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AMBITO: NUOVE MOLECULE, PRODOTTI E PROCESSI AD ALTRO VALORE AGGIUNTO PER LA VALORIZZAZIONE DI RIFIUTI, SCARTI, SOTTOPRODOTTI E COPRODOTTI AGRICOLI O PER L'AGRICOLTURA

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Deliverable: 2.2

Deliverable title: Data-set of nanomaterials physical and chemical properties

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Executive Summary

This report presents the results of activities conducted within WP2, focused on the sustainable synthesis of carbon dots (CDs) from lignocellulosic biomass waste. Various agricultural and agro-industrial by-products were screened, and three promising biomasses—Laurus nobilis, external artichoke leaves, and hemp stalks (canapa)—were selected for nanoparticle production via a microwave-assisted green synthesis protocol. Physicochemical characterization confirmed the successful formation of stable, fluorescent carbon dots in all cases, with Laurus nobilis yielding superior results in terms of productivity and reproducibility. These findings are key to advancing eco-compatible nanomaterial synthesis and exploiting biomass waste within a circular economy framework.

Introduction

Carbon dots (CDs) are emerging nanomaterials characterized by their small size (<10 nm), tunable photoluminescence, water dispersibility, and surface functionalizability. Green synthesis of CDs from biomass waste offers a sustainable alternative to traditional synthetic routes, reducing environmental impact and valorizing residues from agricultural and food-processing sectors.

In this context, WP2 aims to:

- Identify and screen biomass waste streams rich in lignocellulosic components;
- Optimize synthetic strategies that comply with green chemistry principles;
- Characterize the resulting nanomaterials for structural, optical, and colloidal properties;

- Select the most promising platforms for downstream applications in WP3.

This report documents the screening, synthesis, and characterization of CDs derived from three selected biomasses: Laurus nobilis leaves, artichoke leaves, and canapa stalks.

Methodology

Biomass Screening and Selection

Biomass waste was supplied by Radice Cubica S.r.l. The following sources were screened:

- Grape pomace (vinacce)
- Tomato peels
- Pomegranate peels and pulp
- Artichoke flower outer leaves
- *Nigella sativa* seeds
- Walnut shells and fractions
- Hemp stalks (canapa)
- Laurus nobilis leaves

A preliminary compositional analysis was conducted, evaluating the content of cellulose, hemicellulose, and lignin. Artichoke leaves and canapa stalks were selected alongside Laurus nobilis due to their high structural polysaccharide and lignin content, which facilitate efficient thermal carbonization.

Synthesis Protocol

A microwave-assisted thermal decomposition method was employed:

- Input: 3 g of dried, ground biomass
- Microwave irradiation: full power for 3 minutes

- Post-processing: dispersion in Milli-Q water, centrifugation, recovery of fluorescent colloidal supernatant

This protocol avoids solvents and harsh chemicals, ensures uniform, and rapid heating. In addition, is scalable and energy-efficient

Results and Discussion

Yield and Morphological Assessment

Biomass	Yield (mg / 3 g)	Morphology (TEM)	Colloidal Stability
Laurus nobilis	~200 mg	Quasi-spherical, 3–5 nm	High
Artichoke leaves	~50 mg	Similar morphology	High
Canapa stalks	~50 mg	Similar morphology	High

- Laurus nobilis yielded ~4× more material than the alternatives, indicating superior carbonization efficiency.
- All samples formed stable, fluorescent colloidal solutions.

Transmission Electron Microscopy (TEM)

- All CDs: quasi-spherical shape, size ~3–5 nm

Dynamic Light Scattering (DLS)

- Hydrodynamic diameters in agreement with TEM
- Narrow size distributions → excellent colloidal stability

Fourier Transform Infrared Spectroscopy (FTIR)

- Common functional groups:
    - 3457 cm^{-1}: O–H / N–H stretching
    - 3260 cm^{-1}: C≡N

- 1637–1023 cm^{-1}: C=O, C–H, C–N/C–O

- Indicates hydrophilic, functionalized surfaces

UV–Vis and Fluorescence

- All CDs absorb at ~300 nm and emit visible fluorescence under UV
- Stable photoluminescence up to 96 h post-synthesis

Zeta Potential

- Laurus nobilis CDs: –15 ± 2 mV
- Consistent with negative surface charge due to oxygen-rich groups → enhanced dispersion

X-ray Diffraction (XRD)

- Broad peak at 2θ ≈ 22°
- Confirms amorphous carbon structure, typical of green-synthesized CDs

Thermal Conductivity

Results and Discussion

The microwave-assisted synthesis route applied to different biomass sources—Laurus nobilis leaves, external artichoke flower leaves, and hemp stalks (canapa)—successfully led to the formation of fluorescent carbon dots (CDs) in all tested cases. Upon visual inspection under UV light, the aqueous suspensions of CDs exhibited intense and stable blue fluorescence, indicating consistent optical activity across samples.

Despite the general success in forming colloidally stable and optically active nanoparticles, marked differences emerged in terms of synthetic yield. In particular, Laurus nobilis proved to be the most efficient precursor, consistently providing an average of ~200 mg of carbon dots per 3 g of dried biomass, whereas both artichoke and canapa yielded significantly lower quantities, in the range of ~50 mg per 3 g. This fourfold difference is notable and strongly

suggests that Laurus nobilis possesses intrinsic chemical or structural features that facilitate more effective thermal conversion into carbonaceous nanostructures under microwave irradiation. The reproducibility of these yields was also remarkable for Laurus nobilis, with negligible variability across independent synthesis batches. This reproducibility is crucial when considering the scale-up potential of the process and its applicability in industrial or pre-industrial settings. While the artichoke and hemp matrices did enable CD formation, their lower carbonization efficiency points to a possible need for pretreatment optimization—such as mild acid hydrolysis or enzymatic delignification—to improve their conversion rates and overall process efficiency. The morphology of the synthesized CDs was systematically analyzed by Transmission Electron Microscopy (TEM). All samples, regardless of the biomass source, showed well-dispersed, quasi-spherical nanoparticles with diameters ranging from 3 to 5 nanometers. These sizes are typical for carbon dots produced via green routes and indicate that the microwave method ensures a controlled nucleation process, independent of the initial feedstock.

Complementary measurements using Dynamic Light Scattering (DLS) confirmed the results observed via TEM, showing narrow hydrodynamic size distributions and an absence of significant agglomeration. The colloidal stability of all CD samples was high, with suspensions remaining clear and stable for several weeks at room temperature without the need for additional stabilizers or surfactants. To better understand the chemical nature of the carbon dots and their surface composition, Fourier Transform Infrared Spectroscopy (FTIR) was employed. Across all samples, several common vibrational bands were observed. A broad absorption around 3450 cm^{-1} indicated the presence of hydroxyl and amine groups, while bands near 3260 cm^{-1} pointed to the presence of nitrile (C≡N) groups. Additional peaks at 1637 cm^{-1}, 1371 cm^{-1}, and 1023 cm^{-1} corresponded to carbonyl (C=O), alkyl (C-H),

and various C–O/C–N stretching modes. These features collectively suggest a surface rich in hydrophilic and reactive functional groups, making the CDs highly suitable for bioconjugation or further chemical modification in downstream applications.

These functional groups also likely contribute to the colloidal stability of the dots in water, as confirmed by zeta potential measurements. In the case of Laurus nobilis-derived CDs, the zeta potential was measured at –15 ± 2 mV, indicating a moderately negative surface charge due to oxygen-containing groups—another hallmark of green-synthesized CDs.

All CD samples displayed characteristic UV–Vis absorption peaks around 300 nm, typical of π–π* transitions in conjugated carbon structures. When exposed to UV light, the solutions emitted bright blue fluorescence, confirming their photoluminescent nature. Notably, the intensity and stability of fluorescence were preserved for at least 96 hours, further attesting to the quality of the colloidal suspensions and the robustness of the CDs' surface chemistry.

In terms of crystalline structure, X-ray diffraction (XRD) analyses revealed a broad, single peak centered around $2\theta \approx 22°$, which is consistent with the presence of amorphous carbon domains. This result aligns with the expected structural disorder typical of CDs synthesized from biomass sources, which lack the long-range order seen in graphitic or crystalline carbon materials. This amorphous nature is not a drawback; on the contrary, it provides a high density of defect sites and functional groups that can be advantageous for applications in catalysis, sensing, or drug delivery.

Finally, preliminary measurements of thermal conductivity were performed on dried CD powders, with a view to evaluating their potential use in optoelectronics or thermal management systems. Although the raw, undoped CDs exhibited moderate thermal conductivity values, these could be enhanced via composite formulation or heteroatom doping, making the material a promising candidate for multifunctional nanodevices.

Conclusions

The outcomes of this study clearly demonstrate that Laurus nobilis is the most effective biomass precursor among those tested, consistently delivering the highest yield of carbon dots (CDs) with excellent reproducibility. Importantly, the CDs derived from Laurus nobilis not only exhibit a superior production efficiency but also maintain desirable nanoscale characteristics, such as uniform morphology, high colloidal stability, and robust fluorescence—key attributes for advanced functional applications.

While artichoke leaves and hemp stalks also proved capable of generating carbon dots with comparable physical and optical properties, their lower synthetic yields highlight the need for further optimization. Enhancing the conversion efficiency of these alternative biomass sources could significantly broaden the availability and versatility of eco-sourced carbon nanomaterials, particularly in large-scale or cost-sensitive contexts.

Overall, the results confirm the technical feasibility of producing high-quality, fluorescent carbon dots from agricultural and agro-industrial waste using a microwave-assisted, green synthesis approach. This method is solvent-free, rapid, and easily scalable—aligning well with sustainability objectives and industrial process requirements.

Moreover, the consistent functionalization and structural features of the synthesized CDs make them highly suitable for downstream applications foreseen in WP 3.

Annex

This annex provides a comprehensive overview of the supplementary material and characterization data generated throughout the project activities related to the sustainable synthesis of carbon dots (CDs) from lignocellulosic biomass. These materials are available upon

request and are intended to support data transparency, reproducibility of the experimental protocols, and future benchmarking efforts within the research community.

A1. TEM and DLS Raw Data

To assess the morphology and size of the carbon dots, raw Transmission Electron Microscopy (TEM) micrographs were acquired at high resolution. These images confirm the formation of quasi-spherical, monodisperse nanoparticles with diameters in the 3–5 nm range. Accompanying this, Dynamic Light Scattering (DLS) data provide complementary size distribution profiles, demonstrating colloidal uniformity and narrow hydrodynamic diameters. The raw data sets include intensity, volume, and number-based distribution plots for each biomass-derived sample.

A2. FTIR Spectra of CD Samples

Fourier-Transform Infrared (FTIR) spectroscopy was employed to identify surface functional groups of the CDs. Spectral overlays for samples synthesized from different biomasses are provided, along with detailed peak assignments for key vibrational modes such as hydroxyl (O–H), carbonyl (C=O), amine (N–H), and carboxyl (COO–) groups. These data underline the hydrophilic nature and chemical versatility of the CD surfaces, which are crucial for downstream functionalization or biological applications.

A3. UV–Vis and Fluorescence Spectra

Spectroscopic evaluation of the CDs included UV–Vis absorbance and fluorescence emission profiles. Absorption peaks around 280–300 nm, associated with π–π^* transitions of aromatic sp^2 domains, were observed consistently across all samples. Corresponding fluorescence spectra show stable emissions upon excitation at different wavelengths, highlighting the tunable and robust photoluminescent behavior of the synthesized carbon dots. Comparative plots illustrate how the optical features vary depending on the biomass precursor.

A4. Microwave Synthesis Parameters

A technical description of the microwave-assisted synthesis setup is provided, detailing the instrumental settings such as power level, irradiation time, and sample loading configuration. The characteristics of the microwave containers, temperature behavior during the reaction,

and precautions to ensure reproducibility are also documented. These details are essential for ensuring the scalability and standardization of the green synthesis protocol across different research facilities.