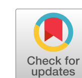
Science of the Total Environment 645 (2018) 411–418

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Replacing calcium with ammonium counterion in lignosulfonates from paper mills affects their molecular properties and bioactivity



Davide Savy [a,b,*], Vincenza Cozzolino [a,c], Marios Drosos [a], Pierluigi Mazzei [a], Alessandro Piccolo [a,c]

[a] Centro Interdipartimentale di Ricerca sulla Risonanza Magnetica Nucleare per l'Ambiente, l'Agro-Alimentare ed i Nuovi Materiali (CERMANU), Università di Napoli Federico II, Via Università 100, 80055 Portici, Italy

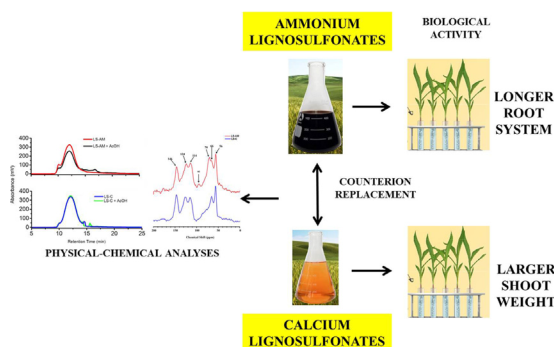
[b] Plant Biology laboratory, Gembloux Agro-Bio Tech, University of Liège, 2 Passage des Déportés, B-5030 Gembloux, Belgium

[c] Dipartimento di Agraria, Università di Napoli Federico II, Via Università 100, 80055 Portici, Italy

HIGHLIGHTS

- Ammonium and Calcium Lignosulfonates (LS) were valorised as plant biostimulants.
- Counterion replacement significantly affected the molecular aggregation of LS.
- The materials showed different molecular size and amount of sulfonates and phenols.
- LS-AM positively affected the root system, LS-C increased Total and Shoot weights.
- Their dose-dependent bioactivity is related to their physical-chemical features.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2018
Received in revised form 11 July 2018
Accepted 12 July 2018
Available online xxxx

Editor: Frederic Coulon

Keywords:
Plant biostimulants
Water-soluble lignin
NMR spectroscopy
High performance size exclusion chromatography (HPSEC)
Maize growth and development
Intensified sustainable agriculture

ABSTRACT

Lignosulfonates are important by-products of the paper industry and may be transformed into different commodities. We studied the molecular properties of ammonium (LS-AM) and calcium Lignosulfonates (LS-C) and evaluated their bioactivity towards the early development of maize plantlets. The FT-IR, ^{13}C NMR and ^{1}H-^{13}C-HSQC-NMR spectra showed that the two lignosulfonates varied in hydroxyl, sulfonate and phenolic content, while DOSY-NMR spectroscopy suggested a similar diffusivity. High Performance Size Exclusion Chromatography (HPSEC) was used to simulate the effects of root-exuded acids and describe the conformational dynamics of both LS substrates in acidic aqueous solutions. This technique showed that LS-C was stabilized by the divalent Ca^{2+} counterion, thus showing a greater conformational stability than LS-AM, whose components could not be as efficiently aggregated by the monovalent $NH4^{+}$ counter-ion. The plant bioassays revealed that LS-AM enhanced the elongation of the root system, whereas LS-C significantly increased both total and shoot plant weights. We concluded that the lignosulfonate bioactivity on plant growth depended on the applied concentrations, their molecular properties and conformational stability.

© 2018 Published by Elsevier B.V.

1. Introduction

With the progressive shortening of fossil fuels, alternative sources of fuel, energy and chemicals are searched. Lignocellulose has considerably attracted the interest of the scientific community (Laurichesse

* Corresponding author.
E-mail address: davide.savy@unina.it (D. Savy).

https://doi.org/10.1016/j.scitotenv.2018.07.153
0048-9697/© 2018 Published by Elsevier B.V.

and Avérous, 2013), as a byproduct of the conversion and exploitation of plant biomasses containing, cellulose, hemicelluloses and lignin (Zakzeski et al., 2010). While cellulose is converted into ethanol, succinic acid, nanocrystals (Cimini et al., 2016; Thambiraj and Shankaran, 2017), and hemicelluloses are transformed into biosurfactants or polymers (Peng and She, 2014), the large aromaticity of lignin is so far envisaged to substitute phenols in phenol-formaldehyde resins or as additive in adhesives (Doherty et al., 2011 and references therein; Kai et al., 2016).

Lignin is a traditional byproduct of the paper production after separation of cellulose by different technologies yielding lignin with diverse physical-chemical characteristics. The sulfate and the sulfite process are the two main processes applied in paper mills to separate lignin (Zakzeski et al., 2010). In the case of sulfate delignification (or kraft process) a mixture of sodium hydroxide and sodium sulfide is used for isolating lignin from cellulose, while the second process may be conducted at different pHs in the presence of sulfite ions to lead to the production of the so-called lignosulfonates (LS) (Holladay et al., 2007). The particular chemical features of LS are extensively exploited in Materials Science, and are being successfully applied to produce formaldehyde resins, emulsifiers or wood preservative (Upton and Kasko, 2016; Angelini et al., 2018, submitted).

The role of LS in crop growth was also the object of scientific investigation. Almås et al. (2014) studied the impact of LS on the rhizochemistry of several soils, while Popa et al. (2008) assessed the role of LS as biostimulants for bean (*Phaseolus vulgaris* L.) cultivations in field trials. The application of LS in agriculture may represent a sustainable exploitation of these materials. In fact, despite their potential as green photosynthate substrates (Laurichesse and Avérous, 2013), LS are still commonly disposed by burning as fuel for energy. A limitation in the exploitation of these substrates as biostimulant in Agriculture is possibly due to the poor knowledge of their compositional and conformational structures (Savy et al., 2016a).

The aim of this work was thus to first elucidate the molecular characteristics and the hydrodynamic behaviour of lignosulfonates with two different conterions, and, then, evaluate their bioactivity towards the early development of maize plantlets.

2. Materials and methods

2.1. Substrates

Two lignosulfonates, ammonium and calcium Lignosulfonates (LS-AM LS-C and, respectively) were kindly provided by the Burgo Group SpA (Altavilla Vicentina, Italy). LS-C was obtained as a byproduct of the sulfite pulping process applied to Norway spruce (*Picea abies* (L.) H. Karst., 1881) wood. The LS-C had been then subjected to ion exchange chromatography (DOWEX 50WX8 200-400) in order to replace the calcium ions with the ammonium ions, thus providing the LS-AM material. The resin was first thoroughly washed with HSO_4 0.125 M in order to saturate the exchange site with H^+, and then rinsed with deionized water until pH 5.5. Then, ammonium hydroxide (0.25 M) was added in order to displace the adsorbed protons with ammonium ions. An aliquot (20 mg mL^{-1}) of LS-C was loaded into the column and eluted down by deionized water. Both LSC and LS-AM were dialyzed against deionized water (membrane cutoff <3500 Da) and freeze-dried.

2.2. Elemental analysis

The elemental composition of both LS was determined by an EA 1108 Elemental Analyzer (Fisons Instruments), while the ash content was measured as by the ASTM E1755–01 "Standard Method for the Determination of Ash in Biomass" (ATSM, 2003). The LS-AM material contained 40.02% of Carbon, 3.78% of Hydrogen, 44.78% of Oxygen, 6.45% of Sulfur, 0.12% of Nitrogen and 4.85% of ashes. The LS-C substrate contained 34.83% of Carbon, 5.93% of Hydrogen, 39.14% of Oxygen, 5.16% of Sulfur, 0.10% of Nitrogen and 14.84% of ashes.

2.3. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT-IR)

DRIFT-IR spectra were recorded with a Perkin Elmer 1720-X FT-IR spectrometer (Waltham, MA, USA), equipped with a Perkin-Elmer Diffuse Reflectance accessory, by accumulating 16 scans with a resolution of 4 cm^{-1}.

2.4. Nuclear magnetic resonance (NMR) spectroscopy

The solid-state ^{13}C-CPMAS-NMR spectra were acquired with a 300 MHz (7.0 Tesla) Bruker Avance wide-bore magnet (Bruker Bio Spin GmbH, Rheinstetten, Germany) equipped with a CPMAS (Cross-Polarization Magic-Angle-Spinning) probe, working at the ^{13}C frequency of 75.47 MHz. Samples were loaded into 4-mm zirconia rotors, closed with Kel-F caps and spun at 10000 ± 1 Hz. The spectra were acquired by applying the cross polarization technique consisting in 1814 time domain points, a spectral width of 300 ppm (22,727.3 Hz), a recycle delay of 2 s, 5000 scans and 1 ms of contact time. The ^{13}C CPMAS pulse sequence was conducted by using a ^1H Ramp pulse to account for the non-homogeneity of the Hartmann-Hahn condition. A TPPM15 scheme was applied to perform the $^{13}C—^1H$ decoupling. The Free Induction Decay (FID) was transformed by applying a 4 k zero filling and an exponential filter function with a line broadening of 100 Hz. All spectra were processed by using MestReC NMR Processing Software (v. 4.9.9.9).

Two–dimensional Heteronuclear Single Quantum Coherence (HSQC) NMR spectroscopy were performed to identify the $^1H—^{13}C$ correlations and assign the most intense NMR signals in samples. The HSQC experiment was acquired by applying a J_{CH} short- range coupling value of 145 Hz and including a 80 μs length (15.6 dB power level) Waltz16 decoupling scheme.

^1H DOSY (Diffusion Ordered SpectroscopY) NMR experiments were conducted by choosing a stimulated echo pulse sequence with bipolar gradients, combined with two spoil gradients and an eddy current delay. This sequence reduced signals loss due to short spin-spin relaxation times. The acquisition was conducted by setting 1400 μs long sine-shaped gradients (δ), that linearly ranged from 0.674 to 32.030 G cm^{-1} in 32 increments, and selecting a diffusion delay of 0.1 s (Δ) between encoding and decoding gradients. DOSY experiments consisted in a recycle delay of 2 s, 4096 points, a spectral width of 14 ppm (5592.8 Hz), 64 scans and 4 dummy scans. DOSY spectra were processed by Topspin software (v.3.1, Bruker Biospin, Rheinstetten, Germany). The Fourier Transform of FIDs was conducted by applying a 2-fold zero filling in F2 dimension and multiplying by a 2 Hz exponential function.

All spectra were processed by using both Bruker Topspin Software (v.2.1, Bruker Biospin, Rheinstetten, Germany) and MestReC NMR Processing Software (v.4.8.6.0, Cambridgesoft, Cambridge, Massachusetts, USA). Zero filling was applied during Fourier transform of free induction decays (FIDs).

2.5. High performance size exclusion chromatography (HPSEC)

The HPSEC system was composed by a Shimadzu LC-10-AD pump equipped with a Rheodyne rotary injector and 100-μL sample loop and a UV/VIS detector (Perkin e Elmer LC295), set at 280 nm. The chromatographic column was a PolySep™ GFC-P3000 300 × 7.80 mm (Phenomenex, USA), preceded by a PolySep GFC-P 35 × 7.80 safety guard (Phenomenex, USA) and a 2 mm inlet filter. The elution flow rate was set to 0.6 mL min^{-1}, while the eluting solution was made of 0.1 mol L^{-1} NaH_2PO_4 solution buffered at pH 7.0 and 4.6 mmol L^{-1} NaN_3. The eluent solution was also used to dissolve both the LS materials at a concentration of 0.6 g L^{-1}. The same LS solutions were then added with glacial acetic acid (AcOH) to lower the pH to 3.5 before

Download English Version:

https://daneshyari.com/en/article/8858484

Download Persian Version:

https://daneshyari.com/article/8858484

Daneshyari.com