

PINEA SPOT CONGRESS

LISBON 2023

21 TO 23 NOVEMBER





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INSTITUTO
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Tailoring the valorization of by-products from the pine nuts industry

Ricardo A. Costa, Helena Patrício, Teresa Quilhó, Ana Lourenço, Jorge Gominho



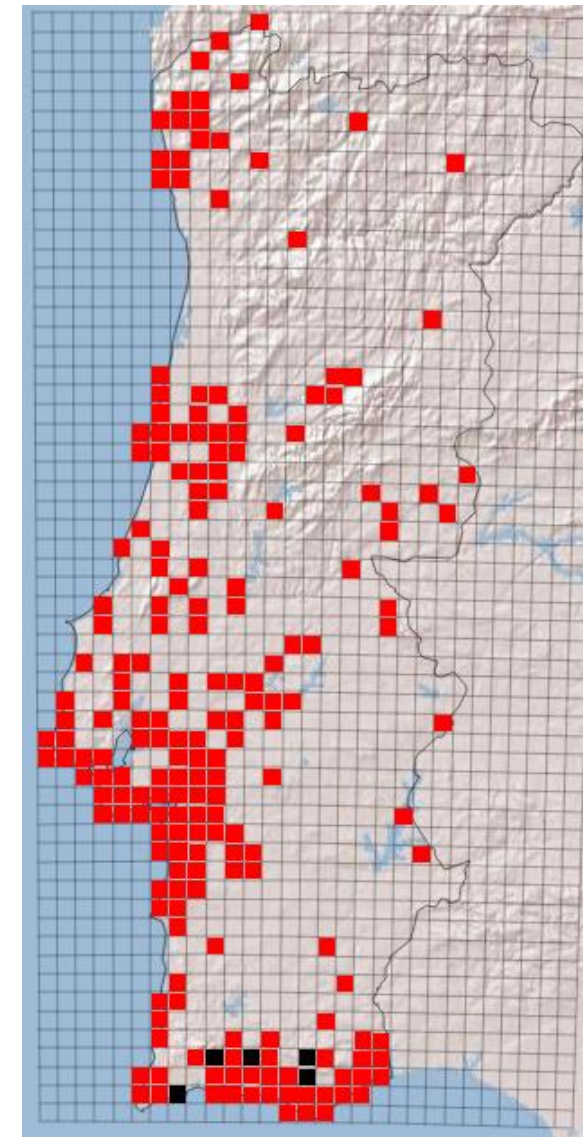
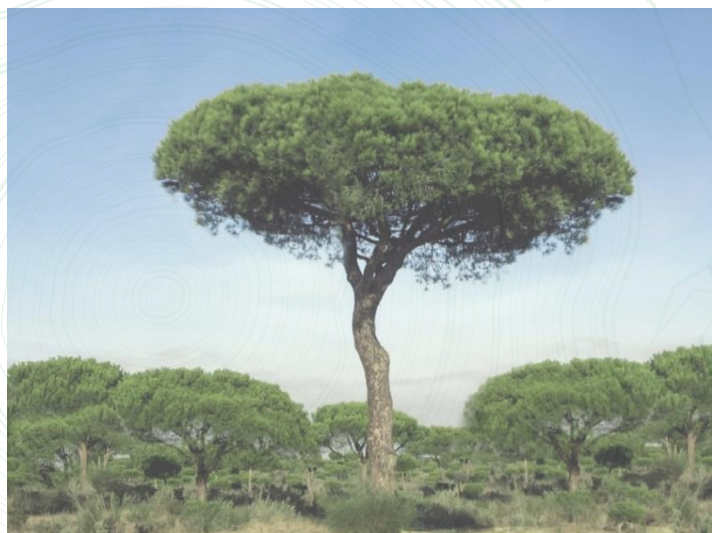
Presentation Structure

1. Introduction
2. Objectives
3. Valorization Potential
4. End Uses



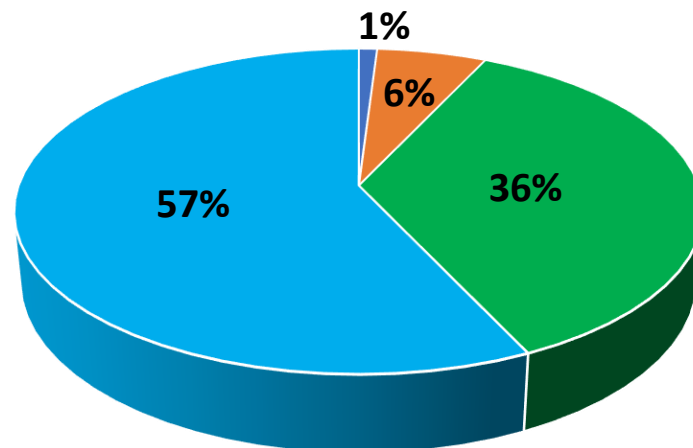
Introduction – Pine nut industry bi-products

- 193 000 ha in Portugal (6 % of Portugal forested area);
- 414 000 tons of pinecones annually produced;
- Explored for its edible seed (12000 tons were harvested in 2020/2021 (UNAC));
- Pinecone (57 % cone itself, 10 % nut shells, 3 % nuts, 30 % moisture content);
- 236 000 tons of pinecone and 41 400 tons of nut shells bi-products.



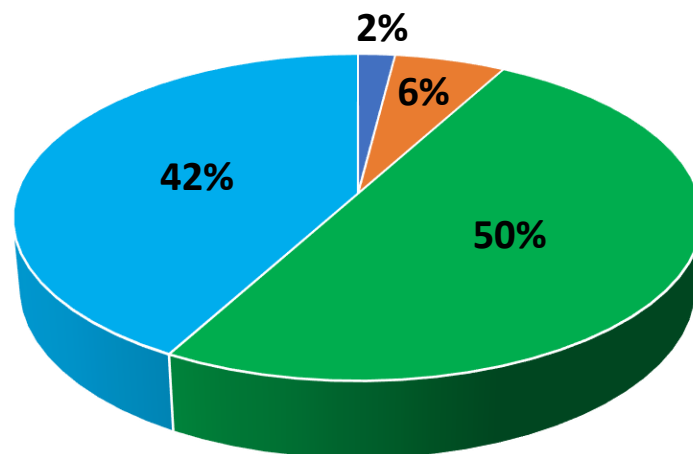
Introduction – Chemical Composition

Pinecones



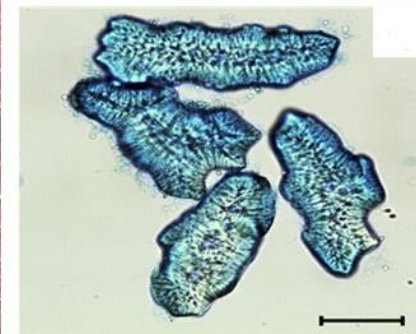
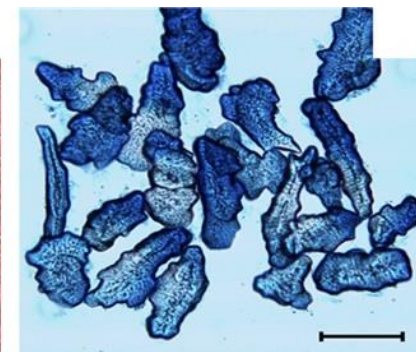
- Ashes
- Extractives
- Lignin
- Polysaccharides

Nut Shells



Introduction - Anatomical Studies

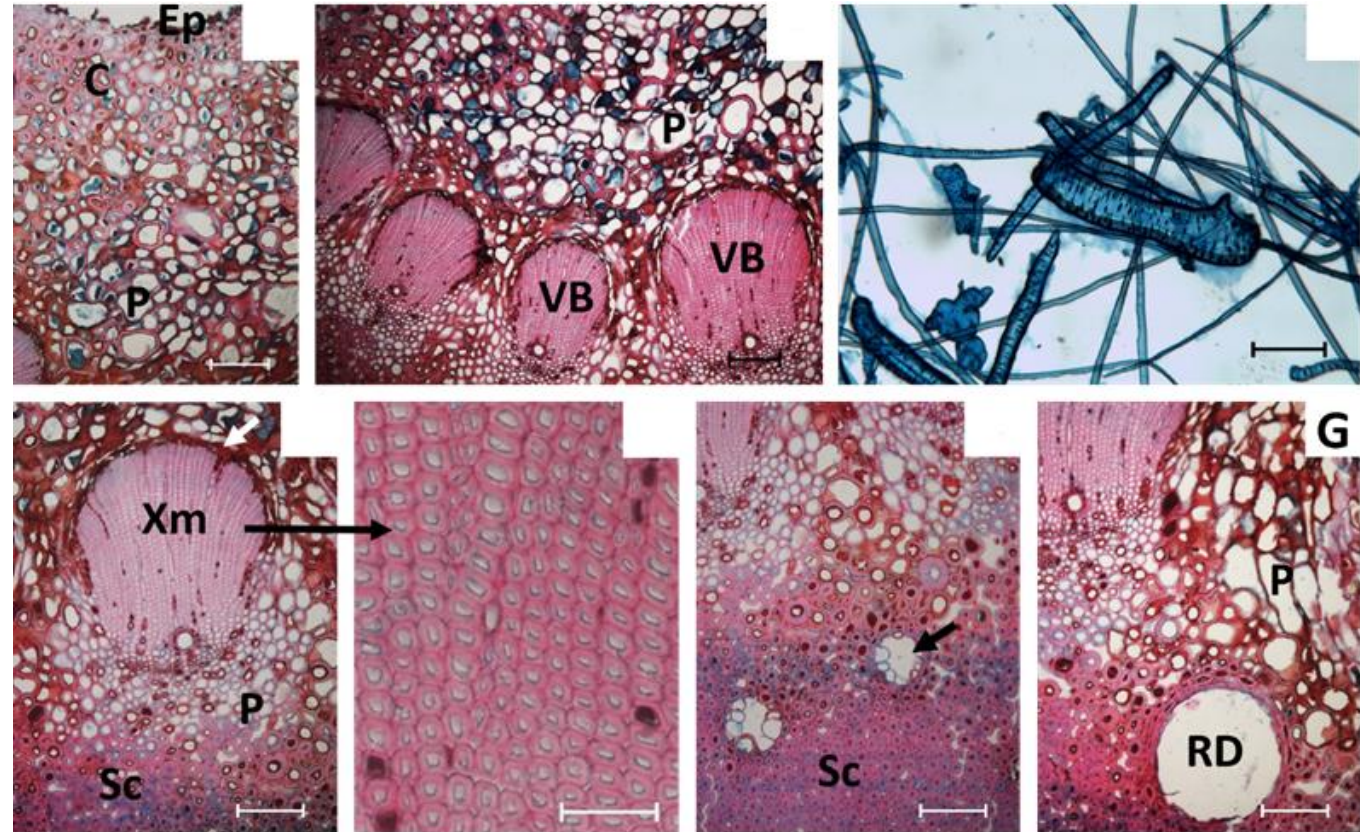
Nut Shells



Sclereids (Sc)

Introduction - Anatomical Studies

Pinecones



Epidermis (Ep), collenchyma (C), parenchyma cells (P); vascular bundles (VB), parenchyma cells (P); xylem (Xm), phloem (white arrow), parenchyma (P), sclereids (Sc); large resin duct (RD) and parenchyma cells between vascular bundles (P).

Scale bar: 200 μ m

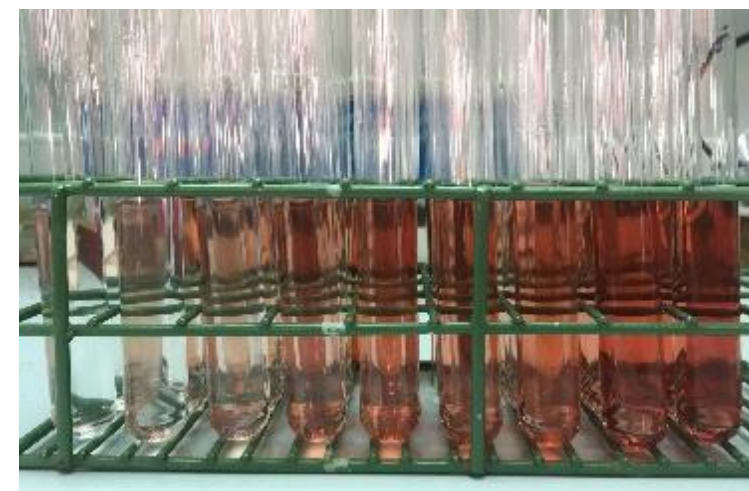
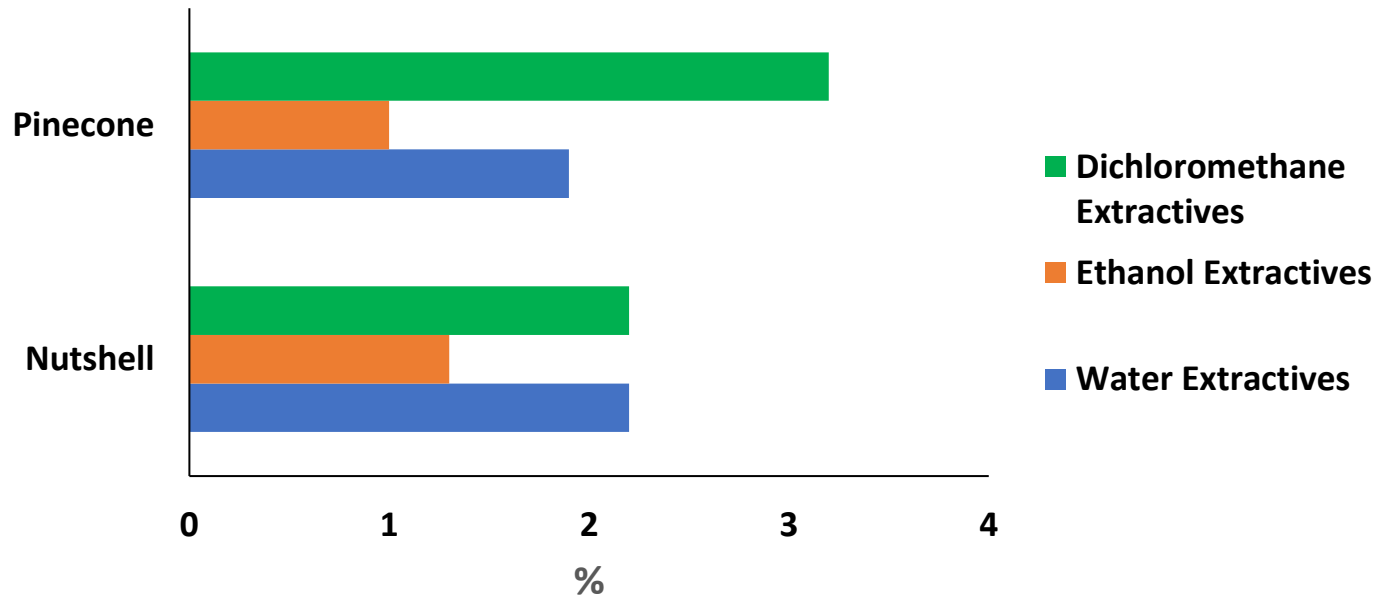
Objectives

- Find an alternative valorization route for *Pinus pinea* industrial bi-products.
- Is it possible to produce lignin nanoparticles with good characteristics and be applied in the industry?

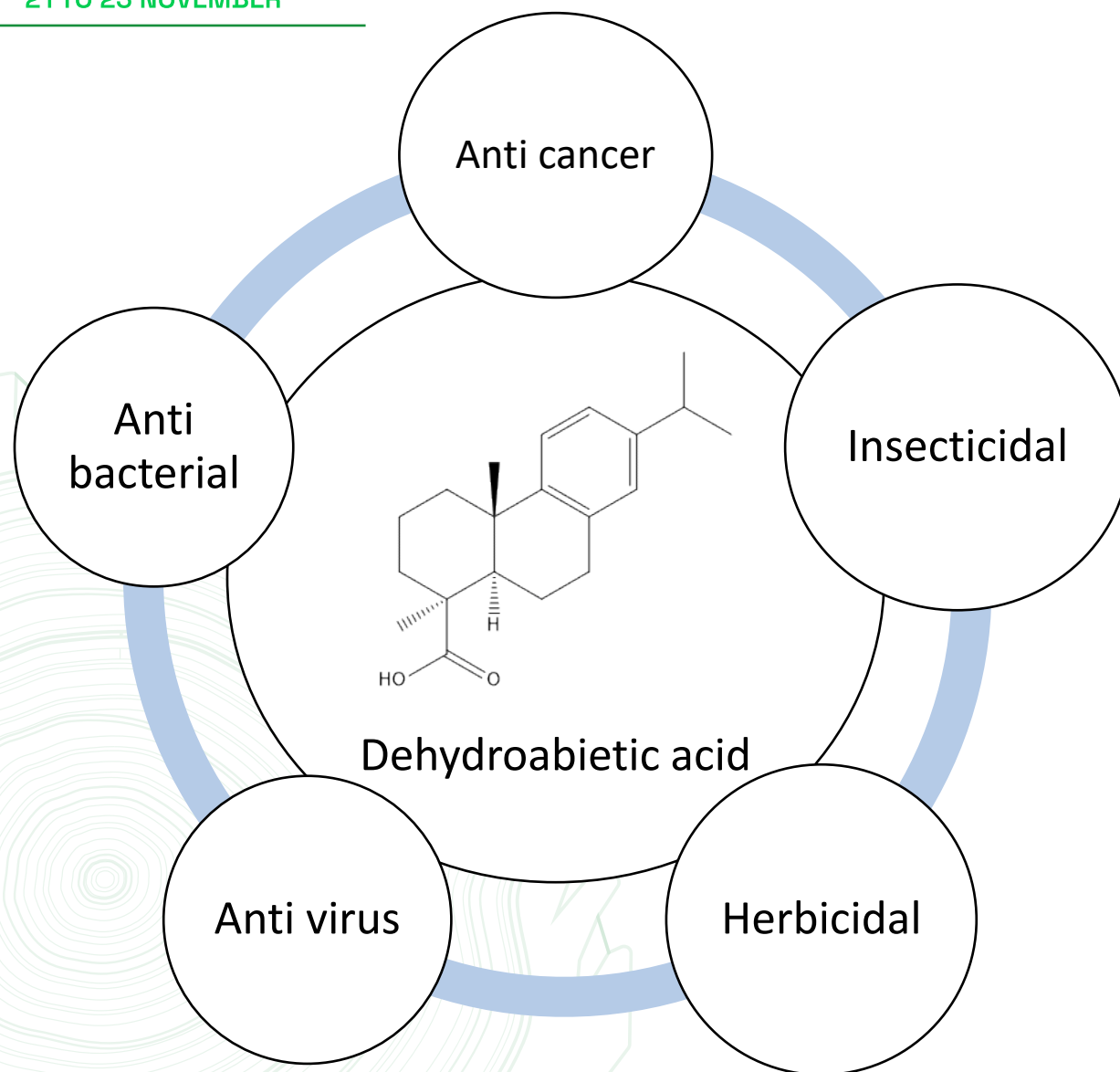


- **Why Lignin??**
- Pinecone – 36 %
- Nutshells – 50 %

Valorization Potential - Extractives



Valorization Potential - Extractives



- **Pinecone**

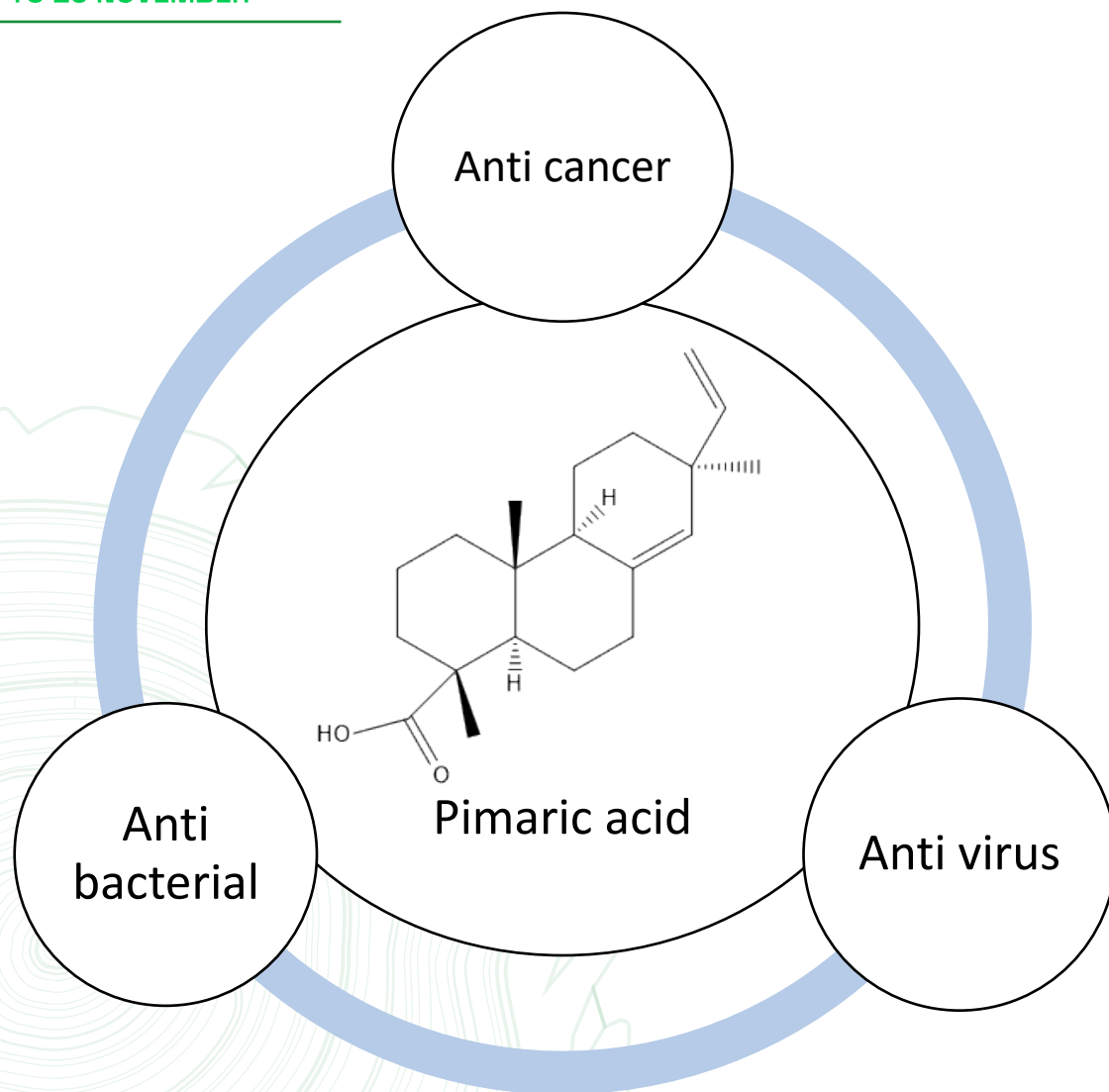
- 9 % DCM extractives
- 2000 mg/Kg cones

- **Nutshells**

- 3.5 % DCM extractives
- 1100 mg/Kg shells

- Standard (1 mg) – 296 € (Merck)

Valorization Potential - Extractives



- **Pinecone**

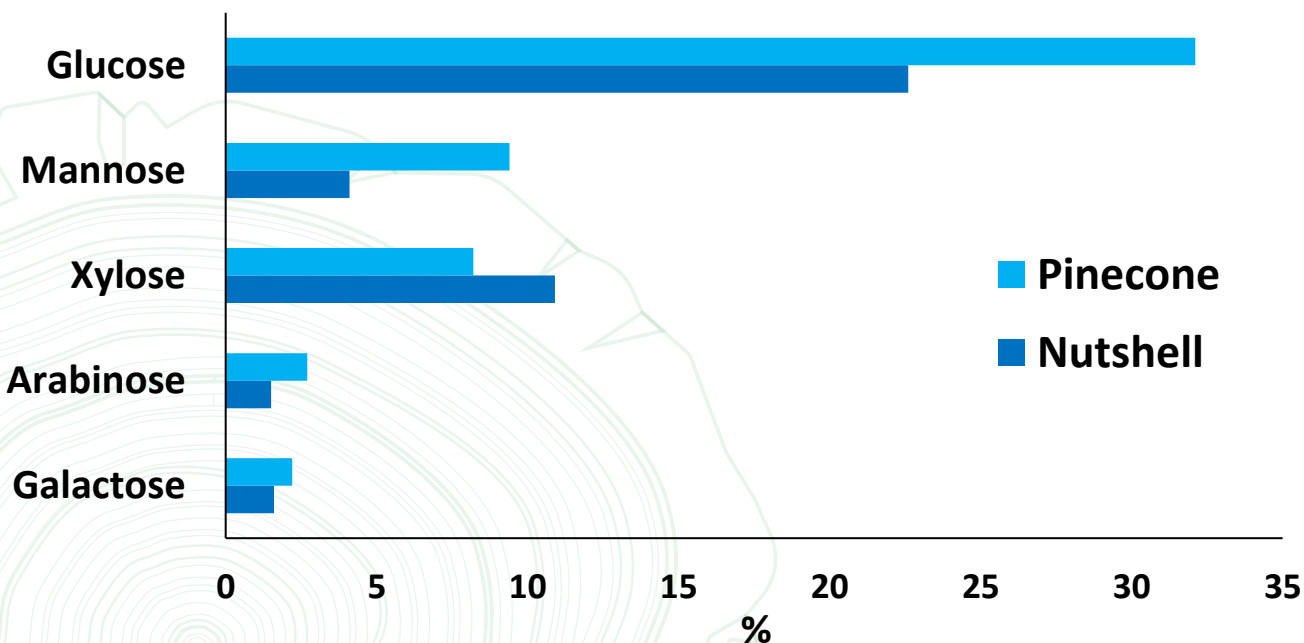
- 9.6 % DCM extractives
- 2100 mg/Kg cones

- **Nutshells**

- 2.6 % DCM extractives
- 830 mg/Kg shells
- Standard (1 mg) – 195 € (Alomone Labs)

Valorization Potential - Polysaccharides

Monosaccharides Composition

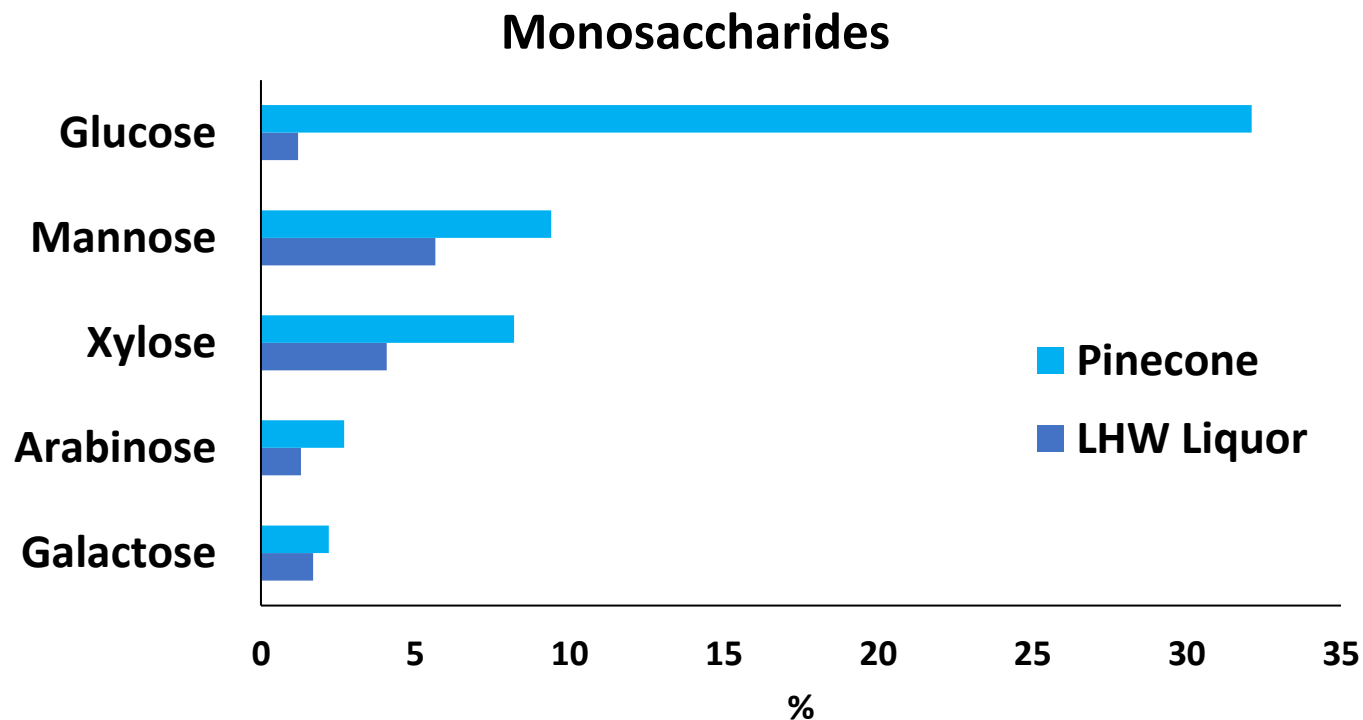


- Hemicelluloses extraction to enhance lignin removal and increase purity (autohydrolysis, steam explosion)
- Bio-ethanol production by fermentation processes

Valorization Potential - Polysaccharides

Liquid Hot Water Pre-treatment:

- 160° C
- 90 min
- Liquid to Solid ratio - 10



Bio-ethanol production – 71 g/Kg of pinecones

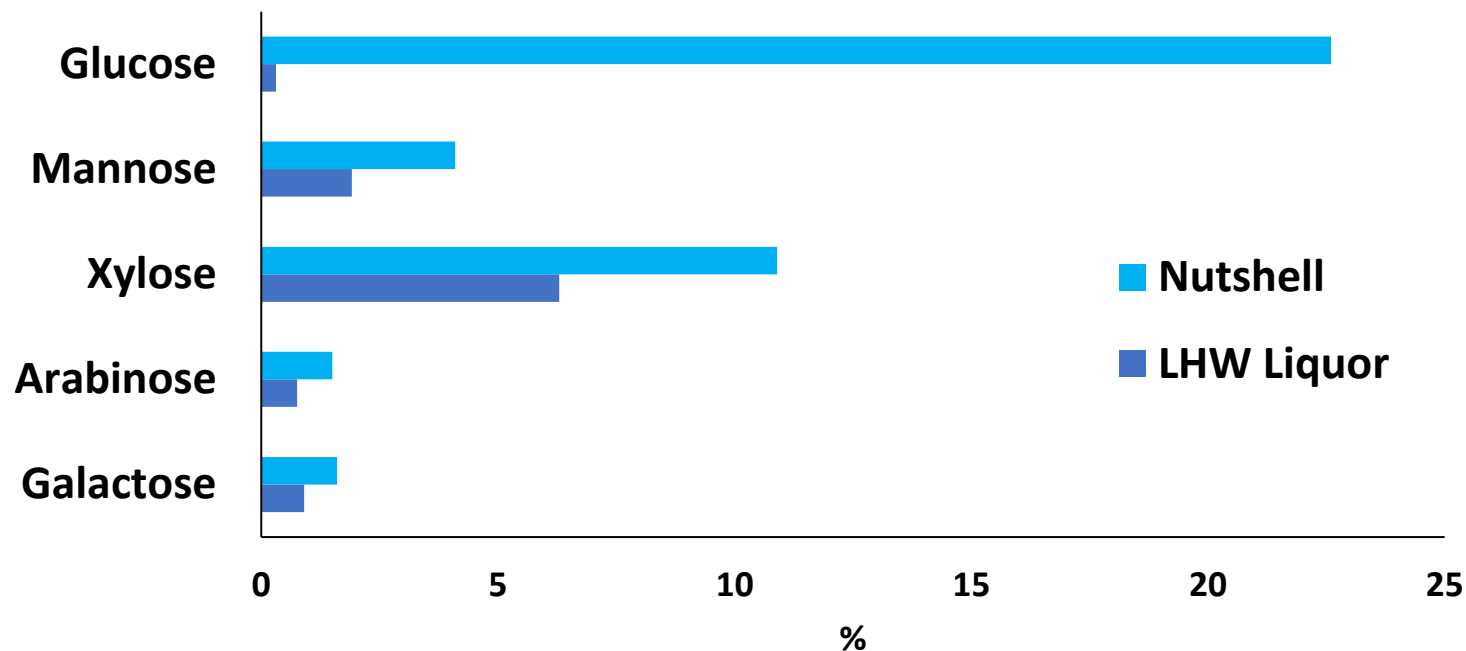
Valorization Potential - Polysaccharides

Liquid Hot Water Pre-treatment:

- 160° C
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- Liquid to Solid ratio - 10



Monosaccharides

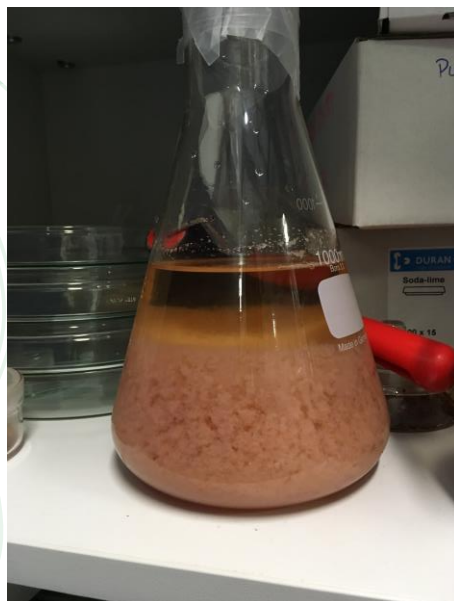


Bio-ethanol production – 52 g/Kg of nutsheels

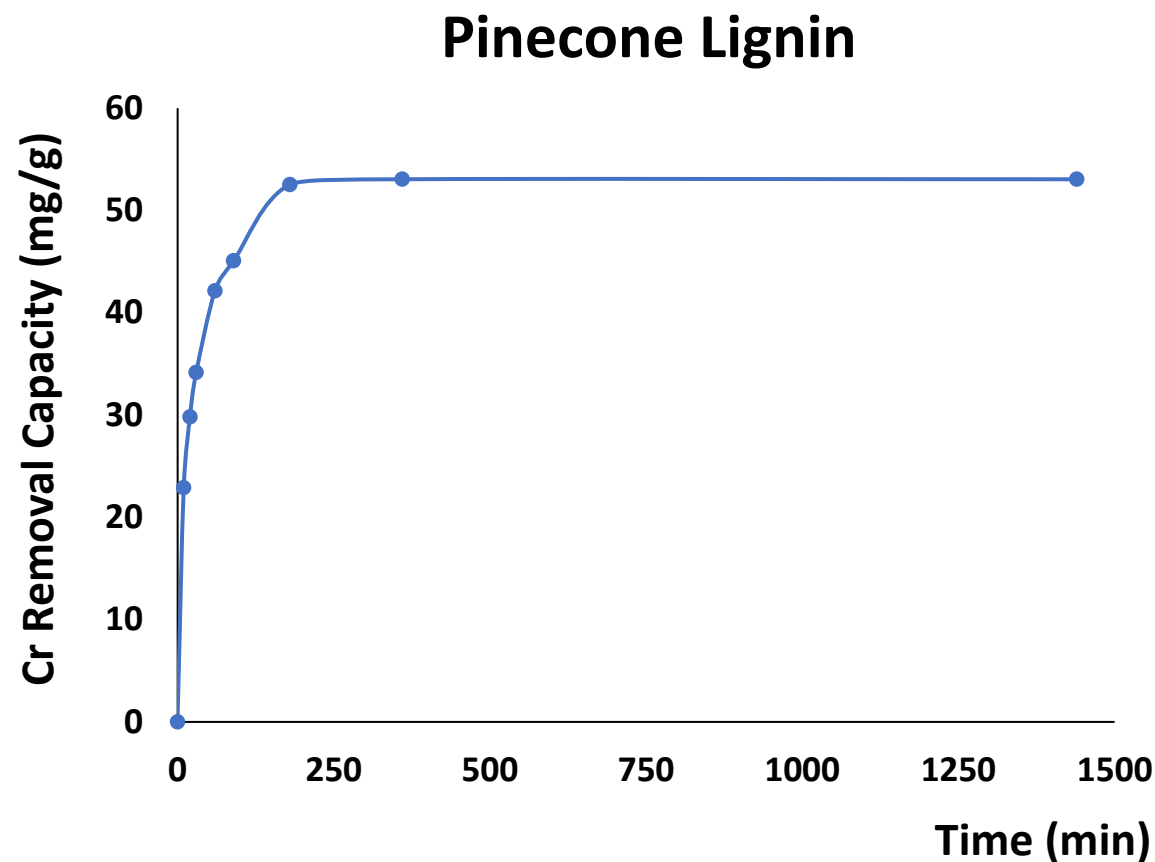
Valorization Potential – Lignin Extraction

Organosolv Extraction

- 180° C
- 120 min
- Ethanol:Water – 80:20
- 1.5% HCl
- Liquid to Solid ratio - 10



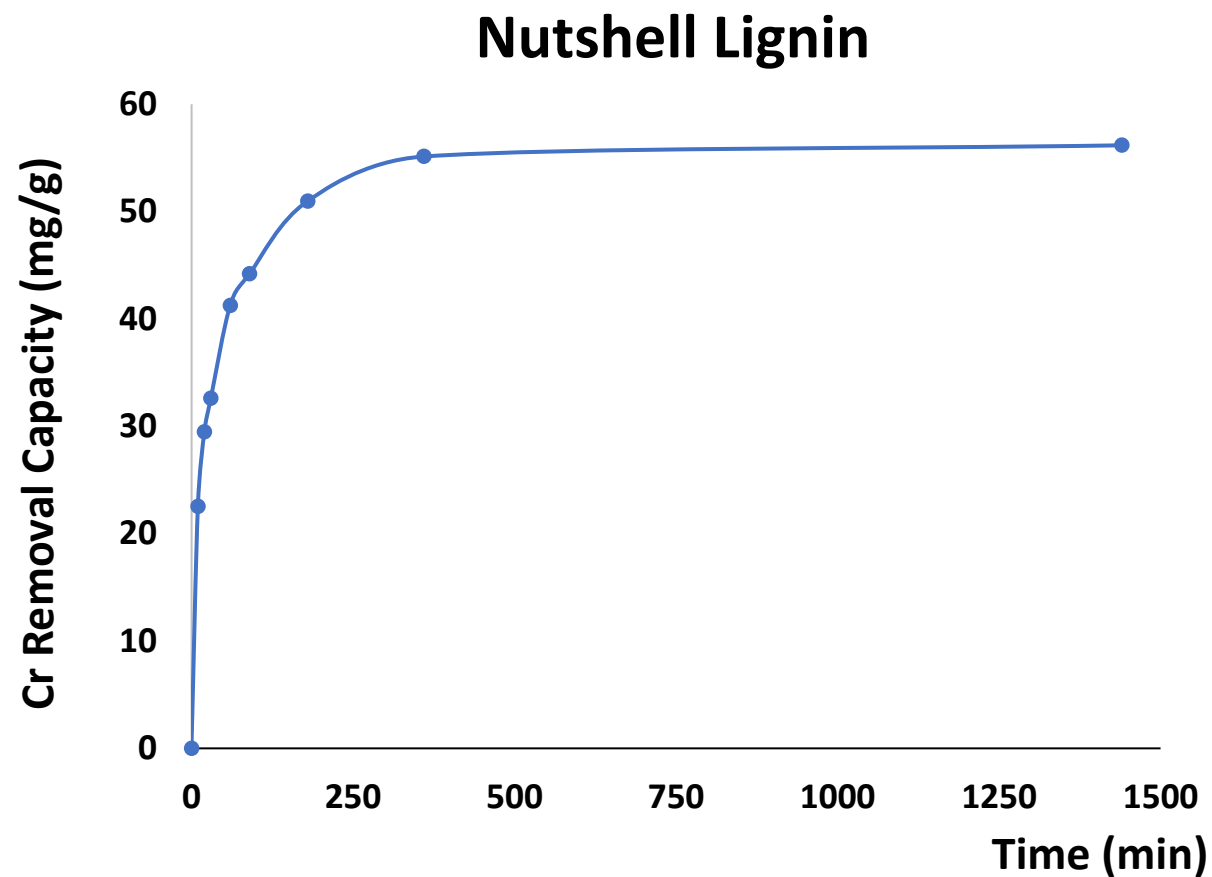
End Uses – Chromium VI Adsorption



Maximum chromium adsorbed:

- Pinecone Lignin – 175 g/Kg

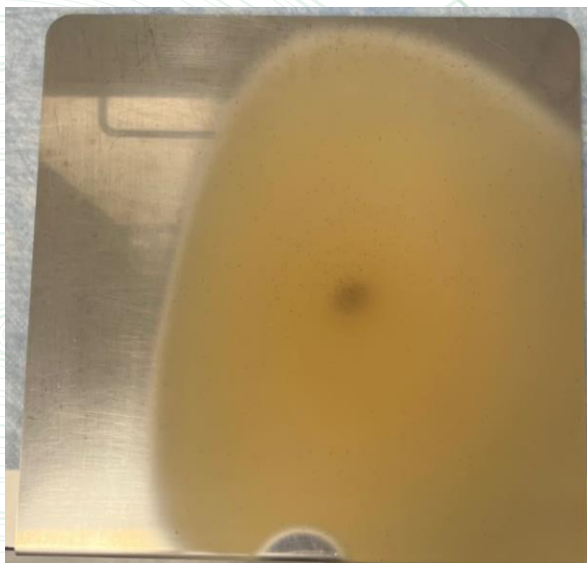
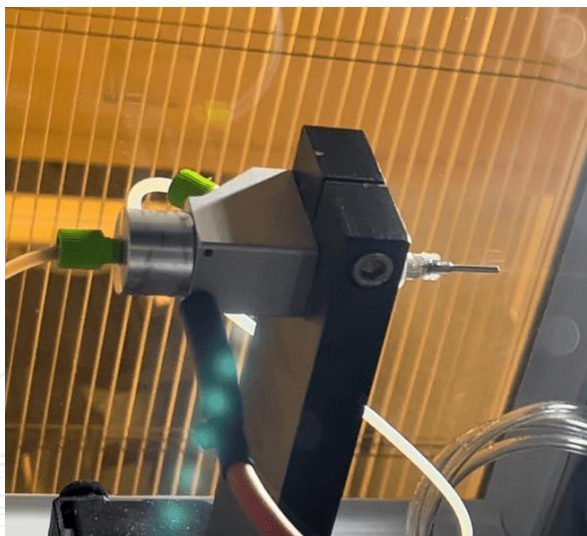
End Uses – Chromium VI Adsorption



Maximum chromium adsorbed:

- **Nutshell Lignin – 365 g/Kg**

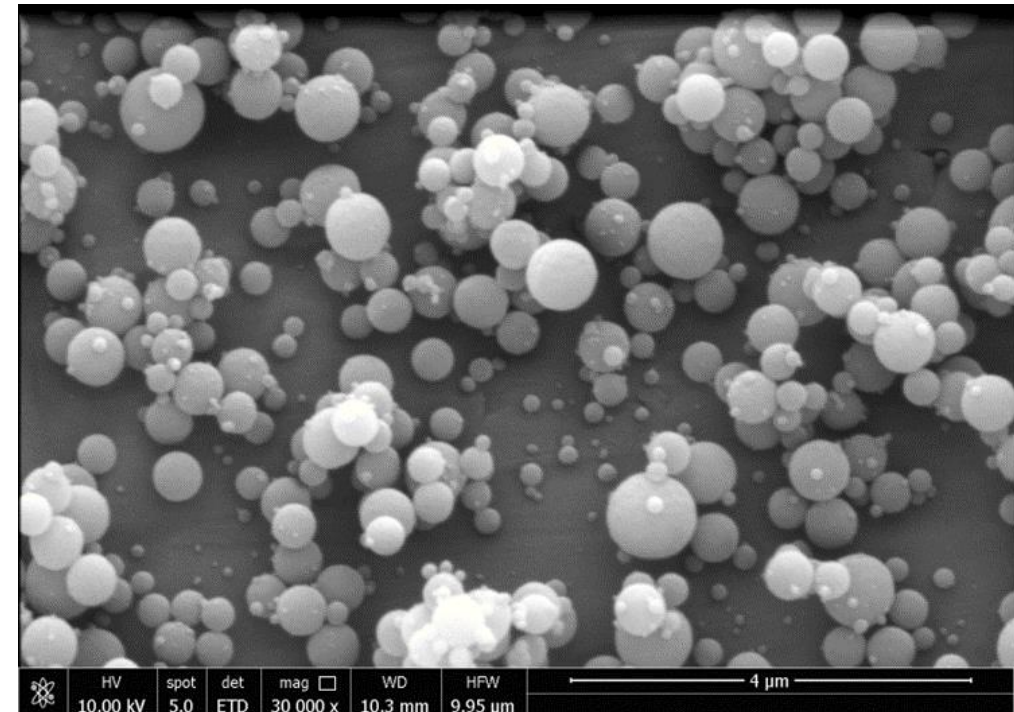
End Uses – Lignin Nanoparticles



- **Higher surface area**
- **Stable in aqueous dispersions**
- **Can be produced in different shapes (spherical/squared, solid/hollow)**
- **Antioxidant and antibacterial properties**
- **UV absorbent**
- **Drug delivery system**

End Uses – Lignin Nanoparticles

- Incorporated in sunscreens formulation to increase UV absorbance
- Incorporation in food packaging to decrease water permeability and increase expiration date
- Incorporation in wood coatings to increase resistance to abiotic factors
- As adhesives to replace phenol formaldehyde resins



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Thank you all!

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