Hydrothermal Humification of Spruce Greenery as an Environmentally Friendly Tool for Production of Synthetic Humic Substances

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There is a rising need for an alternative source of humic substances, that would align with the EU Green Deal.

Spruce greenery is a major forestry waste that is often underutilized and left in the forest, making it a suitable source for production of humic substances.

Hydrothermal humification was conducted in the range of 155-230 ºC for 2-24 hours. Most optimal conditions for synthesis were found to be 185 ºC and 9 hours.

Temperatures above 200 ºC initiate the formation of potentially harmful free semiquinone radicals.
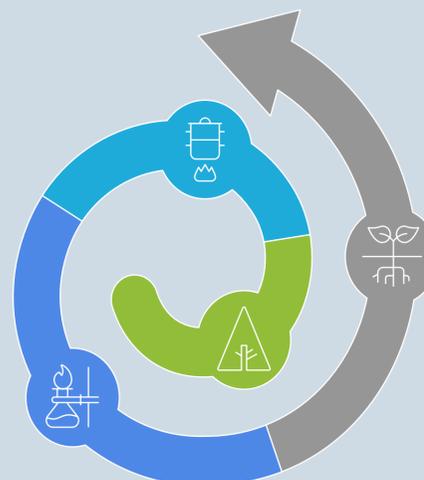
01 Spruce Needles and Branches as Precursors

02 Hydrothermal Humification Process Initiation

03 Biochemical Transformations

04 Formation of Humic Substances

Gradual increase of synthesis temperature leads to formation of more aromatic structures and increased carbon retention, while aliphatic structures decrease.

Introduction

The depletion of non-renewable peat resources and its significant greenhouse gas emissions have prompted the search for sustainable soil amendment alternatives. Norway spruce greenery, a forestry byproduct often left unused after logging, contains high lignocellulose content and is a promising feedstock for producing humic acids.

Hydrothermal humification (HTH) is a climate-neutral, thermochemical process that mimics and accelerates natural humification in an alkaline environment, retaining carbon efficiently. This study investigates the transformation of extracted spruce greenery biomass into humic acids using HTH, supporting circular bioeconomy principles and peat replacement strategies.

Methods

Spruce (*Picea abies*) greenery was harvested, dried, and extracted with isopropanol to simulate post-extraction waste, then subjected to hydrothermal humification. The process was carried out in a Teflon-lined autoclave at six temperatures (155–230 °C) and five reaction times (2–24 h) using 0.65 M KOH. After the reaction, humic acids were precipitated with HCl, isolated, washed, dried, and quantified.

Physicochemical characterization was performed using contemporary methods such as UV-Vis spectroscopy, FTIR, electron paramagnetic resonance (EPR), and solid-state ^{13}C-CPMAS-NMR to assess molecular structure and humification degree. Statistical analysis (ANOVA and Tukey's HSD) was applied to determine optimal synthesis conditions for maximum humic acid yield.

Results

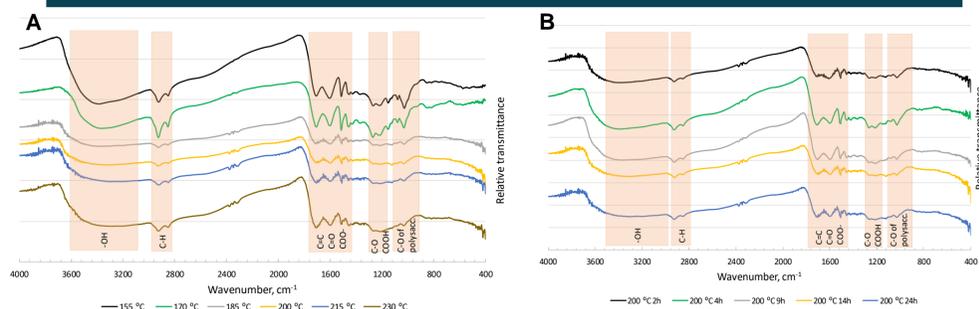Fig. 1. FTIR spectra of artificial humic acids and their dynamics depending on synthesis temperature (A) and synthesis time (B).

Sample	E_2/E_3	E_3/E_4	E_2/E_6	E_4/E_6
155 °C 14h	2.6	7.1	41.5	5.0
170 °C 14h	2.7	7.1	42.6	5.1
185 °C 14h	3.0	7.8	38.3	4.9
200 °C 14h	3.0	7.4	34.6	4.7
215 °C 14h	3.1	7.5	33.2	4.5
230 °C 14h	3.1	6.9	29.0	4.2

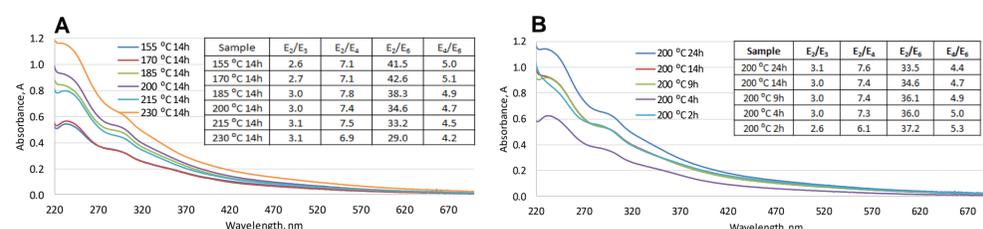| Sample	E_2/E_3	E_3/E_4	E_2/E_6	E_4/E_6
200 °C 24h	3.1	7.6	33.5	4.4
200 °C 14h	3.0	7.4	34.6	4.7
200 °C 9h	3.0	7.4	36.1	4.9
200 °C 4h	3.0	7.3	36.0	5.0
200 °C 2h	2.6	6.1	37.2	5.3

Fig. 2. UV-Vis spectra of artificial humic acids and their dynamics depending on synthesis temperature (A) and synthesis time (B).
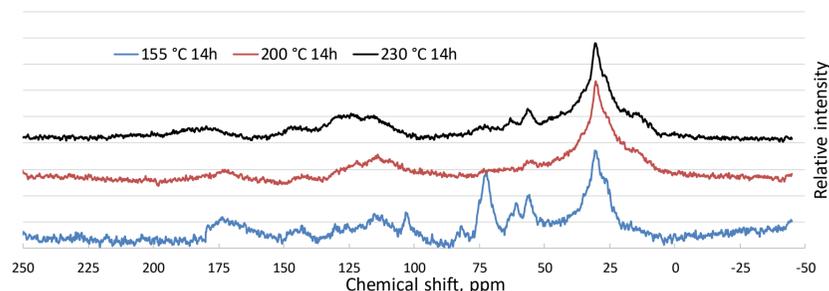

Fig. 3. Solid state ^{13}C-CPMAS-NMR spectra of artificial humic acids and their dynamics depending on synthesis temperature.
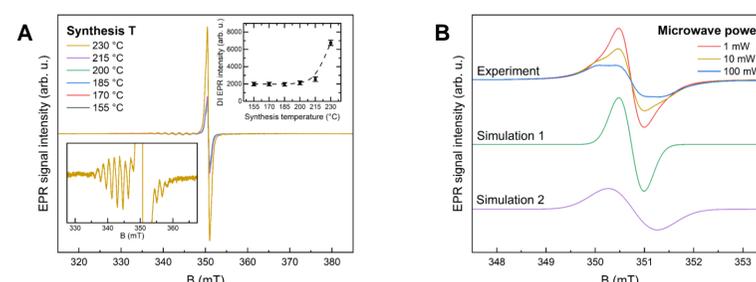

Fig. 4. EPR spectra (10 mW microwave power) of AHA samples after synthesising at different temperatures (A). Inset (lower left corner): magnified EPR spectrum of the HA sample synthesised at 230 °C; inset (upper right corner): double integrated (DI) EPR signal intensity in the 348-357 mT range as a function of synthesis temperature. EPR spectra simulations of the AHA sample synthesised at 230 °C (B)