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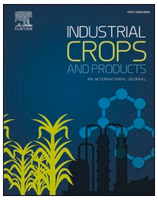

# From black liquor to tinted sunscreens: Washing out Kraft lignin unpleasant odor and improving its properties by lignin nanoparticle preparation

Mariana N.B. Silva, Eupidio Scopel, Camila A. Rezende *

*Universidade Estadual de Campinas, UNICAMP, Instituto de Química, Campinas, SP 13083-970, Brazil*

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ABSTRACT

Kraft lignin is a major byproduct of pulp and paper processing, presenting outstanding properties, including antioxidant action and UV and visible light absorption. Despite being a promising low-cost and renewable ingredient for dermo-cosmetic formulations, lignin use is restricted primarily because of its unpleasant odor and poor dispersibility in water. This study presents an integrated and environmentally friendly method to eliminate lignin odor, followed by improving its dispersibility in water through lignin nanoparticle (LNP) production, and, finally, evaluating their application in cosmetic formulations to act as antioxidant and UV-blocker. Starting with black liquor, Kraft lignin was precipitated and washed with water at 70°C, effectively removing lignin odor by a straightforward method, reducing its sulfur content from 5.6 to 2.9 wt%, and the ashes to negligible values without compromising the lignin structure. LNPs were successfully produced by the self-assembly method, yielding spherical and colloidally stable particles (zeta potential *ca.* −30 mV) with diameters ranging between 25 and 200 nm, outperforming particles prepared by sonication and bulk lignin itself. LNPs prepared by self-assembly method showed exceptional antioxidant activity, eliminating up to 79.2 % of DPPH• radicals (52 % more than bulk lignin) and showing *in vitro* SPF of *ca.* 15 with only 0.5 wt% of particle concentration, in addition to the improved dispersibility in cosmetic formulation.

## 1. Introduction

Lignin is a major component of lignocellulosic biomasses, presenting an aromatic structure with UV-absorbing and antioxidant functional groups (Pereira et al., 2022) that can be taken advantage of in the preparation of renewable products. Despite being a renewable, cost-effective, and non-toxic ingredient, lignin is commonly classified as a byproduct of the pulp and paper production line and currently used primarily for low value-added applications (Österberg et al., 2020).

Lignin is a promising ingredient in the cosmetic sector for preparing water-based formulations due to its antioxidant and anti-UV properties, interesting for its use as active ingredients in sunscreens (Qian et al., 2015). Sunscreens are essential everyday products designed to prevent the adverse effects of excessive sun exposure, including long-term disorders like photodamage, photoaging, and skin cancer (Lyons et al., 2021). Given the widespread incidence of skin cancer globally, with over 325,000 new cases reported in 2020 and projections indicating more than a 50 % increase in cutaneous melanoma by 2040 (Arnold et al., 2022), the significance of sunscreens is undeniable.

Typically, sunscreens protect against UVA (320–400 nm) and UVB (290–320 nm) radiations through tailored formulations incorporating organic and inorganic components that act *via* distinct mechanisms to safeguard the skin (Singer et al., 2019). Inorganic compounds, such as titanium dioxide ($TiO_2$) and zinc oxide (ZnO), serve as physical barriers, reflecting and scattering UV radiation (Diffey and Grice, 1997). Conversely, organic compounds, such as *p*-aminobenzoic acid derivatives, benzophenones, salicylates, and cinnamates, absorb radiation through a chemical mechanism (Diffey and Grice, 1997). However, achieving the recommended minimum sun protection factor (SPF) of 15 (Diaz and Nesbitt, 2013) demands a substantial content of chemical actives (around 20 wt%), raising concerns about skin allergies and environmental harm (Beisl et al., 2017). Currently, available sunscreens are associated explicitly with coral bleaching from aquatic exposure (Tashiro and Kameda, 2013) and toxicity to marine life due to certain ingredients, such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), synthetic organic antioxidants that are highly toxic to aquatic organisms with long-lasting effects (Carocho and Ferreira, 2013).

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* Corresponding author.
*E-mail addresses:* m221871@dac.unicamp.br (M.N.B. Silva), eupidio.scopel@iqm.unicamp.br (E. Scopel), camilaiq@unicamp.br (C.A. Rezende).

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Kraft lignin is available commercially, representing (together with lignosulfonate lignin) *ca.* 90 % of the technical lignin currently produced (Li and Takkellapati, 2018). Although primarily burned for power generation (Kai et al., 2016), it holds potential for higher-value applications following separation from black liquor. However, some challenges make the application of Kraft lignin in the cosmetic sector difficult, mostly related to its unpleasant odor and poor dispersibility in water.

Previous literature contributions indicated that the unpleasant odor of lignin is mainly related to the release of volatile organic compounds (VOCs). Though the specific molecules that causes the smell are still under discussion, they are expected to include formic and acetic acids, guaiacol, and sulfur-containing compounds (Guggenberger et al., 2023, 2019; Kalliola et al., 2012; Kouisni et al., 2016). This poses a challenge for using Kraft lignin in cosmetics. In addition, the presence of sulfur components is an obstacle to industrial operations due to the release of sulfur oxides and because it can poison catalysts in the process of lignin chemical conversion (Vishtal and Kraslawski, 2011).

Some purification strategies aiming to mitigate lignin odor already reported in literature include grafting of functional groups (epoxides, carboxylic acids, etc.) (Siegle et al., 2003), enzymatic treatments (Kalliola et al., 2012), conversion into nonvolatile species (Kouisni et al., 2016), and washing with organic solutions or applying supercritical $CO_2$ treatment (Alvarado and Tomani, 2016; Reynolds et al., 2016). These approaches focused on removing lignin foul odor, but did not consider the next steps for lignin application in cosmetic formulations.

Lignin in its bulk form has poor solubility in neutral water, requiring modifications to increase its polar character, such as chemical reactions to allow lignin solubilization (sulfonation, sulfomethylation, or oxidation) or its conversion into nanoparticles, creating a colloidal suspension (Österberg et al., 2020). The preparation of lignin nanoparticles (LNPs) is an interesting alternative to enhance lignin dispersibility in water and exploit its antioxidant and sunscreen performance (Pavaneli et al., 2024) since LNPs are prepared *via* more environmentally friendly methods and utilizing less aggressive reagents than in chemical modifications (Österberg et al., 2020). The efficiency of LNPs in sunscreens has been demonstrated using technical (Qian et al., 2017; Trevisan and Rezende, 2020) and modified (Wu et al., 2020; Zhang et al., 2019) lignins. However, to the best of our knowledge, there is no report in literature investigating the production of LNPs after strategies to mitigate lignin odor. This study presents relevance since odor removal could modify lignin structure and consequently affect the properties of produced LNPs, including those related to UV-Vis absorption, which are mandatory for application in sunscreens.

Another drawback for Kraft lignin use is its natural brownish color. However, lignin color can be an opportunity for developing new types of cosmetics. Recently, the focus of sunscreens has turned to protect against visible light in addition to the traditional and essential UV protection since visible light can cause long-lasting pigmentation and erythema (Kohli et al., 2019; Mahmoud et al., 2010). In addition, tinted sunscreens are attractive for people with dark skin. Tinted sunscreens currently developed are prepared by blending UV filters with pigments like iron oxides and pigmentary $TiO_2$ (Lyons et al., 2021), but lignin natural pigmentation is quite promising for these products. Therefore, removing chromophores seems to be a counterproductive step and the steps to bleach lignin natural brown color could be avoided if the focus is the preparation of tinted sunscreens (Widsten et al., 2020).

Based on the potential of using lignin as an active agent for tinted sunscreens, this work focused on proposing an integrated strategy to surpass the drawback of Kraft lignin foul odor and its low dispersibility in water using a simple and sustainable method that does not compromise lignin macromolecular structure and allow its application in cosmetic formulations. To remove the foul lignin odor, a purification step using mild hot water (70 °C) washing was applied to the lignin precipitated from the black liquor from Kraft processing. This simple step efficiently lowered sulfur content by reducing VOCs and ashes, while maintaining lignin molecular weight. Washed lignin was used to produce LNPs by the self-assembly method or sonication. The antioxidant capabilities, dispersibility in emulsions, and UV-Vis light blocking of lignin in three different forms were assessed, highlighting the efficacy of the self-assembly method in improving lignin properties.

## 2. Materials and methods

### 2.1. Materials

Black liquor produced from Eucalyptus was kindly donated by Suzano® (Suzano, Brazil). Hydrochloric acid (99.5 % purity), acetone (99.5 % purity), oleic acid P.A., glycerin (99.5 % purity), acetic anhydride (99.8 % purity), ethanol (99.5 % purity), and dioxane (99 % purity) were purchased from Synth® (Diadema, Brazil). Sodium dodecyl sulfate (SDS) (99 % purity), pyridine (99 % purity), and 2,2-diphenyl-1-picrylhydrazyl (DPPH•) were purchased from Sigma Aldrich®. Xanthan gum was purchased from a local market (food grade). Sunscreen (nominal SPF 30) was purchased from Basic+ Care®. All reactants were used as received.

### 2.2. Precipitation of Kraft lignin from black liquor

Kraft lignin was precipitated from industrial black liquor (diluted 10 times before precipitation) through the gradual addition of hydrochloric acid (HCl) until it reached pH 2 under constant magnetic stirring (Camargos and Rezende, 2021). After the acidification, the lignin precipitated was collected by centrifugation at 3500 rpm for 20 minutes (RC-3B, Sorvall Instruments). The supernatant was discarded, and the precipitate was washed with distilled water at room temperature and centrifuged until a more neutral pH was achieved in the same conditions (4–5 cycles). The sample was identified as KL (Kraft lignin).

### 2.3. Kraft lignin washing process

To mitigate the foul odor of Kraft lignin, a portion of the KL was added to a beaker with water preheated at 70°C and kept under magnetic stirring for 15 min (*ca.* 10 mL of water for each gram of lignin). This temperature was selected to increase solubility of sulfur-components and to avoid lignin degradation. After that, the sample was vacuum filtered and identified as WKL (washed Kraft lignin). Part of the WKL was kept in an aqueous suspension (never dried) for further incorporation into the sunscreen or for sonication. The remaining WKL was dried in an oven at 60ºC for 24 h to be used in the preparation of nanoparticles by the self-assembled method, and the washing process yield was calculated (Supplementary Material, S1).

### 2.4. Preparation of lignin nanoparticles by self-assembly induced by the addition of a non-solvent (SA)

The preparation of SA LNP followed the method previously reported (Camargos and Rezende, 2021). Briefly, 0.3 g of WKL was solubilized in 10 mL of a 9:1 (v/v) acetone/water solution, keeping the system under magnetic stirring for 10 minutes to ensure the solubilization. Then, 390 mL of distilled water was added to the WKL solution at once with the system still under stirring to induce nanoparticle formation by self-assembly. Filtration using a paper filter (pore size 28 μm) was used to separate large particles not converted into LNPs. LNP dispersion was stored in amber glass vials, and the yield was calculated (Supplementary Material S1).

### 2.5. Ultrasonication (US)

Ultrasonication was used to reduce the size of bulk lignin particles (Camargos and Rezende, 2021). Batches of 250 mL of the lignin suspension in water (1 g/L) were sonicated in a probe-sonicator (QR 550 W, Eco-Sonics) using a titanium macro tip with 13 mm of diameter, amplitude of 80 %, frequency of 20 kHz, and operating power of 440 W for 1 h. Samples were kept in an ice bath during the process, alternating 5 minutes of operation and 5 minutes of rest to avoid overheating. Finally, the suspension was filtered and stored in amber glass vials, and the yield was calculated (Supplementary Material S1). Samples were identified as US.

### 2.6. Preparation of model sunscreens

To produce the sunscreens, an oil-in-water (O/W) emulsion composed of 35 mL of distilled water (aqueous phase), 0.2 g of sodium dodecyl sulfate (SDS) (surfactant), and 4 mL of oleic acid (oil phase) was prepared by stirring all components together at 4500 rpm in a rotor-stator homogenizer (Ultra-Turrax T25, IKA) for 5 min. In sequence, a paste composed of 0.8 g of xanthan gum and 3 mL of glycerin, was mixed using the rotor-stator homogenizer and then manually with a spatula. Xanthan gum and glycerin were used to enhance emulsion viscosity for a closer thickness of a commercial sunscreen. For the preparation of the formulations containing lignin, the amount of distilled water was replaced by the aqueous suspension of lignin (WKL, SA, or US) to ensure the concentrations of 0.25, 0.5, and 1 wt%, considering the weight of the formulation. To achieve the target lignin concentrations, lignin dispersions were prior concentrated in a convection oven at 60°C. Formulations were named as control (with no lignin), SA for self-assembled, US for ultrasonicated, and WKL for bulk lignin, and the numbers indicate lignin concentration (0.25, 0.5 or 1 wt%).

### 2.7. Characterization

#### 2.7.1. Bulk lignin (KL and WKL)

Elemental analysis (CHNS) was carried out in KL and WKL to determine the content of carbon, hydrogen, nitrogen, sulfur, and oxygen in a Fisons EA1108 Elementary Analyzer (CE Instruments). Ash content was determined according to standard protocols by calcination (Muffle Furnace EDG 10 P-S) (Sluiter et al., 2008).

For VOC detection, gas-chromatography-mass spectrometry (GC-MS) in headspace mode was carried out in an Agilent GC 7890 coupled to an MS 5975 C mass spectrometer using an FFAP column (30 m x 0.25 mm, 0.25 µm) and an automatic sampler MPS Gerstel. Powder samples (1 g) were added in a vial, closed with a sept, and kept under stirring for 20 min at 80 °C. The temperature of the column was kept at 40 °C for 1 min, increased up to 220 °C at a rate of 10 °C/min, and kept at 220 °C for 3 min. The injector, ion source, and quadrupole temperatures were 240, 280, and 150 °C, respectively. Analysis used helium as carrier gas at 1 mL/min.

The determination of the molar mass average number (Mn), the molar mass average weight (Mw), and the dispersity (D) of the KL and WKL were carried by gel permeation chromatography (GPC) (Waters 1525 Binary High-Performance Liquid Chromatography Pump system) calibrated with a polystyrene standard (Hu et al., 2012). Before GPC analysis, lignin was acetylated by dissolving 0.5 g of dried lignin in 3 mL of pyridine and adding 3 mL of acetic anhydride (Pan et al., 2006). Lignin acetylation is the standard method for determining lignin molar mass by GPC and is an essential step to allow a better dissolution of lignin in the analysis solvent (tetrahydrofuran, THF) (Tolbert et al., 2014). The system was kept under constant magnetic stirring (300 rpm) at room temperature and dark for 168 h (1 week). Then, the acetylated lignin was precipitated by adding 50 mL of ice-cold deionized water, followed by the gradual addition of HCl until pH 2. Next, the system was centrifuged at 3500 rpm for 15 minutes (NT-820 Centrifuge, Novatecnica), the lignin was dried in an oven at 60°C for 24 h, and the supernatant was discarded.

Additional characterization of LK and WLK (Fourier-transform infrared spectroscopy - FTIR, and determination of acid-soluble and insoluble lignin) is described in Supplementary Material.

#### 2.7.2. Colloidal and morphological characterizations

To assess the colloidal stability and the hydrodynamic diameter of lignin nanoparticles, zeta potential and dynamic light scattering (DLS) analyses were carried out (Zetasizer Nano Zs-Zen 3600, Malvern) using a disposable capillary cell (DTS1070, Malvern Panalytical). Both measurements were performed in triplicate, with at least 11 scans each and a fixed angle of 173° (Trevisan and Rezende, 2020).

The morphology of the nanoparticles was analyzed by field-emission scanning electron microscopy (FESEM) (Quanta FEG 250, FEI). Secondary electron images were obtained at a 5 kV voltage and 10 mm working distance. Prior to analysis, nanoparticle dispersions were deposited on silicon, dried in a desiccator, and covered with a layer of Ir (current 11.3 mA; 60 seconds) (Baltec MED 20). A histogram with the diameter distribution of SA LNP was obtained by measuring 217 particles in the ImageJ® software.

#### 2.7.3. Determination of antioxidant activity

Lignin in its different structures had their antioxidant activities determined by monitoring the DPPH• (2,2-diphenyl-1-picrylhydrazyl) radical scavenging reaction, more specifically, the absorbance band of this radical at 515 nm ($\lambda_{max}$) at different times (0, 16 and 30 minutes of reaction) (Ultrospec 1000 UV-Vis Spectrometer, Pharmacia Biotech) (Dizhbite et al., 2004). For this, 2 mL of DPPH• (65 µmol/L in ethanol) was added to 1 mL of the lignin suspended in dioxane (90 % v/v dioxane: water) or to 1 mL of the nanoparticle suspension in water (0.15 mg/mL). To prepare the reference samples, 2 mL of DPPH• (65 µmol/L in ethanol) and 1 mL of dioxane (90 % v/v) or 1 mL of distilled water were used. The measurements were performed at room temperature.

#### 2.7.4. Determination of UV-Vis absorption capacity

The formulations (emulsions with different types and concentrations of lignin) and the commercial sunscreen SPF 30 had their UV-Vis absorption capacity (280–750 nm) determined by absorbance measurements in a Diffuse Reflectance Spectrometer with an integrating sphere (Shimadzu UV – 2450) (Trevisan and Rezende, 2020).

The *in vitro* SPF was determined for formulations and commercial sunscreen using the method of UV radiation absorption measurements (Dutra et al., 2004). SPF values were calculated using Eq. 1:

$$FPS_{in\ vitro} = CF \times \sum_{\lambda=290}^{\lambda=320} E_\lambda \times S_\lambda \times Abs_\lambda \tag{1}$$

Where: CF is the empirical correction factor of the *in vitro* method (CF = 10); $E_\lambda$ is the parameter of erythematous spectral effectiveness; $S_\lambda$ is the spectral solar irradiance, and $Abs_\lambda$ is the absorption of UV radiation at a given wavelength. The data ($E\lambda$ x $S\lambda$) are tabulated.

#### 2.7.5. Evaluation of lignin dispersibility in formulations

To verify the presence of lignin agglomerates, optical microscopy images of the formulations (Nikon E800) were obtained in at least 10 regions of each sample.

## 3. Results and Discussion

### 3.1. Isolation and purification of lignin from black liquor

Kraft lignin is generated during pulp and paper production as a byproduct of the Kraft process. In this method, lignin is extracted from wood due to a combination of sodium sulfide ($Na_2S$) and sodium hydroxide (NaOH) applied in a pressurized digester and heated at temperatures around 150 °C (Sjostrom, 1993). After the separation of the solid stream rich in cellulose, lignin is dispersed in a complex mixture known as black liquor. As a consequence of the $Na_2S$ use, the resulting Kraft lignin contains sulfur linked to the macromolecule structure and as small molecules (Mansouri and Salvadó, 2006).

Fig. 1A schematizes the isolation of Kraft lignin from black liquor

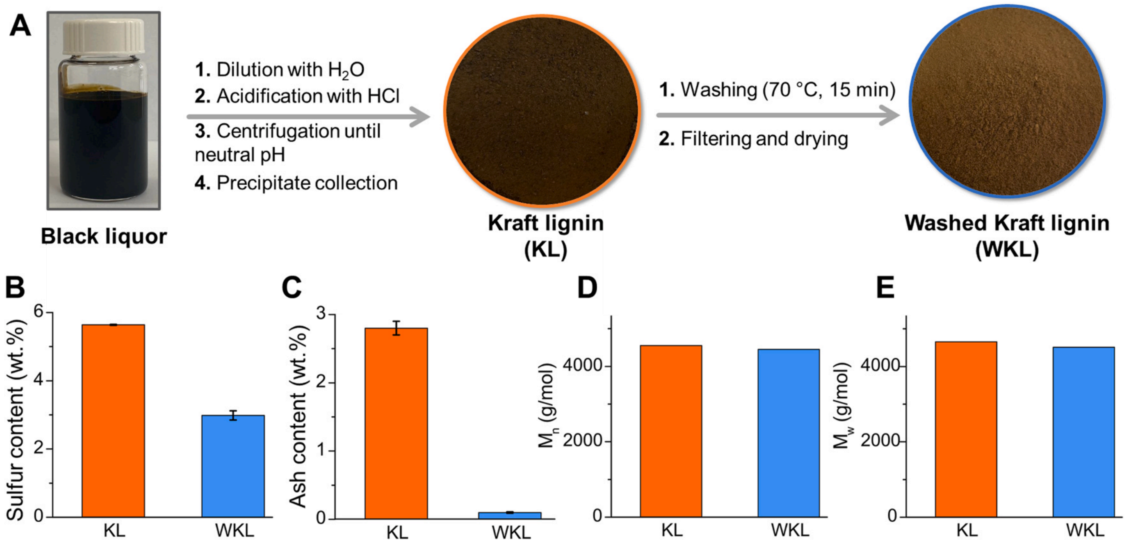

**Fig. 1.** A) Visual appearance of the black liquor (BL), Kraft lignin (KL), and Washed Kraft lignin (WKL); and comparison of B) Sulfur content; C) Ash content; D) Numerical average molar mass ($M_n$); and E) Average molar mass by weight ($M_w$) between KL and WKL. Molar mass dispersity (Đ) is 1.02 and 1.01 for KL and WKL, respectively. Error bars indicate the standard deviation of duplicates.

followed by the washing step designed in this work to reduce the odor, allowing its application of in cosmetics. A common strategy for isolating lignin from liquid phases involves acidification, prompting lignin to precipitate (Österberg et al., 2020). This is then followed by centrifugation or filtration. In the case of the black liquor used in this study, preliminary dilution was needed to reduce the high viscosity of the liquid phase caused by a substantial solid content (470 ± 30 g/L). After precipitation, 122 ± 6 g of KL can be recovered from 1 L of black liquor, representing a 26 % yield in relation to the content of total solids. The unprecipitated solids may contain inorganic elements, degraded wood substances, and smaller lignin fragments, all originated from the Kraft process (Bajpai, 2016).

After that, a purification step was used to address the undesirable odor. KL was washed in water at 70 °C with magnetic stirring for 15 minutes. Notably, the visual comparison indicates that washed KL (WKL) exhibits a lighter color than the original KL. The washing process demonstrated a recovery yield of 96 %, indicating minimal weight losses. Blind tests conducted with different individuals confirmed the elimination of the odor post-washing.

Elemental analysis was performed on KL and WKL to evaluate the effects of the washing process on the sulfur content (Fig. 1B and Table S1). The sulfur content was reduced from 5.6 to 2.9 wt%, a decrease of *ca.* 50 %. The washing process also aided in drastically diminishing the ash content, comprising inorganic materials co-precipitated with lignin during acidification (Fig. 1C).

Sulfur in Kraft lignin is present as VOCs and in ashes, which can be easily removed, as well as chemically bound to lignin macromolecules (Vishtal and Kraslawski, 2011). The sulfur reduction observed in CHNS experiments is potentially due to a reduction of VOCs and ashes since they are most susceptible to being washed out.

GC-MS (Figure S1) in the headspace mode, focused on analyzing the desorption of molecules by heating the solid powder, indicated the removal of small sulfur-containing molecules like methanethiol and dimethyl disulfide after the washing step. These components were found in KL but were not significant in WKL. Besides components with sulfur in their composition, chlorobenzene and furfural were detected in KL but not in WKL, and the intensity in the acetic acid peak was reduced. Indeed, the unpleasant odor of lignin primarily results from the physical desorption of the VOCs, including sulfur components, organic acids, and other small molecules (Guggenberger et al., 2023). The specific VOCs contributing to the odor and the mechanisms causing the smell remain a subject of study (Guggenberger et al., 2023). In this context, the adopted simple washing step likely solubilized the VOCs contributing to the foul odor, notably those linked to sulfur, organic acids, and carbohydrate degradation products.

Kraft lignin ashes comprise a substantial amount of sodium sulfate (Aro and Fatehi, 2017), which has enhanced solubility at higher temperatures (Linke and Seidell, 1965). Therefore, the washing step at 70 °C favored the removal of inorganic materials, as evidenced in Fig. 1C.

Numerical average molar mass ($M_n$) (Fig. 1D), average molar mass by weight ($M_w$) (Fig. 1E), and molar mass dispersity (Đ) (1.02 for KL and 1.01 for WKL) displayed remarkable similarity between KL and WKL. This is interesting for the future applications of lignin to produce LNPs since the method for removing the unpleasant odor does not modify lignin macromolecular structure and does not hinder LNP production. The similarities of molar mass before and after washing can be related to the quantification of acid-soluble and acid-insoluble lignin by Klason method (Table S2). The washing process brought down the acid-soluble lignin content by around 40 % (from 11 to 6.7 wt%). Acid-soluble lignin is defined as the fraction that remains in liquid after the acid hydrolysis (Klason method) and comprises all the small fragments of lignin with smaller molecular weight. Therefore, this fraction is more susceptible to leaching during washing with hot water and did not change the molar mass values. The analysis also confirmed high purity of lignin (up to 98 %) after washing, primarily due to ash removal.

The decrease in sulfur content while maintaining constant molar mass indicates that the washing step predominantly removed small molecules and fragments from KL, leaving the macromolecular structure unaltered. The similarities in FTIR spectra of Kraft lignin before and after washing (Figure S2) underscore the preservation of the basic lignin structure during the process. As lignin is composed of three phenylpropanolic monomers: *p*-coumaryl, coniferyl, and synapyl alcohols (Evdokimov et al., 2018), FTIR spectra indicated the presence of a broad band at 3375 $cm^{-1}$, associated with -OH binding of phenolic groups; a narrow, moderately intense band at 1600 $cm^{-1}$ indicative of C=C binding of aromatic rings; and a narrow, strongly intense band at 1110 $cm^{-1}$ indicative of C-O binding of the ether groups for both KL and WKL.

The characterization of lignin before and after washing demonstrates the efficiency of the straightforward method for reducing its odor without compromising its further applications, specifically for LNP preparation. Washing did not change any chemical properties of lignin important for UV-Vis absorption, according to FTIR, and kept the macromolecular structure of lignin basically unaltered, according to molecular weight determinations. In contrast, it significantly reduced sulfur, VOC, and ash contents. It is important to highlight that precipitating lignin from the black liquor already employs several washing steps during centrifugation using water at ambient temperature, which removes the excess acid and increases the pH. It demonstrates that washing with water at ambient temperature is insufficient to reduce VOCs, ashes, and sulfur content to values as low as those achieved when washing with water at 70 °C was employed. The differences are potentially related to the higher solubility of these components at moderately elevated temperatures. This approach opens opportunities for employing Kraft lignin in cosmetics and also solves VOC challenges during combustion at an industrial scale. Compared to other strategies to reduce lignin smell, like functional group grafting (Siegle et al., 2003), enzymatic treatments (Kalliola et al., 2012), or conversion in nonvolatile components (Kouisni et al., 2016), washing stands out as a straightforward approach. While some studies and patents have explored washing combined with supercritical carbon dioxide (Reynolds et al., 2016) and short-chain alcohols (Alvarado and Tomani, 2016), these methods yield aqueous streams with acids or organic solvents, making treatment more complex than a simple step using neutral water at moderate temperatures, as employed in the proposed strategy.

### *3.2. LNP preparation: colloidal stability, morphology, and antioxidant properties*

WKL was used to produce LNP by self-assembly (SA), which was achieved by adding a non-solvent (water) to the lignin solution in acetone. When the dissolved lignin contacts water, SA LNP assemble with their hydrophilic groups oriented towards the surface and the hydrophobic moieties of lignin hidden in the core (Schneider et al., 2021). The production rate of this method was 93 %, and lignin tends to form spherical particles to minimize the surface area. This is corroborated by microscopy images showing spherical, individual nanoparticles ranging from 25 to 207 nm, with an average diameter of 65 nm (Fig. 2).

Alternatively, ultrasonication (US) was used to reduce the size of lignin aggregates in water. Particles prepared by US exhibited an irregular shape, agglomerates, and diverse sizes, including nanoparticles (Figure S3). This is typical of this preparation method since ultrasonication generates cavitation air bubbles that reduce particle sizes (Gilca et al., 2015), often leading to smaller particles that are heterogeneous in form and with a broad particle size distribution (Schneider et al., 2021). After filtering, it was possible to recover 80 % of lignin (named US), composed of nano and microparticles.

Spherical particles prepared by SA method offer advantages like easier property control, improved packing, and prolonged colloidal stability (Österberg et al., 2020). On the other hand, irregular particles exhibit higher roughness, leading to uneven energy distribution across their surface. Consequently, local inter-particle interactions can differ from predictions, unlike well-defined colloidal systems observed in spherical particles (Lourencon et al., 2020).

The mean hydrodynamic diameter values measured by DLS revealed a single population of nanoparticles for SA LNP, with an average diameter of 85 nm, displaying only a slight variation around the average (Fig. 3A). On the other hand, two populations were measured by DLS after US treatment (peaks in 163 and 651 nm, Fig. 3A), indicating the polydispersity of the sample. Large agglomerates observed in SEM images (Figure S3) cannot be measured by DLS due to the technique limitation.

Samples prepared by SA and US demonstrated robust colloidal stability, as evidenced by zeta potential values more negative than −30 mV (Fig. 3B), even for the polydisperse US samples. These zeta potential values indicate stabilization by electrostatic repulsion, which arises from carboxylic group deprotonation on the particle surface (Leskinen et al., 2017).

To assess the antioxidant capacity of lignin in its different structures, DPPH• radical capture assays were conducted. Fig. 4 presents results for bulk lignin, SA, and US particles. Data at 16 and 30 min were gathered to facilitate literature comparison, given the absence of consensus on the time for measuring radical inhibition percentages (IP). SA LNP presented the best antioxidant activity, showing IP of 79.2 ± 4.2 %. On the other hand, IP remained the same for bulk lignin and US at both points: after 30 minutes, WKL consumed 52.2 ± 0.8 % of radicals, whereas US samples suppressed 57.4 ± 4.8 %, statistically equivalent values. For comparison, at the same concentration (50 mg/mL), BHA and BHT could consume *ca.* 40 % and 50 % of DPPH• (Li et al., 2018), indicating the superior performance of lignin nanoparticles prepared by SA.

The heightened antioxidant properties of lignin, even in bulk form, emanate from phenolic groups that act as hydrogen donors (Lu et al., 2012). SA LNP displayed superior performance primarily due to their small size, offering a larger surface area per volume and a greater arrangement of hydroxyl groups on the surface (Trevisan and Rezende, 2020). As US samples are composed of more heterogeneous particles in

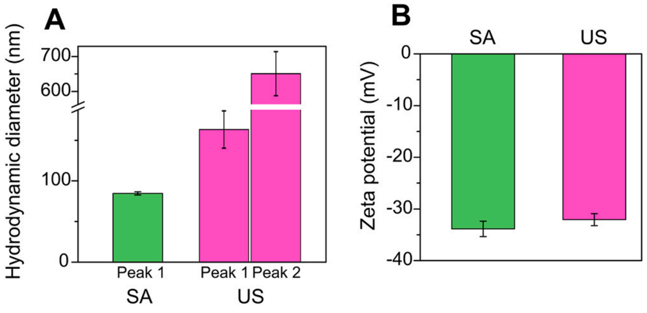

**Fig. 3.** Comparison between LNP prepared by self-assembly method (SA) and ultrasonication (US): A) Hydrodynamic diameter measured by DLS; and B) Zeta potential. Error bars indicate the standard deviation of triplicates.

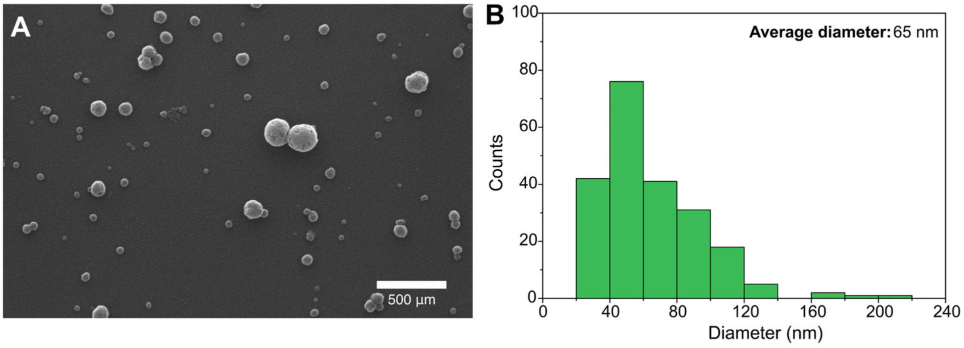

**Fig. 2.** A) FESEM image; and B) Diameter distribution histogram for SA LNP.

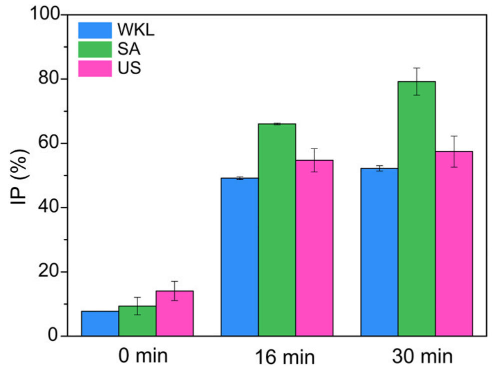

**Fig. 4.** Antioxidant activity of bulk WKL, SA, and US particles indicated as the inhibition percentage (IP) of the DPPH• radical.

size, prepared by cavitation of bulk lignin, they are more similar to bulk lignin values. These robust antioxidant properties position lignin, particularly SA LNP, as potential substitutes for synthetic antioxidants like BHT and BHA in pharmaceuticals and cosmetics (Carocho and Ferreira, 2013).

### *3.3. Dermocosmetic formulations and UV-Vis protection*

UV-Vis protection of lignin originates from its molecular structure (Ragauskas et al., 2014). Chromophores, like aromatic rings and quinones – potentially conjugated with double bonds or bearing carbonyl group as side chains – absorb light in UVA-UVB regions. The presence of phenolic hydroxyl and methoxyl groups act as auxochromes, their free pair of electrons conjugating with chromophores structures. This combination alters chromophore absorption and enhances UV absorption (Qian et al., 2015). Moreover, charge-transfer complexes involving *o*-quinones (electron acceptors) and phenolic groups (electron donors) amplify UV-Vis region absorption (Barsberg et al., 2003; Furman and Lonsky, 1988).

Emulsions were formulated to simulate dermo-cosmetic products using bulk WKL, SA and US particles in various concentrations to explore this attribute. Fig. 5 presents optical microscopy images of control and formulations prepared using 1 wt% of lignin material. Bulk WKL (Fig. 5B) displays sizeable particle agglomerates (indicated by arrows), which are attributed to its poor water dispersibility (Li and Takkellapati, 2018). Conversely, SA LNP formulations (Fig. 5C) exhibited no aggregates visible in the optical microscope and are very similar to the control formulation with no lignin (Fig. 5A). Formulations prepared using US lignin (Fig. 5D) featured smaller particles than bulk WKL, which is still visible in optical microscope, corroborating with SEM images (Figure S3). The better dispersibility of SA LNP in water formulation is likely attributed to their size and shape (Österberg et al., 2020). Moreover, the direct addition of LNP, as prepared without drying steps, into the water phase of the emulsion facilitates dispersibility. Given the simplicity of the LNP preparation method, the recommendation is to prepare the LNP at the formulation site, minimizing water transportation (in the case of the transportation of LNP dispersions) or drying steps that could escalate costs.

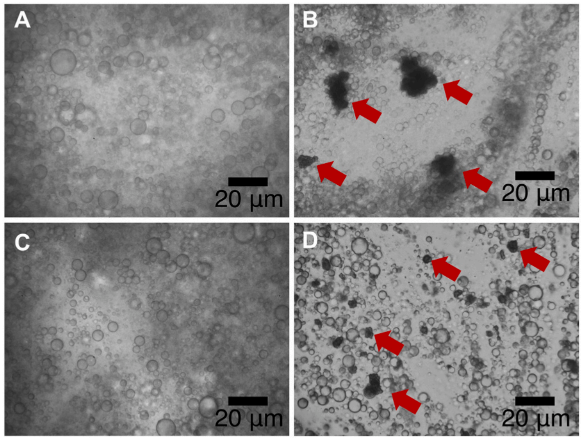

**Fig. 5.** Optical microscopy images of the formulations prepared: (A) control; (B) WKL 1 wt%; (C) SA LNP 1 wt%; and (D) US particles 1 wt%.

Fig. 6A presents transmittance profiles for formulations prepared using bulk WKL, serving as a control, and SA LNPs, which displayed the best water dispersibility and antioxidant activity. These formulations span the UV (280–400 nm) and visible (400–750 nm) regions. Commercial sunscreen with a nominal SPF of 30 containing benzophenone-3, titanium dioxide, and zinc oxide as UV blockers and pure cream – devoid of lignin - were also analyzed as a control. The composition of the commercial sunscreen is described in the Supplementary Material (section S6).

Incorporating bulk or SA LNP significantly reduced UV-transmittance, remarkably boosting UV-Vis protection. Increasing lignin concentration in the same group of lignin entities (bulk WKL or SA LNP) increased the UV (280–400 nm) and visible protection. Significantly, SA LNP outperformed bulk WKL at the same concentrations, reflecting superior UV protection attributed to their large surface area, functional groups, and enhanced dispersibility.

Formulations containing 0.5 and 1 wt% SA nanoparticles displayed transmittance in the UV region (280–400 nm), similar to the commercial sunscreen. It is noteworthy that these quantities of active ingredients are slight compared to the higher chemical amounts usually employed to achieve equivalent sunblock efficiency (Beisl et al., 2017). This success stems from the stable, uniform, spherical LNP acting as antioxidants and UV filters. This approach, coupled with the odor reduction from simple washing, advances Kraft lignin utilization into valuable applications.

Regarding using lignin as an active ingredient in tinted sunscreens, formulations with bulk WKL and SA LNP outperformed commercial sunscreen in protecting against visible light (400–750 nm). This presents prospects for crafting tinted sunscreens (Lyons et al., 2021), in which lignin serves UV and visible filters and antioxidants as a new trend for sunscreens.

Fig. 6B-E illustrate the visual appearance of formulations with SA LNP, ranging from no-added lignin to 1 wt% exhibiting characteristic lignin color. Intriguingly, the efficacy of formulations with 0.5 wt% and 1 wt% is similar; the color turns darker by increasing LNP concentration (Fig. 6D-E). This opens opportunities to tailor product tones by adjusting LNP quantity while maintaining performance. In addition to the trend of preparing tinted sunscreens, these formulations look promising for people with dark skin tones. Presently, tinted sunscreens are already on the market and necessitate pigmentary additives like iron oxide and

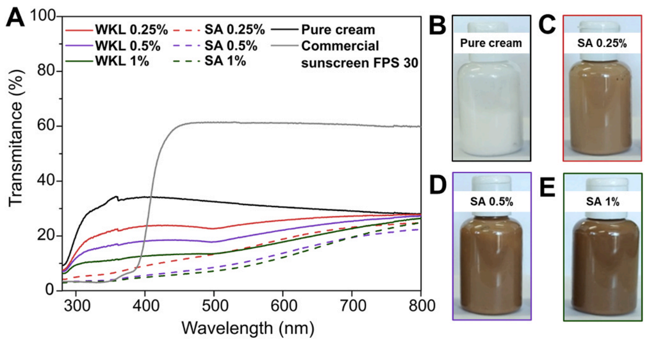

**Fig. 6.** A) UV-Vis transmittance for formulations with WKL and SA LNP, pure cream (control), and commercial sunscreen SPF 30; and photographies of the formulations: B) Pure cream (control, no lignin); C) 0.25 wt% of SA LNP; D) 0.5 wt% of SA LNP; E) 1 wt% of SA LNP.

pigmentary $TiO_2$ alongside UV filters. Lignin application can either substitute or complement these efforts for sustainable and effective tinted sunscreens.

Transmittance profiles of the US particles applied in formulations are in Figure S4, while visual appearances of formulations prepared using bulk WKL and US particles are in Figures S5 and S6, respectively. Similar trends emerge with SA LNP: US samples outperform bulk WKL, and higher lignin concentration augments UV and visible light protection. Within the same concentrations, SA LNPs excel over US particles, possibly due to the smaller size and superior formulation dispersibility.

Table 1 presents calculated *in vitro* SPF values for dermo-cosmetic formulations, offering a quantitative indicator of sunscreen efficacy (Dutra et al., 2004). In addition, the *in vitro* SPF 30 for the commercial sunscreen is included, with the labeled SPF based on *in vivo* methodology. Notably, SPF takes account of UVB ray absorption, not UVA or visible protection, even considering that UVA radiation is more damaging than UVB, up to 9 times (Kamenisch et al., 2018).

Formulations containing 0.5 wt% SA LNP showed an SPF of 14.6, while those having 1 wt% SA LNP showed an SPF of 14.9), mirroring the *in vitro* SPF of the commercial sunscreen (SPF = 14.8) labeled as SPF of 30. Similarly, the formulation with 1 wt% US particles had an SPF of 13.7), approaching the commercial product SPF despite lignin dispersibility challenges. Even at low concentrations in formulations, lignin nanoparticles exhibited potent photoprotective action against UV and visible radiation, promising replacements for active compounds in commercial sunscreens. These tinted sunscreens with LNP outperformed many literature examples using LNP, which achieved similar SPF values of 15 but required notably higher LNP quantities, ranging from 5 (Gordobil et al., 2019) to 10 wt% (Qian et al., 2017).

**Table 1**
SPF of formulations prepared with different types of lignins and commercial sunscreen using the *in vitro* method.

| Formulation | *In vitro* SPF |
|---|---|
| Commercial sunscreen SPF 30 | 14.8 |
| Pure cream | 6.5 |
| WKL 0.25 wt% | 8.2 |
| WKL 0.5 wt% | 9.0 |
| WKL 1 wt% | 10.1 |
| SA 0.25 wt% | 13.0 |
| SA 0.5 wt% | 14.6 |
| SA 1 wt% | 14.9 |
| US 0.25 wt% | 10.4 |
| US 0.5 wt% | 11.7 |
| US 1 wt% | 13.7 |

## 4. Conclusion

This study employed an integrated strategy to apply Kraft lignin as an active ingredient in tinted sunscreens without odor and with improved dispersibility, antioxidant, and anti-UV properties. Starting from black liquor, a straightforward and efficient washing step eliminated lignin undesirable odor. The washing procedure reduced VOCs, led to a 50 % reduction in sulfur content, and practically removed all the inorganic components. Notably, the self-assembly approach proved more adept at producing potent antioxidant lignin nanoparticles, which exhibited superior performance in sunscreen formulations, particularly regarding dispersibility. The tinted sunscreens demonstrated remarkable efficiency, achieving *in vitro* SPF values of 15 even at extremely low concentrations of lignin nanoparticles (0.5 wt%). This achievement is significant considering that, typically, larger quantities of chemical additives are required to attain similar levels of sun protection. This eco-friendly approach using a byproduct from pulp and paper refining and a mild washing step to eliminate its odor holds promise in reducing the reliance on toxic and allergenic synthetic antioxidants and coral bleaching agents. Moreover, it paves the way for advanced cosmetic formulations offering comprehensive protection against UV and visible light with antioxidant ingredients while being environmentally responsible.

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## CRediT authorship contribution statement

**Mariana N.B. Silva:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Eupidio Scopel:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation. **Camila A. Rezende:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2024.118910.

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