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2023 EN-STIMM

Subcritical water, a cleaner nanosizing technique to simultaneously enhance sustainability and circularity of nanocellulose manufacturing

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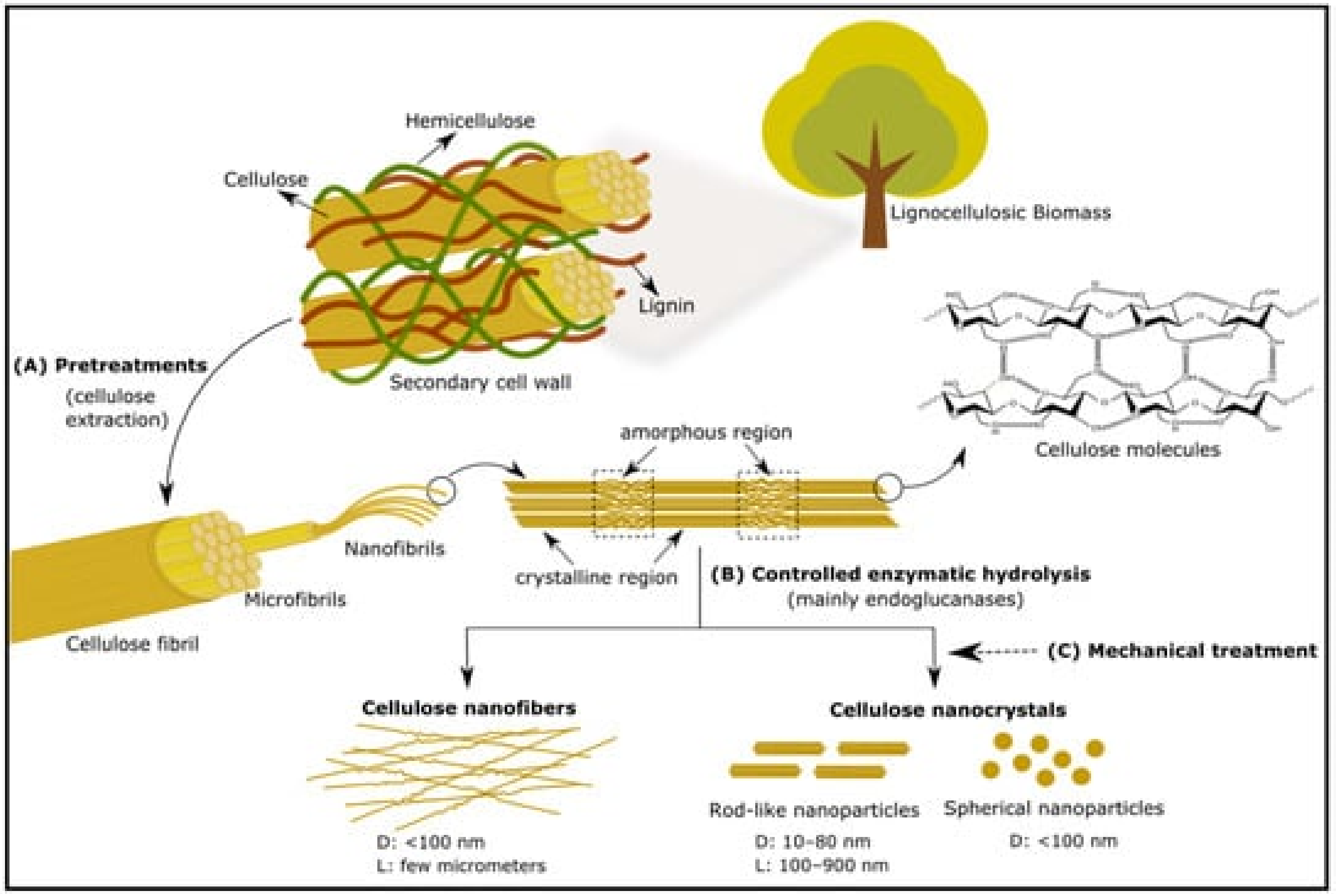
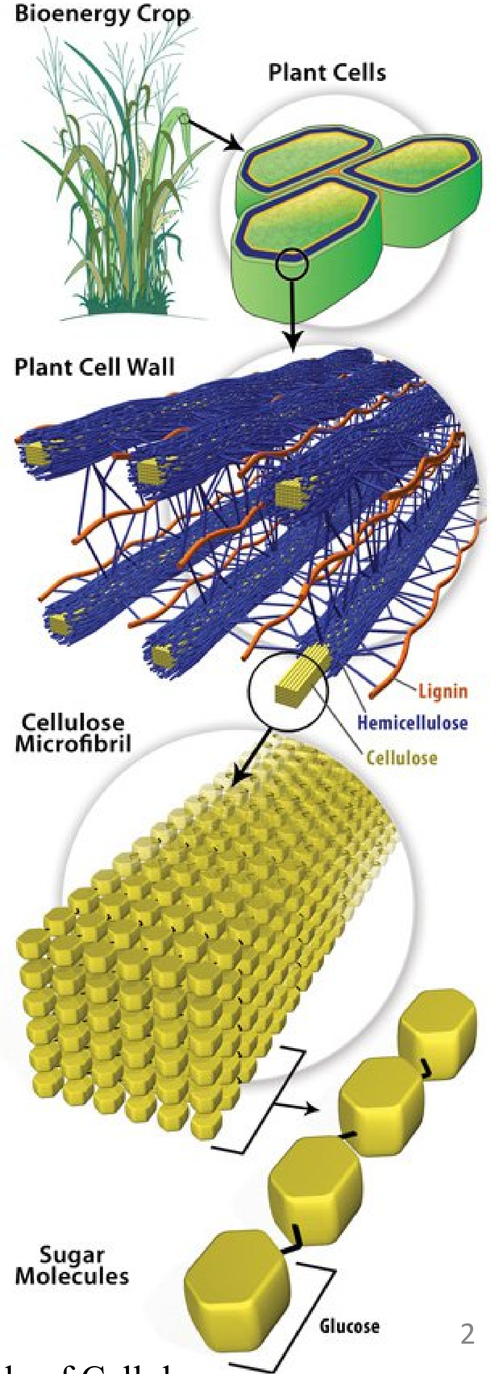
Nanocellulose from cellulose



Michelin et al. (2020)



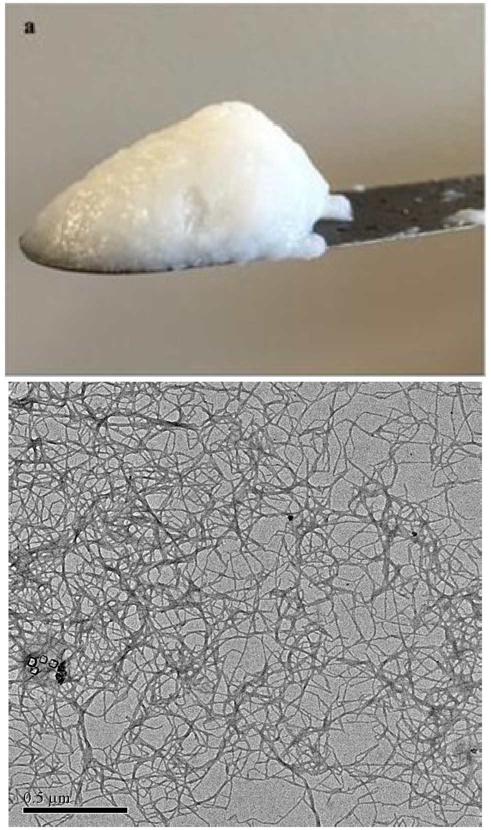
Cellulose, being one of the most important natural polymers on Earth and virtually inexhaustible, is a key source of sustainable materials suitable for industrial applications (Klemm et al. 2011).

Figure1: Structural Chemical formula of Cellulose

Different types of nanocellulose depending on the process

Cellulose nanofibrils (CNF) Mechanical treatment

Tajvidi et al. (2017)



Cellulose nanocrystal (CNC): Acid Hydrolysis

Bacterial Cellulose: *Acetobacter Xylinum*

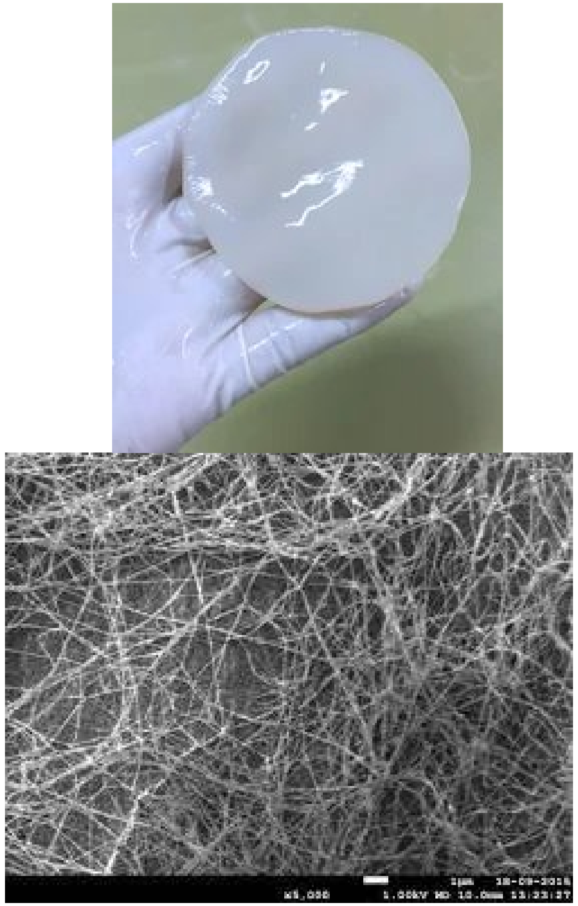
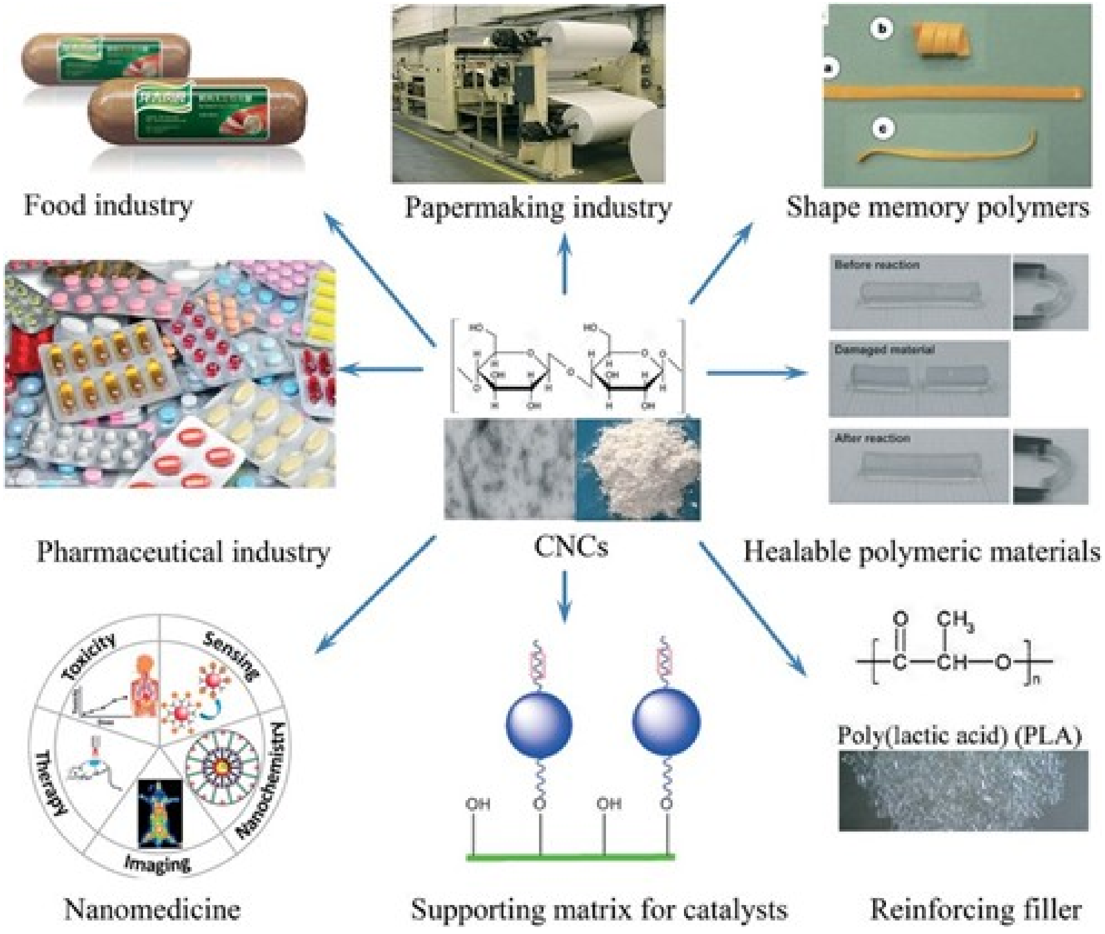


Figure 2: The different types of nanocellulose: Macrostructure and Nanostructure

Potential industrial applications of nanocelluloses

Nanocellulose Characteristics	Performance
• Young's modulus: 138 GPa strength: 2 to 3 GPa	• prospective mechanical properties
• reactive surfaces containing —OH side groups	• chemical modification /integration
• high aspect ratio entangled web-like structures	• flexible substrates
• nano-order scale high specific surface area thermal stability	• thermal stable nanoporous materials
• desired constituents with relatively high carbon content	• precursor for carbon-based materials
• various resources and multiple fabrication methods	• various structures and surface chemistry properties



Xie et al. (2018)

Figure 3: Characteristics and potential industrial applications of nanocellulose

Most common cellulose nanocrystal (CNC) production route

Bleached cellulose

↓

Sulfuric acid (H_2SO_4)
Hydrolysis: 64% (w: v)

↓

Quenching with distilled water to precipitate

↓

Excess acid removal

↓

Dialysis

↓

Sonication

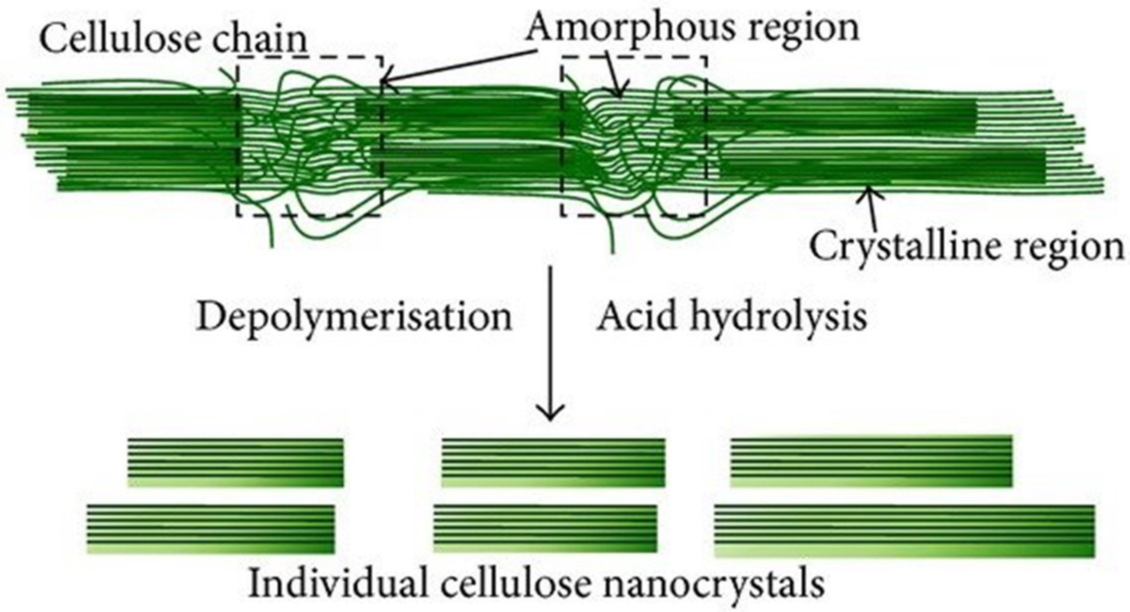
↓

Centrifugation

↓

Colloidal suspension

T˚C = 45˚C
Time: 60-90 min



Lee et al.(2014)

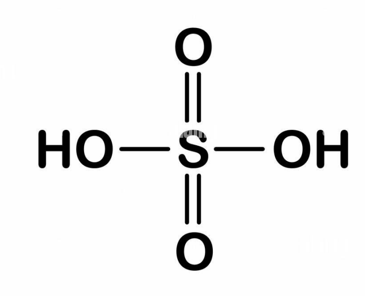
Rod-like particles: 15 – 300 nm length

Figure 4: Formation of rod-like particle of cellulose nanocrystal via acid hyhdrolysis: principle

Advantage and Drawbacks of sulfuric acid hydrolysis route of Cellulose nanocrystal production

Figure 5: Concentrated sulfuric acid solution

Strong mineral acid } pKa of sulfuric acid is 1.92 at 25 °C



Advantages:

- fast reaction
- Produce surface charged rod like particles
- Stable coloidal suspension
- low energy consumption but is not ecofriendly and pretreatments are necessary starting from lignocellulosic matrices

Main drawbacks:

- - For every 25 kg CNCs production it require:
  - 296 kg sulphuric acid,
  - 37200 L water are consumed (Reiner and Rudie, 2013)
- High corrosivity
- Environmental impact: dischargesof high quantity acidic waste,
- Acid recycling challenging and costly
- Result in costly CNCs as high as $25/kg

Alternative: Assesmsent of more sustainable CNC routes via subcritical treatment.

Exploitation of the autoHydrolysis potential of water molecules at high temperature (100 -374˚C) and high pressure → acidification of the medium.

Method 1: Dilute-sulfuric acid Pressurized hot liquid (Subcritical) hydrolysis

Reduction of the [H_2SO_4] : 1.5 to 3% Vs 64% (w: v)

Temperature: 130˚C,

Time: 60 minutes.

Results

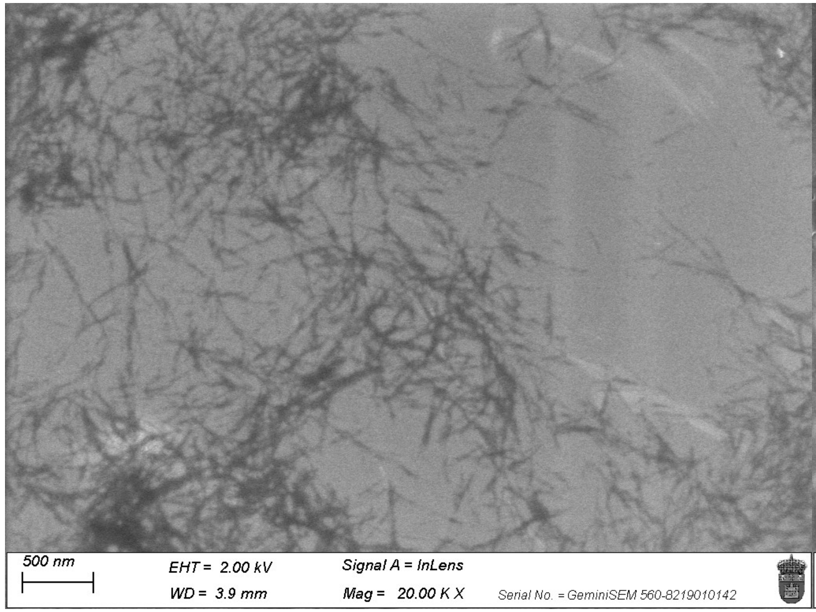
Table 1: Surface Elemental Analysis of Cellulose Nanocrystal CNC isolated from **Method 1**

	% N	% C	% H	% S	% O
CNC regular	-	39.8 ± 0.1	5.4 ± 0.3	1.4 ± 0.3	48.5 ± 0.3
Pressurized hot water 0% H_2SO_4	-	42.4 ± 0.5	6.2 ± 0.1	0.0 ± 0	51.7 ± 0.1
Pressurized hot water 1.5% H_2SO_4	-	41.9 ± 0.4	5.4 ± 0.1	0.6 ± 0.4	51.6 ± 0.1
Pressurized hot water 3% H_2SO_4	-	42.6 ± 0.1	5.6 ± 0.1	0.7 ± 0.2	50.9 ± 0.1

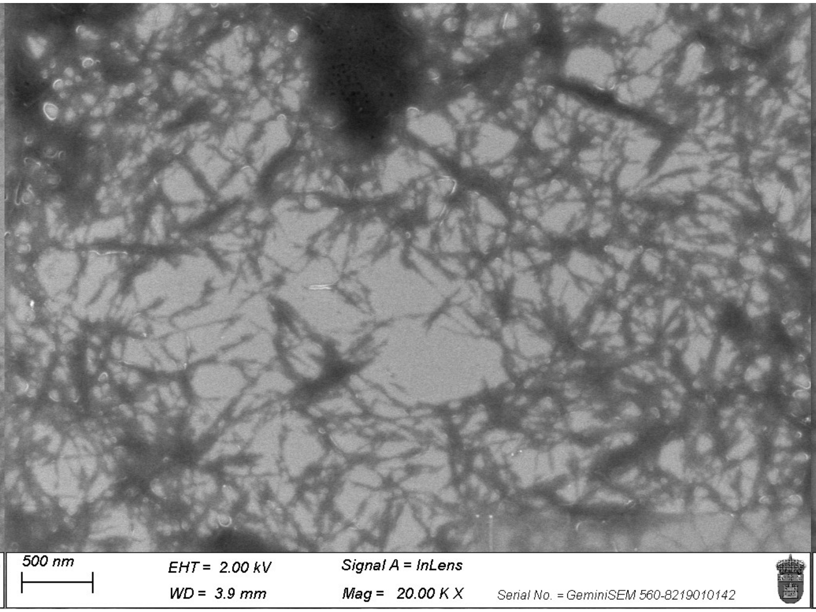
- Elemental Analyser EA Flash 2000 (Thermo Fisher Scientific)

FE-SEM Microstructure of CNC isolated from dilute sulfuric acide / PLE

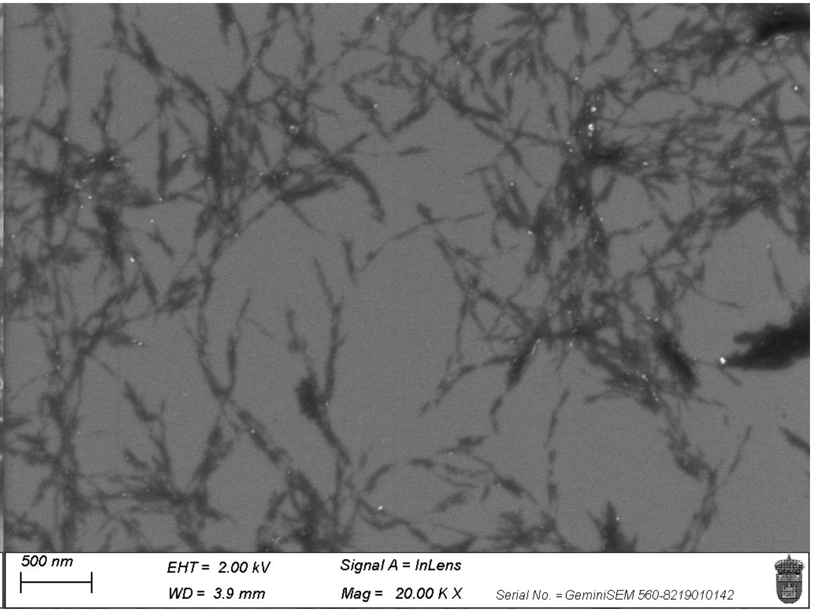
Method 1



Regular CNC



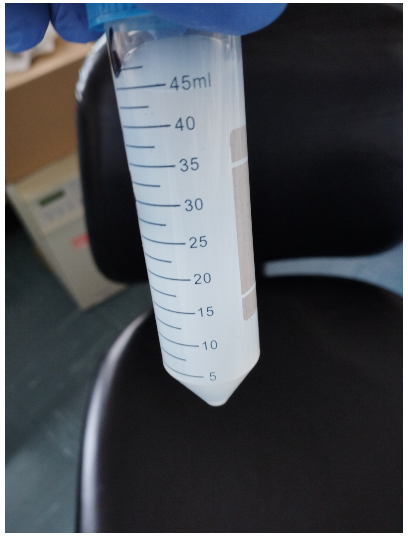
PLE-3% H_2SO_4



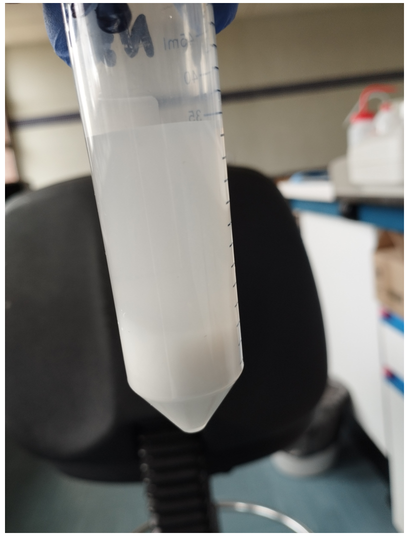
PLE-1.5% H_2SO_4

Yield = 42%

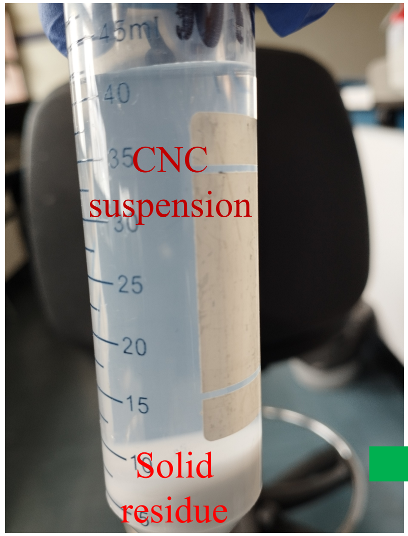
Production of sugar residues



Yield = 20%



Yield = 10%



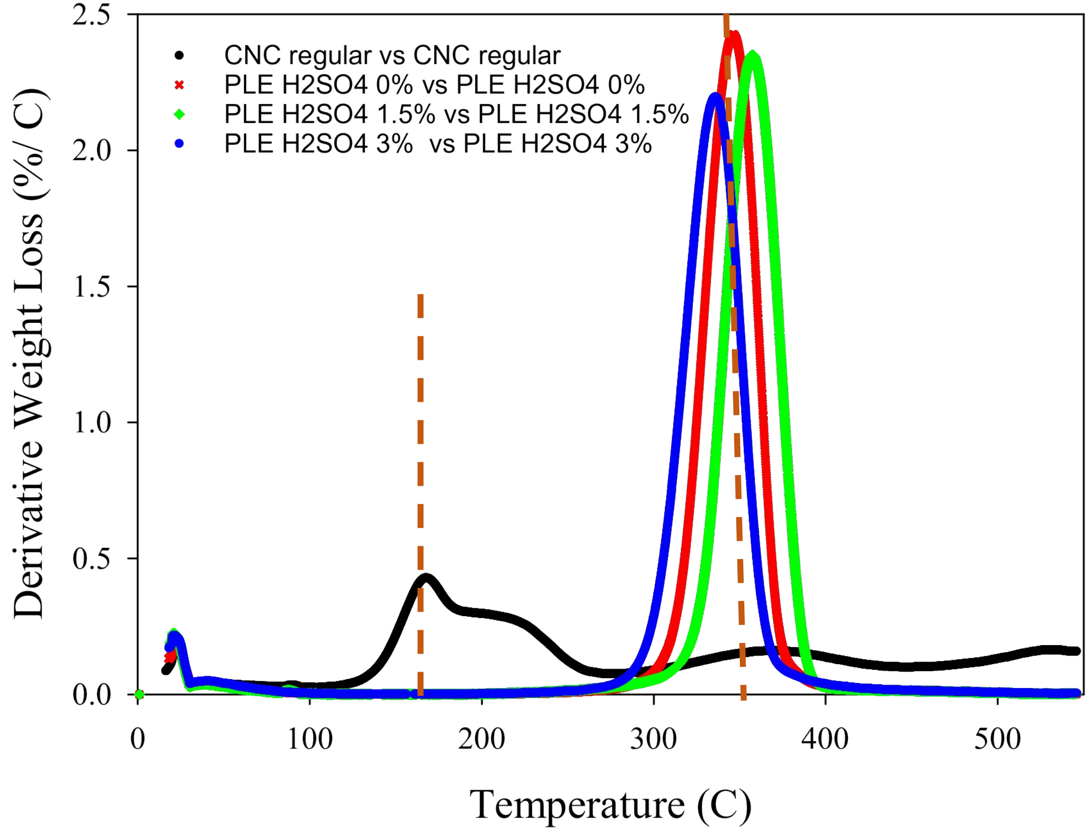


Figure 8: Thermal stability of the CNC via dilute acid PLE hydrolysisis

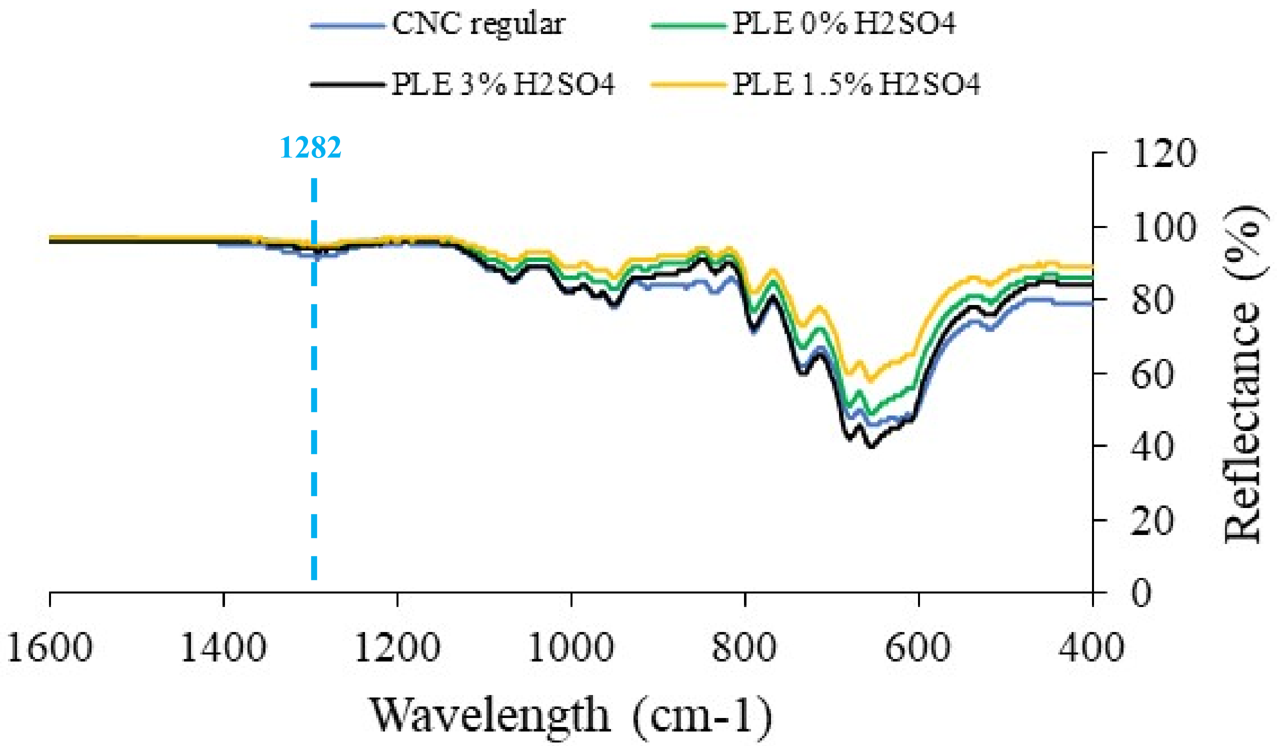
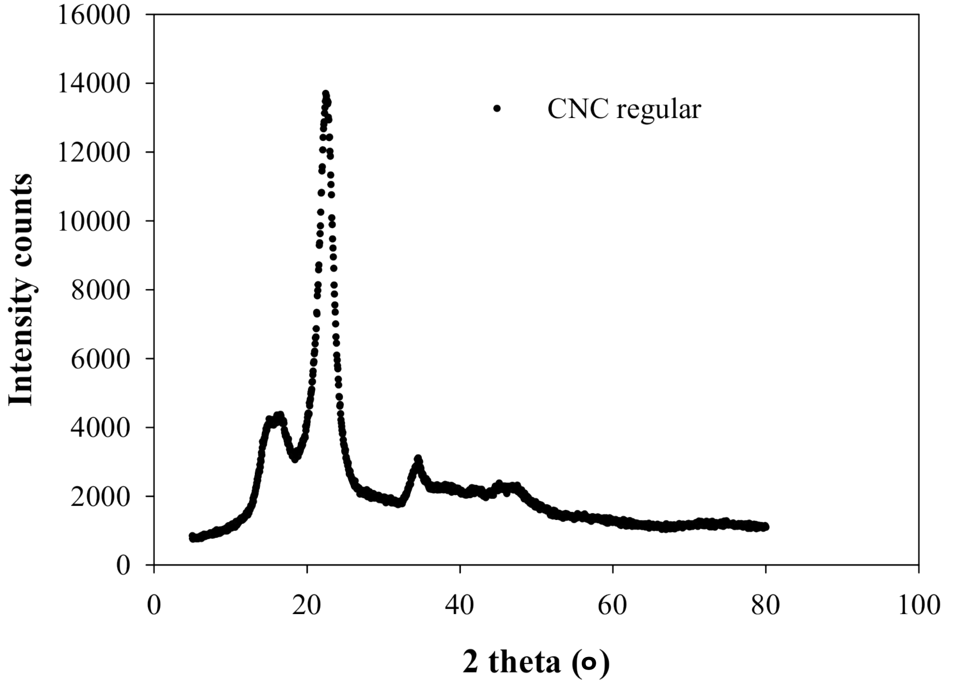
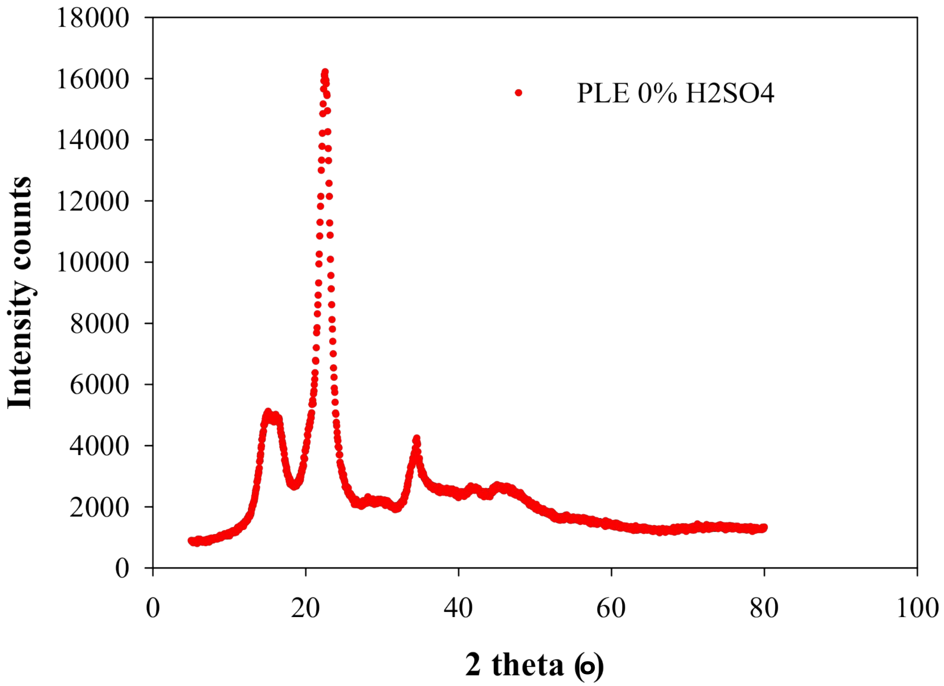
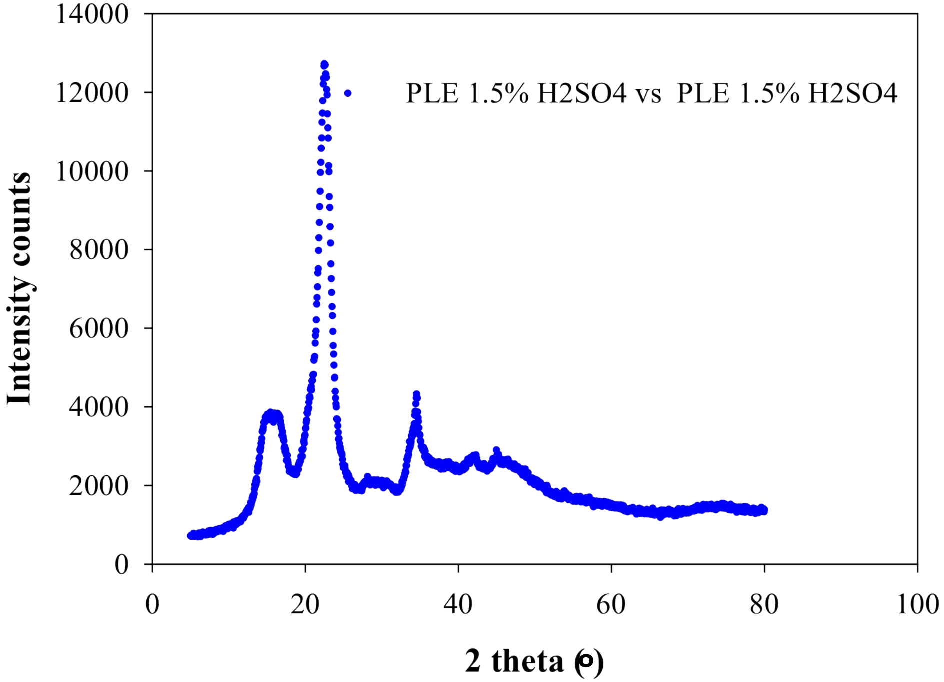
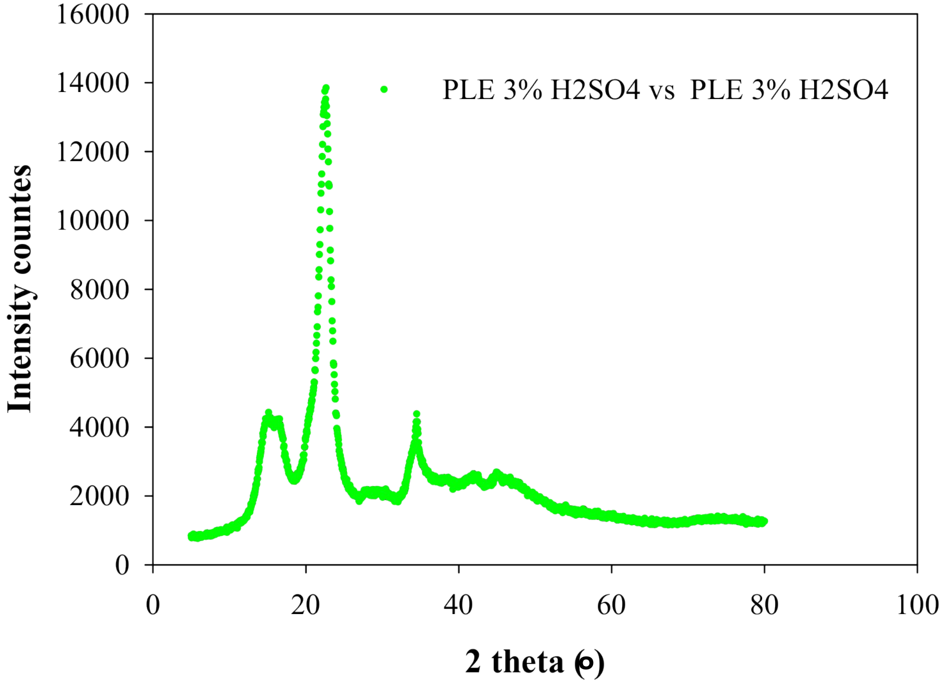


Figure 9 : Structural composition of the CNC via dilute acid PLE hydrolysisis


CNC regular
Intensity counts
2 theta (o)
0
2000
4000
6000
8000
10000
12000
14000
16000
0
20
40
60
80
100

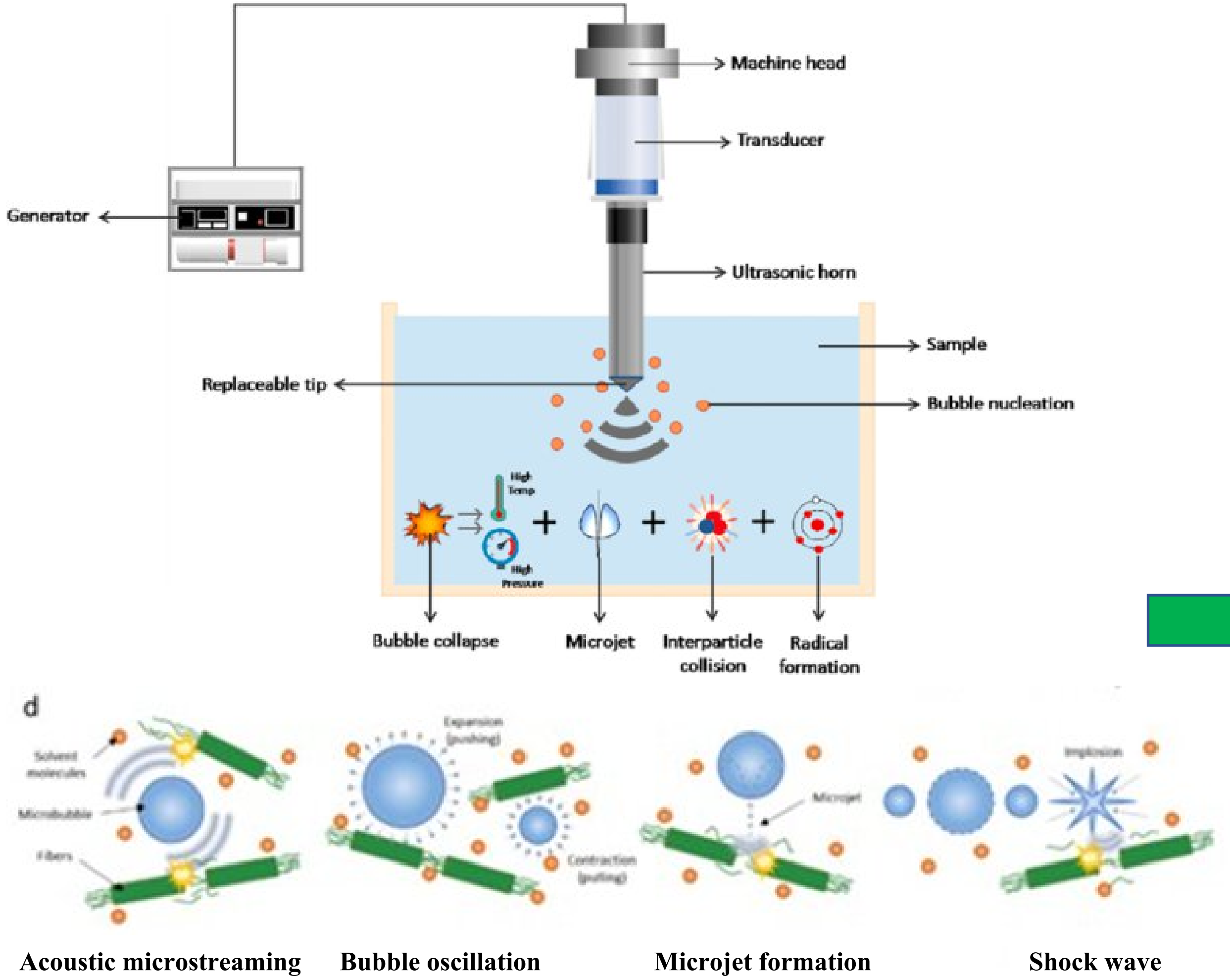

PLE 0% H2SO4
Intensity counts
2 theta (o)
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
0
20
40
60
80
100


PLE 1.5% H2SO4 vs PLE 1.5% H2SO4
Intensity counts
2 theta (o)
0
2000
4000
6000
8000
10000
12000
14000
0
20
40
60
80
100

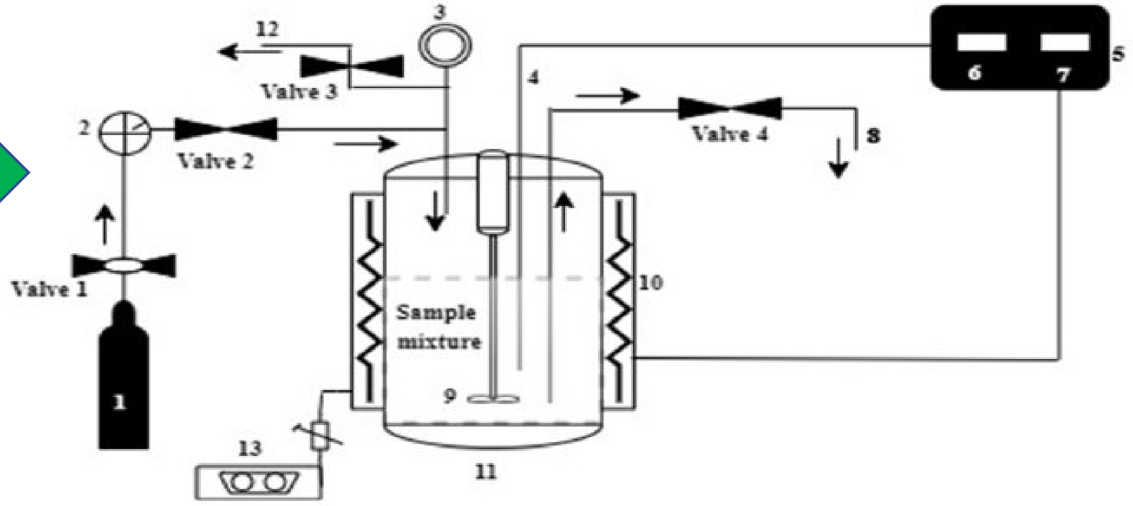

PLE 3% H2SO4 vs PLE 3% H2SO4
Intensity countes
2 theta (o)
0
2000
4000
6000
8000
10000
12000
14000
16000
0
20
40
60
80
100

Method 2: Ultrasounds pretreatment assisted Pressurized hot maleic acid hydrolysis.

Ultrasound principle



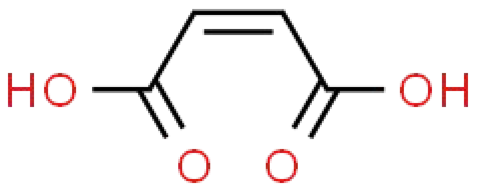
Subcritical water reaction principle



1- N_2 gas tank
2- Pressure source regulator
3- Extractor pressure controller
4- Thermocouple temperature recorder
5- Centralized temperature control board
6- Extracor temperature controller
7- Heating jacket temperature controller
8- Sample collector
9- Propeller
10- Heating jacket
11- Pressurized liquid extractor vessel
12- Pressure release system
13- Resistor linked to a PID controller

Figure 5: functionment prínciple of ulstrasound and pressurized hot (subcritical) liquid

Maleic acid used as sulfuric acid replacement



Chemical structure of maleic acid

Figure 6: Maleic acid cristal salt

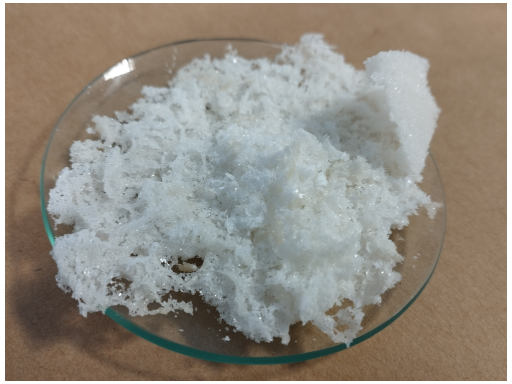
- Weak, colorless organic crystal acid salt
- Safe storage
- Low transportation cost
- soluble in water.
- Able to hydrolyze cellulose
- Non-corrosive to equipment
- environmentally friendly: Easily recyclable
- Stable up to 130˚C
- pKa = 1.83

Table 2: Evaluation of the ultrasound /PLE assited maleic acid hydrolysis

Code	**Maleic acid**	**Ultrasound**	**Glass reactor**	**PLE**	**Temperature (˚C)**	**Time (min)**	**Yield (%)**
MA-85	**50%**				80	90	≈ 16
MA-PL	**50%**				130	60	≈ 29
MA-UR	**50%**			**-**	80	60	≈ 33
MA-UP	**50%**				130	60	≈ 41

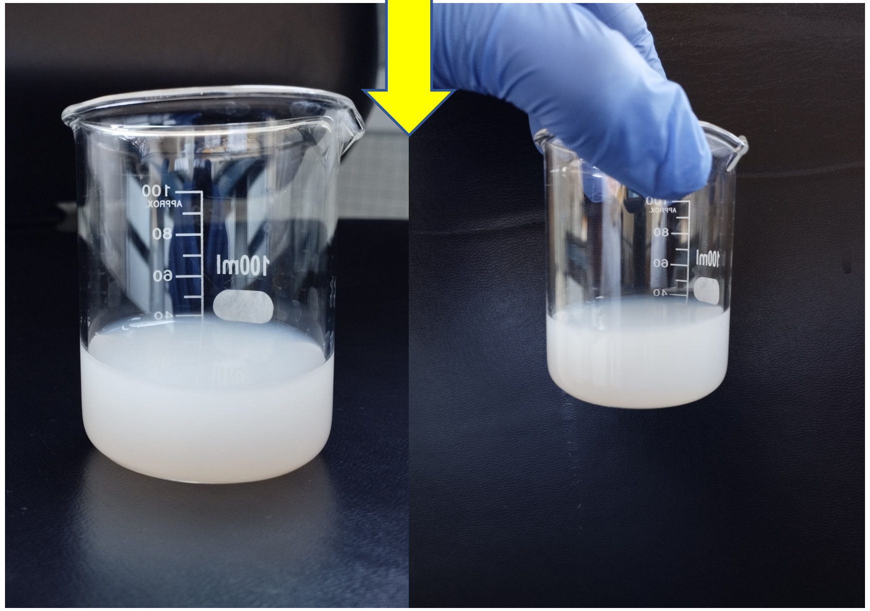
Maleic acid Hydrolysis → Cleanimg → Dialysis → sonication → centrifugation

Evaporation
75 ˚C

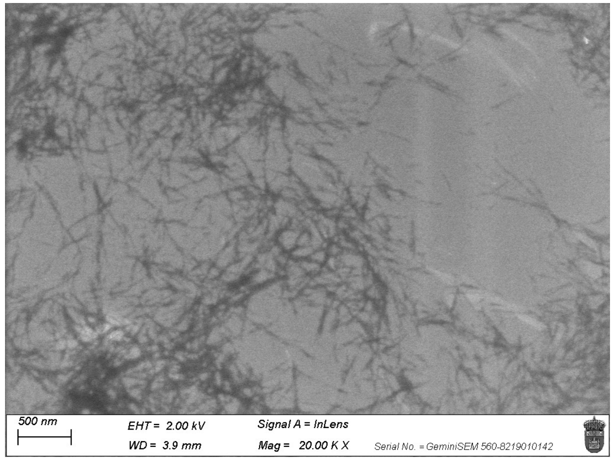


Maleic acid recovey

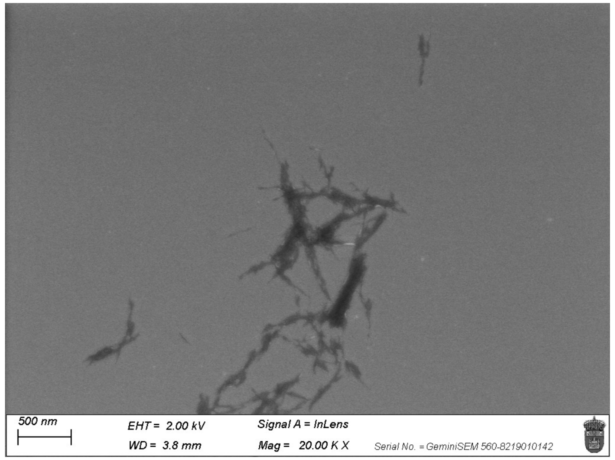
- ❑ Recycled
- ❑ Reutilizable efficiently



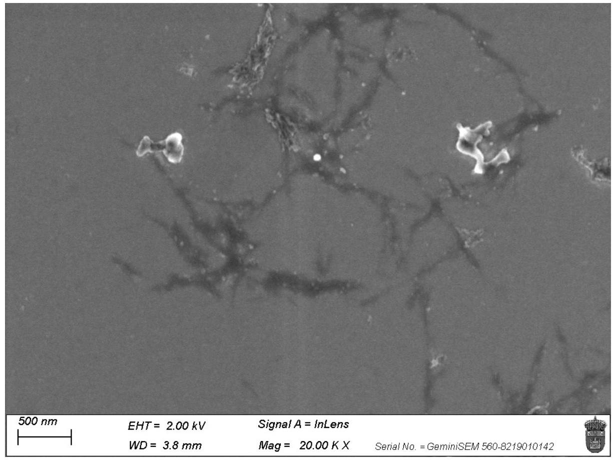
Cellulose nanocrystal suspensions



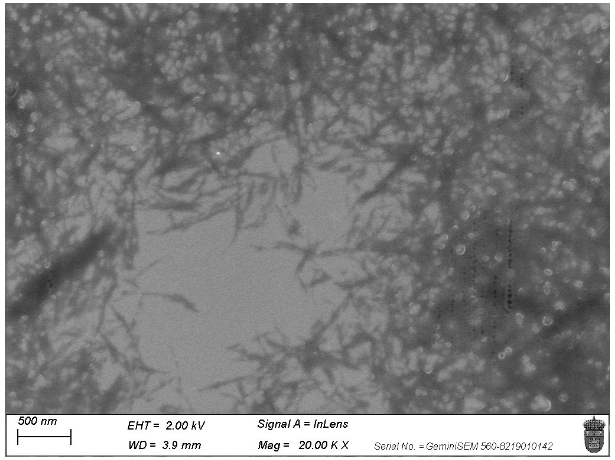
Regular CNC



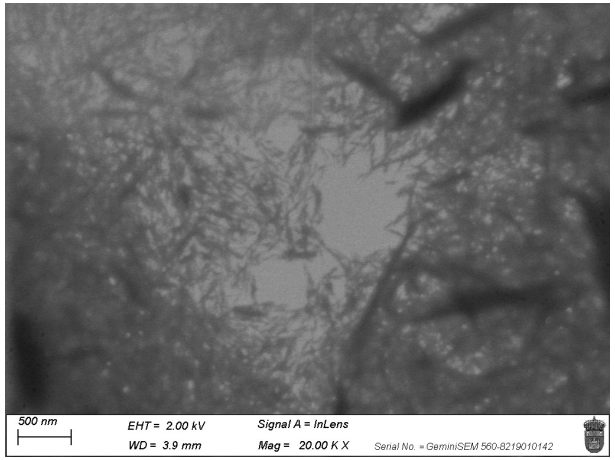
MA-85



MA-PL



MA-UR



MA-UP

Figure: FE-SEM nanostructure of maleic acid hydrolysi CNC production

Conclusion

- Pressurized liquid or subcritical liquid technology showed strong potentialities for rendering more sustainable the manufacturing route of cellulose nanocrystal.

- Dilute acid at concentration as low as 3% (W:V) was able to produce CNC at aceptable yield (21%) when combined to subcritical water.
- isolation of esterified rod-like particles, with thermostability comparable to neat cellulose.
- However: corrosivity at concentration > 3% for equipment reduced their potential use at higher scale.

- Combining utrasound treatment and subcritical treatment Foster the hydrolysis potential of maleic acid.
- Maleic acid as a weak acid, can foster CNC at yields comparable to the common sulfuric acid hydrolysis route.

- The possibility of recovering and reusing maleic acid at the end of the process make the process highly scalable and environmentally friendly.

- Therefore Subcritical treatment can simultaneously enahnce the sustainabilit and circularity of nanocellulose manufacturing.

THANK YOU FOR YOUR ATTENTION!

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