Hybrid Synthesis Route for Stable and Swellable Lignin Nanoparticles

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Highlights

- A hybrid route for nanoparticles synthesis combining antisolvent and ultrasonication strategies.
- Lignin nanoparticles production with high stability in solvents and reversible swelling features.
- Lignin is a biowaste converted into a high-value chemical compound.

1. Introduction

Lignin, the main by-product of the pulp and paper industry, is now emerging as a low-cost and renewable raw material for the development of new products and processes. In fact, its biocompatibility, intrinsic multifunctional features and safety make it a sustainable promising source for obtaining novel and value-added materials. However, its complex chemical structure and heterogeneous self-assembly behaviour pose several challenges. Nanostructured systems using lignin could address these issues, finding applications in food science, cosmetics, and healthcare. The current study focused on the development of a novel hybrid synthesis method for lignin nanoparticles that combines top-down and bottom-up strategies. A significant improvement in the performance of lignin nanoparticles is achieved. Not only the obtained nanoparticles (LNP) feature improved the stability in various organic solvents, but they also exhibited reversible swelling features, thereby expanding their potential applications in various fields. Therefore, the present research lay the foundations for an efficient and low-cost technological route for lignin valorization.

2. Methods

First, 600 mg of Kraft Lignin (KL) have been dissolved for three hours and at room temperature in a 10 ml mixture of acetone/water (7:3 (v/v)) to obtain a stock solution S600, as described elsewhere [1].
LNP have been synthetized using a hybrid procedure that combined antisolvent (AS) and ultrasonication (US) strategies. Specifically, 1 ml of S600 was added dropwise into 9.2 ml of distilled water, and the resulting mixture has been sonicated in a probe tip sonicator, operating at a 20 kHz frequency and 40% amplitude for 10 minutes to obtain LNP nanoparticles (IB600).
LNP stability was investigated in various organic solvents, as reported elsewhere [2]. The hydrodynamic diameter (D_h) of the LNP was measured using a Dynamic Light Scattering (DLS) Instrument to detect any changes in size when exposed to various solvents (ethanol, acetone, acetonitrile, 1M NaOH aqueous medium) at room temperature and different contact times. The Atomic Force Microscopy (AFM) was used to conduct morphological analysis of LNP in various organic solvents.

3. Results and discussion

The colloidal stability was analyzed by putting in contact a specific amount of LNP with the chosen organic solvent (acetone is reported as the most significant example) for 30 minutes, 60 minutes, 5 hours, 15 hours, and 24 hours, at room temperature. DLS results are reported in **Figure 1.** IB600 displayed an initial D_h of about 117 nm which increased to 280 nm after 30 minutes, and then stabilized at around 320 nm after 24 hours (red curve). On the other hand, AS600 showed an initial D_h value of about 86 nm which increased to 330 nm within the first 30 minutes and to about 820 nm after 24 hours, but without reaching a constant value (black curve). AS600 sample evidenced complete dissolution after

24h, whereas for IB600 it was observed an increase of D_h of about 60%, without dissolving further proving the greater colloidal stability of IB LNP. The distinct behavior of the AS sample could be ascribed to the system response to an unfavorable solvent environment for LNP, leading to a complete dissolution of the system.

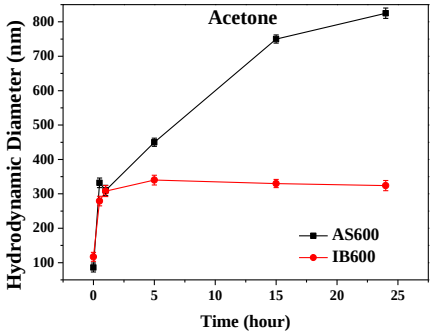

Figure 1 D_h over time of IB600 (red curve) and AS600 (black curve) in in acetone solution.

Moreover, the reversible swelling behavior of IB600 sample has been investigated. Briefly, when LNP are soaked into acetone solvent, their D_h value increases due to the swelling phenomena associated to the interaction between the nanoparticles and the solvent. On the other hand, when LNP are redispersed in water, D_h restricts back to 150 nm, close to starting diameter. This can be associated to a squeezing phenomenon: the ability of nanoparticles to undergo such reversible size changes, expanding when exposed to certain solvents, such as acetone, and subsequently contracting when re-immersed in water.

4. Conclusions

This study proposes a green and simple method for producing stabilized LNP by combining antisolvent and ultrasonication procedures through a hybrid procedure. The method provides a high yield of LNP in water with a fine size distribution and reproducibility in just 10 minutes, without the need for further purification such as the dialysis step required by most previously proposed routes. Additionally, the nanoparticles obtained demonstrated significant stability in organic solvents and alkaline environments, in contrast to those prepared using the conventional AS route, which showed marked aggregation phenomena in non-aqueous environments. Furthermore, the IB nanoparticles exhibited reversible swelling characteristics upon changing the dispersant medium, making them suitable for a variety of applications. The proposed LNP synthesis approach adheres to green chemistry principles, as the production method is not environmentally hazardous, and waste prevention has been addressed. Moreover, this is a bio-waste material that can be utilised to produce multifunctional nanostructures composed entirely of organic matter, without any inorganic support.

References

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Keywords

Waste-to-wealth; lignin nanoparticles; hybrid approach; colloidal stability.