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ARTICLE

Simple process for lignin nanoparticle preparation

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The lack of renewable resources and their inefficient use is a major challenge facing the society. Lignin is a natural biopolymer obtained mainly as a by-product from pulp- and paper-making industry, and is primarily burned to produce energy. However, the interest for using lignin in more advanced applications has increased rapidly. In particular, lignin based nanoparticles could find potential use in functional surface coatings, nanoglues, drug delivery, and microfluidic devices. In this work, a straightforward method to produce lignin nanoparticles from waste lignin obtained from kraft pulping is introduced. Spherical lignin nanoparticles were obtained by dissolving soft wood kraft lignin in tetrahydrofuran (THF) and subsequently introducing water into the system through dialysis. No chemical modification of the lignin was needed. Water acts as a non-solvent reducing lignin's degrees of freedom causing the segregation of hydrophobic regions to compartments within the forming nanoparticles. The final size of the nanoparticles depended on the pre-dialysis concentration of dissolved lignin. The stability of the nanoparticle dispersion as a function of time, salt concentration and pH was studied. In pure water and room temperature the lignin nanoparticle dispersion was stable for over two months, but very low pH or high salt concentration induced aggregation. It was further demonstrated that the surface charge of the particles could be reversed and stable cationic lignin nanoparticles were produced by adsorption of poly(diallyldimethylammonium chloride) (PDADMAC).

Introduction

Lignin is the second most abundant polymer from biomass after cellulose and the main available renewable resource based on aromatic units. Native lignin is mostly present in the middle lamella between wood cells and the secondary cell wall. Thus, it plays an important role in the structural properties of plants by adding strength to the cell walls, controlling the fluid flow as well as protecting the plant against biochemical attacks.¹ Annually, over 70 million tons of industrial lignin is produced mostly as a side stream of biomass separation processes. Around 95 % of this lignin is burned due to its good heat value. Currently only 5 % of the industrial lignin is used for value added products. One challenge with lignin utilization is the imprecisely defined and varying structure depending on the origin of the lignin. Additionally, the separating and fragmentation processes still limit its usage. Current commercial applications of industrial lignin grades include additives, binders, dispersants and surfactants.²

Due to its aromatic structure, lignin has lately attracted increasing interest in new application fields. To name a few, the use of lignin as a raw material for carbon fibre production has achieved promising results.³ Furthermore, lignin has been investigated as a raw material for the wood adhesives industry. Main focus has been on replacing phenol-formaldehyde adhesives with lignin based substances.⁴ However, the poor dispersability of lignin in the adhesives has been a challenge.⁵ The possible antimicrobial activity and feed additive properties of industrial lignins has also gained interest.⁶

The insolubility of lignin in water is a major limitation for its industrial processing and large scale applications. However, recently it has been shown that it is possible to prepare aqueous lignin nanoparticle dispersions.^{7,8} These water dispersed lignin nanoparticles (LNP) could have potential in applications such as bio based adhesives, stabilizers, crops additives, etc. Successful utilization of lignin nanoparticles to reinforce phenolic foams, to stabilize Pickering emulsions, and to carry silver ions or silver nanoparticles has been reported in the literature.⁹⁻¹³ Furthermore, as water dispersed polymer nanoparticles have been widely investigated in drug delivery systems,¹⁴ lignin nanoparticles could be a potential precursor for drug delivery applications.

Despite the obvious need for well-defined aqueous lignin nanoparticle dispersions only a few scientific articles on lignin based nanoparticles have been published. Frangville *et al.*

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were among the first ones to report on aqueous lignin nanoparticle dispersion. They produced nano sized lignin particles through dialysis by using ethylene glycol as solvent.⁸ However, the obtained particles were rather irregular in size and shape. Qian et al. prepared spherical nanoparticles from acetylated lignin using tetrahydrofuran (THF) as solvent and inducing the particle formation by drop-wise addition of water to the lignin solution.⁷ Yiamsawas et al. introduced a lignin based nanocapsules which may have potential in agricultural applications,¹⁵ and Gilca et al. modified lignin with ultrasonication in order to produce nanoparticles.¹⁶ Gonogunta et al. produced lignin based carbon nanoparticles by freeze-drying a lignin solution followed by thermal carbonization process.¹⁷ Moreover, Qian et al. proposed a novel method of using CO₂ and N₂ gas responsive lignin based nanoparticles as a surfactant for Pickering emulsions.¹⁸

The lignin nanoparticle preparation methods reported so far have major limitations considering potential industrial processes. Qian et al. used acetylated lignin⁷. This step required environmentally hazardous chemicals such as acetyl bromide. Additionally, in order to get high concentrated nanoparticle dispersions significant amount of water would need to be evaporated, consuming energy. Furthermore, in the methods described by Yiamsawas et al.,¹⁵ Frangville et al.,⁸ and Gilca et al.¹⁶ the final lignin nanoparticles had irregular shape. This may lead to application challenges if spherical particles are desired. Moreover, hazardous chemicals were utilized in these particle preparation methods including toluene diisocyanate by Yiamsawas et al.,¹⁵ and pyridine by Qian et al.¹⁸

In this work we present a straightforward method for the preparation of lignin nanoparticles that yields a spherical particle morphology and colloidal stability over time without the need for chemical modification of lignin. The method uses a limited amount of organic solvents and produces the particles as an environmentally friendly aqueous dispersion. The characteristics of the lignin nanoparticles (size and zeta potential) and their stability against time, added electrolyte and pH were studied. Furthermore, coating with a cationic polyelectrolyte, poly(diallyldimethylammonium chloride) (PDADMAC), allowed the modification of the nanoparticle surface charge.

Results and discussion

Effect of solvent on nanoparticle properties

The chemical composition of lignin varies depending on wood species, process conditions and separation methods. This affects the solubility of the lignin and potentially the applicability of various nanoparticle preparation methods. Based on previous research the most interesting solvents were ethylene glycol, THF and water (as non-solvent). The lignin used in this work was originally soft wood lignin extracted from the kraft pulping process (SW). It dissolved relatively well in THF while it did not dissolve in water or ethylene glycol. For

comparison, another kraft lignin grade (Sigma-Aldrich) was tested, which showed opposite dissolving properties, i.e. low solubility in THF but good solubility in ethylene glycol and partial solubility in water.

Table 1 presents the chemical structure of the lignin used in this work obtained by ³¹P-NMR spectroscopy. It can be observed that the major difference between the lignin grades is the amount of hydroxyl groups. Especially the portion of phenolic hydroxyl groups vary considerably between the two samples, possibly explaining the difference in solubility.

Water dispersions of lignin nanoparticles were produced by solvent exchange via dialysis. The particle size and structure was observed to be dependent on the solvent used for dissolving lignin prior to the solvent exchange step (Figure 1). The lignin nanoparticles that were prepared using THF as the solvent (upper two images) are more symmetric and have uniform round shape compared to the particles prepared with ethylene glycol (lower two images). This is due to either better lignin solubility in THF and worse solubility in water or more suitable solvent exchange interactions with water. THF is less polar compared to ethylene glycol which might be an advantage for the nanoparticle formation. Since spherical lignin nanoparticles were obtained from the combination of SW lignin and THF as solvent, the rest of the experiments were performed with this setup. It must be highlighted that spherical nanoparticles were also obtained from the THF-soluble fraction of lignin from different sources (pine kraft, leaf kraft, spruce EMAL, birch organosolv), which indicates that the nanoparticle preparation method described in this work could be applied to any lignin or lignin fraction soluble in THF (results not shown). Negligible amounts of THF were detected in the final nanoparticle dispersions by headspace gas chromatography-mass spectrometry (GC-MS) and ¹H-NMR spectroscopy (Supplementary Information), indicating that THF was efficiently removed during dialysis.

Compared to other preparation methods for lignin-based nanoparticles or capsules previously reported by Yiamsawas et al.,¹⁵ Frangville et al.,⁸ and Gilca et al.,¹⁶ the method presented in this work yields more spherical nanoparticles, which represent an important advantage for advanced applications.

Effect of pre-dialysis lignin concentration on the characteristics of lignin nanoparticles

Pre-dialysis lignin concentration had an effect on the final particle diameter (Figure 2). The average particle size seems to have a minimum at around 1 mg/ml concentration. The particle diameter then increases until the dispersion becomes unstable at around 20 mg/ml. The average polydispersity indexes (PDI) range from 0.15 to 0.56 in a scale from 0 to 1 (the higher the PDI, the more polydisperse the particles are). The highest PDI was obtained for the maximum lignin concentration studied, 20 mg/ml. However, there was no trend observed in PDI between the concentrations from 0.1 to 10 mg/ml.

Table 1. Amounts of different hydroxyl group species in lignin samples according to ^{31}P -NMR data.^a The sulfur was assumed to be as thiol group.^b Data provided by Sigma-Aldrich.

	Aliphatic OH (mmol/g)	Carboxylic (mmol/g)	Phenolic OH (mmol/g)	Total OH (mmol/g)	Mw (g/mol)	Sulfur (%)	-SH ^a (mmol/g)
SW kraft lignin	1.78	0.41	3.64	5.83	> 4800	3.1	0.94
Sigma-Aldrich kraft lignin	1.39	0.50	1.55	3.44	~ 10000 ^b	3.3 ^b	1.00

The lignin nanoparticles were probably formed via a nucleation-growth mechanism as the THF solvent was replaced with water during the dialysis. Higher concentration of lignin in the system means more lignin available for the growth of the nanoparticles, which explains the slight increase in average diameter with pre-dialysis lignin concentration observed in Figure 2. An increase in particle size as a function of the initial polymer concentration has also been observed in the synthesis of other polymeric particles.¹⁹⁻²¹ At very high lignin concentration (20 mg/ml) the nucleation-growth mechanism during the dialysis seems to occur so fast that nanoparticles with very different sizes are formed (high polydispersity). The minimum in size at lignin concentration around 1 mg/ml could be explained considering the lower probability of nucleus formation at very low lignin concentrations, which eventually leads to the formation of a smaller number of lignin nanoparticles with, nevertheless, larger average diameter.²² Curiously, Frangville et al.⁸ did not observe a minimum but a maximum when studying the effect of the initial lignin concentration in ethylene glycol on the final nanoparticle size.

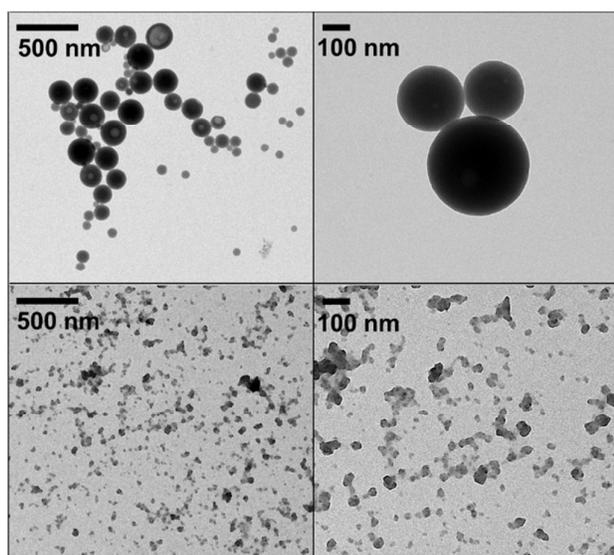


Figure 1. TEM images of lignin nanoparticles prepared from SW lignin dissolved in THF (top) and Sigma-Aldrich lignin dissolved in ethylene glycol (bottom).

The lignin nanoparticles prepared by the method described in this work could be dried (either by evaporation or freeze-drying) and redispersed in water by sonication. These additional treatment possibilities make the lignin nanoparticles suitable to be used in many industrial processes like the fabrication of glues and composites.

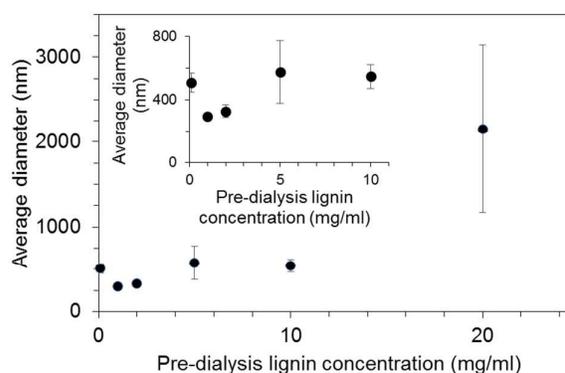


Figure 2. Effect of pre-dialysis lignin concentration on lignin nanoparticle size. The inset shows average particle diameter at low pre-dialysis lignin concentration in more detail.

Effect of time, salt concentration and pH on particle stability

For some applications, such as coatings and drug delivery, it is crucial that the nanoparticles retain their nanosize and stay well dispersed to reach desired performance. Thus, the stability of the dispersion was evaluated as a function of time and medium conditions.

When lignin nanoparticles are dispersed in water, the phenolic hydroxyl groups and possible carboxyl groups provide the particles a surface charge that promotes the formation of electrical double layers, which can stabilize the nanoparticle dispersion via electrical double layer repulsion. Additionally, negative surface charge occurs partially due to the adsorption of hydroxyl ions on the nanoparticle surface when the hydrophobic surface of lignin nanoparticles is in contact with water.

Figure 3 illustrates the stability of a lignin nanoparticle dispersion that was prepared with 2 mg/ml initial lignin concentration leading to average particle size between 320 and 360 nm in pure water. The lignin nanoparticle dispersion

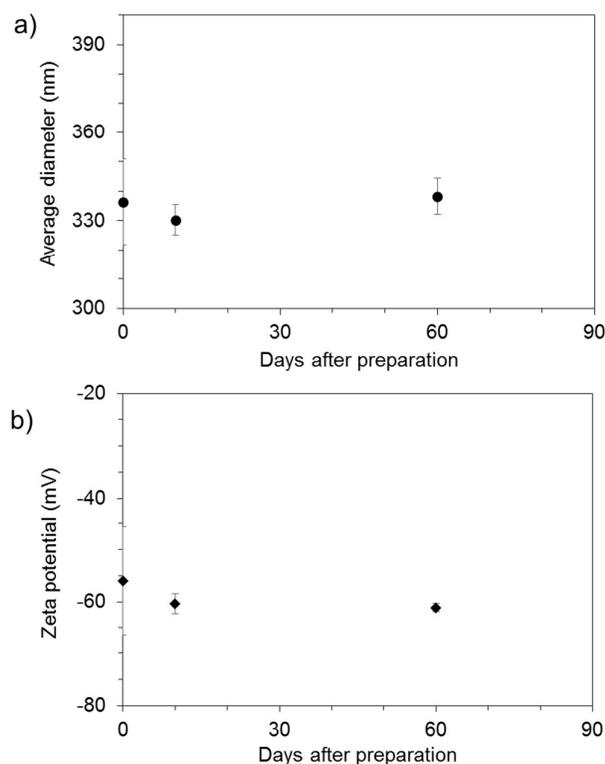


Figure 3. Stability of lignin nanoparticles: a) average hydrodynamic diameter and b) zeta potential of lignin nanoparticles in pure water as a function of time.

was very stable in pure water and no specific aggregation occurred within 60 days (Figure 3a). The relatively high negative zeta potential, about -60 mV, induces sufficient electrical double layer repulsion between the particles to hinder aggregation (Figure 3b). Zeta potentials around -40 mV have been previously reported for other types of lignin nanoparticles.^{8,23} Wei *et al.* measured zeta potentials up to -91.5 mV for lignin nanoparticle dispersions at pH 11.¹⁰

The stability of the nanoparticle dispersions cannot be ascribed to the presence of THF in the system. GC-MS and ¹H-NMR results indicated that a negligible amount of THF was present in the final dispersions after dialysis (Supplementary Information). THF cannot generate repulsive forces between the particles. If entrapped inside the nanoparticles, THF would only reduce slightly –but not cancel– the Van der Waals attraction according to the small difference in dielectric constants and refractive indexes between THF (7.52 and 1.4, respectively) and lignin (about 2.4 and 1.6, respectively). On the other hand, excess of THF in the medium could make deprotonation of charges more difficult (smaller dielectric constant) and decrease the double-layer repulsion, making the system less stable. However, that effect is negligible for the traces of THF detected in the final nanoparticle dispersions.

To evaluate the sensitivity of the lignin nanoparticle dispersion to changes in its environment, the stability of the dispersion was also studied at different salt concentrations and pH. Figure

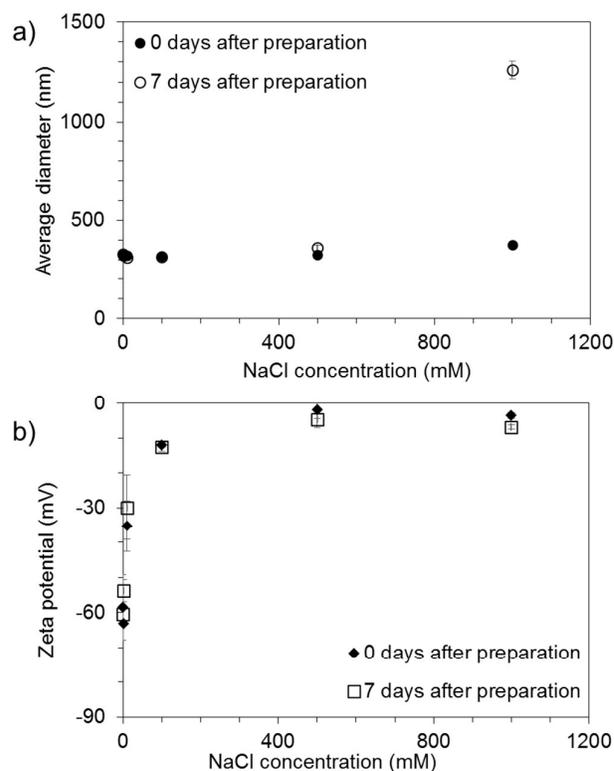


Figure 4. Effect of salt concentration on a) average hydrodynamic diameter and b) zeta potential of lignin nanoparticles.

4 shows the effect of NaCl on the nanoparticle size and zeta potential over a 7-day period. Although a clear reduction in the absolute value of the zeta potential was observed upon increasing NaCl concentration, the lignin nanoparticle dispersion was still stable at 500 mM NaCl, with no significant change in the average particle size after 7 days. However, particle aggregation occurred at 1 M NaCl, with an increase in average particle size 7 days after sample preparation (Figure 4a). These results are in agreement with the DLVO theory, which predicts the decrease in range of double layer repulsion between particles when salt is added to the dispersion.^{24,25} As a consequence, the van der Waals forces become dominant, and may eventually lead to particle aggregation. The decrease in the absolute value of the zeta potential when the salt concentration increased (Figure 4b) is due to the accumulation of Na⁺ counter ions around the particles and the consequent reduction in the thickness of the electrical double layer.

The average particle size of the lignin nanoparticles was observed not to depend on the pH at pH values between 4 and 12 (Figure 5a). The nanoparticle dispersion was stable for at least one week time within the given pH range, with no significant change of average particle diameter after 7 days. However, at pH below 4 the reduction in particle surface charge led to particle aggregation, which was observable after 7 days. At pH 13 the particles were observed to start dissolving as the colour of the dispersion turned yellowish. The dependence of the particle surface charge on the pH is apparent from zeta potential measurements (Figure 5b).

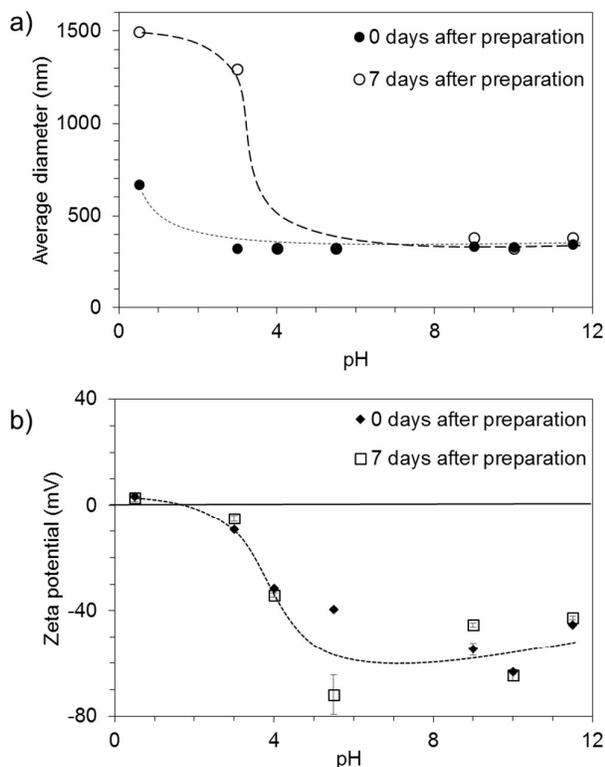


Figure 5. Effect of pH on a) average hydrodynamic diameter and b) zeta potential of lignin nanoparticles. The lines are only visual guides.

Protonation of charged groups at pH below 4 gave rise to a drastic decrease in the absolute value of zeta potential. The isoelectric point of the nanoparticles was around pH 2. The small reduction in absolute value of zeta potential at pH above 10 was due to the slight increase in ionic strength associated with the addition of NaOH to the dispersion for pH adjustment. Similar trends for pH-dependence of zeta potential of kraft lignin were observed by Dong *et al.*²³ These results correlate well with earlier findings regarding polymer particle stability and dispersion behaviour in increasing salt concentrations and pH changes.²⁶

From the results above it can be concluded that the lignin nanoparticle dispersion was very stable and rather insensitive to variations in pH from 4 to 12 and ionic strength up to 500 mM, thus facilitating industrial use. Considering its good colloidal stability, the lignin nanoparticle dispersion could be used in applications where a uniform distribution of the nanoparticles is required, for instance, in drug delivery, Pickering emulsions, wound healing and coating formulations. Understanding the relationship between the dispersion stability and salt as well as pH changes can also be used when programming nanoparticle systems that are desired to react in certain environments such as low pH or high salt concentrations. The effect of surface coating on the nanoparticle properties do also deserve further research.

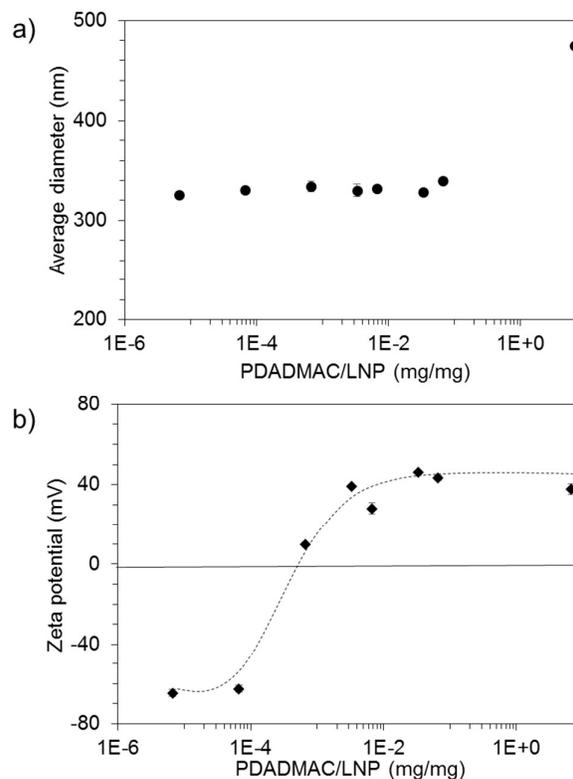


Figure 6. Effect of PDADMAC coating on a) average hydrodynamic diameter and b) zeta potential of lignin nanoparticles. The line is only a visual guide.

Particle surface modification

Lignin nanoparticles were coated by PDADMAC in order to demonstrate the potential surface functionalization possibilities. Figure 6 shows how the zeta potential of lignin nanoparticles changes from negative to positive values when the relative PDADMAC concentration increases in the coating solution. No change of the average particle size was observed, demonstrating that no particle aggregation took place during the particle coating process. As could be expected, the dispersion is stable, most likely due to electrical double layer repulsion between the particles as it is dominant in the case of high charge and low molecular weight polymers such as PDADMAC. This is due to slight overcompensation of the charge upon PDADMAC adsorption, which is common for polyelectrolyte adsorption on oppositely charged surfaces.²⁷ Additionally, steric repulsion created by the cationic polymer adsorbed on the particle surface may be present, further stabilizing the dispersion.

The highest PDADMAC concentration is observed to lead to higher average particle size. The larger particle diameter can be due to different adsorption conformation of the polymer. At high PDADMAC concentration the polymer may adsorb in a more extended conformation on the particle surface forming tails and loops as there is not enough space for flat adsorption.

PDADMAC was used as a model compound showing that the nanoparticles can be surface modified by simple polyelectrolyte adsorption. By changing the surface charge the affinity to certain surfaces can be enhanced. The results indicate that the surface of these lignin nanoparticles can be modified by coating. This may open up new research opportunities in the field of nanoscience. Considering medical applications, these particles could potentially be coated by silver or other substances to, for example, enhance the antimicrobial properties. Additionally, from the drug delivery point of view it would be interesting to investigate whether these particles could be modified so that they would obtain certain targeting properties inside biological systems such as human body.

In summary, earlier Qian et al. described a method for lignin nanoparticle preparation.⁷ This method was based on acetylation of lignin where relatively hazardous chemicals such as acetyl bromide was used. Furthermore, the nanoparticles were prepared utilizing drop-by-drop solvent exchange which leads to very dilute nanoparticle dispersions unless energy is used to evaporate water in addition to removing the THF after acetylation. In contrast, the new method described in this work is simpler and thus more environmentally friendly as no lignin acetylation is needed. One key issue allowing the simple particle preparation method is the structure of the extracted lignin raw material and the origin of the plant from which the lignin has been extracted. The lignin should be soluble in nonpolar solvents like THF to obtain spherical particles. Utilizing dialysis bag solvent exchange gives better control over the nanoparticle dispersion concentration than drop-by-drop method. Alternative filtration techniques could also be utilized to make drop-by-drop solvent exchange more efficient.

Experimental

Chemical characterization of lignin via ³¹P-NMR

The chemical composition of lignin was determined using ³¹P-NMR with a procedure based on the method by Granata and Argyropoulos.²⁸ For ³¹P-NMR analyses, lignin sample was accurately weighted (25 mg) and dissolved in 150 µl of N,N-dimethylformamide in a 10 ml vial. After total dissolution, 100 µl pyridine, 200 µl (0.05 M) of internal standard solution (ISTD) of *endo*-N-Hydroxy-5-norbornene-2,3-dicarboximide (e-HNDI, 0.01 mmol) in pyridine/CDCl₃ (1.6/1, v/v) and 50 µl of the Cr(acac)₃ solution (11.4 mg/ml) in pyridine/CDCl₃ (1.6/1, v/v) were added. Then, 200 µl of the phosphorylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane [P.R.(II)] was added drop-wise. Finally, 300 µl of CDCl₃ was added to the solution and a clear brown to black solution was achieved. Dissolution was aided by slow stirring with magnetic stirrer and gentle heating at 45 °C.

Freshly prepared samples were measured with ³¹P-NMR immediately at room temperature. Bruker 500 MHz NMR spectrometer was used for the measurement. Chemical shifts

are reported relative to the sharp signal (132.2 ppm) originating from the reaction between water and P.R. II. The following NMR parameters were used: 512 scans, 5 s pulse delay, 90° pulse, and line broadening 2.

Lignin nanoparticle preparation

Kraft process extracted lignin (LignoBoost) was provided by VTT Technical Research Centre of Finland. Lignin was dissolved in THF in various concentrations of 0.1, 1, 2, 5 and 10 mg/ml. Subsequently, each solution was filtered through a 0.45 µm syringe filter and introduced into a dialysis bag (Spectra/Por® 1 Standard RC Dry Dialysis Tubing, 6-8 kD, Spectrumlabs, USA) which was then immersed in excess of (periodically replaced) deionized water. Lignin nanoparticles were formed during the dialysis process, which took place for at least 24 hours under slow stirring in a fume hood. Negligible amount of residual THF remained in the nanoparticle dispersions after dialysis, as revealed by GC-MS and ¹H-NMR spectroscopy (Supplementary Information). In the experiments to study the effect of the pre-dialysis lignin concentration on the particle size at least 2 batches of each sample were prepared.

TEM

Transmission electron microscopy (TEM) was performed on a FEI Tecnai 12 (USA) operating at 120 kV. Water dispersions were applied on a carbon film support grid, incubated for 2 minutes and excess water was removed by blotting the side of the grid onto a filter paper. Imaging was done in bright-field mode with slight underfocus.

Particles dispersion characterization

Mean particle size and electrophoretic mobility of the lignin samples were measured using a Malvern Zetasizer Nano-ZS90 instrument (UK). Zeta potential data were obtained from electrophoretic mobility data by applying the Smoluchowski model. Measurements were repeated three times for each sample to check the reproducibility.

Particle dispersion stability

The stability of lignin nanoparticle dispersions was analysed by measuring the particle size and zeta potential at different times (up to 60 days) with a Malvern Zetasizer Nano-ZS90 instrument. The stability of the dispersions in different conditions of pH and salt concentration was also studied. The pH of the particle dispersions was adjusted to values ranging from 0.5 to 13 using HCl or NaOH solutions. Particle dispersions containing NaCl concentrations of 1 mM, 10 mM, 100 mM, 500 mM, and 1 M were also prepared at pH 7. The particle size and the zeta potential of lignin nanoparticle dispersions were measured on the day of preparation and 7 days later for samples at different pH and NaCl concentrations.

Particle surface modification

The surface of the lignin nanoparticles was modified by the adsorption of cationic poly(diallyldimethylammonium chloride)

(PDADMAC, Mw 100-350 kDa, Polysciences, USA). Lignin nanoparticle dispersions were gradually added into PDADMAC solutions at different concentrations. The extension of surface charge modification of the lignin nanoparticles was monitored by zeta potential measurements at different PDADMAC:LNP ratios.

Conclusions

In this work we demonstrated a simple, scalable method to prepare spherical lignin-based colloidal nanoparticles with average diameter between 200 and 500 nm. The nanoparticles, prepared from soft wood kraft lignin, showed predictable dispersion behaviour in varying pH and salt environments, being very stable at pH 4-10 and ionic strength up to 500 mM. Additionally, these nanoparticles were found to be surface modifiable through adsorption of oppositely charged polyelectrolytes. The nanoparticle production method is potentially up-scalable as THF could be recycled in the process via evaporation.

In the future, these nanoparticles could be used in a large range of applications like coatings, glues, composites, drug delivery, Pickering emulsions, wound healing, and antimicrobial materials. Further investigations towards various properties such as surface interactions and biological compatibility will be carried out.

Acknowledgements

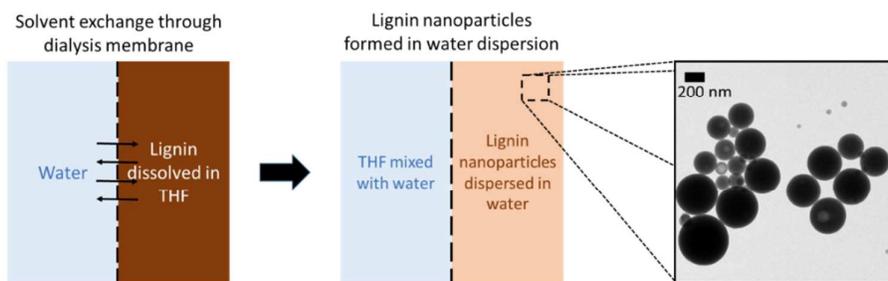
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A simple method to produce stable aqueous dispersions of spherical anionic or cationic lignin nanoparticles from soft wood kraft lignin was developed.