CSAC 2021

1st International Electronic Conference on Chemical Sensors and Analytical Chemistry
01-15 July

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VALIDATION OF SPENT COFFEE GROUNDS AS PRECURSORS FOR THE DEVELOPMENT OF SUSTAINABLE CARBON DOT-BASED FOR Fe^{3+} OPTICAL SENSING

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INTRODUCTION: Carbon Dots (CDs)

- **Fluorescent carbon-based nanoparticles** with typical size below 10 nm.

CDs possess several properties such as:

- ✓ water-soluble
- ✓ highly stable
- ✓ biocompatible
- ✓ nontoxic

- They can be fabricated from a large variety of precursors

- However, most available organic molecules are still expensive, and their use or synthesis can lead to significant challenges to the environment and human health.

BIOMASS WASTE
as alternative precursors in the synthesis of CDs

INTRODUCTION: Carbon Dots (CDs)

- Biomass waste material is ubiquitous, nontoxic, cheap and renewable

Coffee consumption has increased significantly in recente years

↓

Over 9.5 million tons in 2017 →

Increase in waste products, including used coffee capsules containing coffee grounds

Spent coffee grounds (SCGs) ⟶ residues of the treatment of coffee powder

POTENTIAL CARBON SOURCE to a more environmentally sustainable synthesis route

METHODOLOGY: **CDs synthesis**

- **Three different SCG** samples were obtained from three different used expresso capsules.

Chave D`Ouro® decaffeinated blend (Decaf-CDs)

Nicola® Rossio (intense) blend (Rossio-CDs)

Chave D`Ouro Prestige blend (Prestige-CDs)

Citric acid and Urea (CA@U-CDs) as reference CDs

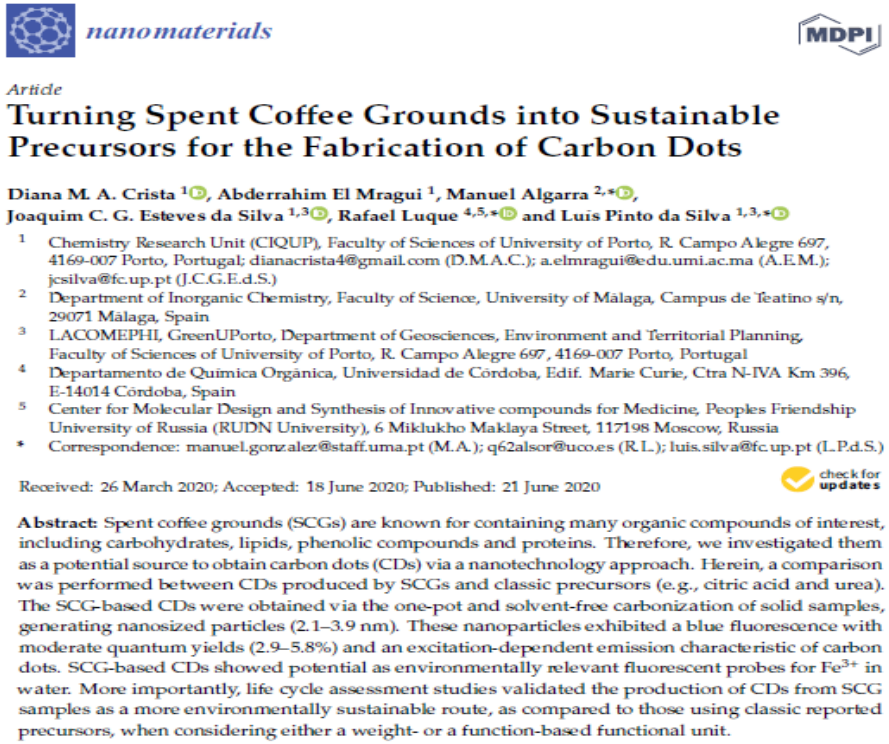
SCG-based CDs were synthesized via one-pot and solvent-free carbonization

2.5 g of each SCG sample
200ºC/ 4 hours

- The synthesized CDs were subsequently dissolved in water and the purification done by centrifuging and dialysis.

METHODOLOGY: CDs synthesis

The work was already published at Nanomaterials journal (DOI: 10.3390/nano10061209)



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Article

Turning Spent Coffee Grounds into Sustainable Precursors for the Fabrication of Carbon Dots

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Received: 26 March 2020; Accepted: 18 June 2020; Published: 21 June 2020

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Abstract: Spent coffee grounds (SCGs) are known for containing many organic compounds of interest, including carbohydrates, lipids, phenolic compounds and proteins. Therefore, we investigated them as a potential source to obtain carbon dots (CDs) via a nanotechnology approach. Herein, a comparison was performed between CDs produced by SCGs and classic precursors (e.g., citric acid and urea). The SCG-based CDs were obtained via the one-pot and solvent-free carbonization of solid samples, generating nanosized particles (2.1–3.9 nm). These nanoparticles exhibited a blue fluorescence with moderate quantum yields (2.9–5.8%) and an excitation-dependent emission characteristic of carbon dots. SCG-based CDs showed potential as environmentally relevant fluorescent probes for Fe^{3+} in water. More importantly, life cycle assessment studies validated the production of CDs from SCG samples as a more environmentally sustainable route, as compared to those using classic reported precursors, when considering either a weight- or a function-based functional unit.

Crista, D. M. A.; El Mragui, A.; Algarra, M.; Esteves da Silva, J. C. G.; Luque, R.; Pinto da Silva, L. Turning Spent Coffee Grounds into Sustainable Precursors for the Fabrication of Carbon Dots. *Nanomaterials* **2020,** *10* (6), pp. 1209. DOI: 10.3390/nano10061209

RESULTS AND DISCUSSION: CDs synthesis

- SCG-based CDs were obtained by solvent-free carbonization of solid samples.

Table 1. Synthesis and fluorescence quantum yields (in %) for the four CDs.

	Decaf-CDs	Rossio-CDs	Prestige-CDs	CA@U-CDs
Synthesis yield (%)	0.5	0.8	1.9	9.9
Quantum yield (QY_{FL}) (%)	4.3	2.9	5.8	22.5
Particle size (nm)	2.1±1.0	3.9±1.0	2.3±0.8	1.0±0.3

RESULTS AND DISCUSSION: Surface Characterization of CDs

Table 2. Atomic composition (%) obtained by XPS for the four different CDs.

	Decaf-CDs	Rossio-CDs	Prestige-CDs	CA@U-CDs
C (%)	59.1	57.1	59.0	58.9
O (%)	35.3	34.9	34.1	27.2
N (%)	2.8	6.2	4.4	13.9
K (%)	2.7	1.8	2.5	-

- All types of CDs samples were composed mostly of C (~57-59%) and O (~27-35%).

RESULTS AND DISCUSSION: Fluorescent Characterization of CDs

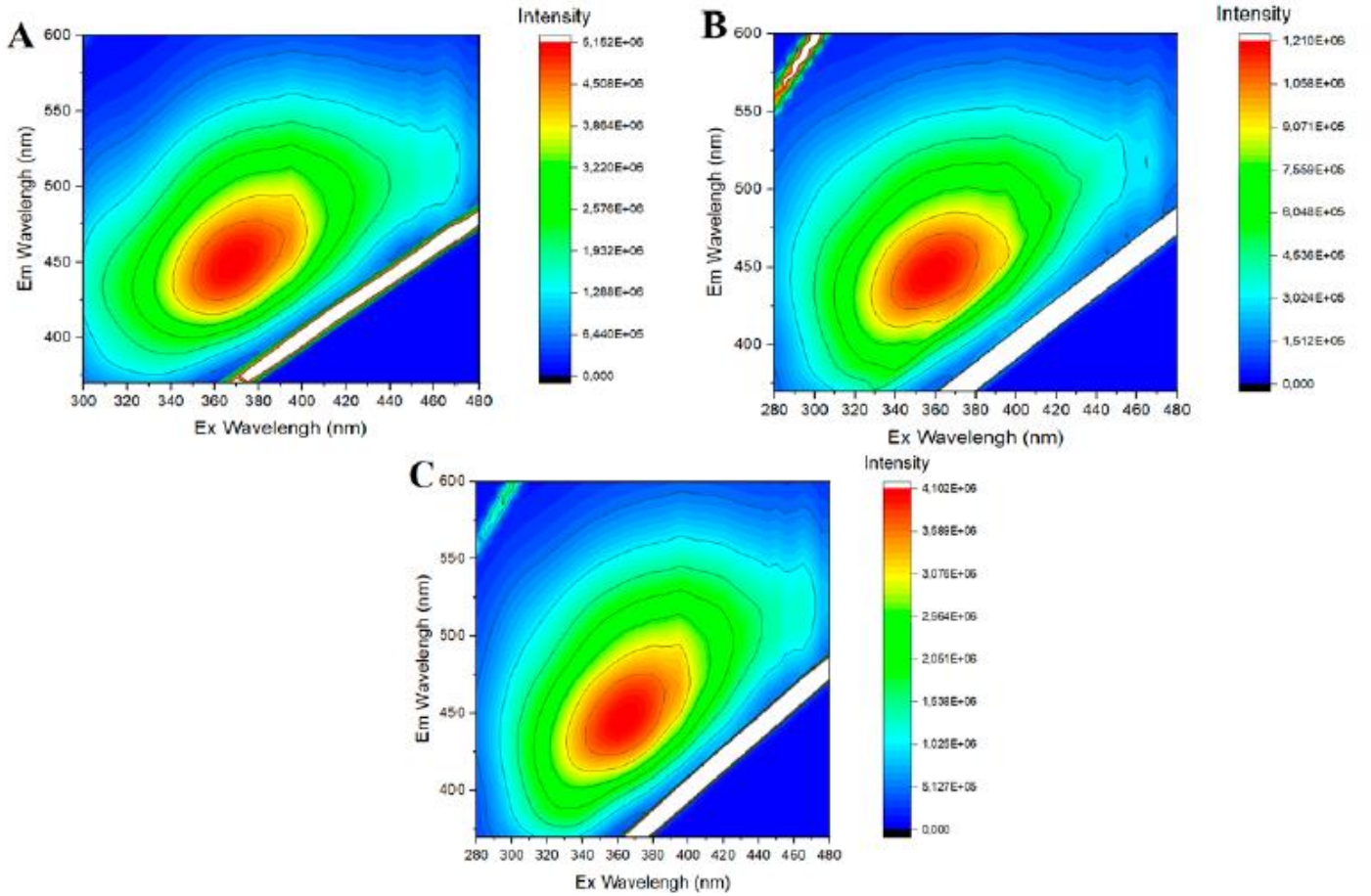

Figure 1. Two-dimensional excitation-emission matrices (EEMs) for decaf-CDs **(A)**, rossio-CDs **(B)** and prestige-CDs (**C**).

- The EEMs show only a well-defined luminescent region for each SCG-based CD, with a maximum in the blue region of the spectrum and similar luminescent centers.

RESULTS AND DISCUSSION: Fluorescent Characterization of CDs

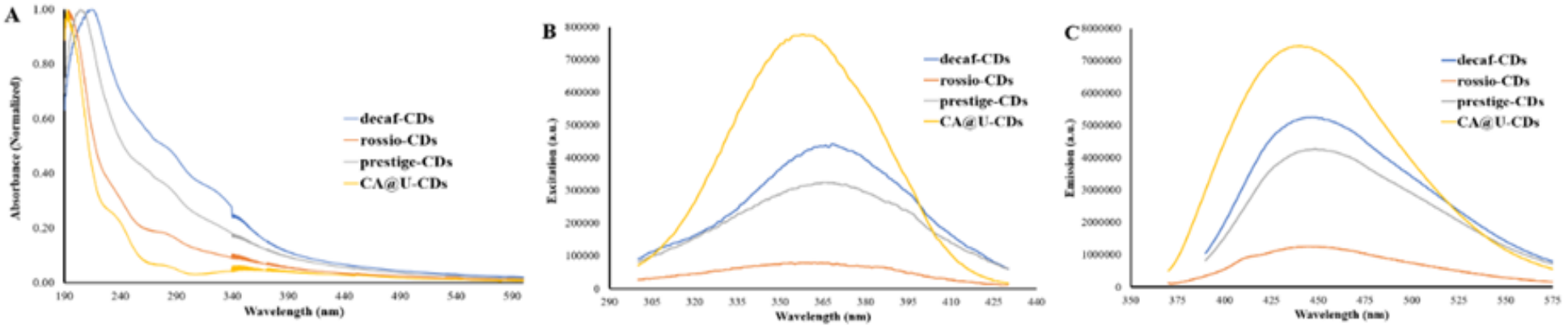

Figure 2. (A) absorption, **(B)** excitation and **(C)** fluorescence spectra in aqueous solution for decaf-CDs, rossio-CDs, prestige-CDs and CA@U-CDs.

- All four CDs present a quite similar excitation (350-370 nm) and emission wavelength (440-450 nm).

RESULTS AND DISCUSSION: Fluorescent Characterization of CDs

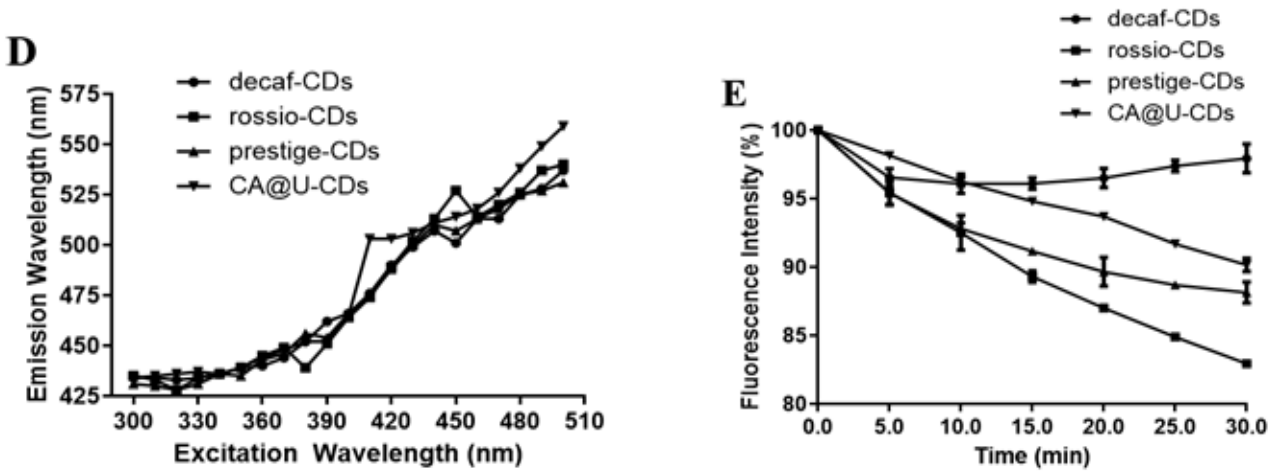

Figure 3. D) Emission wavelength (in nm) as a function of the excitation wavelength (in nm). **(E)** photostability of the four CDs, measured as the variation of the fluorescence intensity as a function of irradiation time under a UV light source (365 nm).

- All samples present na excitation-dependent emission.
- Decaf-CDs and Prestige-CDs can be considered to be photostable (with decreases of just ~3% and ~10% when subjected to 30 min of UV irradiation)

RESULTS AND DISCUSSION: Sensing of Fe^{3+}

- One of the most commom application of CDs is their use as fluorescent probes in sensing of heavy metal cations.
- Elevated intake of Fe3+ can lead to health hazards due to production of reactive oxygen species (ROS) that can cause severl diseases, such as Alzheimer´s and Parkinson´s diseases

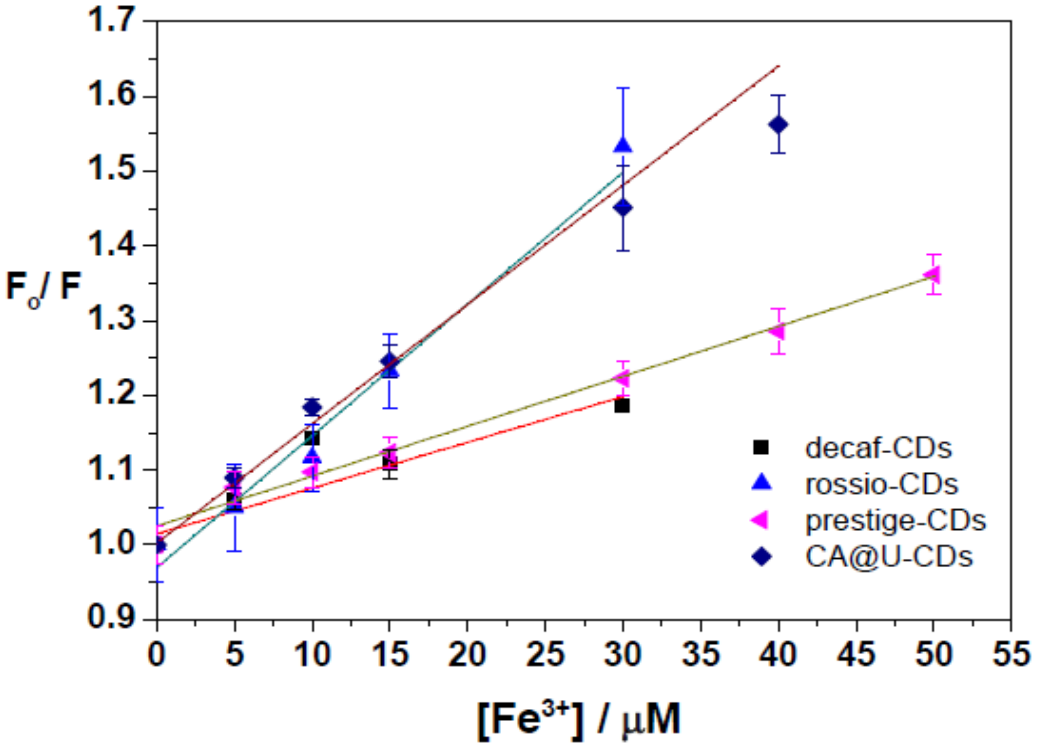

Figure 4. Emission profiles as a function of concentration of the Fe3+ (in mM), in aqueous solution.

- Fe3+ induced a concentration-dependent quenching for all four CD samples.
- Except for Decaf-CDs, their LoDs were below the permissible limit for Fe3+ (5,357 µM) in drinking water, as estabilished by USEPA

RESULTS AND DISCUSSION: Comparative LCA Study

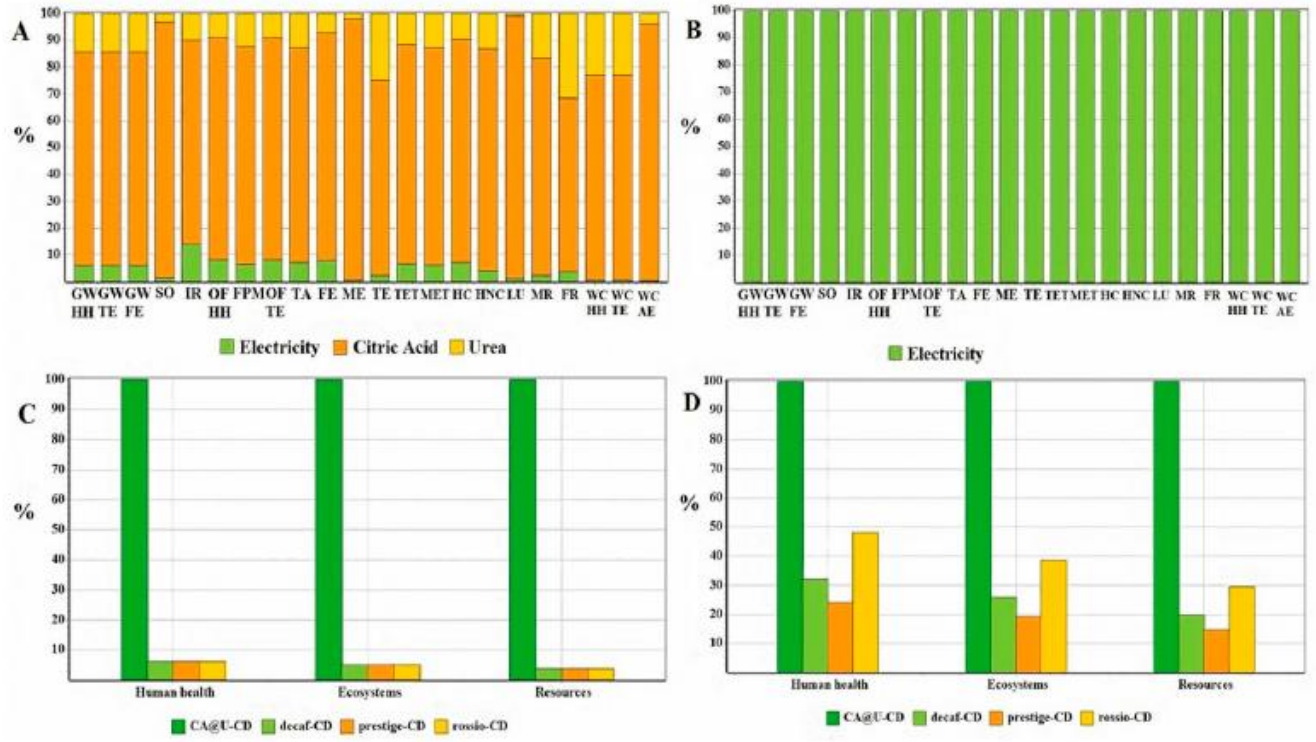

Figure 5. Comparative damage assessment for all four synthesis using (I) reaction yield and (II) quantum yield (QY) unit.

- **LCA** studies validated the production of CDs from SCG samples as a **more environmentallly sustainable route.**

CONCLUSIONS

- The fabrication of fluorescent CDs using either SCG or standard precursors was compared;
- The one-pot and solvent-free carbonization of the different samples led to the formation of nanoparticles with an average size of 1.0-3.9 nm and a similar blue emission;
- SCG-CDs present moderate quantum yields (2.9-5.8%) and quite low reaction yields, when compared to CA@U-CDs (22.5% quantum yield and 9.9% resction yield);
- LCA study demonstrated that the fabrication of SCG-CDs is more environmentally sustainable;
- SCG-CDs also demonstrated their potential as sensing probes for Fe3+ in water.

ACKNOWLEDGMENTS

- To my Supervisor Prof. Dr. Joaquim Esteves da Silva and my Co-Supervisor Dr. Luís Pinto da Silva.

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FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

PhD Grant (SFRH/BD/144423/2019)

THANK YOU