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FULL PAPER

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Fungicide-loaded and biodegradable xylan-based nanocarriers

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Abstract

The delivery of agrochemicals is typically achieved by the spraying of fossil-based polymer dispersions, which might accumulate in the soil and increase microplastic pollution. A potentially sustainable alternative is the use of biodegradable nano- or micro-formulations based on biopolymers, which can be degraded selectively by fungal enzymes to release encapsulated agrochemicals. To date, no hemicellulose nanocarriers for drug delivery in plants have been reported. Xylan is a renewable and abundant feedstock occurring naturally in high amounts in hemicellulose - a major component of the plant cell wall. Herein, xylan from corncobs was used to produce the first fungicide-loaded xylan-based nanocarriers by interfacial polyaddition in an inverse miniemulsion using toluene diisocyanate (TDI) as a crosslinking agent. The nanocarriers were redispersed in water and the aqueous dispersions were proven to be active *in vitro* against several pathogenic fungi, which are responsible for fungal plant diseases in horticulture or agriculture. Besides, empty xylan-based nanocarriers stimulated the growth of fungal mycelium, which indicated the degradation of xylan in the presence of the fungi, and underlined the degradation as a trigger to release a loaded agrochemical. This first example of crosslinked xylan-based nanocarriers expands the library of biodegradable and biobased nanocarriers for agrochemical release and might play a crucial role for future formulations in plant protection.

KEYWORDS

agriculture, emulsion polymerization, hemicellulose, nanocarrier, xylan

1 | INTRODUCTION

Xylan is the second most abundant plant-polysaccharide on earth and can be extracted from lignocellulosic biomass, which is generated in billions of tons annually as an industrial byproduct of agriculture and forestry.[1,2] The biopolymer belongs to the class of hemicelluloses and is a major component (25-35% dry mass) of the plant cell wall. Naturally, hemicelluloses form together with lignin a branched matrix that embeds the cellulose nanofibrils. This natural composite material is referred to as lignocellulose and is essential for the structure and toughness of plant tissue.[2] Industrially, xylan is valorized mainly by the production of the low-calorie sugar replacement xylitol or in various biorefineries for biofuel production without previous isolation from biomass.[1,3,4] Hence, in comparison to cellulose that finds numerous large-scale applications such as in the article or the tissue industry, hemicellulose and xylan are significantly less used until now. The reasons for this might be the complex and heterogeneous molecular structure of the polysaccharides

and the broad molecular weight distribution (10000-40 000 g/mol) depending on the plant origin.[2] Characteristic structure for xylans is a β(1→4) glycosidically linked xylose backbone decorated with various amounts and types of side groups. Depending on the plant, the backbone can be acetylated or is functionalized partially with mono- and oligosaccharides composed of for example, glucuronic acid and arabinofuranose. Likewise, linkages to lignin-derived moieties such as *p*-coumaric, coniferic, or sinapic acid can occur. These side groups lead to an amorphous structure and strongly determine the solubility of the polymer.[2,5,6]

As xylan is a renewable, biocompatible, and relatively cheap feedstock, it is of high interest as a carrier material for advanced drug delivery. To date, most investigations used xylan hydrogels to load drugs and very few studies dealt with the encapsulation of pharmaceuticals.[7–12] Aside from applications in medicine, xylan is ideal as a carrier agent in agrochemical formulations due to its plant origin. However, to the best of our knowledge, no studies have reported the formation of pesticide-loaded xylan nanocarriers yet.

A powerful tool to generate hollow nanocarriers is the interfacial polymerization of toluene diisocyanate (TDI) in an inverse miniemulsion.[13] The stable nanodroplets act as a template where the crosslinker can react at the interface with various nucleophiles like hydroxyl groups or amines, and core-shell structures are obtained that can be loaded with versatile active ingredients. Recently, our group produced TDI-crosslinked nanocarriers from lignin sulfonate or lignin-containing biomass extracts, which released the encapsulated drug only on-demand in the presence of lignin-degrading enzymes.[14,15] This approach was extended herein to prepare xylan-polyurea/polyurethane nanocarriers for the encapsulation of the broad-spectrum fungicide pyraclostrobin (Figure 1). The crosslinking of biopolymers by the reactive TDI is a straightforward approach to prepare nanocarriers with a core-shell structure that can be loaded with cargo as long as it does not react with the isocyanate groups during the crosslinking reaction. The resulting urethane bonds further stabilize the polymer network through hydrogen-bonding. The nanocarrier dispersions obtained are based on a degradable and biomass-derived feedstock; we are convinced that the developed formulation is a powerful tool for the encapsulation of various agrochemicals (pesticides or fertilizers) which could help to increase the sustainability of plant protection.[6]

2 | EXPERIMENTAL SECTION

2.1 | Materials

Xylan from corncobs (Art. 8659.2) and beechwood (Art. 4414.2) was obtained from Carl Roth. Toluene diisocyanate (TDI) (98%), sodium dodecylsulfate (99.9%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%) and endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (98%) were purchased from Sigma Aldrich. Pyraclostrobin was bought from Toronto Research Chemicals. All materials were used without further purification. Poly[(ethylene-*co*-butylene)-*b*-(ethylene oxide)] (=P[E/B-*b*-EO]) consisted of a poly(ethylene-*co*-butylene) block with a molecular weight of (*Mw* = 3700 g/mol) and poly(ethylene oxide) block of (*Mw* = 3600 g/mol). The surfactant was synthesized according to the protocol of Schlaad *et al.*[16]

2.2 | NMR spectroscopy

^{31}P NMR spectroscopy was performed at a Bruker AVANCE spectrometer at 300 MHz. Xylan's hydroxyl groups were quantified after derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in a $CDCl_3$-pyridine-d_5 (4/6 v/v ratio) mixture in the presence of the internal standard endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide and the relaxation agent Cr(III)acetylacetonate using the method of Balakshin *et al.*[17]

2.3 | Dynamic light scattering

The hydrodynamic diameters of the nanocapsules was measured by DLS with a NICOMP 380 submicron particle sizer (Nicomp Particle Sizing systems) at a fixed angle of 90° and a laser diode running at 635 nm. The sample was diluted to a concentration of 0.01 wt% with water or cyclohexane before measurement.

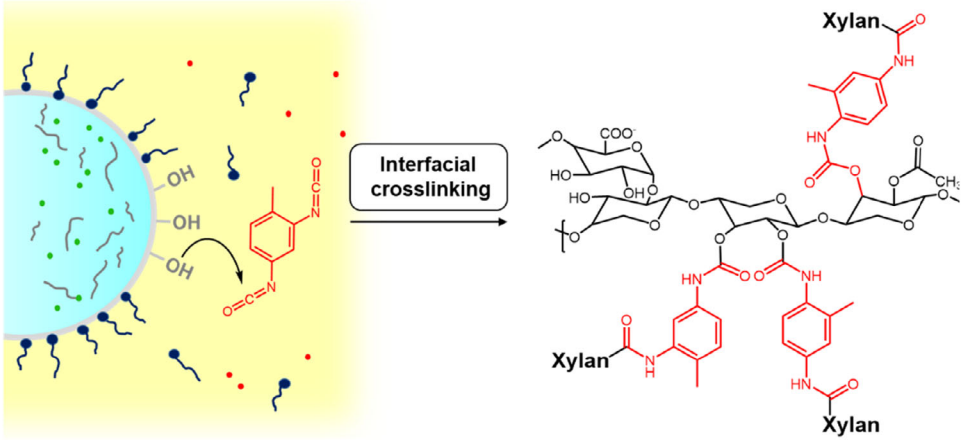


FIGURE 1 Crosslinking of xylan at the droplet interface to generate nanocarriers with core shell structure

2.4 | FTIR spectroscopy

After crosslinking the dispersion was washed twice with cyclohexane and then dried in vacuo. The solid obtained was analyzed with a Nicolet iS10 FTIR spectrometer with Vertical ATR Accessory. Spectra were recorded between 600 and 4000 cm^{-1}.

2.5 | Scanning electron microscopy

The morphology of the nanocarriers was examined with a Gemini 1530 (Carl Zeiss AG, Oberkochem, Germany) scanning electron microscope (SEM) operating at 0.35 kV. The samples were prepared by casting a diluted and purified nanocarrier dispersion on silicon wafers.

2.6 | Size exclusion chromatography

The molecular weight of the xylans was determined using a 0.07 M Na_2HPO_4 solution as an eluent. The measurement was performed at an Agilent 1100 Series (Agilent Technologies 1260 Infinity) as an integrated instrument, including a PSS Suprema linear XL column at 30 °C, a RI detector at a flow rate of 1 ml/min.

2.7 | Encapsulation efficiency

To quantify the amount of loaded cargo, the dispersion was transferred to water without prior purification and then filtered through an Amicon ultra centrifugation filter (MWCO: 3000 Da) to separate the capsules from the aqueous supernatant. Pyraclostrobin was detected in the aqueous solution by HPLC.

2.8 | High pressure liquid chromatography

Before measurement, all samples were passed through a 0.2 µm filter and analyzed by Agilent Eclipse Plus RP18 HPLC system using THF: water/ 0.1%wt as mobile phase and a TFA-gradient. The injection volume was 10 µl and the column temperature maintained at 20 °C. The analysis was performed at a flow rate of 0.2 ml/min with the UV detector at 280 nm for pyraclostrobin.

2.9 | Germination assay

Conidia of *Phaeomoniella chlamydospora* (Pch) and *Phaeoacremonium minimum* (Pmi) from 18-day-old agar plate cultures were harvested. After centrifugation at 4000 rpm for 10 min, the conidia were re-suspended in YMG-medium optaining a concentration of $1{\cdot}10^5$ spores per milliliter. The degradation test was carried out in 96-well microtiter plates (Greiner Bio-One GmbH, Frickenhausen). One microliter of the nanocarrier dispersion (10 mg/ml; without loading, 1 wt% SDS solution as continuous phase) was then added to 200 µl MM1G medium containing 10.000 spores. After an incubation time of 72 h at 27 °C, the optical density was measured at a wavelength of 600 nm (Benchmark Plus Microplate reader, BioRad, Munich). Tests were conducted in triplicates. As references, the germination of conidia in YMG medium (ideal growth conditions), in MM1G medium (minimal growth conditions), and the germination of spores in MM1G medium containing an additionally 1 µl SDS solution were taken.

The media had the following composition: YMG: 10.00 $g{\cdot}L^{-1}$ malt extract, 10.00 $g{\cdot}L^{-1}$ glucose, 4.00 $g{\cdot}L^{-1}$ yeast extract, pH 5.5; MM1G: 1 $g{\cdot}L^{-1}$ glucose, trace elements, pH 5.5.

2.10 | Preparation of xylan nanocarriers

Xylan (156 mg, 2.85 mmol OH) extracted from corncobs was dissolved at 60 °C in 1.3 ml dimethyl sulfoxide (DMSO). To load the nanocarriers, pyraclostrobin (20 mg) was added additionally to the xylan solution in DMSO. The mixture was then added to 9.6 ml cyclohexane containing 100 mg of the surfactant P(E/B-*b*-EO). To generate

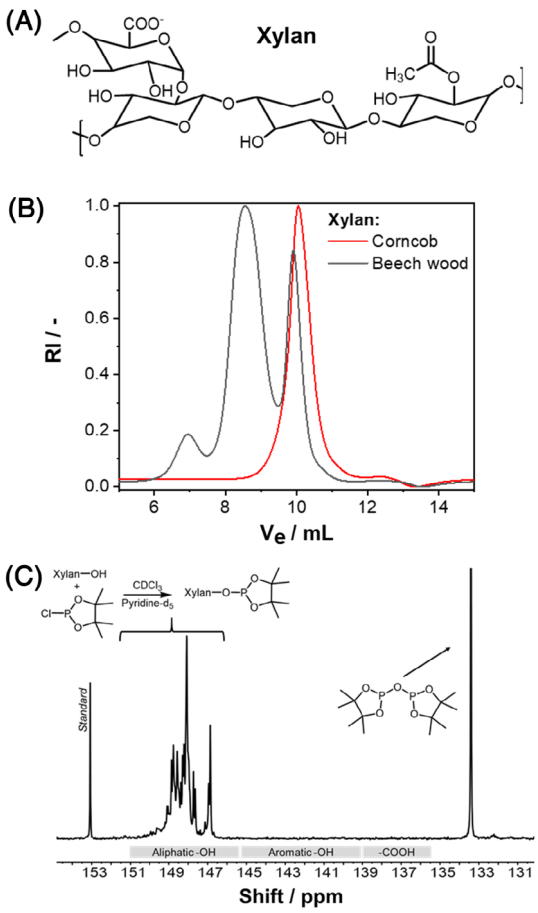


FIGURE 2 (a) Molecular structure assumed for the herein used corncob xylooligosaccharides (Carl Roth, Product number: 8659.2). (b) SEC elugram in 0.07 M Na_2HPO_4 solution of xylans isolated from corncob or beechwood. (c) ^{31}P-NMR spectrum of corncob xylan after phosphorylation according to the method of Balakshin *et al.*[17]

a miniemulsion, the two-phase mixture was ultrasonicated (Branson Digital Sonifier W450-D, 1/2″ tip, 70% amplitude, 3 min, 20 s ultrasound followed by 10 s\ pauses) while cooling with ice water. The two-phase mixture was stirred at 25 °C and was then ultrasonicated to generate a miniemulsion. To achieve efficient crosslinking, no catalyst was used as the interface accelerates the interfacial crosslinking as demonstrated for various other interfacial reactions in miniemulsion previously.[18] Finally, a cyclohexane solution containing P(E/B-*b*-EO) (57 mg surfactant in 6.4 ml) and toluene diisocyanate (TDI, 123 µl, 0.86 mmol) was added dropwise via a cannula while stirring (1000 rpm). The interfacial polyaddition reaction between xylan's nucleophilic hydroxyl groups and the isocyanate groups of TDI was performed overnight at room temperature. The reaction was allowed to process for ca. 12 h at 25 °C and 250 rpm. The obtained dispersion did not phase separate for several weeks. To remove excess P(E/B-*b*-EO), the dispersion was centrifuged at 1400 g and resuspended in pure cyclohexane twice. The dispersion was then added dropwise to an aqueous solution containing the anionic surfactant sodium dodecyl sulfonate (SDS, 0.1 wt%) under sonication and shaking. Then the cyclohexane was evaporated under vigorous stirring overnight to yield the final aqueous dispersion of the nanocarriers typically with solid contents of ca. 1 wt%.The dispersions were characterized by DLS and SEM microscopy regarding their size distribution and morphology.

3 | RESULTS AND DISCUSSION

Xylan (Figure 2(a)) is a major component of hemicellulose and represents the third most abundant biopolymer on Earth. The polymer is composed of β-1,4-linked xylose with side branches of α-arabinofuranose and α-glucuronic acids and is found in the secondary cell walls of dicots and all cell walls of grasses. To find a xylan feedstock that is suitable for nanocarrier preparation, we characterized two commercially available xylans isolated either from corncobs (Carl Roth, product number: 8659.2) or from beechwood (Carl Roth, product number: 4414.2). Both materials significantly differed in their solubility properties and in their molecular weight. When adding beechwood xylan to DMSO a yellowish, viscous gel was formed, whereas corncob xylan yielded a clear solution with comparably lower viscosity. As the latter carbohydrate had a lower molecular weight distribution according to SEC (Figure 2(b)), we assume that a less viscous solution was formed due to a limited ability to form chain entanglements. The emulsification of viscous solutions requires strong sonication or shear forces as the droplet break down needs a high-energy input. For this reason, corncob xylan was preferred as a starting material for the nanocarrier preparation. For further characterization, we quantified the hydroxyl groups of the xylan with ^{31}P-NMR spectroscopy after derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane according to the method of Balakshin *et al.* (Figure 2(c)).[17] After the derivatization, ^{31}P NMR can be used to calculate the number of aliphatic (or aromatic or acidic OH-groups) in the spectrum as the ^{31}P NMR shift is characteristic to each OH-group (typical signals are detected between ca. 150–130 ppm and are compared to an internal standard of known molarity at ca. 153 ppm, compare Figure 2(c), note: also the signal of the dimeric form of the dioxaphospholane at ca. 133 ppm is detected which is present as a typical impurity in the commercial product which does not correspond to the product distribution). As only signals between 153 and 145 ppm were detected, we assume that the herein-used corncob xylan is purely carbohydrate-based, containing no aromatic side

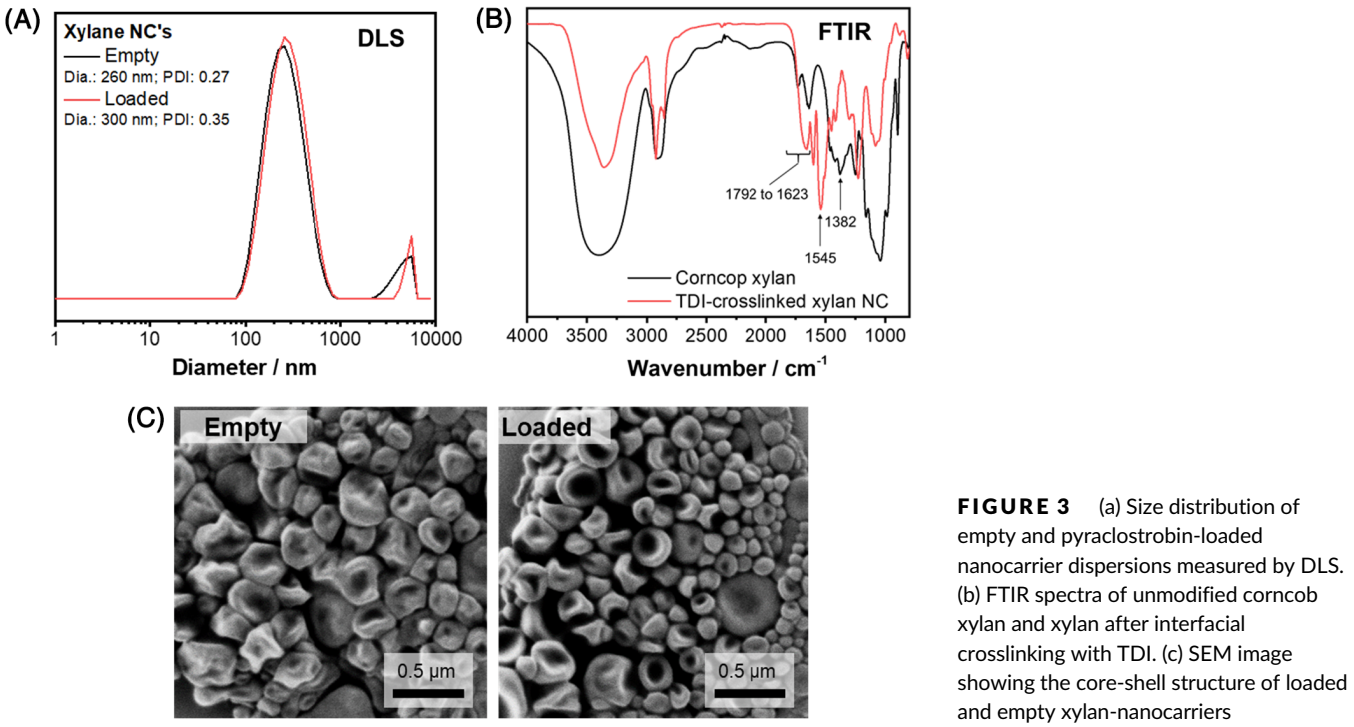


FIGURE 3 (a) Size distribution of empty and pyraclostrobin-loaded nanocarrier dispersions measured by DLS. (b) FTIR spectra of unmodified corncob xylan and xylan after interfacial crosslinking with TDI. (c) SEM image showing the core-shell structure of loaded and empty xylan-nanocarriers

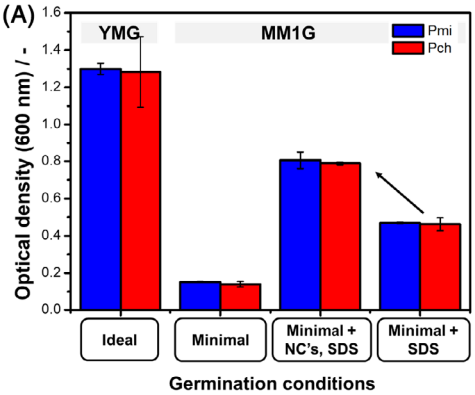
groups like ferulic acid or lignin residues. From the NMR spectra, 18.3 mmol hydroxyl groups per gram xylan were calculated, which allow further functionalization or crosslinking.

According to DLS, the generated xylan nanocarriers had a size distribution in cyclohexane and in water of 200–300 nm (PDI ca. 0.3, some larger aggregates might be formed, Figure 3(a)). SEM showed hollow capsules with a wall thickness of 10–20 nm, proving that xylan and TDI formed a dense shell surrounding the DMSO core during the crosslinking reaction (Figure 3(c)). When reducing stepwise the ratio of hydroxyl to isocyanate groups from 1.65 over 1.29 to 0.86, no nanocarrier formation was observed by SEM. Hence, a monomer/crosslinker ratio of at least 1.65 is needed to form stable core-shell structures. To use the nanocarrier dispersion for drug delivery in agriculture, loaded the broad-spectrum fungicide pyraclostrobin to the xylan nanocarriers. Pyraclostrobin belongs to the class of strobilurins and inhibits the mitochondrial respiratory chain of numerous fungi.[19] It was used previously in our studies on lignin nanocarriers to treat the grapevine trunk disease Esca.[20] As pyraclostrobin is soluble in DMSO as well as xylan, it was mixed with the biopolymer in the dispersed phase of the miniemulsion. A fungicide loading of 8 wt% relative to xylan did not affect the crosslinking at the interface by TDI as outlined above. In these cases, a capsule morphology according to SEM, which proved the robustness of the method. Therefore, this approach might be extended to further pesticides to enable safer and easier handling of toxic agrochemicals.

As pyraclostrobin has a very low water solubility (ca. 1.9 mg/L), it needs to be formulated to be utilized in aqueous dispersion.[21] However, pyraclostrobin has a high solubility in DMSO, which makes it compatible with the xylan used herein. Besides, only relatively low amounts of pyraclostrobin can be dissolved in hydrocarbons.[22] To quantify the amount of encapsulated pyraclostrobin in the xylan nanocarriers, the cyclohexane dispersion was transferred to water without prior purification and then filtered through an Amicon ultracentrifugation filter (MWCO: 3000 Da) to separate the particles from the continuous aqueous phase. Only trace amounts of fungicide (< 0.01%) were detected in the aqueous solution by HPLC, proving almost quantitative encapsulation. As pyraclostrobin has very low solubility in water (ca. 1.9 mg/L), we assume no leakage when stored in an aqueous suspension similar to our previous findings to lignin nanocarriers.

To prove the interfacial crosslinking, SDS was removed by dialysis from the suspension and the nanocarriers were investigated as a solid by FTIR spectroscopy after lyophilization (Figure 3(b)). In comparison to pristine xylan, a broad additional band between 1792 and 1623 cm^{-1} was monitored after crosslinking. The broad signal indicates the overlapping of three bands, which belong to the carbonyl stretching of urethane and urea linkages formed during the shell formation as well as the carbonyl stretching (1738 cm^{-1}) *e.g.* of O-acetyl side groups attached to the xylan backbone. Next to the addition of xylan's hydroxyl groups to TDI forming a polyurethane capsule wall, the isocyanate can hydrolyze at the droplet interface by a trace amount of water, which is dissolved in the DMSO phase. The formed amine can react with TDI's isocyanate groups and lead to a polyurea by-product.[15] Besides the carbonyl signals, we further monitored a strong band of aromatic skeletal vibrations at 1545 cm^{-1} as well as a reduced intensity of the OH stretching band at 1382 cm^{-1} and between 3700-3000 cm^{-1} in comparison to unmodified xylan. Both proved the formation of a covalently crosslinked xylan-polyurea/polyurethane shell, which were visualized by SEM indicating the formation of a core-shell structure (Figure 3(c)).

The enzymatic degradability of the carrier material was analyzed by quantifying the germination of spores and subsequent growth of mycelium belonging to the xylan-degrading fungi *Phaeomoniella chlamydospora* (Pch) or *Phaeoacremonium minimum* (Pmi) in the presence of an only minimal amount of nutrition (Figure 4). More mycelium was formed in comparison to references containing SDS in equal concentration or the minimal medium alone, indicating that the incorporated xylan acted as a degradable breaking point which allowed the metabolization of the carrier material by the fungi. This mechanism might be applied to trigger the carrier degradation and by this the drug release in the presence of microorganisms. At a solid content of <1-10 mg/ml, the pyraclostrobin-loaded nanocarriers prevented the growth of several fungi (strains listed in Figure 4(b)), suggesting the feasibility of the formulation in plant protection. Besides Esca-associated fungi *Pmi* and *Pch*, which proved to be effective degrading xylan, we detected a very high activity against *Pyricularia oryzaethe*,



(B)

Organism	MIC / mg/mL
Pyricularia oryzae	< 1
Botrytis cinerea	< 5
Phaeomoniella chlamydospore	< 10
Phaeoacremonium aleophilum	< 10
Neonectria ditissima	< 10

FIGURE 4 (a) Germination of fungal spores of Pmi and Pch quantified by optical density. The amount of mycelium formed depending on the growth conditions and the respective nutrition provided. (b) Minimal inhibitory concentration (MIC) of pyraclostrobin-loaded xylan nanocarriers (concentration: mg/ml of nanocarriers). Different fungal strains were tested

the cause of the rice blast disease, which is one of the most widely distributed and destructive diseases of rice, and leads to up to ca. 30% loss worldwide.[23] The xylan-based nanocarriers were also active against *Botrytis cinerea* - a devastating fungus in viticulture and horticulture - which is known to produce high amounts of xylanases.[24] These values were comparable to the previously described MIC of lignin-based nanocarriers against pathogenic fungi,[25] expanding their range to the abundant biopolymer class of xylans.

4 | CONCLUSION

This work describes the preparation of degradable xylan-based nanocarriers by interfacial crosslinking of corncob xylan with toluene diisocyanate in an inverse miniemulsion. Xylan extracted from corncobs was found to be a more suitable monomer than xylan from beech wood, as it forms a less viscous dispersed phase more suitable for emulsification and subsequent crosslinking. The obtained xylan dispersions were colloidally stable in cyclohexane or aqueous dispersions for several weeks and contained nanocarriers with diameters between 200-300 nm and a core-shell structure. When adding the fungicide pyraclostrobin to the dispersed phase, the particle size distribution, the morphology, and the stability of the dispersion did not change. This allowed us to prepare pyraclostrobin-loaded nanocarriers, which proved to be active against several pathogenic fungi responsible for devastating plant diseases in horticulture or agriculture. Additional studies monitoring mycelium growth indicated that the xylan-based nanocarriers could be degraded by fungi. The approach is considered a promising tool to generate bio-based nanoformulations, which could help to increase the use of degradable biopolymers in plant protection.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

All data will be made available on request.

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