Sustainable extraction of cellulose nanofibers using deep eutectic solvent

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Abstract

Lignocellulosic biomass, omnipresent in nature, play a crucial role in the transition to a green economy. Among them, cellulose biopolymer stands for the first most abundant organic polymer on Earth. Nowadays, nanocellulose occupies a leading position as a renewable nanotechnology material. The focus on cellulose-based nanotechnology is driven by their exceptional physical and chemical properties [1]. Nanocellulose generally consists of three main types: cellulose nanocrystals (CNC), bacterial nanocellulose (BNC) and cellulose nanofibrils (CNF) [2]. Cellulose nanofibers, in particular, exhibit nano-sized cellular structures that are characterized by alternating crystalline and amorphous regions. Traditionally, CNFs extraction involves a mechanical shearing process, leading to the lateral disintegration of cellulose fibers into nanoscale substructural units [3]. However, this method is generally energy-intensive, raising concerns in the ongoing global warming challenge. In this context, deep eutectic solvents (DES) have emerged as a promising eco-friendly pre-treatment for lignocellulosic biomass, potentially facilitating the nanofibrillation process [4]. In the present study, investigate the effects of DES on the morphology of cellulose fibers. Our approach includes the use of a pre-treatment combining a DES (triethylmethylammonium chloride and imidazole, TID) and microwave energy (MW), optimized by a response surface methodology (RSM) to enhance the solubility of cellulose fibers, and optimize the subsequent nanofiber extraction process.

Materials and methods

1. Materials

Wet bleached cellulose pulp extracted from Eucalyptus globulus was kindly provided by a local producer (Papelera Guipuzcoana de Zicuñaga). All chemicals, were provided by Sigma-Aldrich, as reagent grade and thoroughly dried at 50°C overnight to remove moisture prior use.

2. Methods

Ttriethylmethylammonium chloride/imidazole DES (TID DES) and microwave irradiation combined with a statistical response surface methodology, was employed to determine the critical factors impacting TID DES pre-treatment and identify the optimal conditions for maximizing solubility rates. Subsequently, the effectiveness of TID DES pre-treatment on CNF production was evaluated by comparing the morphology of cellulose nanofibers mechanically extracted from native and pre-treated fibers using transmission electron microscope (TEM).

3. Results and discussion

A microwave-assisted irradiation process was employed to dissolve the amorphous components of fibers, which include lignin, hemicellulose, and cellulose, in TID DES. The optimization of the solubilisation yield ($_{SY}$) was conducted using a response surface methodology combined with a full three-level factorial design. Analysis of the results presented in Table 1 reveals that Y_{SY} values ranged from 8,3% (exp.6) to 25,4% (exp.4). The lowest value was obtained under less severe conditions (5 min and 50°C), while the highest Y_{SY} value was recorded under the most severe conditions (30 min and 100°C). A response surface plot depicted in Figure 1 illustrates the influence of independent variables and their interactions on the solubilisation yield. It is evident from the plot that time and temperature significantly impact the response, with the highest solubilisation yield observed at maximum values of these variables. Following the DES pre-treatment, both untreated and pre-treated cellulose suspensions underwent high-pressure homogenization to produce CNFs. TEM images provided in Figure 2 depict the nanofibrillated

Table 1. Independent normalized and not normalized variables, Time (min) (X_1) and Temperature (ºC) (X_2) along with dependent variable, Solubility Yield (Y_{SY}) (%), of the full three-level factorial design.

Exp.	Independent variables				Dependent variables
	Not normalized variables		Normalized variables		
	Time (min)	Temperature (ºC)	X_1	X_2	Y_{SY} (%)
1	5	75	-1	0	11.6
2	30	75	1	0	22.1
3	17.5	75	0	0	11.6
4	30	100	1	1	25.4
5	30	50	1	-1	19.0
6	5	50	-1	-1	8.3
7	17.5	75	0	0	13.6
8	17.5	50	0	-1	10.3
9	17.5	75	0	0	17.8
10	17.5	100	0	1	17.4
11	5	100	-1	1	16.9

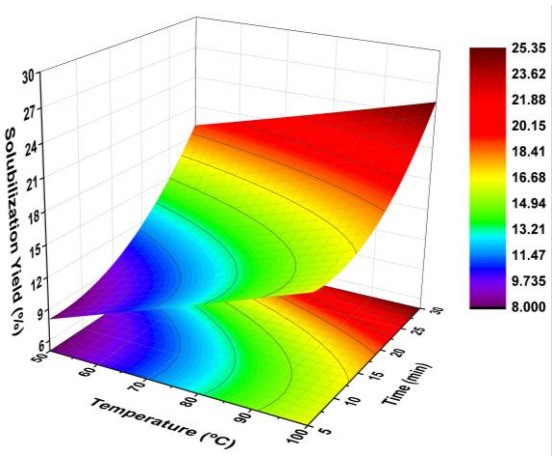

Figure 1. Response surface for solubilization yield of cellulosic fibers in the extraction process.

samples after exposure to mechanical shear force. These images illustrate the effective disintegration of both pulps into nanoscale dimensions, displaying a varied size distribution ranging from approximately 10 nm (individual nanofibrils) to several tens of nanometers (aggregated nanofibrils). In the case of untreated cellulose fibers, the presence of large bundles of microfibrils suggests incomplete fibrillation. However, DES pre-treated cellulose fibers exhibit a slight reduction in diameter and a more uniform distribution of CNFs, indicating enhanced accessibility and improved pulp disintegration. Consequently, a stable nanocellulose suspension with a narrower diameter distribution is achieved, featuring 11% of CNFs with diameters below 10 nm and few remaining thick nanofibers.

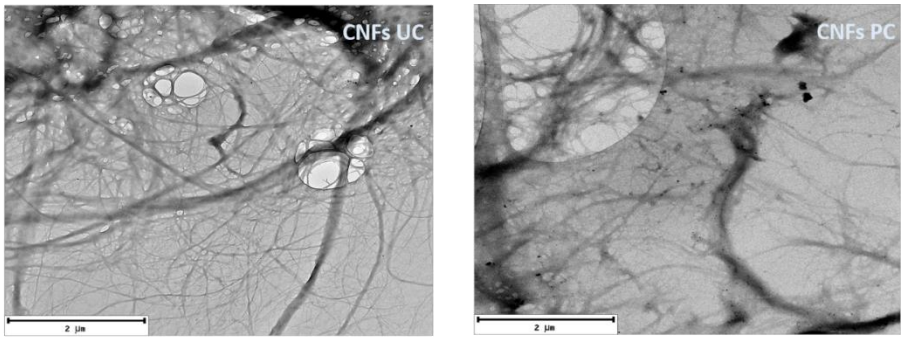

Figure 2. TEM images of CNFs obtained with untreated cellulose fibers (CNFs UC) and DES pre-treated cellulose fibers (CNFs PC).

Conclusion

Cellulose nanofibers were successfully produced through the effective combination of microwave irradiation, TID DES pre-treatment and high-pressure homogenization. The DES pre-treated fibers produced cellulose nanofibers with a narrower diameter distribution. These results provided valuable insight into the effects of DES pre-treatment on the production of cellulose nanofibers and, more specifically, in terms of its role in facilitating the microfibrillation process.

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