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LIGNIN NANOPARTICLES AS A GREEN ALTERNATIVE FOR LIGNIN VALORIZATION: EVALUATION OF PREPARATION PROCEDURES

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ABSTRACT

The development of nanomaterials through advances in technology has enabled their evolution and application in areas such as medicine, pharmaceuticals, food, genetics, polymers and cosmetics. In recent studies, an increasing number of trials have shown that lignin nanoparticles (LNP) present a new green and sustainable material, with non-toxic characteristics, that can be used as vehicles to encapsulate various organic compounds. In this study different parameters for the preparation of lignin nanoparticles by the solvent exchange method have been investigated. LNP were characterized through techniques such as dynamic light scattering (DLS), electrokinetic potential, and SEM, which provided information about particle size, homogeneity, appearance and colloidal stability. The use of ethanol to solubilize Kraft lignin at pH 7 resulted in a minimum particle size of 225.7 ± 5.0 nm, PDI of 0.181 ± 0.027 and Zeta potential of -47.00 mV. The negative charge on the LNP surface is due to the deprotonation of acidic groups (phenolic OH and COOH) of lignin.

Keywords: Kraft lignin. Nanoparticles. Biopolymer. Biomass

1 INTRODUCTION

Industrial lignin is produced as high-volume byproduct, mainly by the pulp and paper industries and in the cellulosic ethanol process. Kraft lignin is obtained from the kraft pulping process, which accounts for the highest proportion (approximately 85%) of industrial lignin[1]. This process generates lignin in the form of "black liquor"[2], which is traditionally directed to a recovery boiler to recycle chemicals and generate bioenergy[3]. Lignin has potential for applications that span across various sectors including textiles, pharmaceuticals, biomedical, cosmetics, food, and packaging[4-6]. However, despite its abundance most of the lignin is burned as fuel to generate energy and only 5 % are recovered and its use in value-added applications has been a challenge[5].

Nanostructured materials can be produced from a large variety of renewable biopolymers. However, lignin stands out in this scenario, as it is the second most abundant macromolecule of biological origin in the world[3]. It is a complex irregular polymer encountered in the plant cell wall, representing 20 to 35 %   of lignocellulosic biomass, and its annual global production accounts for approximately 300 billion tons[3.]

Lignin nanoparticles (LNP) provide a sustainable alternative for valorizing lignin. They are biodegradable, non-toxic, and have the capability to serve as carriers for encapsulating a variety of organic compounds such as antimicrobial agents, fragrances, mosquito repellents, drugs, selected therapeutics, as well as inorganic particles[8].

Due to its aromatic chemical structure with phenolic and methoxy groups, lignin and its degradation products or extracts have antimicrobial and antioxidant properties. To prepare NP from lignin, different methods have been described in the literature, such as acid precipitation from a lignin solution, using castor oil, ethylene glycol and water as an antisolvent[9]. The formation of LNPs occurs basically through self-assembly, which has been described as a promising green chemistry methodology in industrial applications.

The main objective of this research is to value lignin from agro-industrial waste for the preparation of nanostructured materials. In this study the preparation of LNP based on kraft lignin has been investigated by the solvent exchange method, and the influence of different parameters has been evaluated.

2 MATERIAL & METHODS

The Kraft lignin (KL) batches were obtained from an undisclosed source. Solvents and reactants employed in this work were purchased at high purity grades from commercial suppliers without further treatment.

Lignin nanoparticles (LNP) were prepared by the solvent exchange method, where lignin was first dissolved in commonly used water miscible solvents, such as tetrahydrofuran (THF) and ethanol. Then an excessive amount of the antisolvent water was added gradually, leading to the formation of nanoparticles via self-aggregation[10]. With ethanol as lignin solvent, saline water (10^{-3} mol L^{-1}NaCl solution) was used as antisolvent. To achieve homogenous dispersion or dissolution of lignin in ethanol the dispersing device Ultra-turrax T25 digital (IKA) was used, then the antisolvent was added dropwise into the lignin solution under constant agitation, controlling time, agitation and temperature of 20 °C. The colloidal properties of the different LNP preparations

were analyzed with DLS and electrokinetic techniques using the Zetasizer Nano ZS particle analyzer (Malvern Panalytical). Morphology, surface characteristics and dimensions were analyzed by scanning electron microscopy (SEM) carried out with an Oxford instrument, model X-ACT.

The electrokinetic stability of NPs in different pH values from 2 to 12 were evaluated by acid and basic titration in Zetasizer Nano instrument coupled to autotitrator (MPT-2 Multi-Purpose Titrator - Malvern) at 25°C. Two stock solutions were used: HCl at 0.0972 mol L^{-1} and NaOH at 0.2394 mol L^{-1}. These solutions were integrated into autotitrator, which in triplicate performed pH measurements simultaneously and added HCl or NaOH solution according to the programming in the software, adjusting until the desired specific pH is reached.

3 RESULTS & DISCUSSION

The use of ethanol for the solubilization of Kraft lignin batch 1 resulted in an average particle size of 383.9 ± 7.1 nm, PDI of 0.253 ± 0.010 and Zeta potential of -30.6 ± 3.4 mV. The use of ethanol to solubilize Kraft lignin from batch 2 resulted in an average particle diameter of 329.0 ± 4.7 nm, PDI of 0.174 ± 0.032 and Zeta potential of -24.2 ± 1.9 mV.

The use of THF as lignin solvent resulted in particles sizes of 678.0 ± 36.3 nm, approximately double in diameter. A reduction in PDI was observed from 0.357 ± 0.056 to 0.253 ± 0.010 with lignin batch 1 and to 0.174 ± 0.032 with lignin batch 2 when alcohol was used, indicating the predominance of particles of similar diameters in the colloidal system. The Zeta potential of the THF preparation has not been determined (nd). Additionally, the use of ethanol stands out as an environmentally safer option compared to THF, due to the possibility of obtaining it through biotransformation, in addition to having smaller nanoparticle diameters when ethanol was used as a solvent. Furthermore, the cost of the THF solvent is higher than that of ethanol, which is another important factor when choosing.

Table 1 Influence of the solvent and filtration of the lignin solution in ethanol before the addition of the antisolvent on the characteristics of LNP

Solvent	Filtration	Diameter (nm)	PDI	x (mV)
THF	nd	678.4± 36.6	0.357± 0.056	nd
ethanol (1)	nd	383.9± 7.1	0.253± 0.010	-30.6
ehtanol (2)	nd	329.0± 4.7	0.174± 0.032	-24.2
ethanol (2)	7.5 µm	225.7± 5.0	0.181± 0.027	-47.0

The Zeta potential of analysis was monitored over 20 days (Figure 1 A), resulting in a value of -30.6 ± 3.4 mV on the first day and -53.2 ± 4.0 mV at the end of this period, suggesting LNP become more stable. The negative charge on LNP surface is the deprotonation of acidic groups (phenolic OH and COOH) of lignin[11].
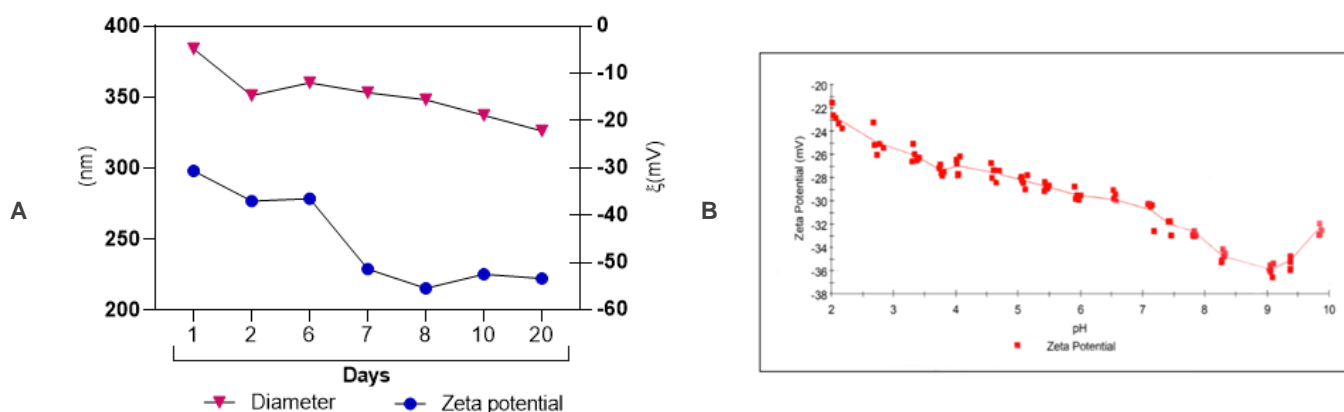

Figure 1 A Evaluation of stability of LNP over time in relation under diameter and Zeta potential; **B** Electro-kinetic stability of LNP at pH 2 to 10 using the Malvern MPT-2 Autotitrator, 25°C

The results showed that LNP exhibit a range of colloidal stability, especially greater at pH values above 6.0 (Figure 1 B), indicating Zeta potentials greater than -30 mV. It is noted that it is in an alkaline environment, with a pH of 9, that LNPs manifest a more negative Zeta potential, approximately -36.4 mV ±1.81. That phenomenon confers greater stability, due to the increased propensity of the particles to repel each other due to the negative charge effect of the deprotonated groups, resulting in a lower probability of aggregation. Thus, an important characteristic of LNP is the wide pH range with colloidal stability, with repulsive effects, due to the negative charges in the interface with the dispersion medium.

The Zeta potential plays an extremely important role in the analysis of physical stability of colloidal systems. Notably, NPs with Zeta potential situated outside the range of -30 mV to 30 mV demonstrate a high level of colloidal stability[12]. It is observed through the values of the Zeta potential, of -24.2 mV for LNP without filtration and -47.0 mV for NPs with filtration of the lignin solution, which the application of the filtration technique provided greater electrokinetic stability of the nanoparticles, suggesting that filtration of the lignin solution in ethanol selects lignin fractions prone to forming smaller NPs in addition to removing impurities that would serve as a nucleus for the formation of unwanted particles.
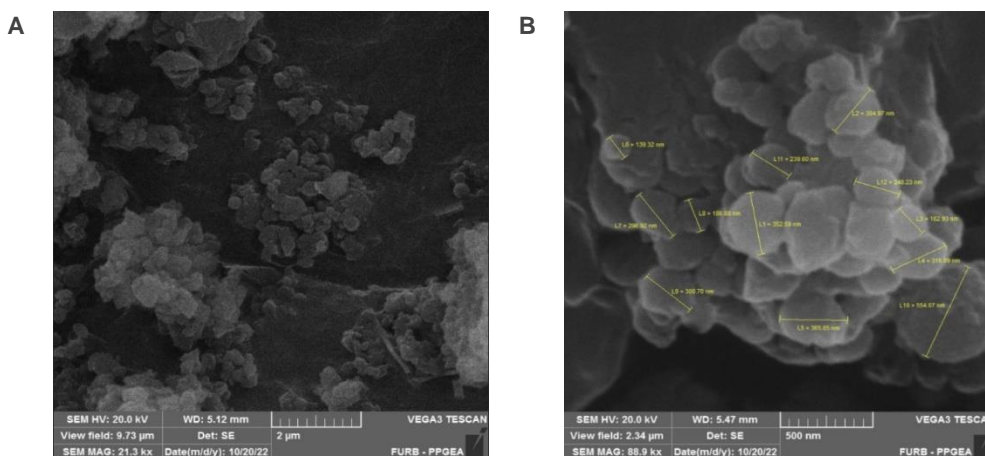
Figure 2 SEM of LNP synthesized with Kraft lignin lot 1 A and B represent images of LNP synthesized with Kraft lignin from batch 1 with 20000x magnification and 90000x

It was observed that the NPs presented an almost spherical and irregular structure and a narrow size distribution range between 200 and 350 nm (Figure 2: SEM of LNP synthesized with Kraft lignin batch 1B). The LNP microscopy results confirm the trend shown by the DLS technique. The SEM images demonstrate that LNPs are prone to agglomeration upon solvent evaporation, which can also be seen in the images presented below.

4 CONCLUSION

The present study investigated the influence of different solvents, specifically ethanol and THF, on the solubilization of Kraft lignin and the formation of lignin nanoparticles (LNP). The results obtained demonstrate that the use of ethanol as a solvent result in nanoparticles with a smaller average diameter, greater uniformity, and better electrokinetic stability compared to the use of THF. In addition to the physical characteristics of the nanoparticles, the choice of ethanol as a solvent stands out as a more environmentally safe option compared to THF, due to the possibility of obtaining it through biotransformation and due to its lower cost. This suggests that ethanol should be the preferred solvent for the solubilization of Kraft lignin in the synthesis of lignin nanoparticles, providing benefits both in terms of process efficiency and environmental sustainability.

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