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Published in:
Green Chemistry

DOI:
10.1039/c8gc00064f

Published: 01/01/2018

Document Version
Peer reviewed version

Please cite the original version:
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Lignin Nano- and Microparticles as Template for Nanostructured Materials: Formation of Hollow Metal-Phenolic Capsules

Blaise L. Tardy1,2,*, Joseph J. Richardson1, Junling Guo3, Janika Lehtonen4, Mariko Ago5, Orlando J. Rojas1,4,6

Hollow polymeric, submicrometer-sized capsules show promise in applications ranging from water remediation to drug delivery, and the preferred method for their synthesis includes templating from sacrificial particles. Such particles are typically non-renewable and the process of selective dissolution used to produce the capsules often requires harsh and/or toxic solvents. Thus, there is a critical need to develop inexpensive, sustainable templates that can be dismantled under mild conditions. Lignins have recently been introduced as renewable precursors for the synthesis of solid particles and can favorably substitute solid particles based on petrochemicals (such as latex) or minerals (such as silica) precursors. Conveniently, widely available by-product streams of biomass processing can be used for the supramolecular assembly required for lignin particle formation. Herein, we introduce two common lignin sources (kraft and alkali lignins) as renewable and easily degradable particulate templates for the preparation of hollow polymeric capsules. The polymeric nanocoating, or wall of the capsules, was synthesized from renewable tannins, which self-assemble around the lignin particle template in the presence of metal ions, thereby coordinating into metal-phenolic networks (MPNs). The lignin template particles were easily degraded with aqueous or organic solvents under ambient conditions. Thus, the nanocoating assembly and template disassembly processes can be considered fully “green”. Finally, the synthesized hollow capsules were successfully demonstrated for water clean-up through the degradation of an organic dye, exemplifying a cost-effective and facile route for using environmentally friendly nanomaterials for environmental remediation.

Introduction

Polymeric nanocoatings hold unique promise for a variety of applications as they can selectively control interactions between the coated material and the surrounding environment. Alternatively, polymeric nanocoatings can be isolated by selectively removing the coated material, which acts as a template, yielding free-standing polymeric films useful for separation, catalysis, self-healing and drug-delivery, among others applications.1-4 When the nanocoatings are deposited on spherical particle templates, freestanding hollow “capsules” can be formed. In this case, the selective removal or etching of the underlying template is critical to the process as it requires a solvent that preferentially leaves the nanocoating intact.5 The final capsule morphology (shape, size, etc.) are determined by the detailed template geometry.6 It is often desirable to load the templates with functional cargo, where the nanocoatings retain the cargo in a concentrated form and prevent it from being released during template dissolution and capsule formation.7 Additionally, larger mesoporous structures such as inverted opals can be obtained via templated synthesis. Therefore, the appropriate choice of template is crucial for the preparation of functional templated polymeric materials such as hollow capsules. Desirable qualities for the templating particles include facile sourcing or synthesis, low-cost, tailorable surface chemistry and, importantly, no inherent toxicity. Moreover, the template and template etching molecules ideally should not be toxic as they can attach to the capsule walls during template removal or remain in solution. For example, organic templates such as polystyrene particles dissolve into individual polystyrene chains, which have been shown to be toxic to a variety of human cells.8,9 Similar issues arise for another common template material, silica, as it is often etched with hydrofluoric acid,10,11 which not only requires strict safety protocols for use, but also poses serious health risks.12,13 In a related manner, the template should also be easy to remove in terms of processing (simple dissolution) and versatility (susceptibility to a variety of etching solutions) so that a variety of polymeric nanocoatings can remain intact during dissolution, allowing
Herein, we introduce lignin nano- and microparticles as soft templates for the fabrication of metal-phenolic networks (MPN) capsules. Additionally, as templates, lignins offer the benefits of an easily controllable surface chemistry and also the possibility to tailor the solubility properties depending on the lignin source used for particles preparation. MPNs are an emerging class of “green” nanocoatings composed of phenolic molecules (often derived from plants) crosslinked with metal ions. The most common MPNs utilize Fe(III)-tannic acid chelation through the 1,2,3-benzenetriol (gallo) molecules on tannic acid, which allows for an interconnected nanofilm due to the dendritic and multivalent structure of tannic acid. Other phenolic molecules and metal ions can also be used to construct MPNs, thereby allowing for diverse applications to be realized, including catalysis, artificial-sporulation, bio-imaging, and drug delivery. The several reported examples of lignin particles loaded with therapeutics and active compounds (biocides and antimicrobials among others) suggests promise for new uses, such as templating, where lignin can provide significant synergies for the development of loaded MPN capsules. Here, we demonstrate that lignin particles act as an ideal template for MPN capsule formation, as they dissociate in given solvents depending on the type of lignin. Additionally lignins are rich in aromatics, which have been shown to interact well with tannins. The diffusion of the dissolved lignin across the nanostructured capsules is also favored due to the fact that it has a low molecular mass, and we study the dissolution process thoroughly as a function of pH or DMF fraction in water. We first deposited Fe(III)-tannic acid MPNs on the kraft lignins particles followed by their dissolution, which is crucial for the formation of nanostructured capsules. We also demonstrate the versatility of lignin particles as soft templates for the fabrication of nanostructured materials by forming MPN films in acetone around alkali lignin particles, which are solubilized in water to form free-standing MPN capsules. The formation of MPN capsules from lignin particles also exemplifies the possibility to choose solvents that comply with the concept of green processing.

Previous templates for MPN capsule formation have either required harsh, toxic solvents like tetrahydrofuran (THF), for dissolving polystyrene particles or chelating agents and low pH (for dissolving CaCO₃ particles), which can lead to the disassembly of the free-floating MPN films themselves. Template production has been relatively streamlined for many inorganic and organic templates, so any new template should be able to be modularly inserted into current production and experimental methods. Lastly, we demonstrate an unexplored environmental benefit of MPN capsules by using the inherent properties of MPNs for water clean-up. This is in contrast with previous reports, which mostly focus on the loading of active cargo such as therapeutics or catalytic nanoparticles. We demonstrate the exceptional ability of these capsules to catalyze the degradation of a model compound, the sodium salt of 4-(2-Hydroxy-1-naphthylazo)benzenesulfonic acid (orange II). Overall, we expect the sum of the results presented herein to further push the development of lignin particles and tannin-based structures as “green” nanostructured materials for environmental applications.
Figure 1. Schematic illustration of the formation of an MPN nanocoating on a lignin particle (1) using Fe(III) and tannins as building blocks for film (nanocoating) formation (2). The dissolution of the lignin particle template (3) results in hollow, high surface area MPN capsules (4).

Results and Discussion

I. MPN nanocoating preparation and subsequent dissolution of the sacrificial lignin particle templates. The lignin particles used herein were obtained by the aerosol flow reactor method. The method allows for the preparation of spherical particles as a dry powder with diameters ranging between 30 nm and several microns from virtually any lignin source. The aerosol flow reactor method is particularly relevant to the template-based preparation of functional capsules as active compounds (cargo) can be directly loaded during template formation. Additionally, the particles can also be separated by size for specific applications and suspended in aqueous or organic media. Herein, the majority of experiments utilized polydisperse lignin particles to establish a flexible, robust protocol for the formation of nanostructured Fe(III)-tannic acid MPN capsules of various sizes via lignin-based template assembly. Principally, particles with an average size of 1.9 µm were used, smaller fractions were also used with an average size of 330 nm (Figure S1).

Prior to the formation of the MPNs on the surface of the kraft lignin particles, the particles were washed at pH 9 to develop a reproducible surface charge (ζ = -42,6 ± 1,8) and to remove any residual, soluble lignin molecules. Furthermore, this washing step ascertained that the steps leading to the formation of the MPN coating were not affected by the release of lignins as a pH 9 buffer was used in the formation of the nanocoating used herein. Washing steps were performed by centrifuging the suspension (10000 rcf, 1 min) to form a particle pellet, followed by replacing the particle-free supernatant with a given solution. Initially, the suspension and pellet (after centrifugation) appeared light brown, with no aggregates visible to the naked eye in the suspension, which suggested the formation of a homogeneous particle dispersion (Figure 2a). The MPN coating was rapidly (<10 s) formed on the lignin particle templates. Briefly, Fe(III) solution was first added to the lignin particle suspension followed by addition of the tannins solution. As expected, the color of the suspension darkened within seconds after addition of the tannins, and turned into a vivid hue of purple upon further addition of HEPES buffer (pH 9), as the Fe(III)-tannin complex transitioned to the tris complex. The excess buffer, tannins, and Fe(III) were removed by washing the coated suspension three times with water. A single MPN coating process was sufficient to obtain capsules after lignin removal, but application of a second coating step (double coating) rendered the capsules tougher to the lignin solubilization process and made the capsules more robust to the centrifugation and separation steps. The double MPN coating process and washing cycles were rapid and only took a total of 20 minutes. The lignin particle suspension appeared slightly darker after MPN coating (Figure 2a), and due to the high polydispersity of the lignin particles (Figure 2b), the pellet itself had a color gradient with a very dark fraction corresponding to the smaller particles and a very brown fraction at the bottom corresponding to the larger particles sedimenting first (Figure 2a).

Upon selective removal of the lignin particle template by the addition of pH 12 buffer (sodium phosphate, 100 mM) or N,N-dimethylformamide (DMF), the supernatant rapidly became brown due to the dissolved lignin. After separation of the dissolved lignin from the capsules by centrifugation, the capsules were washed with DI water and the pellet, as well as the re-dispersed capsule suspension, were black (Figure 2a). Because of the small molecular weight of the lignins, a slow dissolution process was required to avoid excess osmotic pressure during dissolution, thus preventing the capsules from bursting. We found that the structural integrity of the capsules was conserved if the dissolution process was slightly slowed down, i.e., over several seconds (Figure 2c). The large polydispersity of the lignin particles translated to the capsule
suspension, as the capsules had a similar polydispersity to the particles, as expected for templated polymeric capsules. The dissolved lignin could be isolated after formation of the capsules and reprecipitated using concentrated hydrochloric acid. In this process the collected lignin amount corresponded to 87% of the original lignin mass. The difference in mass corresponded to dissolved lignin lost during the particles preparation steps. Additionally, as can be seen in Figure 2c, some capsules appeared fused, which resulted from the coating of lignin particles aggregates. This highlights that the redispersion of lignin nano- and microparticles from the dry state into a suspension with less aggregation may require severe redispersion steps such as high energy tip sonication.

Figure 2. (a) Appearance of a suspension of Kraft lignin particles during the MPN coating process and after dissolution of the lignin particle templates. (b) Lignin particles coated with MPNs as observed by bright field microscopy before template removal and (c) after removal of the lignin template with a solution of sodium phosphate at pH 12. (d) Time-lapse images highlighting the dissolution of a single lignin particle and stabilization of a hollow MPN capsule. Scale bars are 20 μm.

We further analyzed the dissolution process of MPN-coated Kraft lignin particles as a function of the solvency (pH or DMF fraction) by measuring the absorbance of the supernatant of 0.25 mg mL⁻¹ MPN-coated lignin particles. High pH and aprotic polar solvents (namely DMF, THF or ethanol) have been commonly used for the dissolution of Kraft lignins. We evaluated DMF because DMF was the solvent used for the synthesis of the particles and is thus favorable for recycling lignins as suggested in Figure 1. Pure DMF and buffered, aqueous, medium at pH 12 led to complete dissolution of the lignin particles (Figure 3). The spectra were significantly different after complete dissolution of the lignin at pH 12 and in DMF because of the formation of phenolates at pH 12. A pH of 10.5 marked the onset of lignin particle dissolution, which corresponds well with the hydrolysis (i.e. deprotonation) of phenolic’s alcohol groups to phenolate, rendering the lignin soluble in the process (Figure 3a). Interestingly, although the pKa of phenols is around ca. 10, complete dissolution of the lignin particles did not occur below pH 12. This is because the pKa of lignins’ phenols is higher, as reported previously. Other phenolic acids are present and, also, a higher degree of hydrolysis was required for dissolution of larger lignins. Additionally, lignin particle dissolution took longer at pH < 12. It is worth noting that the undissolved suspension did not have a specific absorbance, highlighting that the undissolved particles principally reflect light by scattering (i.e., non-specifically) (Figure 3a inset).

Adding small amounts of water to DMF significantly reduced the dissolution of the Kraft lignin particle templates. At a DMF:water ratio of 3:1, hollow capsules could be obtained after letting the solution incubate for at least an hour (data not shown), whereas at a 1:1 ratio the remaining lignin could clearly be observed by the presence of a brown hue under brightfield microscopy (Figure S2). This highlights the versatility of different lignins for use as template particles for the formation of nanostructured materials. Whereas the formation of phenolates is the principal drive behind dissolution of the lignin particles at higher pH, solubilization of non-polar segments of lignin is the principal reason for dissolution of lignin in DMF, and therefore the presence of DMF resulted in less hydrophilic fractions of lignin becoming dissolved. Similar fractionation has been reported by using different mixtures of ethanol and water. Importantly, MPN capsules could also be formed from lignin particles formed from alkali lignin. The MPN coating process was conducted in acetone, and the alkali lignin particles were dissolved in water (Figure S3). The capsules formed from alkali lignin particle templates appeared slightly rougher by SEM. This is possibly a result of the different processes occurring during the formation of the capsules in this case, which occurred somewhat simultaneously as the template dissolved. Although we demonstrate the generation of nanostructured capsules from two types of lignin particles, we believe that other nanostructured architectures, such as MPN capsules or layer-by-layer capsules, could be generated from the broad library of lignins currently available.
Figure 3. Dissolution of lignin from MPN-coated lignin particles as a function of (a) pH and (b) DMF fraction in water. In (a) the inset highlights the suspensions UV-Vis adsorption (red). It can be noted that the suspension made of lignin particles absorbs light non-specifically due to scattering as the absorption spectra is homogeneous.

II. Morphology of MPN capsules and evaluation of residual lignin.

The double MPN coating resulted in capsules with a double layer thickness of 20 nm (minimum AFM height in Figure 4c resulting from the shell of the capsule collapsing onto itself) and thus the thickness of a single layer was estimated to be 10 nm (Figure 4a-c). This corresponds well with the thickness reported for MPN capsules formed on latex particles. The capsules described in Figures 4a,c and S3 were obtained from a polydisperse sample whereas the capsules described in Figure 4b were obtained by preparing capsules from a sample containing smaller lignin particles (fraction 5 as described by Ago et al., corresponding to an average particle size of 330 nm as measured by dynamic light scattering). The thickness of the capsules was constant for the capsules sizes ranging from 40 nm to several microns (Figures 4a-c and S3), suggesting that the MPN coatings were uniformly deposited on every particles, regardless of their size. The capsules were smooth and collapsed into a folded structure for capsules larger than 100 nm, as is usually observed for thin film polymeric hollow capsules (Figure 4a,b and Figure S4). The smaller dried capsules did not collapse, likely because of their higher thickness-to-diameter ratio. The particles dissolved in 1:1 DMF water yielded capsules with a spherical structure in the dry state. Additionally, the capsules appeared more rigid when DMF was used to dissolve the lignin particles (Figure S5), possibly as a result of the MPN capsules becoming more rigid by dehydration in DMF.

Figure 4. Atomic force microscopy images of hollow MPN capsules obtained from a double coating process with sizes of (a) ca. 450 nm and (b) 40 nm. The capsules were obtained from a polydisperse sample of lignin (template) particles and a size-fractionated sample (fraction 10 and 5 reported in Ref.34, corresponding to average sizes of 1.9 µm and 330 nm, respectively and after collapse on the supporting surface, upon drying. (c) profilometric analysis obtained from (a) (top) and (b) (bottom). (d) SEM micrograph of collapsed MPN capsules. The core was dissolved at pH 12 (sodium phosphate, 100 Mm). The folds observed are typically observed for hollow capsules with a thickness significantly smaller than their diameter.

We studied the effect of the lignin template dissolution conditions on MPN capsule degradation and on the presence of residual lignin. As can be seen in Figure 5a, the capsule suspension had a spectrum similar to the MPN coating obtained on a planar substrate, with the presence of a broad peak at 570 nm corresponding to the chelated Fe(III) (Figure...
5a). The capsules obtained at pH 12 and in DMF had a similar spectra, whereas the capsules obtained in 1:1 DMF:water had a significantly higher non-specific adsorption and also less defined peaks (Figure 5a) due to the residual lignin. All of the different capsule suspensions lost the broad specific peak at 570 nm upon addition of acids due to the dissociation of the MPN (Figure 5b). Importantly for MPN capsules suspension formed from alkali lignin or kraft lignin particles, no significant peaks corresponding to residual lignins could be observed (Figure 5b and S2a). The MPN capsules had relatively fast degradation kinetics at pH 3, similar to previous reports (Figure S6). Interestingly, when the capsules obtained by dissolving lignin in 1:1 DMF:water were degraded with acids, a clear brown suspension with objects observable by the naked eye were produced, which under the microscope appeared to be aggregates of single component lignin capsules (Figure 5b inset). These capsules are speculated to consist of the fraction of lignin having a higher M₇₈₈, different inter-unit linkages, or with a more apolar chemical makeup, which remained after dissolution of the other lignins composing the template. This lignin fraction either migrated to form a shell during the dissolution process or highlights that the flow aerosol method yields to less hydrophilic lignins on the outer shell of the formed lignin particles.

Figure 5. UV-Vis absorption spectra from (a) MPN capsules obtained at different degradation conditions of the lignin microparticles and (b) 5 min after degradation of the chelated MPN using HCl (100 mM).

III. MPN capsules for water clean-up. We studied the potential of the “all-green” MPN capsules for water remediation. Besides their negligible toxicity, the removal of the lignin core to form capsules resulted in hollow structures that can be easily kept in suspension or separated by sedimentation over the course of several hours of centrifugation or filtration cycles. Furthermore, the free-floating capsules had a significantly higher relative amount of Fe(III) available for the Fenton reaction. Also, the relatively large size of the capsules made them easily processable and safe for such applications, while keeping a highly accessible high surface area with access to the MPN shell from both inside and outside the capsules as MPN shells show high permeability to small molecules. Furthermore, the products of the capsules consisted principally of tannins and a small amount of Fe(III) (97% and 3%, respectively, as estimated from XPS), suggesting that the potential negative environmental effects and hazards for human consumption would be negligible upon degradation.
Because the capsules contained chelated, stable Fe(III), we investigated their use as catalysts for Fenton reactions. Fenton-catalyzed reactions are efficient and low cost with few potential hazardous side effects, and can be used to process and remove organic contaminants.6,57 Previously, Fe(III) has been immobilized onto collagen fibers to form heterogeneous catalysts for the Fenton reaction, and the collagen fibers prevented the release of excess metal ions into the treated water. Heterogeneous catalysis using immobilized, chelated, Fe(III) minimizes Fe contaminants released during the Fenton reaction when compared with the homogeneous Fenton reaction, occurring with free Fe ions equilibrated in solution.57,58 Herein, we demonstrate that the high surface area of the Fe(III) crosslinked capsules allowed for the Fenton reaction to occur in deionized water or under mildly acidic conditions.

The Fenton reaction occurs in the presence of hydrogen peroxide (H₂O₂) and sunlight, which in this experiment was artificially simulated using a UV-light source. We used a UV chamber at a fixed wavelength of 254 nm to study the potential of MPN capsules as catalysts for the Fenton reaction. MPN capsules have previously been demonstrated as catalysts for the degradation of H₂O₂ into reactive species, however MPN capsules can also be degraded in the presence of a large amount of H₂O₂.55 As expected, the MPN capsules formed herein degraded rapidly in the presence of higher concentrations of H₂O₂ (50 mM) at pH 6 (Figure S7). Even at higher concentrations of H₂O₂, at pH 6 the Fenton kinetics were only mildly faster in the presence of MPN capsules (data not shown). Nevertheless, at lower H₂O₂ concentrations the capsule stability improved significantly (Figure S7), and when the Fenton reaction occurred in the absence of buffer, the capsules rapidly degraded with proportionally faster degradation kinetics of orange II (Figures S7 and S8). This degradation is likely the result of the acidification process occurring during the Fenton reaction from the measured native pH of orange II solution (5.8) to a pH below 4 after the reaction. Therefore, we explored the catalytic activity of MPN capsules at pH 4 and 4.5, where the capsules were stable in the absence of H₂O₂ and catalyst by the Fenton reaction could be studied. At pH 4 and 4.5 the degradation of orange II occurred with considerably faster kinetics in the presence of capsules. In the control experiments in the absence of MPN capsules, the signal of 0.15 mM orange II (absorbance at 484 nm) only decreased by ca. 20%, whereas the signal decreased by more than 80% in the presence of capsules obtained from 0.5 mg of lignin particles (Figure 6 and S8). Importantly, the decrease in the specific absorption peak (484 nm) and in the 400 to 600 nm band measured by UV-Vis highlight the initial degradation stages of Orange II (Figure S10). The complete degradation of Orange II occurs over several oxidative steps during which oxidized aromatics are formed and finally small hydrocarbons, thereby acidifying the solution.59 These results suggested that the MPN capsules acted as efficient catalysts for the degradation of orange II with minimal amounts of H₂O₂ in mildly acidic conditions. Additionally, minimal quantities of Fe were released along with the non-hazardous release of tannins.
Preparation of suspensions of MPN-coated lignin particles and subsequent preparation of MPN capsules suspensions: The nano- and microparticles were dispersed in deionized water (kraft lignin) or acetone (alkali lignin) at concentrations ranging from 0.1% to 1%. The dispersions were homogenized by using several cycles of vortexing and low power ultrasonication. In the case of the kraft lignin particles, the solvent was exchanged to a pH 9 solution buffered with HEPES (20 mM). Solvent exchange process and washing steps were performed by centrifuging the particle suspension at 10000 rpm for 1 min using an Eppendorf Minispin device and then replacing the supernatant from the formed pellet with the adequate solvent. In a typical MPN formation process using the kraft lignin particles, the homogenized aqueous suspension (1 mL, 1%) was washed 4x using pH 9 HEPES buffered solution (20 mM); following this, the solvent was replaced by water (750 μL) and 10 μL of Fe(III) solution (0.1 mg mL⁻¹) was mixed into the suspension followed by mixing 10 μL of tannin solution (0.4 mg mL⁻¹). The solution rapidly became darker and the complexes formed were stabilized by addition of 750 μL HEPES solution (pH 9, 20 mM). This process was repeated twice and the solvent was replaced by water prior to dissolution of the core of the obtained MPN-coated lignin particles, i.e., dissolution of lignin in order to obtain hollow MPN capsules. The dissolved lignin was removed by washing the MPN capsules suspension 3x; following this, the suspension was washed 3x using deionized water to obtain the final, suspended capsules. For the systems with alkali lignin particles, the process was the same as described above using fraction 8 (1050 nm average size) as previously described, but the initial lignin suspension as well as the tannins and Fe(III) solutions were prepared in acetone and the MPN film was the result of a one step coating procedure.

Bright field and scanning electron microscopies: Bright field micrographs were obtained using a Leica ICC 50 camera mounted on a Leica DM750 with an oil immersion objective (100x magnification). For scanning electron microscopy, substrate immobilized capsules were obtained by dip coating suspensions onto poly(ethylene imine) coated silicon wafers. Briefly, the silicon wafers were cut into pieces of ca. 1 x 1 cm² and then dipped into a solution of 0.1 % of PEI (MW ~ 30 kDa). The wafers were then washed by dipping into DI water and directly dipped into the suspension of MPN-coated particles, Lignin particles or MPN capsules. The morphology of the capsules was examined using a field emission scanning electron microscope (FE-SEM) (Zeiss SigmaVP, Germany) operating at 1.6 kV and a working distance of 3 mm. The samples were sputtered with Pt/Pd alloy (4 nm).

Atomic force microscopy: The substrate immobilized capsules were prepared as for SEM observations and imaged on a MultiMode™ Scanning Probe Microscope (Digital Instruments, Inc., USA) in intermittent contact mode using a cantilever with an 8 nm radius spherical tip (spring constant of 40 N/m and a resonance frequency of ca. 260 kHz).

UV-Vis spectroscopy: The absorbance of the solutions was recorded by using a Shimadzu UV-2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) in the range of 250-800 nm. All experiments were carried at room temperature.

Dissolution of lignin particles to form MPN capsules as a function of solvent mixtures: Buffered solutions were prepared at 100 mM and given pH using Na-carbonate (for solutions of pH between 9 and 11) or Na-phosphate (for solutions above pH 11). Mixtures of DMF and water were prepared using micropipettes. 15 min after exposure of a 0.5 mg of MPN-coated kraft lignin particles suspension to 2 ml of the test solution, the particles were centrifuged and the supernatant was separated from the pellet and directly measured.

Degradation of MPN capsules: The capsules were suspended in the respective solvent and their absorbance was directly measured by UV-Vis in order to prevent potential sedimentation. The same suspensions were measured after exposure to the solution dissolving the MPN network.

Catalytic assays: The experiments were conducted using quartz cuvettes. 3 mL of orange II (concentration 0.15 mM) in the appropriate solution (i.e. water, sodium phosphate pH 6 50 mM, sodium acetate pH 4 or 4.5 50 mM) was added to each cuvette. 50 μL of capsule suspension (corresponding to 0.5 mg of initial lignin particles mass) and H₂O₂ (to achieve a concentration of 2.5 mM) were then added and the solution was thoroughly mixed. The cuvettes were placed into a UV chamber (UVITEC Cambridge) with wavelength 254 nm. The absorbance of the solutions was measured at given intervals with a Shimadzu UV-1800 spectrophotometer at a wavelength of 484 nm. The absorbance for samples with capsules and H₂O₂ in buffer (no Orange II) were also measured and subtracted from the results to eliminate the contribution to the absorbance from the capsules. Data obtained at pH 4, as described in Figure 6, were normalized to concentration using a linearly fitted calibration curve ( [Orange II] (mM) = Absorbance x 18.6⁻¹).

Conclusions

We demonstrated the use of lignin nano- and microparticles as templates for the formation of nanostructured MPN capsules with minimal processing steps. We thoroughly investigated the dissolution of the lignin template particles as a function of the solvent type. We find that a DMF fraction above 75% or a pH of 12 led to effective dissolution of the lignin template and that no residual lignin could be observed after dissolution in those conditions. The resultant capsule morphologies observed are typical of previously reported MPN capsules synthesized from other templates, further supporting the potential of lignin particles as templates to be modularly inserted into the formation process of hollow superstructures by templated assembly. Finally, we introduced MPN capsules as catalysts for the degradation of organic residues using the Fenton reaction for the first time, and we demonstrated that the degradation rates are highly improved in mildly acidic conditions in the presence of MPN capsules. Importantly, although lignin particles are promising materials, there are still few studies on their key characteristics; herein we analyzed the stability and degradability of the tested types of lignin particles. Additionally, since MPN nanocoatings form...
ubiquitously on precursor supports, the findings demonstrated herein are also directly applicable to lignins particles formed via any other process. Furthermore, despite lignins complex molecular architectures we demonstrate that the surface of lignin particles can be coated uniformly and homogeneously. More complex morphologies such as inverted opals or mesoporous architectures can be envisioned. Lignins’ worldwide abundance, versatility in chemical functionalities, and low/non-toxicity to humans make them an interesting material as building blocks for structured materials. This is particularly true as nanometer and micrometer sized particles have remarkably similar physico-chemical properties, which is not the case for many metal-based particles. Additionally, the use of lignins for higher end applications is clearly supported by growing socio-economical concerns pointing to the need of entering a circular economy. Indeed, lignins are naturally the result of plant-based carbon capture and thus their use is positive when considering carbon neutrality.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
We are grateful for the support of the Academy of Finland through funding of the SIRAF Project, the Center of Excellence “Engineering of Biosynthetic Hybrid Materials Research”, HYBER (2014-2019) and funding support from NordForsk under the Project “High-Value Products from Lignin”.

Notes and references


