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TECNOLOGIA TÊXTIL

Universidade do Minho
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CELLULOSE NANOWHISKER OBTAINED FROM COTTON REJECTED BY TEXTILE INDUSTRY

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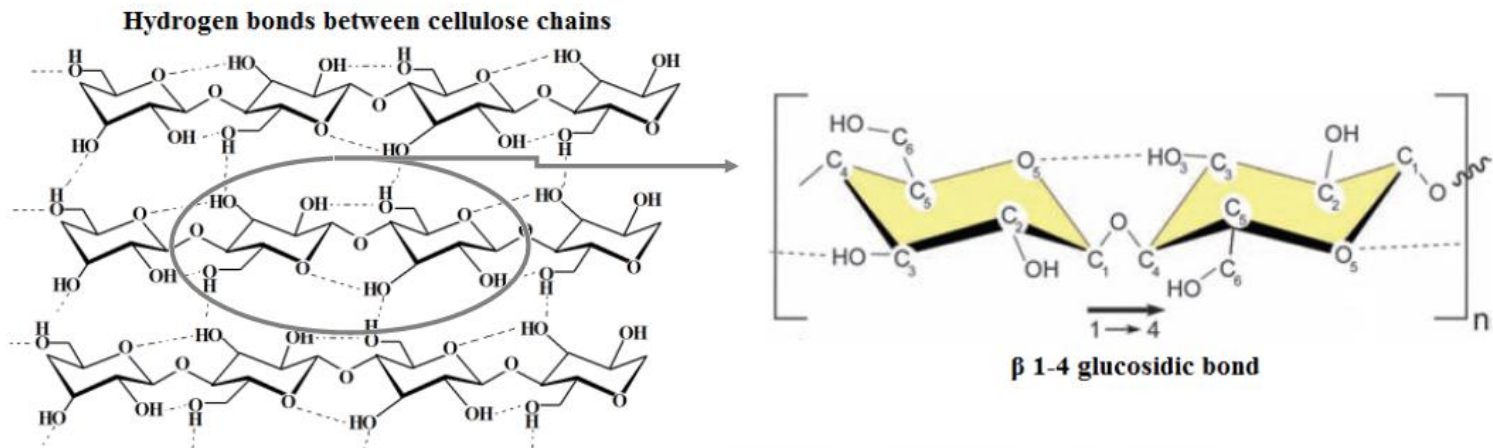
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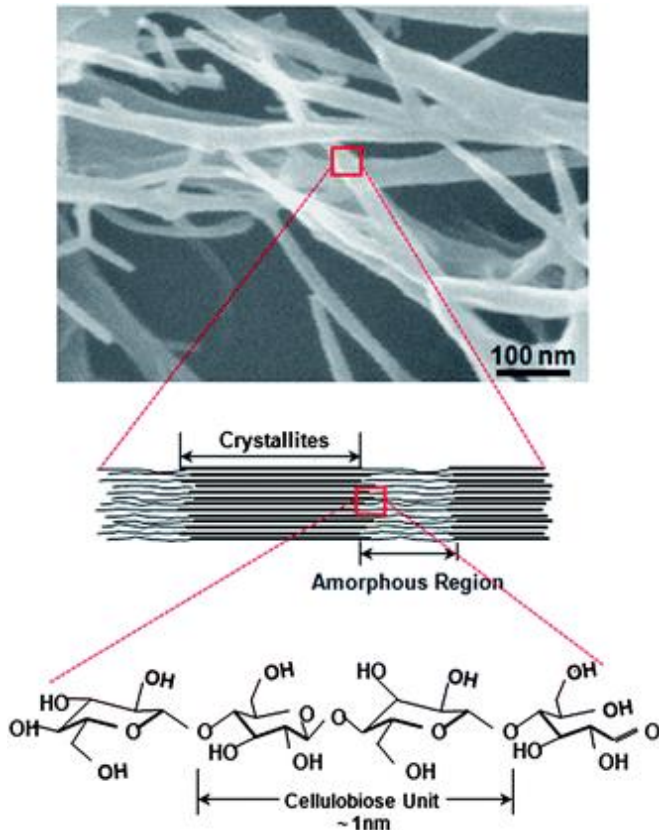
Cellulose

- Cellulose is a homopolymer of β -1,4-d-glucose molecules linked in a linear chain that can be found in nature among various sources like plants, algae, marine creatures and bacteria.





Cellulose



- The single cotton fibre consists of superfine fibrils having diameter in the range of nanometer.
- Within these fibrils there are regions where the cellulose chains are arranged in a highly ordered crystalline structure and amorphous regions.



Cellulose

- Cellulose sources are not completely crystalline. The presence of paracrystalline or amorphous cellulose makes the structure susceptible to acid hydrolysis, and the eventual breakdown into individual crystallites.

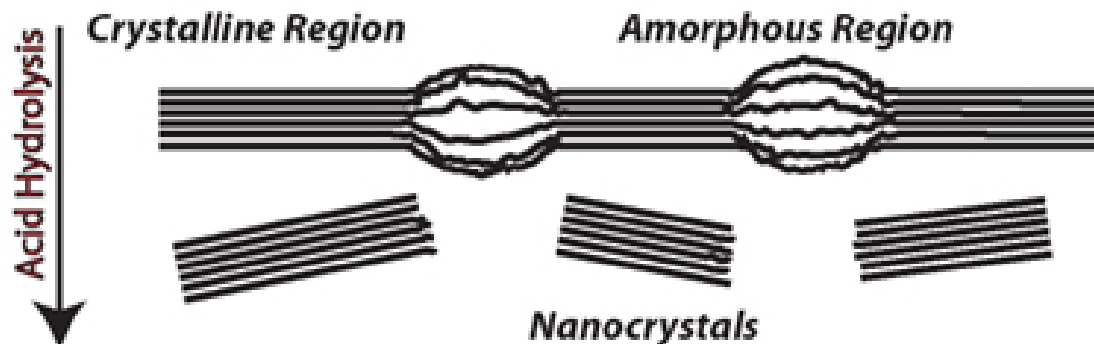
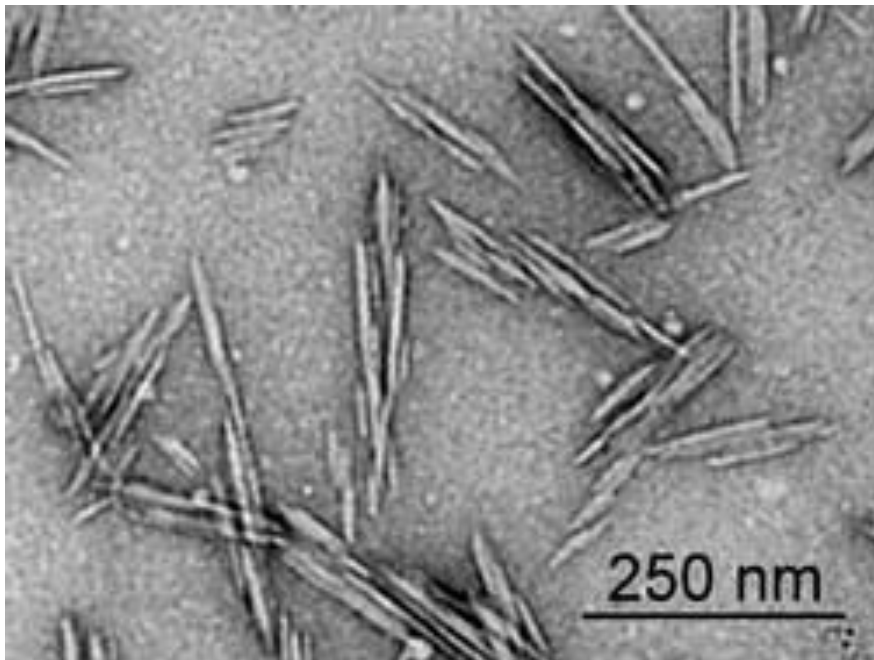


Figure 1: Acid hydrolysis breaks down disordered (amorphous) regions and isolates nanocrystals.



Nanowhiskers

- Nanowhiskers are defined as the nanocellulose with diameters ranging from 2 nm to 20 nm and length ranging from 100 nm to 2.1 μm .



Main properties:

- Biodegradability
- Biocompatibility
- High strength and modulus
- High surface area
- Dimensional stability
- Chemical functionality



Nanowhiskers



- Due to their aspect ratio (length/diameter), high stiffness and reinforcing capabilities are potentially suitable for composite materials.
- A high aspect ratio to the fibres is desirable as this enables a critical length for stress transfer from the matrix to the reinforcing phase.
- Can be applied in a wide range of applications such as nanocomposites, construction materials, intelligent or active package, functional surface, etc.



Aims



- The aim of this work was to extract and characterize the cellulose nanowhisker obtained from cotton rejected by textile industry.
- The physical and chemical properties of CNC obtained were studied by analysis of surface charge, crystal size dimension and morphology, crystallinity and chemical structure.



Cotton pre-treatment

Discarded 100% cotton fabric
(textile industry residue)



Milled and hydrolysed
Alkali treatment in a solution of NaOH 5% o.w.f. (of weight of fabric)
80 °C for 2 hours



Bleaching process
Silicate (Na₂O/SiO₂)- 3.5% o.w.f.
Non-ionic surfactant 1% o.w.f.
Na₂CO₃ 1% o.w.f.
NaOH 1% o.w.f.,
35% H₂O₂-4% o.w.f.
1 h at 90°C.



Nanowhiskers preparation

Method of acidic hydrolysis

(W.J. Orts, L. Godbout, R.H. Marchessault, J.F. Revol (1998) Macromolecules 31, 5717-5725)

Clean cellulose mill to pass through a **20 mesh**

Cellulose concentration of 10% (w/w) in **60% sulfuric acid** at 46 °C for 15 min.

Reaction stopped by adding 10-fold excess of cold deionized water

Centrifuged colloidal suspension for 20 minutes at 13.000 rpm

Ultrasonicated to prevent agglomeration and dialyzed with water until **pH was above 6**

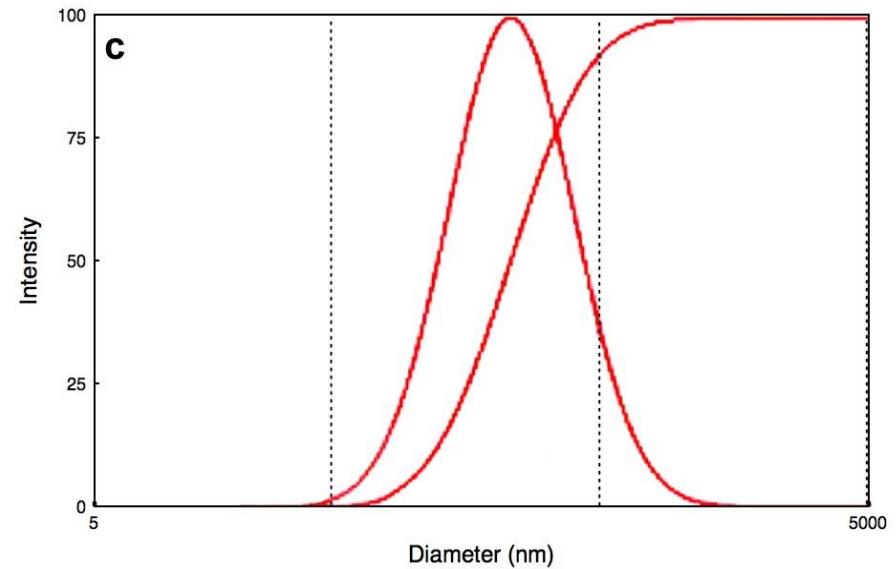
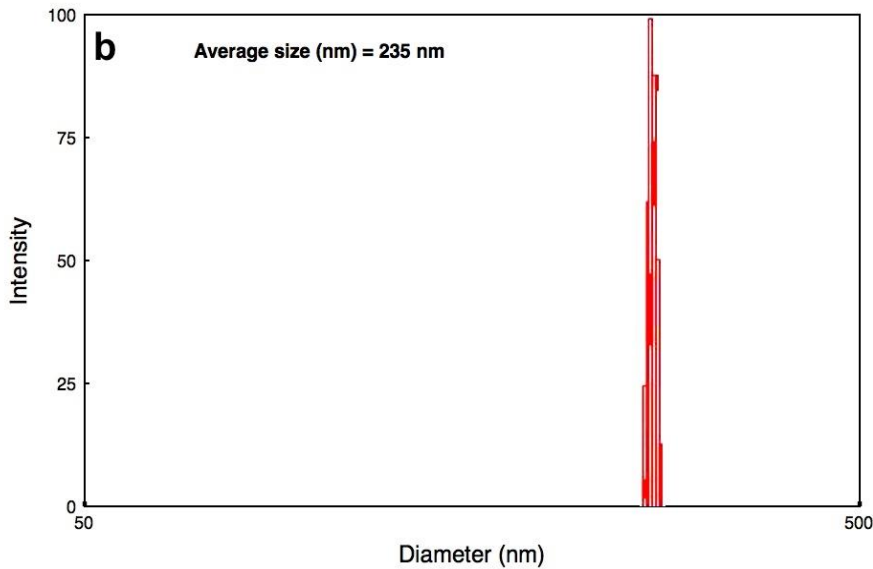


Nanowhiskers preparation

- Under the used controlled conditions it was possible an efficient disruption of the amorphous regions surrounding and embedded within cellulose microfibrils leaving the microcrystalline segments intact.
- Since the geometrical characteristics of cellulose whiskers depend on the origin of cellulose microfibrils and acid hydrolysis process conditions such as time, temperature, and purity of materials is extremely important.



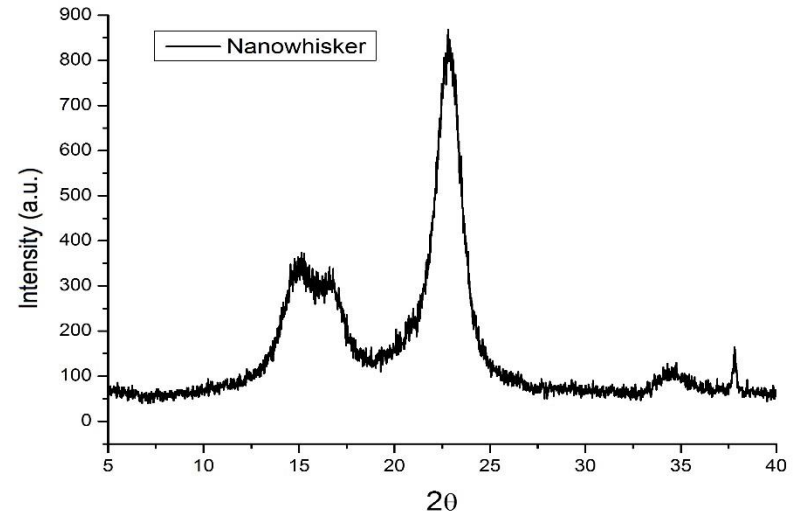
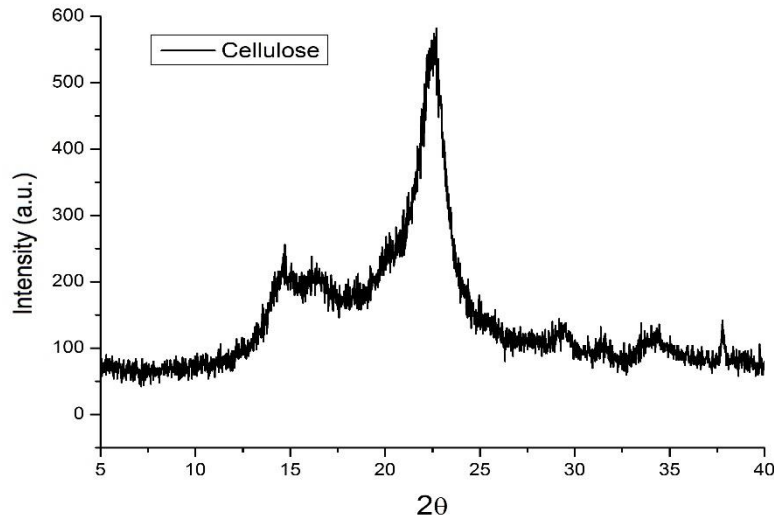
Dynamic Light Scattering (DLS)



- Zeta potential of 25.35 ± 1.5 mV.
- Monodisperse size distribution between 100 and 300 nm and an average size of 235 nm.
- Precipitate with high dispersion of sizes in micro range.



X-ray powder diffraction (XRD)



- High crystallinity of the extracted nanowhiskers (C.I. 86%) compared to the cellulose fibers (C.I. 72%).
- Characteristic peaks of cellulose I at 22.5° and 34.5°.
- The superimposed lattice peaks between 14.8° and 16.7° are better defined in the nanowhiskers cellulose



Scanning

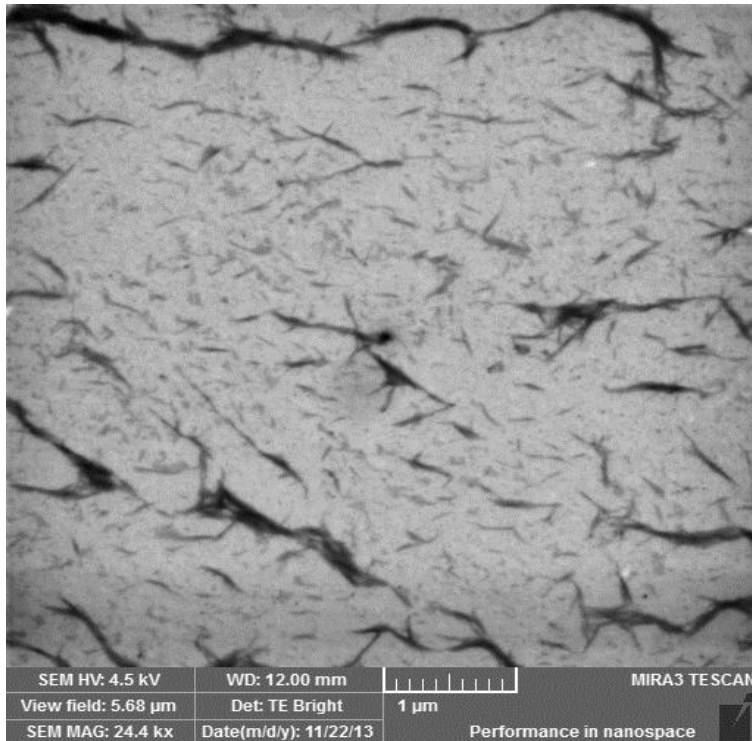
Transmission

Microscopy (STEM)



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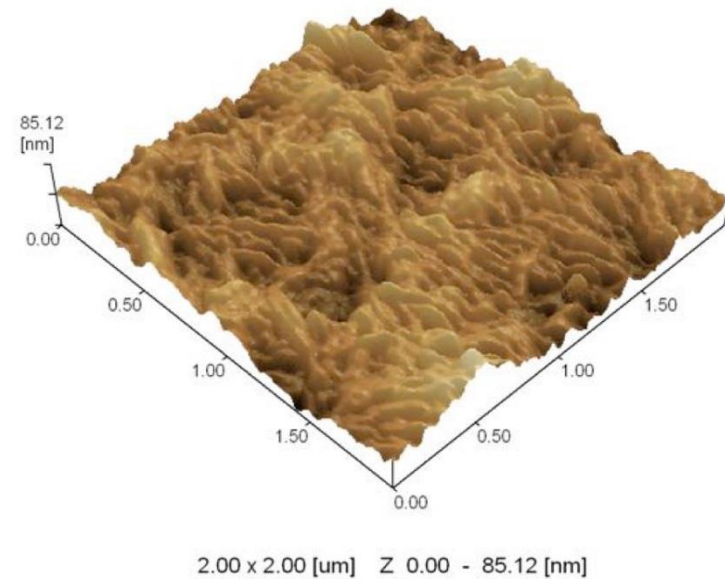
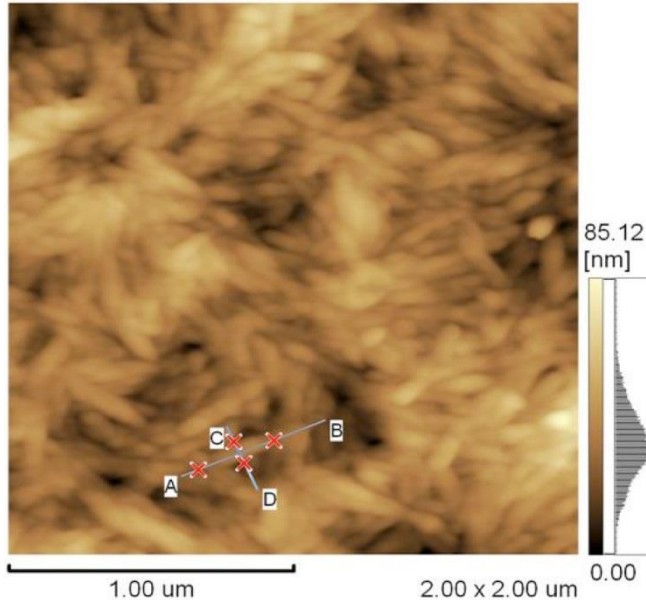
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- STEM picture reveals that cellulose nanowhiskers have a high surface area to volume ratio.
- Presence of agglomeration zones of nanocellulose with dispersed crystallites and individual crystals.



Atomic force microscopy (AFM)

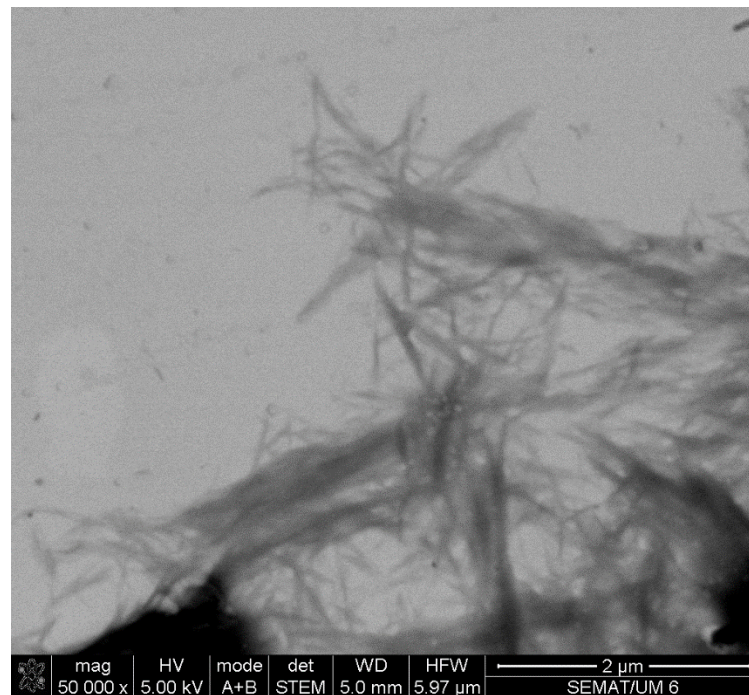
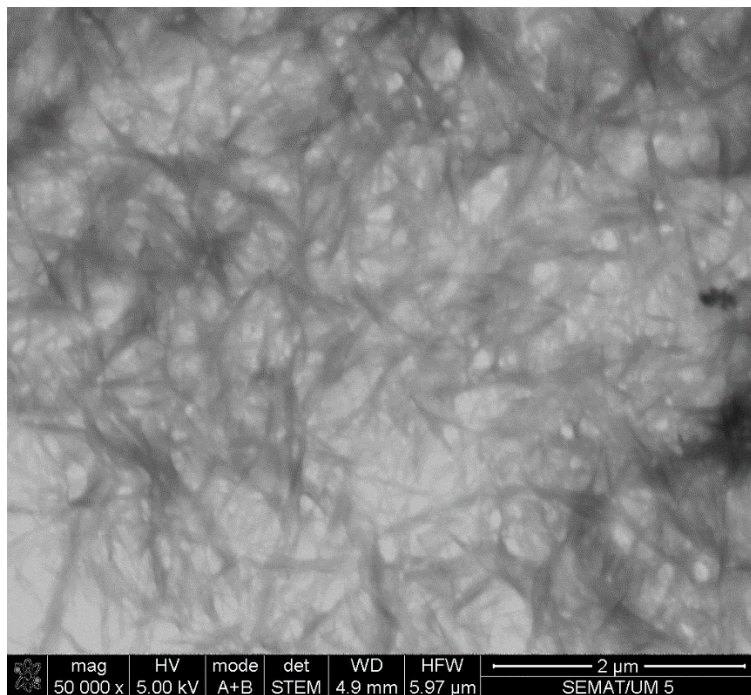


- The average length and diameter with values of 98.1 ± 4.7 and 8.0 ± 3.4 nm, respectively.
- Aspect ratio of the fibers, around 12.3, was higher than the average values usually reported in literature (~ 10).



Effect of hydrolysis time

- Preliminary test with a 10 min of acid hydrolysis.





Conclusions



- Cellulose nanowhiskers were successfully extracted by acid hydrolysis from cotton residues showing an aspect ratio of 12 and high crystallinity of 86%.
- Acidic route is an efficient alternative for obtaining monodisperse cellulose nanowhiskers from industrial cotton wastes.
- Control of time and temperature of the acid hydrolysis step is a fundamental variable for an efficient production.



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Thank you for your attention

