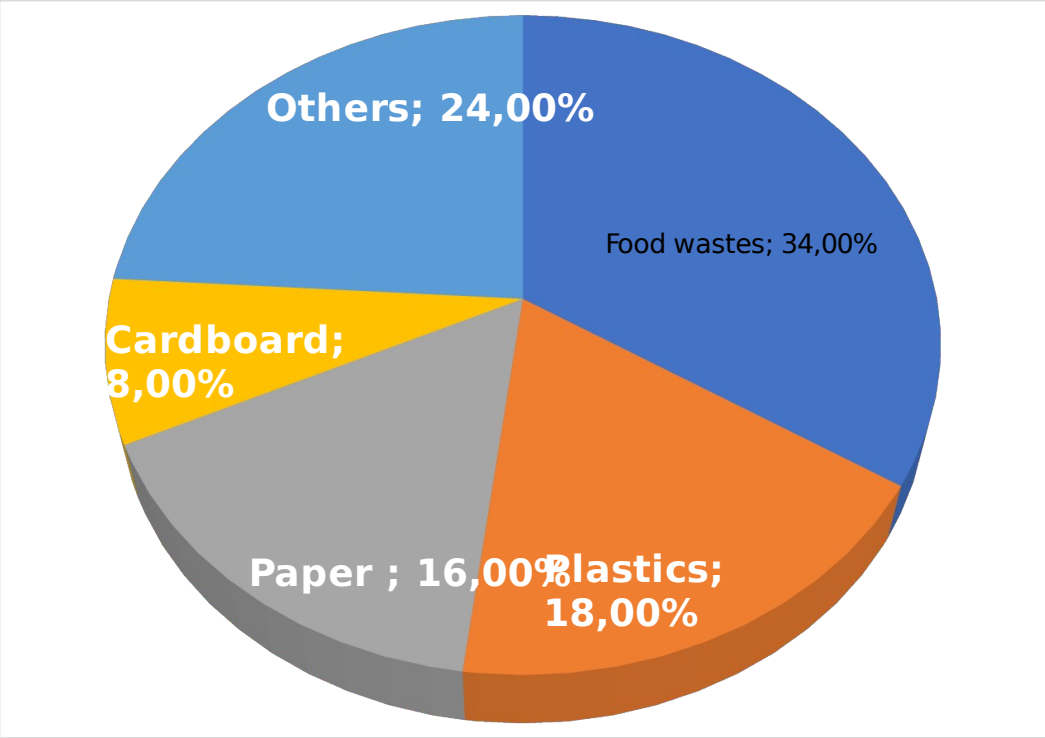
School of Mechanical engineering, Environmental ,engineering program

TEL AVIV UNIVERSITY אוניברסיטת תל אביב

# Production of nanocellulose from Israeli paper mill sludge by ozonation pretreatment followed by recyclable maleic acid hydrolysis

Peretz, E. Sterenzon, Y. Gerchman, V. Kumar Vadivel, T. Luxbacher, H.




Israeli Ministry of Environmental Protection, 2014

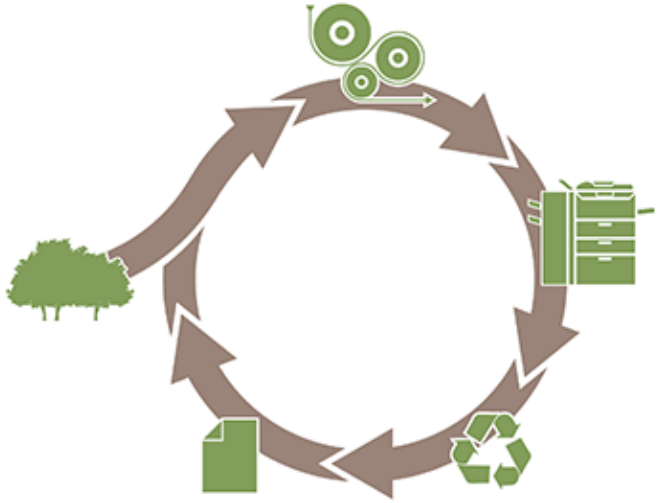
- **4.8 million tons of MSW are produced annually.**
- **The predominant types of municipal wastes are of organic source with 34% of food residues and 24% of paper and cardboard (by weight).**
- **Total amount of paper and cardboard wastes are about 1.15 million ton/year**
- **Each year ~ 0.23 million**

# Recycled Paper Sludge


**31,000 tons of RPS in Israel alone!**


# What can we do with it???

– **As paper is made from wood material**



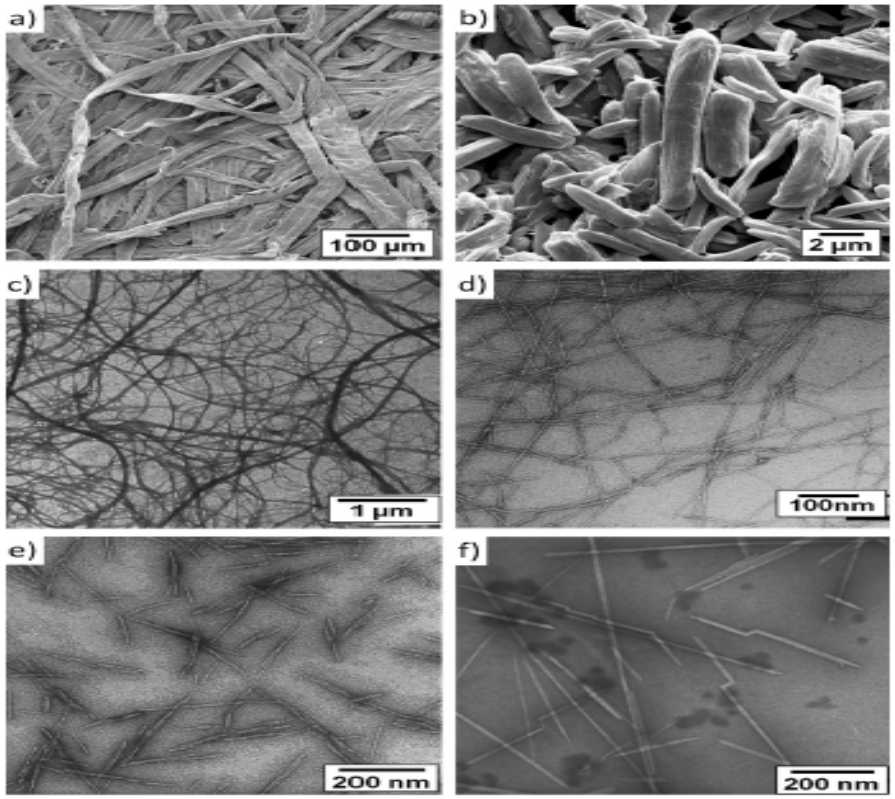
# RPS contain cellulose, ?Lignin

RPS characteristics.

| Isoelectric point (IEP) | pH ~ 2 |
|---|---|
| Insoluble lignin | 8.22% ± 0.22% |
| Soluble lignin (ABSL) | 10.71% ± 2.21% |
| Crystallinity index (CI) | 70.68% ± 0.55% |
| Crystalline cellulose | 75.3% ± 20.2% |
| Ash | 16.64% ± 2.21% |

**Peretz et al. 2019**

# Nanocellulose




Moon et al. 2010

**Properties:**

- **Low density (1.6 gr cm-3)**
- **High light transmittance**
- **High strength and stiffness**
- **Surface (-OH) for chemical modifications.**
- **Biodegradable & biocompatible.**
- **High surface area.**
- **Green disposal/ recycle at end of life.**
- **Thermal stability.**

**Environmental friendly nanomaterials.**
**Key component in many industrial applications.**

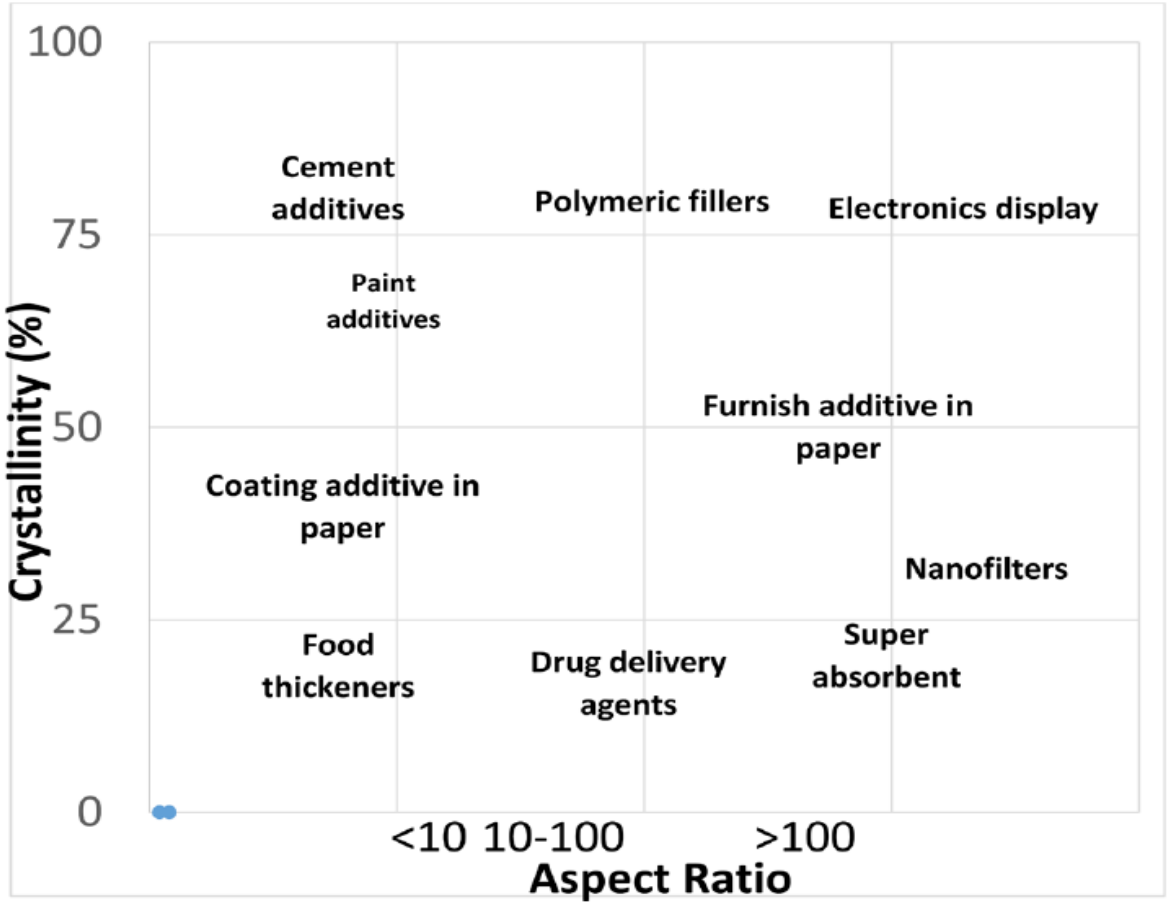
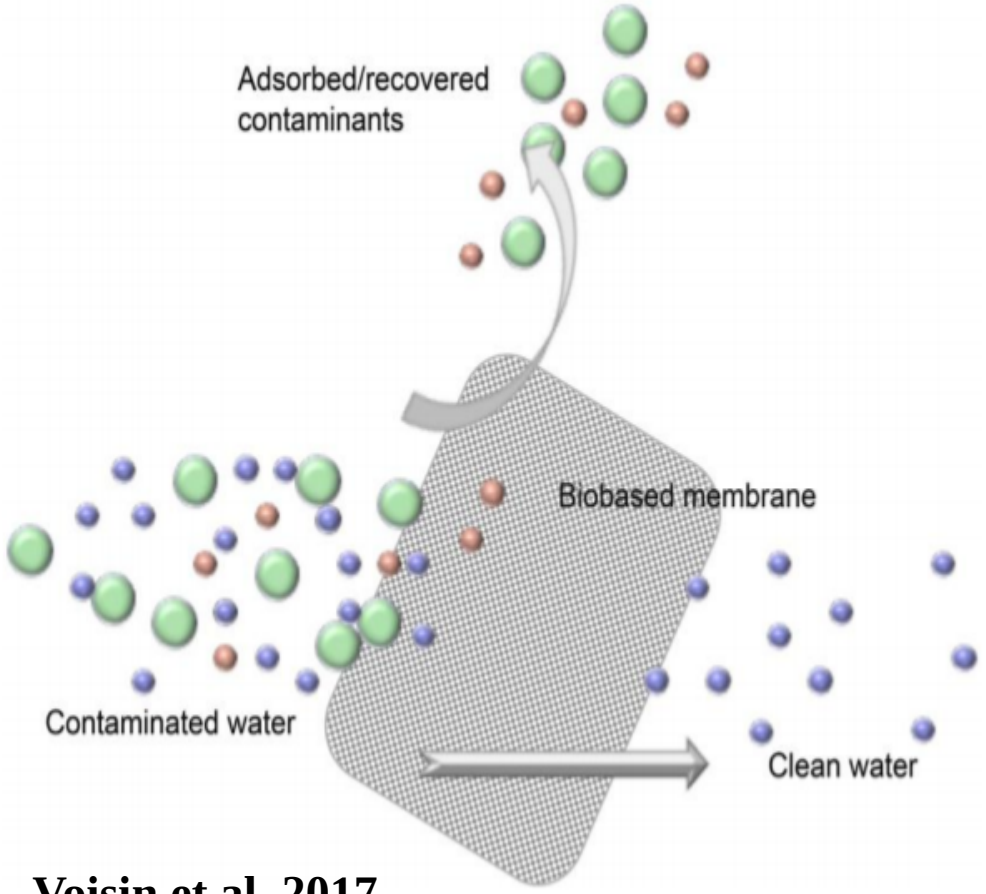



Figure 4. Nanocellulose Quality Index based on aspect ratio and crystallinity for various applications.

**Bharimalla et al. 2015**

# Example: Water treatment




**Voisin et al. 2017**

# Nanocellulose production is not so easy

**Based on Bian et al. 2017***

## Pre-treatment

De-lignification

Drying
Overnight ; 105 C

Grinding

Sieving
hr ; 0.5 mm<..>4mm 1

## Hydrolysis

Acid hydrolysis
70 wt% maleic acid

Filtration

Dilution
total solids in DI 1%~

Sonication
.min 20

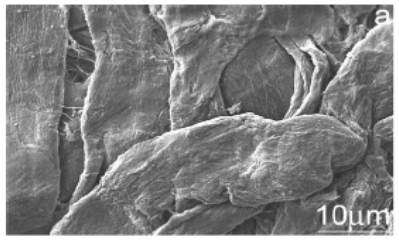
Centrifugation
.X g ; 10 min 15,000

## CNC separation

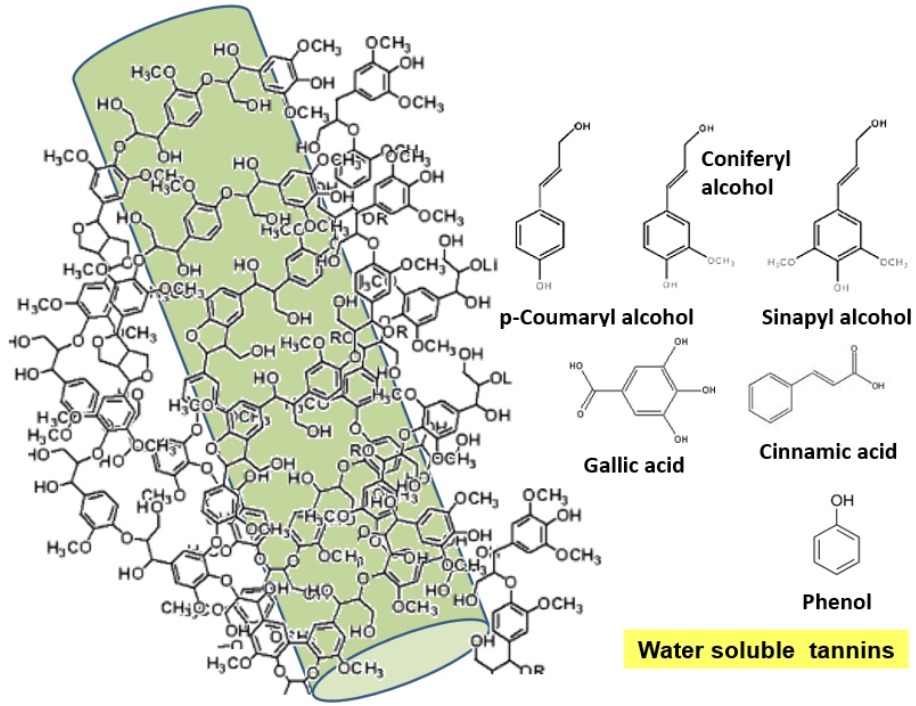
Repeat centrifugation until turbidity

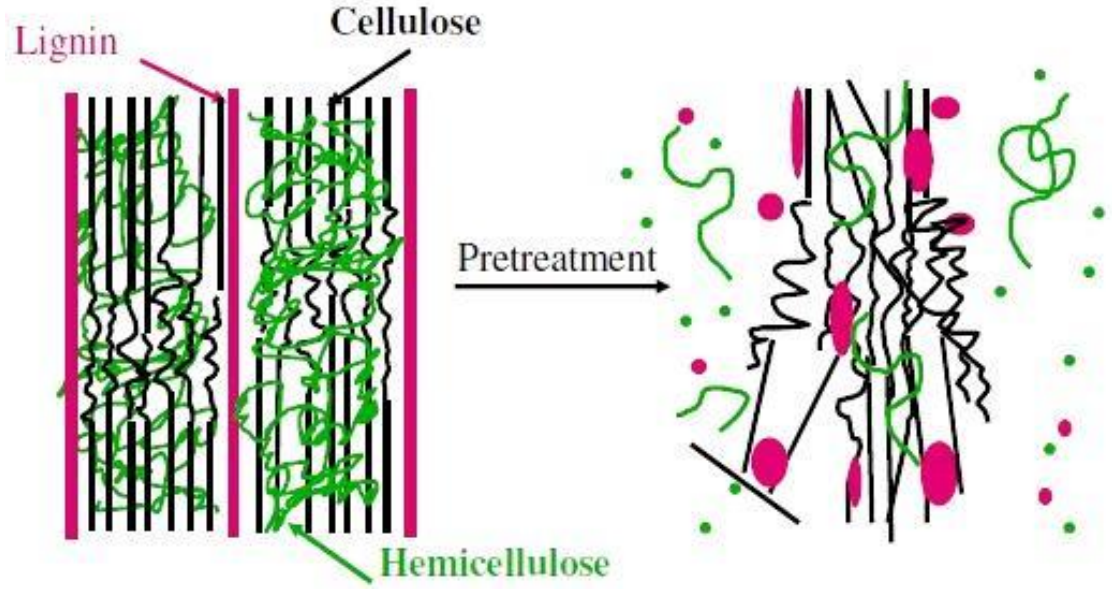
Dialysis

Centrifugation
.X g ; 10 min 5,000

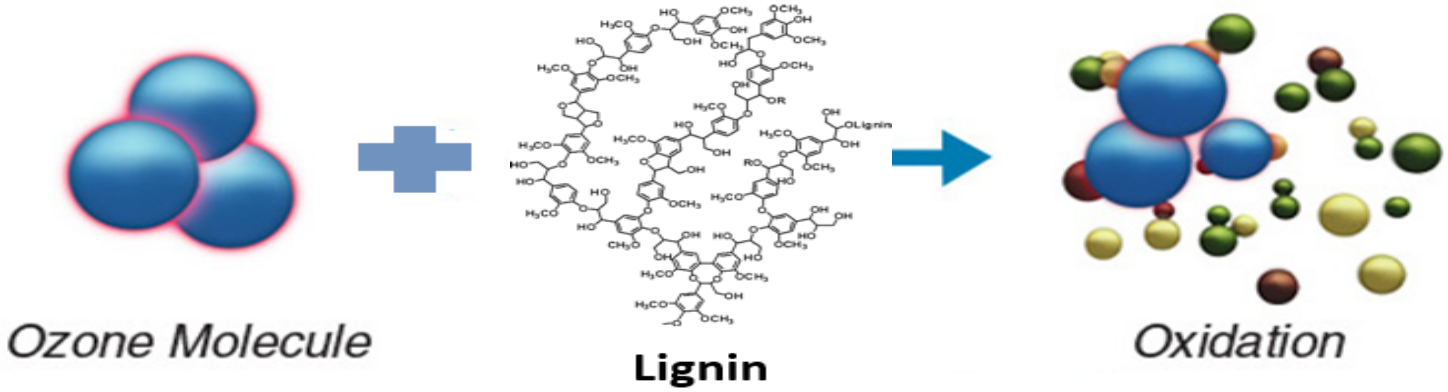


# Pre-treatment (De-lignification)



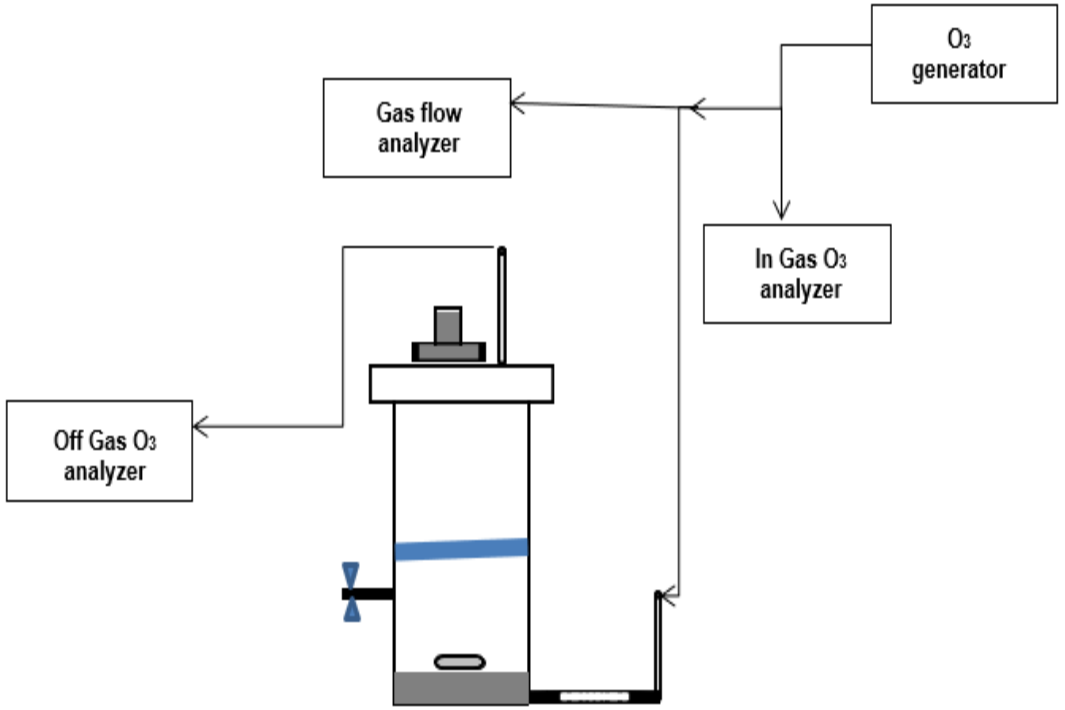

**Akhtar, 2014**



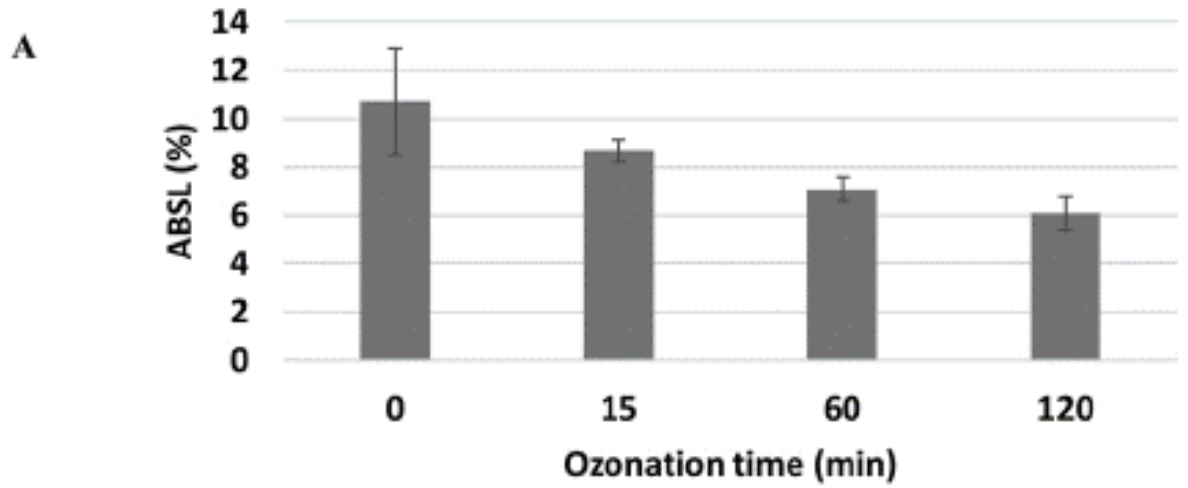

- **Very high reaction rate with phenols than sugars/cellulose chains.**

- **Short half-life (t1⁄2) in water – 20 min. (at 20 °C) – cleaning step is not necessary.**

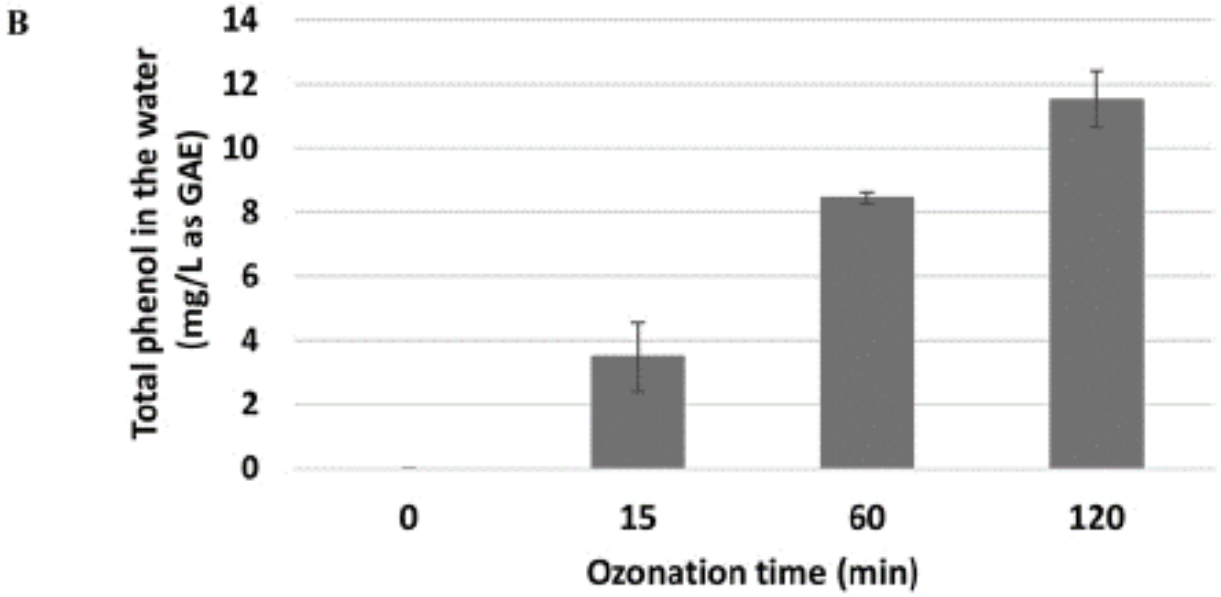
- **None to little inhibitors formation**



# Soluble lignin (RPS)




# Total phenols (process water)




Peretz et al. 2019

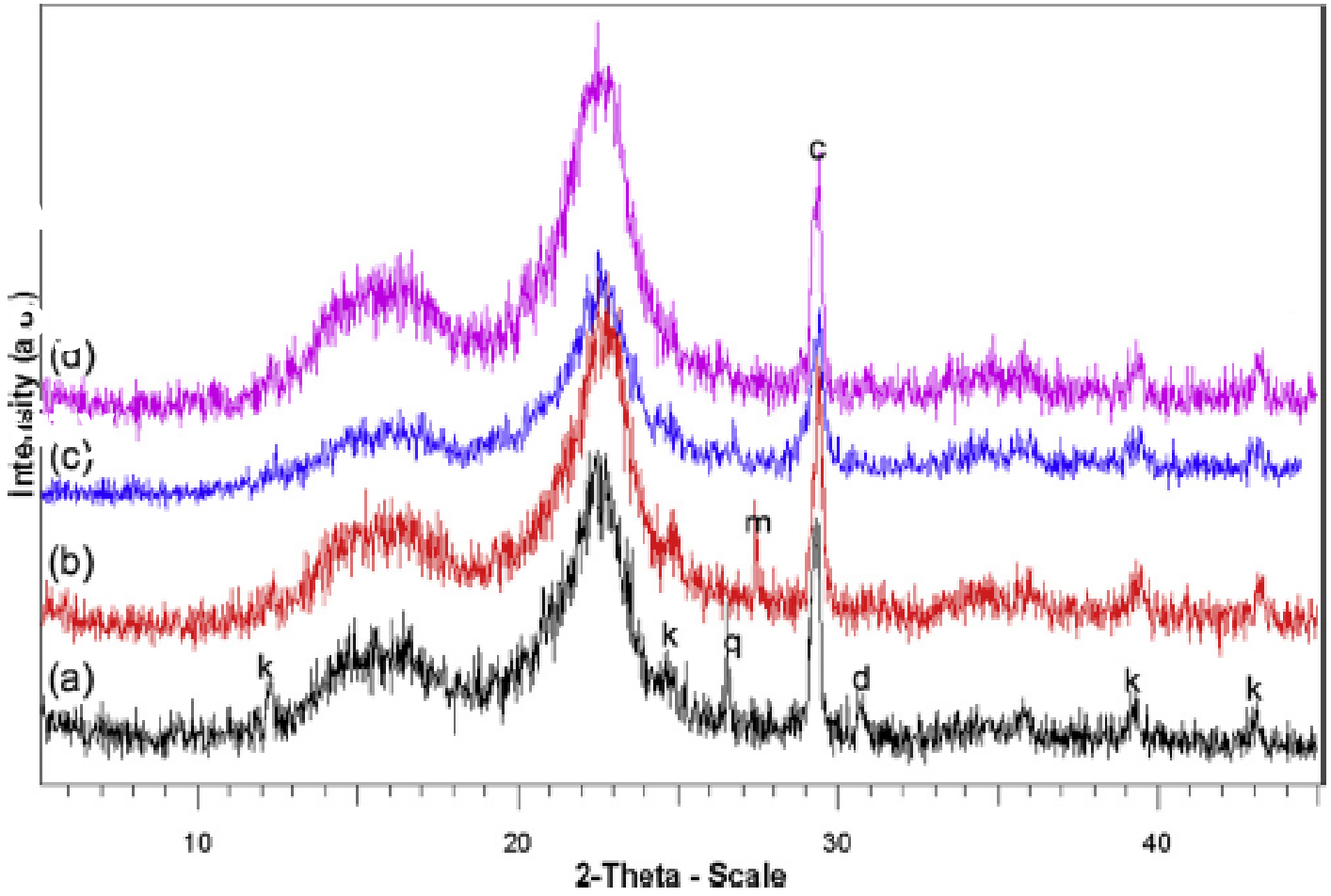
# XRD

0 min.

120 min.

60 min.

15 min.



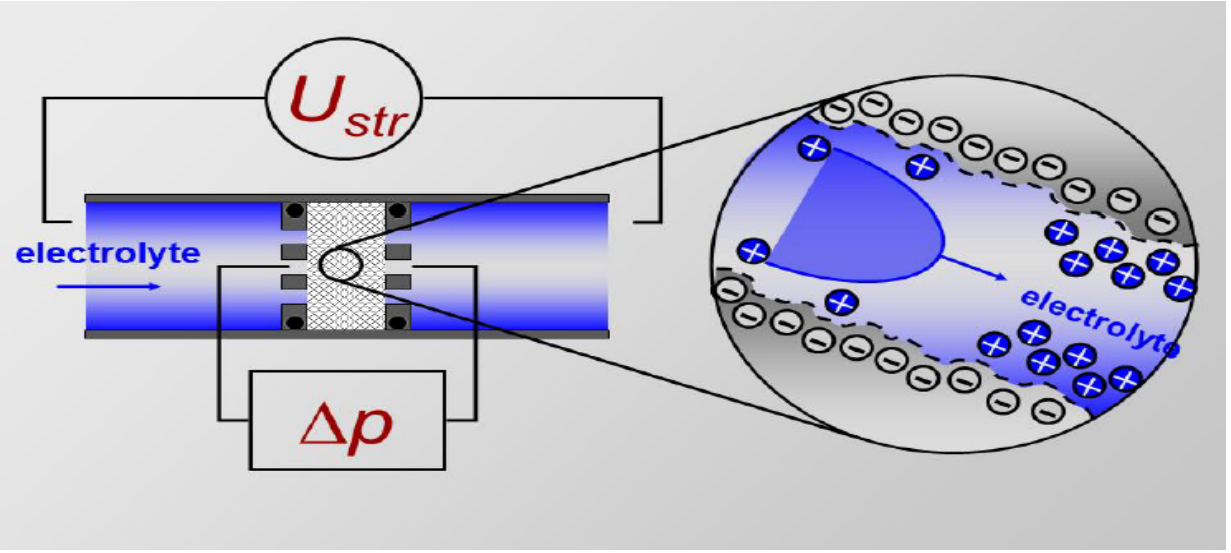

Peretz et al. 2019

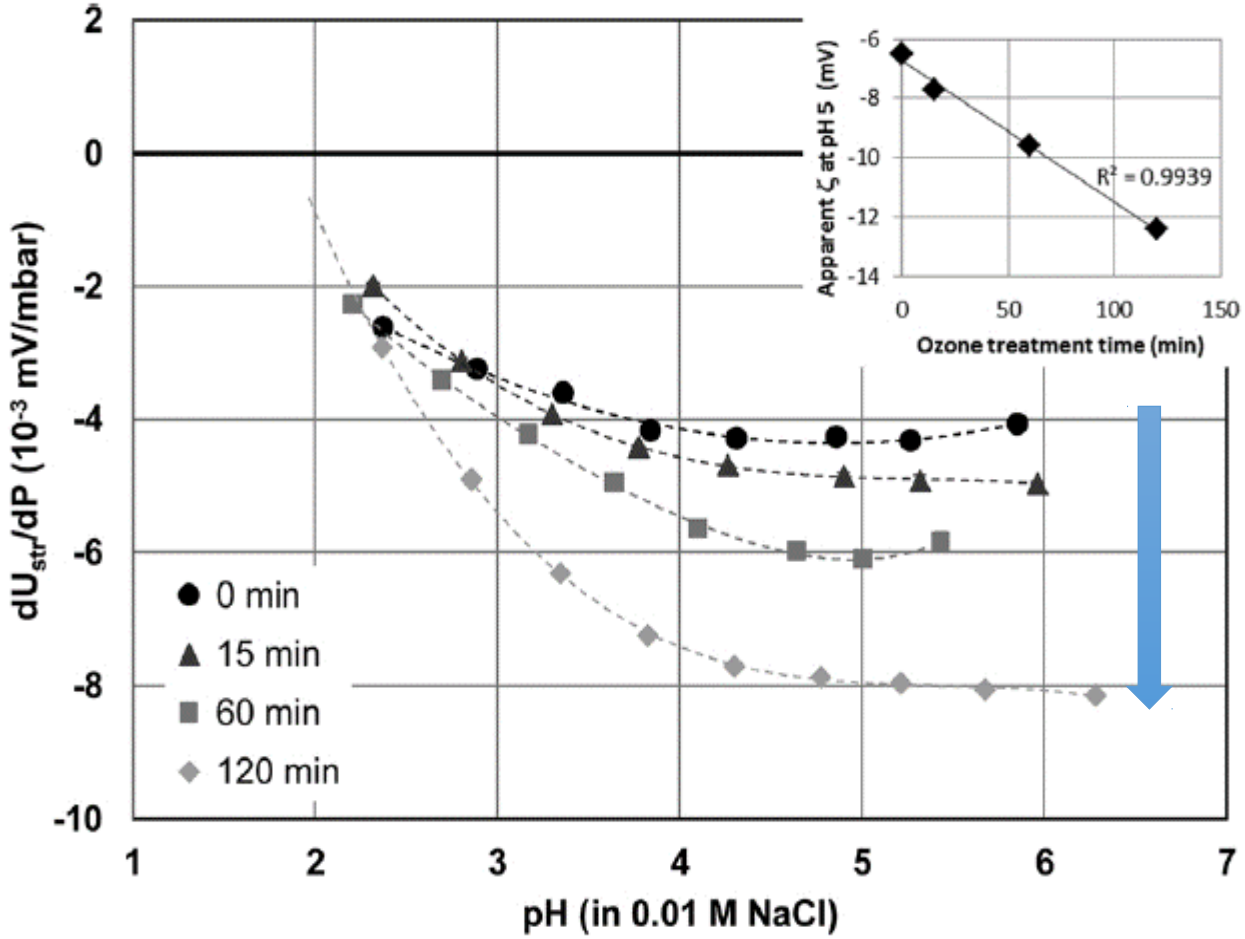
* Typical cellulose-I structure- was not affected
* Slight increase of cI index from 70% to 77%

**Lignin (and other impurities) removal!**

# Streaming

$$\zeta = \frac{dU_{str}}{dP} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times k_B$$



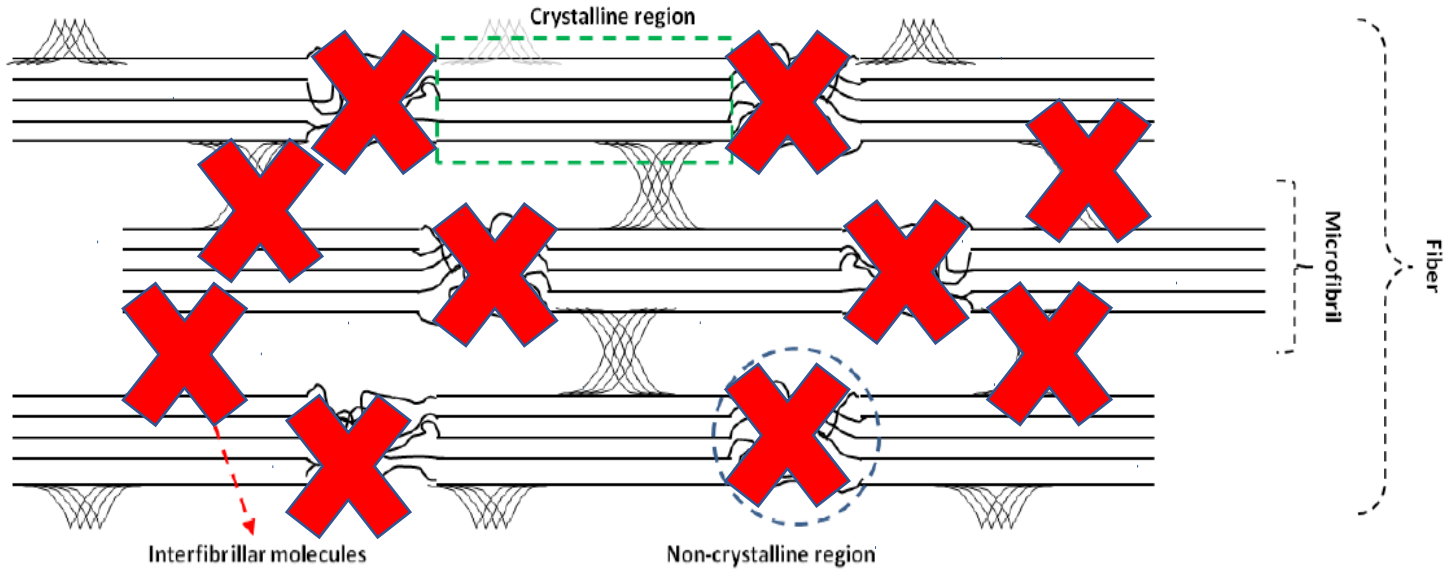




Peretz et al. 2019

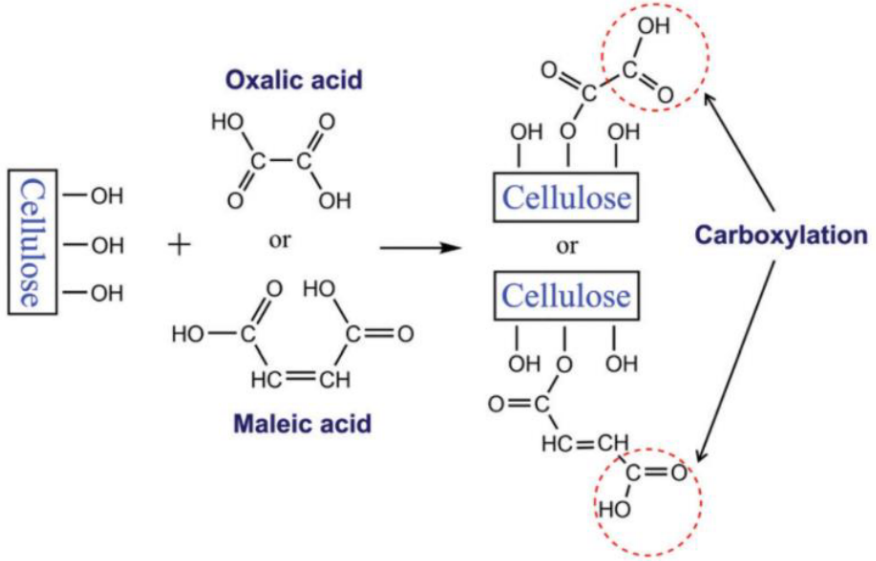
**Ozone dose** ↑ **Streaming potential** ↑

**Lignin and other impurities removal!**

# Acid hydroly

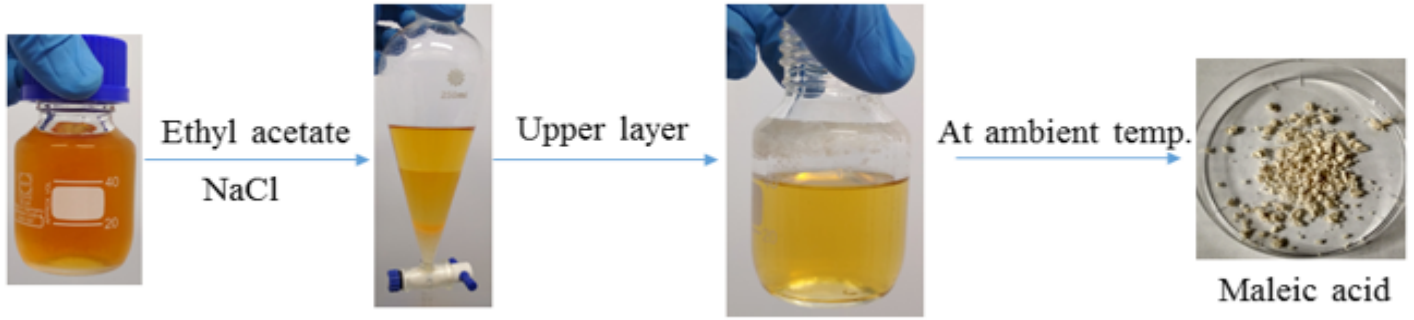


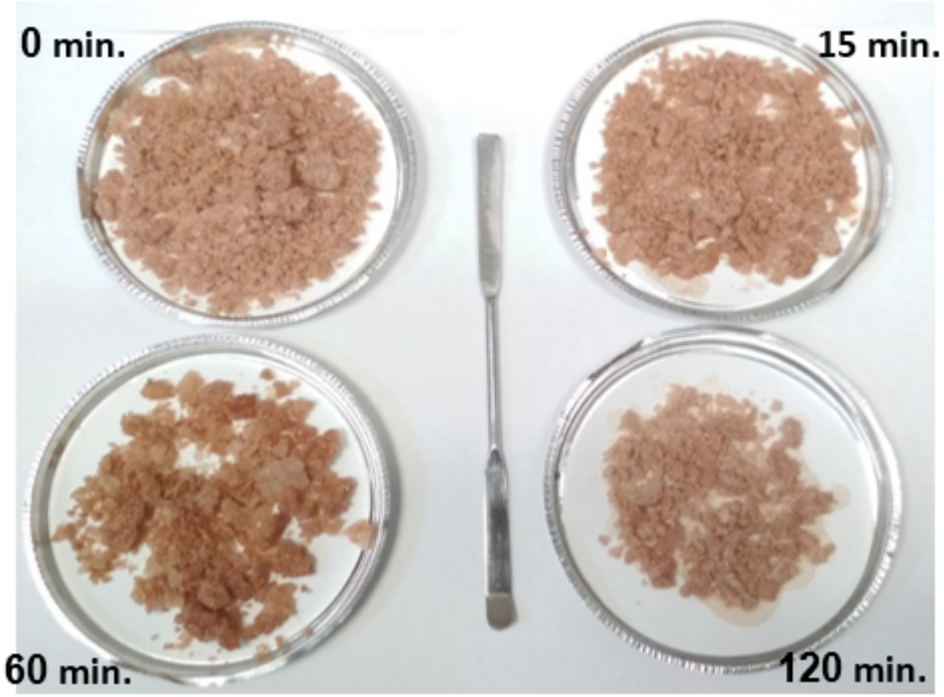

**Borjensson et al. 2019**

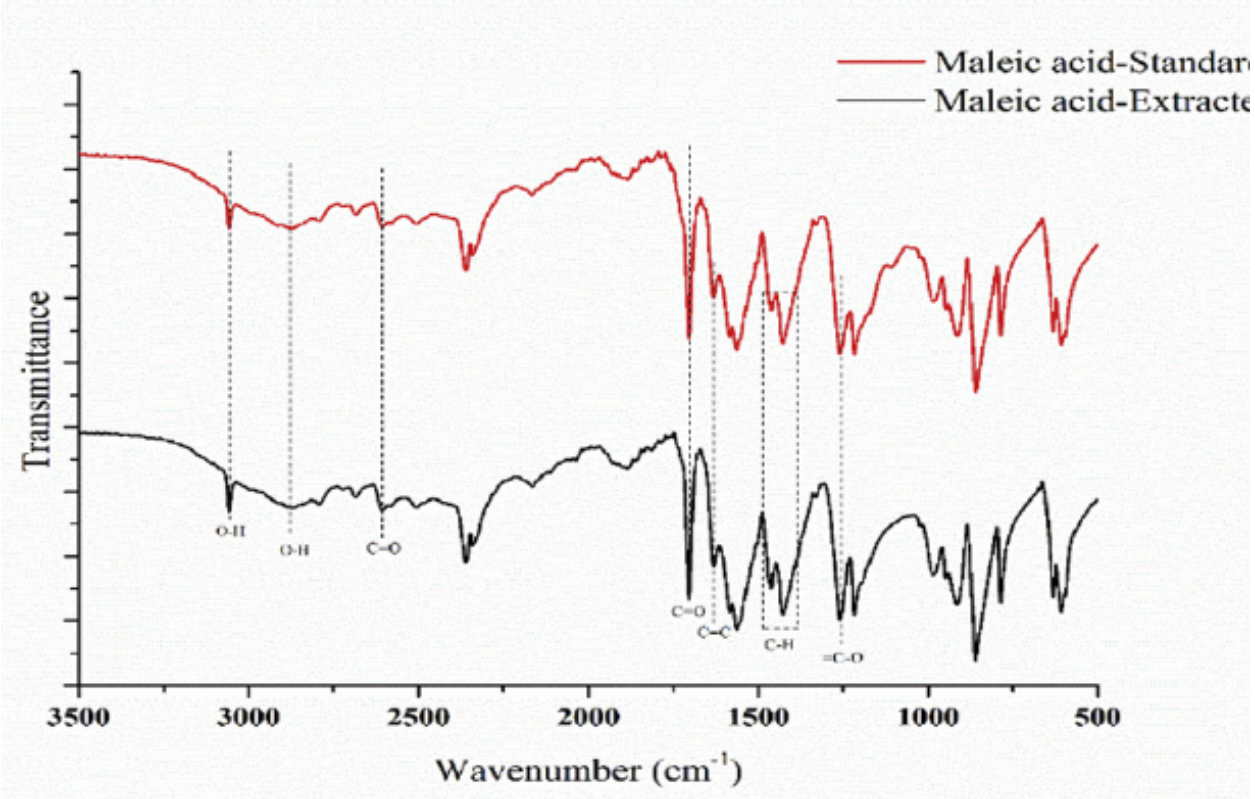


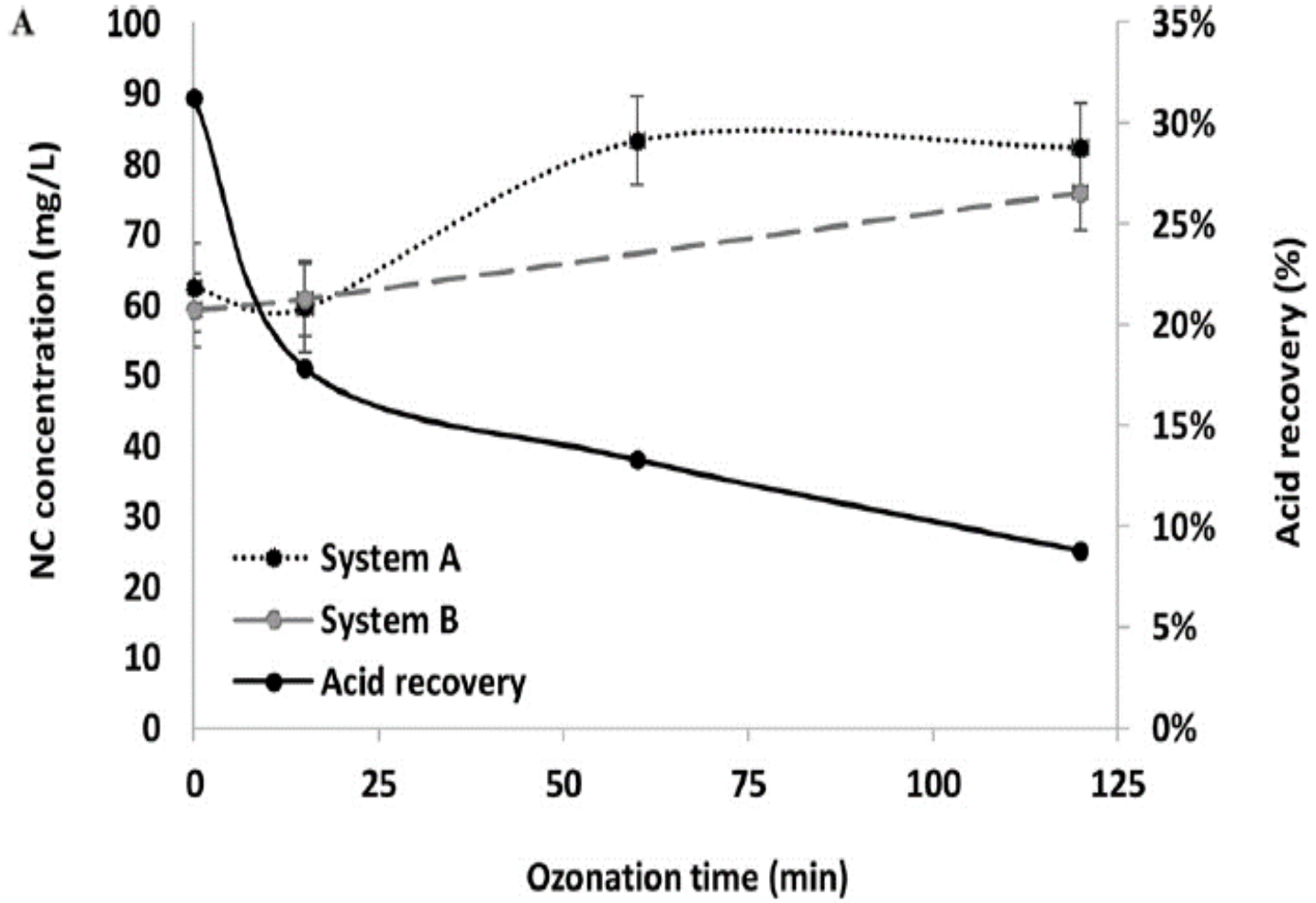

**Chen et al. 2016**

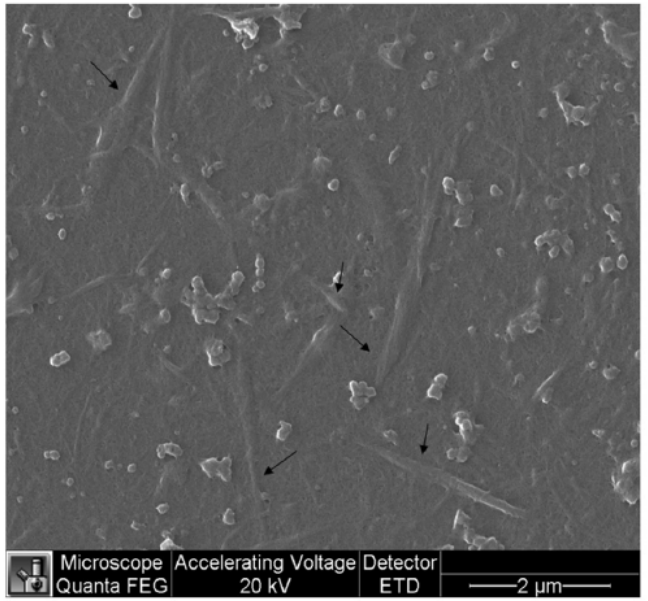
# Acid recove


Ethyl acetate
NaCl
Upper layer
At ambient temp.
Maleic acid


0 min.
15 min.
60 min.
120 min.


Maleic acid-Standar
Maleic acid-Extracte
Transmittance
O-H
O-H
C=O
C=O
C=C
C-H
=C-O
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)




**nm in length** 571 ± 2,431
**nm in width** 37 ± 165

# Conclusions

- **RPS contain high amounts of crystalline cellulose, making it a very good source for NC production.**
- **Ozonation was examined as a pretreatment stage for NC recovery from RPS.**
- **Ozonation showed to result in effective lignin removal from the RPS.**
- **NC yield remained low (~1 %wt), even after high ozone doses, suggesting process optimization is required.**
- **"Green-industry" concept- no chemical traces, and can applied at ambient conditions**

# Thank you!

:For more

Peretz et al. (2019), *Carbohydrate Polymers*, 216:343-351

https://doi.org/10.1016/j.carpol.2019.04.003