Cationization and conversion into nanoparticles of lignin from olive tree pruning using eutectic solvents

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1. Introduction

Lignin is the most abundant natural biopolymer (Yadav et al., 2022). Lignin aromatic nature and specific structural features (eg the presence of non-polar and polar moieties) enable it to self-assemble into lignin nanoparticles (LNPs), characterized by hydrophobic cores and hydrophilic outer layers (Almeida et al., 2024).

Antisolvent precipitation is the most common method of self-assembly used to produce LNPs, by dissolving lignin in polar protic solvents (such as ethanol, ethylene glycol, etc.) or aprotic solvents (such as γ-valerolactone, tetrahydrofuran, etc.), followed by the addition of an antisolvent, usually water (Ma et al., 2023). Due to their unique morphology, biodegradability, and structural features, LNPs have high potential for application in the fields of tissue engineering, drug delivery, food packaging, nutraceuticals, among others (Yadav et al., 2022).

However, apart from lignin macromolecular properties LNPs features such as size, surface charge, and morphology are decisive for their performance in such applications. LNPs tend to have a negative zeta potential due to the surface orientation of hydroxyl and carboxyl groups (Matsakas et al., 2020). To broaden their field of application, it is necessary to develop LNPs with a positive surface charge. In this context, the cationization of lignin using eutectic solvents (ES) emerges as a sustainable and integrated alternative in line with green chemistry principles, as these systems have proven are inherently sustainable and have demonstrated to be effective for lignocellulosic biomass delignification processes (Gómez-Cruz et al., 2024).

Olive groves dominate the eastern part of Andalusia (Spain), with olive tree pruning (OTP) being their main waste product. Current management of this by-product is mainly based on burning in the field or shredding and direct application to the soil; however, these practices can have significant environmental impacts. OTP is a lignocellulosic waste with a high lignin content, close to 20 %, whose fractionation and comprehensive recovery are key to the development of lignocellulosic biorefineries aligned with circular economy principles.

The objective of this research was to develop an integrated, sustainable, and environmentally friendly process for the delignification of OTP and the subsequent cationization of LNPs using eutectic solvents (ES).

2. Materials and methods

OTP underwent a delignification process using a ternary mixture of eutectic solvents (ES) composed of choline chloride (ChCl), *p*-toluenesulfonic acid (*p*TSA), and ethylene glycol (EG) in a molar ratio of 1:1:9. The treatment was carried out at 80 °C for 4 h, with a dry solids load of 10 % (w/w).

Cationized LNPs were obtained using two strategies:

(i) solvent exchange method using directly the liquid fraction resulting from the OTP delignification process;
(ii) isolation of the lignin present in this liquid fraction, followed by its redissolution in ethanol and γ-valerolactone, and subsequent nanoprecipitation by solvent exchange assisted by dialysis at pH values of 6.5, 2, and 1.

The physicochemical properties (particle size, polydispersity, and zeta potential) of the LNPs were determined by dynamic light scattering (DLS) and scanning electron microscopy (SEM) (Figure 1).

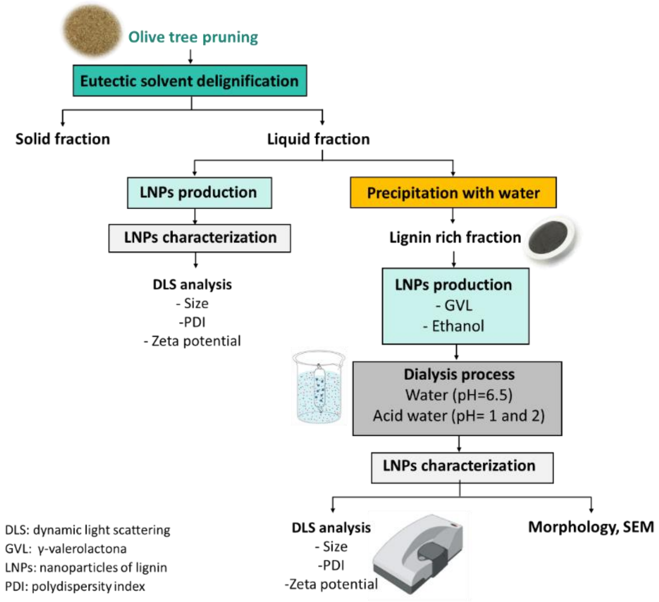

Figure 1. Scheme of the work carried out in this study.

3. Results and discussion

The high z-average value (8271 nm) of LNPs obtained when directly using the liquid fraction from the delignification stage for lignin self-assembly evidenced the formation of large aggregates, confirming the unfeasibility of forming LNPs from this fraction. However, GVL and ethanol allowed the assembly of homogeneous and uniform nanoparticles with a hydrodynamic diameter of 118 and 200 nm, respectively.

In terms of zeta potential, both solvents showed positively charged LNPs with values around +30 mV. Subsequently, the LNPs obtained by nanoprecipitation with GVL and washed by dialysis showed that at pH 2 they clearly produce homogeneous and uniform spheres, which corroborates the PDI value determined by DLS (0.099). In addition, half of the NPs produced at this pH show an average hydrodynamic size of 80-120 nm.

This work has developed a simple, novel, and environmentally friendly method for obtaining cationized lignin with a high capacity to form homogeneous, spherical LNPs with a positive surface charge. This process represents a substantial improvement in the valorization of lignocellulosic biomass due to the great potential of cationized NPs in various industrial fields.

4. References

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