Nanotechnology has consolidated itself as a strategic field with applications in sectors such as healthcare, electronics, energy, composites, and packaging. In 2024, the global market was estimated at USD 14.56 billion, with projections to reach USD 227.54 billion by 2032, reflecting a compound annual growth rate (CAGR) of 41% [1]. This expansion is driven by the integration of advanced technologies into production processes and the development of innovative materials, although it still faces challenges such as high production costs, specific regulations, and communication barriers with the end consumer.

In the nanocellulose segment, the global market reached USD 700 million in 2024 and is expected to reach USD 4.6 billion by 2034, with a CAGR of 20.6%, highlighting its potential as a sustainable, high-performance material applied in areas ranging from packaging to engineering composites. Europe maintains its leadership in production and R&D, while the Asia-Pacific region stands out for its rapid growth, favored by abundant raw materials and qualified labor [2].

Scientific progress follows this trend: in 2024, more than 256,000 articles on nanotechnology were indexed in the Web of Science, representing a 4% increase compared to 2023. In the field of patents, the European Patent Office received 199,264 applications in 2024, maintaining the previous year's level, with 2,934 of these related to nanotechnology, accounting for approximately 29% of the total. These indicators reinforce the relevance and competitiveness of the sector, as well as the need for technically efficient and economically viable production processes [3-5].

Among the most prominent materials, cellulose — an abundant polymer from renewable plant sources — offers great versatility. When processed at the nanoscale, it gives rise to cellulose nanofibrils (CNF), cellulose nanocrystals (NCC), or bacterial nanocellulose (BNC). CNF and NCC, of plant origin, can be obtained through chemical, mechanical, enzymatic, or combined routes, generally preceded by pretreatments to remove hemicellulose, lignin, and other constituents, thereby increasing fiber accessibility [6-7].

Mechanical methods apply shear forces to delaminate the cell wall, while chemical methods promote surface modifications and selective removal of amorphous regions, releasing crystalline structures. The choice of the nanocellulose extraction method, associated with parameters such as time, temperature, concentration, and processing intensity, directly affects the yield, morphological properties, and cost of the nanomaterial [8-9]. In this context, the application of statistical tools is essential to quantify the effect of these variables and identify optimal combinations. Analyses such as ANOVA, Tukey's test, and response surface modeling (RSM) allow group comparisons, evaluation of interactions, and process optimization based on indicators such as yield, aspect ratio, crystallinity, and homogeneity.

This study will use the PRISMA method to select articles presenting quantitative data on yield and cellulose nanofibril quality, correlating them with total production time and cost. Based on this systematic approach and statistical data analysis, at least three extraction methods will be identified that stand out in mechanical strength, cost-effectiveness, and lower environmental impact, providing insights for future research and industrial applications.

2. METHODOLOGY

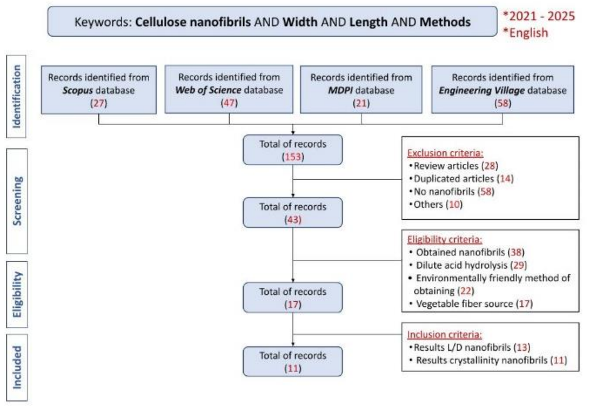
The systematic review was conducted according to the PRISMA protocol (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) [10], with the aim of identifying studies that described the process of obtaining cellulose nanofibrils from plant fibers, using chemical and/or mechanical methods, and that presented quantitative results related to the morphology, crystallinity, and yield of the nanomaterial.

The searches were carried out between 2021 and 2025 in four databases: Scopus, Web of Science, MDPI, and Engineering Village, restricted to articles published in English. Two distinct search strategies were employed, maintaining as common descriptors the terms "cellulose nanofibrils" and "methods," while varying the other parameters according to the research objective:

- Search 1 (Figure 1): "Cellulose nanofibrils AND Width AND Length AND Methods" — aimed at obtaining data on width, length, and aspect ratio.

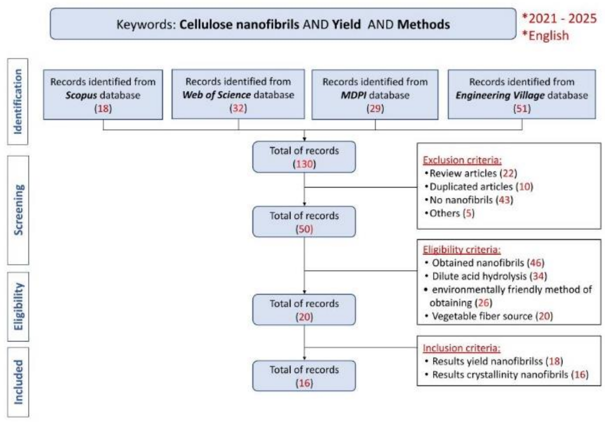
Figure 1. Methodological flowchart based on the PRISMA protocol considering "length" and "width" as keywords for the selection of articles that presented these data related to the developed nanofibrils.

ISSN: 2357-7592



- Search 2 (Figure 2): "Cellulose nanofibrils AND Yield AND Methods" — aimed at obtaining yield data.

Figure 2. Methodological flowchart based on the PRISMA protocol considering "yield" as a keyword for the selection of articles that presented this data related to the developed nanofibrils.



In both strategies, after the initial identification, a screening stage was carried out, excluding review articles, duplicate articles, studies that did not address nanofibrils, and publications outside the scope or with insufficient information (classified as "others").

In the eligibility stage, the remaining articles were evaluated according to the following criteria: (i) effective production of nanofibrils, (ii) use of diluted acid hydrolysis, (iii) application of an environmentally friendly method, and (iv) use of plant fiber as raw material.

Finally, in the inclusion stage, only studies presenting at least one of the predefined results of interest for each search were considered:

- For Search 1: results for the L/D ratio of nanofibrils and crystallinity values.
- For Search 2: yield and crystallinity results.

This process resulted in the final inclusion of 11 articles for Search 1 (Figure 1) and 16 articles for Search 2 (Figure 2). These studies formed the analytical basis of the present research, serving as references for comparing and discussing the most efficient methods for obtaining cellulose nanofibrils.

3. RESULTS AND DISCUSSION

The aspect ratio (length-to-diameter ratio) is an essential parameter for characterizing cellulose nanofibrils (CNF), as it directly influences their mechanical and viscous properties. High aspect ratios confer greater surface area and enable more efficient load transfer in composite materials, while also promoting intermolecular interactions such as hydrogen bonding and Van der Waals forces, which are fundamental for rheological behavior and the formation of structured networks. Techniques such as AFM and TEM provide precise measurements of this ratio.

Well-established methods for obtaining CNFs include TEMPO-mediated oxidation, which introduces anionic carboxylate groups onto the fibril surface, resulting in highly stable and well-defined dispersions. Studies such as Lorevice et al. (2023) [11] demonstrated the production of nanofibrils with diameters between 1.2 and 2.0 nm in just three and a half hours, combining TEMPO oxidation with microfluidization—an efficient but chemically demanding method. Alternatively, deep eutectic solvents (DES), such as a mixture of choline chloride and lactic acid, have emerged as a sustainable route, offering excellent cellulose solubilization when coupled with mechanical fibrillation. Xu et al. (2023) [12] reported nanofibrils with an average thickness of 8.8 nm in about four hours, highlighting the potential of this approach for greener processing. However, what truly stands out in the context of the present investigation is the method combining single-screw extrusion with glycerol swelling followed by dilute acid hydrolysis. This protocol enables the production of nanofibrils in reduced time, without the need for expensive reagents or highly complex processes. As demonstrated by Lu et al. (2022) [13], glycerol acts as a pre-treatment agent by penetrating the cell walls and reducing interfibrillar cohesion, thereby facilitating physical delamination during extrusion. The subsequent hydrolysis, carried out with sulfuric acid at concentrations of 0.15–0.6 %, selectively removes amorphous regions without significantly compromising crystallinity, resulting in nanofibrils with diameters between 20 and 60 nm and yields ranging from 62 to 75 %, with total processing times of approximately 3.5–4 hours.

The work of Zhang et al. (2022) [14] further reinforces the applicability of this strategy by developing lignocellulosic nanofibril (LCNF) composites with polylactic acid (PLA) for use as 3D-printable filaments. In this study, single-screw extrusion not only promoted mechanical fibrillation after the prior glycerol swelling of fibers but also preserved part of the internal lignin, which contributed to improved interfacial compatibility with the polymeric matrix and enhanced mechanical performance of the composite. The presence of residual lignin provided additional strength, greater thermal stability, and rheological properties suitable for 3D printing, without compromising PLA processability. These results indicate that single-screw extrusion, when properly tuned for parameters such as L/D ratio, temperature, and screw speed, can simultaneously promote structural fiber opening and optimize integration with biodegradable polymers, adding value to the produced nanomaterial.

In comparison, methods such as TEMPO-mediated oxidation and DES processing offer advantages in terms of chemical functionalization and achieving highly stable dispersions but require specific reagents and additional purification steps. In contrast, extrusion with glycerol, particularly in bench-scale single-screw configurations (L/D ≈ 10.3), stands out as a simpler, lower-cost route, significantly reducing the use of aggressive chemicals while enabling the valorization of low-value lignocellulosic sources. This makes the process especially attractive for large-scale applications and the development of sustainable products, such as structural composites, barrier films, and filaments for 3D printing.

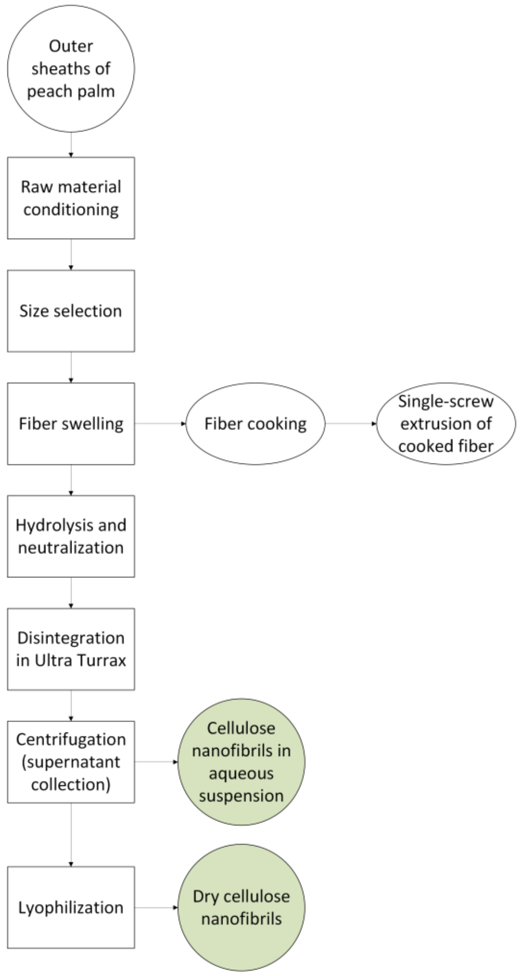
3.1 JUSTIFICATION AND STRUCTURING OF THE EXPERIMENTAL PROCESS

The selection of the single-screw extrusion method as the central stage of the pre-treatment was based on its ability to promote controlled mechanical shear in fibers previously swollen in glycerol, facilitating the opening of the cellular structure and exposing the amorphous regions of the plant cell wall to the subsequent action of dilute acid hydrolysis. This process offers relevant advantages for lignocellulosic fibers with high structural rigidity, such as the outer sheaths of peach palm, as it combines operational simplicity, low cost, and reduced energy consumption compared to high-energy mechanical fibrillation methods such as high-pressure homogenization and disc milling. In addition, single-screw extrusion provides greater tolerance to raw material particle size variability, reducing the need for strict sieving and enhancing its applicability at pilot and industrial scales.

The methodological design was structured based on the studies by Zhang et al. (2022) and Lu et al. (2022), adapted to the available conditions and equipment, aiming at the production of cellulose nanofibrils from agro-industrial residues. The choice of glycerol swelling as a pre-treatment is grounded in its ability to penetrate cell walls, plasticize amorphous regions, and reduce the rigidity of the lignocellulosic matrix, thereby increasing internal accessibility to subsequent chemical attack. Combined with the moderate shear of single-screw extrusion ($L/D \approx 10.3$), this process enhances the action of dilute acid hydrolysis (0.4–0.6% H_2SO_4), enabling the selective depolymerization of amorphous regions with minimal degradation of crystalline portions.

The methodology (Figure 3) was organized into sequential and integrated steps: selection and preparation of peach palm outer sheaths, discarding degraded samples; cutting into 3–5 cm fragments; drying and milling to the target particle size; glycerol swelling; single-screw extrusion according to parameters defined in the experimental plan; dilute acid hydrolysis under controlled conditions; neutralization; mechanical defibrillation using an Ultra-Turrax; centrifugation for phase separation; and freeze-drying to obtain the dry nanofibrils.

Figure 3. Simplified methodological flowchart of the nanofibril production process.



The experimental design was developed according to a 2^3 factorial arrangement, without replication at the central point, to evaluate the combined influence of critical parameters in three process stages: (i) swelling – variation of screw rotation speed (15–35 rpm) and number of passes (1–3), with assessment of swelling degree; (ii) acid hydrolysis – variation of temperature (80–100 °C), time (60–90 min), and acid concentration (0.4–0.6%), with crystallinity analysis by XRD; (iii) mechanical defibrillation – variation of speed (14,000–18,000 rpm) and residence time (10–20 min), with colloidal and structural characterization by zeta potential, DLS, TEM, XRD, TG, and DSC.

This approach, built from the literature and systematized in the experimental flowchart, does not yet aim to present results, but rather establishes a solid methodological basis for the future evaluation of the effect of operational conditions on the physicochemical and structural properties of nanofibrils. The proposed process remains aligned with sustainability principles, reducing the use of aggressive reagents, utilizing agro-industrial residues, and prioritizing low energy consumption, which favors its feasibility in industrial scale-up contexts.

4. CONCLUSIONS

From the application of the PRISMA protocol, articles were selected that provided the technical–scientific basis for defining the parameters and stages of the proposed method. The systematic screening allowed the identification of gaps and opportunities in the routes for obtaining cellulose nanofibrils, with emphasis on processes employing glycerol swelling, single-screw extrusion, and dilute acid hydrolysis as a combined strategy for physicochemical pretreatment and controlled delamination.

Based on a thorough analysis of the eligible studies, a process flowchart and an experimental design were developed to evaluate critical variables, covering steps from fiber preparation and granulometric selection to hydrolysis and final product recovery. The choice of single-screw extrusion, preceded by glycerol swelling, was supported not only by its operational simplicity and pilot-scale feasibility, but also by bibliographic evidence indicating its potential to plasticize the cell wall, increase the exposure of amorphous regions, and reduce the demand for energy and aggressive reagents.

The designed framework provides a solid basis for future trials, in which it will be possible to correlate operational conditions with crystallographic parameters obtained by XRD, enabling process optimization from a sustainable perspective and in line with the valorization of agro-industrial residues. The integration between the systematic review conducted under the PRISMA protocol and the experimental design ensures that the selected route is not only technically grounded but also supported by quantitative and qualitative evidence, reinforcing its scientific relevance and industrial applicability.

Acknowledgement
The authors thank the Federal University of Bahia (UFBA) for academic, institutional, and infrastructure support, and TRL9 LAB for providing the technical resources essential for carrying out this study.

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