UNIVERSIDADE FEDERAL DE SANTA CATARINA

CENTRO TECNOLÓGICO

PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

Valentina Arias Velasco

Towards Sustainable Obtention of Carbon Quantum Dots: Life Cycle Analysis and Synthesis

Florianópolis

2023

Valentina Arias Velasco

Towards Sustainable Obtention of Carbon Quantum Dots: Life Cycle Analysis and Synthesis

Dissertação submetida ao Programa de Pós-Graduação em Engenharia Química da Universidade Federal de Santa Catarina como requisito parcial para a obtenção do título de Mestra em Engenharia Química.

Orientador(a): Prof. Sergio Yesid Gómez González. Dr.
Coorientador(a): Prof. Dachamir Hotza. Dr.

Florianópolis

2023

Valentina Arias Velasco

Towards Sustainable Obtention of Carbon Quantum Dots: Life Cycle Analysis and Synthesis

O presente trabalho em nível de Mestrado foi avaliado e aprovado, em 1 de setembro de 2023, pela banca examinadora composta pelos seguintes membros:

Prof. Agenor de Noni Junior, Dr.
Instituição Universidade Federal de Santa Catarina

Profa. Larissa Nardini Carli Dra.
Instituição Universidade Federal de Santa Catarina

Certificamos que esta é a versão original e final do trabalho de conclusão que foi julgado adequado para obtenção do título de Mestra em Engenharia Química.

> Insira neste espaço a
> assinatura digital

Coordenação do Programa de Pós-Graduação

> Insira neste espaço a
> assinatura digital

Prof. Sergio Yesid Gómez González Dr.

Orientador

Florianópolis, 2023.

À minha família.

AGRADECIMENTOS

Agradeço a todos os que de alguma forma ou de outra tenham colaborado para a realização deste trabalho, de forma especial agradeço:

Aos meus pais William e Mariluz e minha irmã Ximena, por terem apoiado sempre.

À minha professora Ana Cecilia Agudelo Henao por compartilhar sua paixão pelo conhecimento e sua disponibilidade permanente em me apoiar.

Ao meu orientador Sergio Yesid Gómez González, a quem muito admiro por sua grande capacidade de trabalho e sabedoria e por me motivar a continuar.

Aos meus amigos por me ouvirem e serem uma parte importante do meu bem-estar geral.

À banca, por ter se disponibilizado a avaliar este trabalho.

Aos laboratórios PROCER e LABMASSA, pela estrutura oferecida para que fosse possível realizar os experimentos necessários para este trabalho.

À Universidade Federal De Santa Catarina, que tem professores de excelente qualidade.

À CAPES, pelo apoio financeiro à pesquisa.

RESUMO EXPANDIDO

Introdução
Na busca por avanços tecnológicos sustentáveis, os Pontos Quânticos de Carbono (CQDs) emergiram como candidatos promissores devido às suas propriedades únicas e aplicações potenciais em áreas como energia, biomedicina e detecção ambiental. À medida que cresce o interesse pelos CQDs, torna-se imperativo avaliar de forma abrangente o seu impacto ambiental ao longo do seu ciclo de vida, para garantir que os seus benefícios não sejam ofuscados por efeitos prejudiciais no bem-estar humano.

Este estudo aborda uma Avaliação do Ciclo de Vida (LCA) Cradle-to-Gate (berço ao portão) dos processos de síntese de CQDs. Os objetivos principais abrangem a avaliação da sustentabilidade de métodos de síntese comuns e a síntese de CQDs em conformidade com os princípios de síntese verde. Estes objetivos alinham-se com a crescente ênfase em práticas sustentáveis na investigação científica e no desenvolvimento tecnológico.

Metodologia
Este trabalho abrange uma avaliação LCA que visa identificar os potenciais impactos ambientais associados ao processo de síntese de CQDs. A avaliação foi iniciada pela identificação de tendências nos parâmetros de síntese para CQDs puros em escala laboratorial obtidos a partir de fontes de carbono derivadas de biomassa. Aproveitando os resultados da pesquisa do banco de dados Scopus, foram selecionadas técnicas de síntese comumente empregadas (oxidação química, tratamento hidrotérmico, micro-ondas e pirólise). Um conjunto de dados de 70 estudos foi considerado para delinear o inventário do ciclo de vida com base nos parâmetros modais de cada método de síntese usando Ecoinvent® 3.7. Além disso, foram investigados três cenários distintos em relação à fonte de carbono. O primeiro cenário abrangia matéria orgânica bruta, enquanto o segundo envolvia fontes secas de carbono. O terceiro cenário substituiu a biomassa por ácido cítrico, um reagente comercial típico para produção de CQDs. Este estudo concentrou-se predominantemente na fase de produção de nanopartículas em escala laboratorial, abrangendo emissões imediatas da produção de CQD e efeitos consequentes decorrentes da extração de recursos e o consumo de energia. As avaliações de impacto ambiental foram realizadas utilizando uma unidade funcional baseada na massa, em que 1 grama de CQDs produzidos serviu como referência.

O procedimento de síntese teve como objetivo diminuir os tempos das etapas e eliminar reagentes perigosos, utilizando fontes orgânicos como casca de banana (BP), casca de laranja (OP) e casca de pinhão (PS) para síntese de CQDs. Esses resíduos foram escolhidos devido à sua abundância e potencial para gestão de resíduos no setor agroindustrial. A síntese foi conduzida usando um reator de micro-ondas sob condições variadas de temperatura e tempo. As características ópticas das amostras foram analisadas através de espectroscopia UV-Vis e de fluorescência. Os grupos funcionais de superfície foram determinados via espectroscopia FTIR, enquanto as propriedades cristalográficas foram avaliadas por análise de Difração de Raios X (DRX).

Resultados

Foram identificadas as condições operacionais mais comuns dos métodos de síntese mencionados, constatando-se que os principais fatores ambientais afetados estão relacionados ao aquecimento global, à eco toxicidade terrestre, à toxicidade humana não cancerígena e ao consumo de água. Entre os três cenários de fonte de carbono (matéria orgânica bruta, fonte de carbono seco e ácido cítrico), o uso da biomassa como fonte de carbono (cenário 2) surgiu como a opção mais sustentável, oferecendo menor impacto ambiental. O processo de síntese seguiu diretrizes verdes, utilizando de carbono como biomassa.

Se identificaram variações significativas nas contribuições de impacto entre métodos de síntese. O método de micro-ondas demonstrou o menor impacto ambiental, seguido pela oxidação química, enquanto os métodos de pirólise e tratamento hidrotérmico exibiram maiores impactos. Este estudo não só esclarece as implicações ambientais da síntese de CQDs, mas também fornece insights sobre como otimizar a sua produção para se alinhar com práticas sustentáveis.

Os CQDs obtidos exibiram propriedades ópticas com elevada similaridade, sendo PS a amostra que apresentou diferenças mais notáveis devido à composição de sua fonte de carbono. Os espectros UV-Vis demonstraram forte absorção na região UV e absorção mais fraca na região visível para todas as três fontes. As respostas de fluorescência diferiram levemente com base nas fontes de carbono e nas condições de reação. A análise da estrutura cristalina revelou que os CQDs exibiam uma estrutura amorfa grafítica. As condições de síntese de 180°C e 20 minutos foram selecionadas porque produziram CQDs com propriedades melhoradas e homogêneas de absorção e fluorescência.

Considerações finais

Em conclusão, este estudo avaliou a sustentabilidade ambiental de vários métodos de síntese de CQDs e avaliou seu potencial como uma tecnologia sustentável. Os métodos de síntese mais comuns têm a possibilidade de serem modificados para obter mais sustentabilidade no processo sem afetar mais o produto alvo. Os diferentes CQDs obtidos com uma abordagem sustentável exibiram características ópticas e estruturais similares, com propriedades de absorção e fluorescência influenciadas pela fonte de carbono e condições de síntese. No geral, este estudo fornece informações valiosas sobre as implicações ambientais dos métodos de síntese de CQD e contribui para a compreensão de suas propriedades ópticas e estruturais. As descobertas sublinham a importância de selecionar fontes de carbono e condições de síntese adequadas para alcançar as propriedades desejadas, avançando ainda mais as aplicações potenciais dos CQDs em tecnologias sustentáveis.

RESUMO

Este estudo apresenta uma Avaliação do Ciclo de Vida (ACV) para medir o impacto ambiental da síntese de Pontos Quânticos de Carbono (CQDs). Através de tendências em parâmetros em escala laboratorial, foram selecionados métodos de síntese comuns com base em 70 estudos. Foram analisados três cenários envolvendo diferentes fontes de carbono. A avaliação centrou-se nas emissões imediatas e nos efeitos consequentes da produção de nanopartículas, com uma unidade funcional baseada na massa dos CQDs. Os dados para a avaliação foram derivados de tendências de síntese em escala laboratorial, abrangendo matérias-primas, eletricidade e subprodutos, usando Ecoinvent® 3.7. Para a síntese do CQD, foram utilizadas fontes de resíduos orgânicos como Casca de Banana (BP), Casca de Laranja (OP) e Casca de Pinhão (PS). Um reator de micro-ondas foi empregado para produzir CQDs em temperaturas e tempos variados. A caracterização envolveu espectroscopia UV-Vis e de fluorescência, cálculo de energia bandgap, espectroscopia FTIR para grupos funcionais de superfície e análise XRD para cristalografia. Este estudo apoia o papel dos CQDs em tecnologias sustentáveis, avalia metodologias de síntese e adere aos princípios de síntese verde, contribuindo com conhecimentos essenciais para a sua integração em aplicações sustentáveis.

Palavras-chave: nanotecnologia, impactos ambientais, nanomateriais de carbono, biomassa, pontos quânticos de carbono.

ABSTRACT

This study presents a Life Cycle Assessment (LCA) to evaluate the environmental impact of Carbon Quantum Dots (CQDs) synthesis. Through trends in laboratory-scale parameters, standard synthesis methods were selected based on 70 studies. Three scenarios involving different carbon sources were analyzed. The assessment focused on nanoparticle production's immediate emissions and consequential effects, with a functional unit based on CQD weight. Data for the evaluation were derived from laboratory-scale synthesis tendencies, encompassing raw materials, electricity, and subproducts. The foreground system was modeled using Ecoinvent® 3.7 data. For CQD synthesis, organic waste sources like Banana Peel (BP), Orange Peel (OP), and Pinion Shell (PS) were utilized. A microwave reactor was employed to produce CQDs at varying temperatures and times. Characterization involved UV-Vis and fluorescence spectroscopy, bandgap energy calculation, FTIR spectroscopy for surface functional groups, and XRD analysis for crystallography. This study supports CQDs' role in sustainable technologies, evaluates synthesis methodologies, and adheres to green synthesis principles, contributing essential insights for their integration into sustainable applications.

Keywords: nanotecnologia, impactos ambientais, nanomateriais de carbono, biomassa, carbon quantum dots.

FIGURE LIST

TABLE LIST

LIST OF ABBREVIATIONS AND ACRONYMS

BP	Banana Peel.
CQDs	Carbon Quantum Dots.
CO	Chemical oxidation.
FET	Freshwater eutrophication.
FEX	Freshwater ecotoxicity.
FPM	Fine particulate matter formation.
FRS	Fossil resource scarcity.
FTIR	Fourier transformed infrared spectroscopy.
GW	Global warming.
H	Hydrothermal.
HCT	Human carcinogenic toxicity.
HNCT	Human non-carcinogenic toxicity.
IRAD	Ionizing radiation.
IS	Impact score.
LCA	Life cycle assessment.
LU	Land use.
M	Microwave.
MEX	Marine ecotoxicity.
MET	Marine eutrophication.
MRS	Mineral resource scarcity.
OP	Orange peel.
OZH	Ozone formation, Human health.
OCT	Ozone formation, Terrestrial ecosystems.
P	Pyrolysis.
PS	Pinion shell.
QDs	Quantum Dots.
QY	Quantum yield.
SOD	Stratospheric ozone depletion.
TER	Terrestrial acidification.
TEO	Terrestrial ecotoxicity.
UV-Vis	Ultraviolet-Visible.
XRD	X-ray diffraction.

WC   Water consumption.

SUMMARY

1   INTRODUCTION

In the face of pressing environmental challenges such as pollution control, resource depletion, and energy demands, integrating sustainable strategies has emerged as a critical approach to safeguarding the planet (FANTONI; TOLOMELLI; CABRI, 2022; MURATOGLU; YUCE, 2015; PEIJNENBURG et al., 2021). The essence of sustainability lies in pursuing development that harmonizes present needs while preserving the potential of coming generations (NATIONS, 2019). The attempts to link human development with the environment's well-being bring alternative strategies, such as implementing nanotechnology, which allows the manipulation of matter at the nanoscale (Chaudhary et al., 2023). Nanomaterials can address some improvements in technologies like water purification (ZEKIĆ; VUKOVIĆ; HALKIJEVIĆ, 2018), solar cells (WU et al., 2020; ZHOU et al., 2015), energy storage devices (THANGARAJ; SOLOMON; RANGANATHAN, 2019), air pollution mitigation (ASHOURI et al., 2021; THULASI; KATHIRAVAN; ASHA JHONSI, 2020), food packaging (SOHAIL et al., 2019; ÜNLÜSAYIN et al., 2016), and intelligent textiles (DULGER et al., 2016; YETISEN et al., 2016), among others.

Nevertheless, the emergence of sustainable or green nanotechnologies requires critically examining the "green" façade since these practices often conceal complexities that mask more profound ecological implications and demand rigorous assessments (CIAMBELLI; LA GUARDIA; VITALE, 2019; GOTTARDO et al., 2021; ROCO; HERSAM; MIRKIN, 2011). The production processes of specific nanomaterials can require substantial energy consumption and involve the use of hazardous substances, raising questions about their actual environmental benefit. Moreover, the full extent of their impact on human health and ecosystems is not often noticeable, mainly when novel nanomaterials are introduced without comprehensive prior assessment (FOJTŮ; TEO; PUMERA, 2017; KHARISSOVA et al., 2019; SOHAIL et al., 2019).

Some suitable assessments that can be adopted in sustainable nanotechnology are the green metrics, which come from the 12 principles of green chemistry. The green metrics are quantitative measures used to assess and quantify the environmental impact and sustainability performance of products, processes, technologies, or

systems (LENOIR; SCHRAMM; LALAH, 2020; REID; REED, 2016), which present specific scopes according to the different principles of green chemistry, focusing on stoichiometry relations, waste generation, energy consumption, etc. (detail description of green metrics can be found in section 2.2). For example, Life Cycle Assessment is a comprehensive approach that evaluates the environmental impact of a product or process throughout its entire life cycle, including raw material extraction, manufacturing, use, and disposal; thereby is considered one of the completest metrics to assess sustainability (GIROUX et al., 2021; PATI; MCGINNIS; VIKESLAND, 2014; SHELDON, 2018).

Carbon Quantum Dots (CQDs) emerge as greener nanomaterials in green nanotechnology since their synthesis can be adapted to sustainable guidelines and presents low toxicity behavior (JOHN; ABRAHAM; MATHEW, 2022). Nevertheless, the synthesis processes for CQDs obtention are varied, differing in synthesis technique and operational parameters, giving place to particles with distinctive properties, which hinders comparative analysis, formation mechanisms, and overall appropriate environmental assessments (DAS; BANDYOPADHYAY; PRAMANIK, 2018; HIMAJA; KARTHIK; SINGH, 2015; KUMAR et al., 2022). Therefore, upcoming research should address the development of environmental assessments of nanomaterials like CQDs to promote their incorporation into safe technologies. As the nexus of nanotechnology and sustainability continues to evolve, this research attempts to contribute to the paradigm of superficial green labels in CQDs synthesis by exploring the intricate synergy between nanotechnology and sustainability.

Previously, Pati, McGinnis, and Vikesland 2014 carried out an LCA to synthesize gold nanoparticles varying the reducing agent. The authors found that the significant environmental contribution corresponded to the embodied energy in gold. Furthermore, utilizing various biological reducing agents did not reduced environmental impacts compared to conventional commercial reactants. For example, in terms of cumulative energy demand, it is more beneficial to use borohydride, citrate, and grape pomace, which have consumption almost three times lower than using coriander and soybean seed extract.

Similarly, F. Wu, Zhou, and Hicks 2019 studied the sustainable manufacturing of titanium dioxide nanoparticles (TiO_2) by comparing six synthesis processes (physical, chemical, and biological). The chemical synthesis presented more influence on the precursors than the physical approach. In contrast, the physical approach demands notable volumes of auxiliary gas and significant energy infusion to sustain elevated temperatures, resulting in an escalated ecological load. Similarly, a substantial environmental burden is also anticipated within the biological approach owing to the necessity for bacterial culture media. In this case, biological synthesis is not the greener method and requires more development in laboratory-scale operations, focusing on energy efficiency and conversion rate.

The literature review conducted within the scope of this study (using the Scopus database) allows us to identify that, to date, there is just one research group (Chemistry Research Unit (CIQUP) from Portugal) that studies the synthesis and LCA of CQDs with a total of 6 published research. The core of the research group in this topic lies in the LCA for the synthesis (laboratory scale) of CQDs using citric acid and urea as carbon precursors with hydrothermal, microwave, and thermal oxidation techniques (CRISTA; DA SILVA; DA SILVA, 2020; FERNANDES; DA SILVA; DA SILVA, 2022; FERNANDES; ESTEVES DA SILVA; PINTO DA SILVA, 2021; SENDÃO et al., 2020). Additional synthesis process changes included commercial coffee grounds glucose and nitrogen doping strategies (CHRISTÉ; DA SILVA; DA SILVA, 2020; CRISTA et al., 2020; FERNANDES; DA SILVA; DA SILVA, 2022).

The main findings reported are the synthesis of CQDs from citric acid and urea with similar properties in morphology and photoluminescence (6-7 nm of size, blue-to-green emission, and similar types of surface functional groups) using the three different methods (hydrothermal, microwave, and thermal oxidation) (CRISTA; DA SILVA; DA SILVA, 2020; FERNANDES; ESTEVES DA SILVA; PINTO DA SILVA, 2021). The LCA developed points that microwave synthesis is a greener option due to its higher reaction yield and lower chemical need. Later, using different carbon sources (coffee grounds and glucose) in a thermal oxidation synthesis showed that the precursors lower the synthesis yields and fluorescence intensity compared to citric acid; nevertheless, these methods present lower environmental impacts (CRISTA et al., 2020; FERNANDES; DA SILVA; DA SILVA, 2022). Additionally, incorporating

ethylenediamine as a nitrogen source yielded the synthesis (CHRISTÉ; DA SILVA; DA SILVA, 2020).

Overall, the key to minimizing the environmental impacts of carbon dot synthesis lies in carefully selecting carbon precursors, optimizing electricity consumption, and adopting cleaner production strategies that reduce the use of additional chemicals. These studies found a good starting point to identify the differences among the sustainability of synthesis methods for CQDs. Nevertheless, they are focused on specific synthesis parameters using mainly citric acid as a carbon source, and there still needs to be a gap in some issues, like 1) identifying the critical points in carbon dot synthesis that contribute to environmental impacts and understanding their relative significance. 2) Evaluating the environmental impacts of different carbon precursor choices and their implications for the overall sustainability of carbon dot synthesis. 3) Identifying opportunities for improving the sustainability of carbon dot synthesis through selecting carbon precursors, optimizing synthesis routes, and adopting cleaner production strategies. To support this gap, a literature review named "Context and Prospects of Carbon Quantum Dots Applied to Environmental Solutions" was published in the Environmental Nanotechnology Monitoring and Management journal (https://doi.org/10.1016/j.enmm.2023.100884). Additionally, another publication involving the LCA and synthesis of sustainable CQDs is about to be submitted.

1.1 OBJECTIVES

1.1.1 General objective

Develop a life cycle analysis on existing Carbon Quantum Dots synthesis methods to identify and propose a green synthesis methodology for CQDs that optimizes environmental sustainability.

1.1.2 Specific objectives

- Identify and analyze the current Carbon Quantum Dots synthesis trends regarding sustainable technologies.
- Evaluate the sustainability of existing synthesis methods for Carbon Quantum Dots obtention by life cycle assessment.
- Synthesize Carbon Quantum Dots following green synthesis guidelines considering the environmental impact factors identified in the life cycle assessment.

1.2 RESEARCH STRUCTURE

This dissertation aims to tackle the comprehension and development of green synthesis methodologies of Carbon Quantum Dots intended for sustainable technologies. The work is divided into four chapters as follows:

Chapter 1 introduces the relevance and aim of the studied research problem. Chapter 2 discusses the role and history of CQDs in nanotechnology and sustainable technologies. Chapter 3 shows the LCA's methodological details and the synthesis process of the CQDs. Chapter 4 exhibits the results and discussions of the LCA study and the synthesis performed following green guidelines. Finally, a general conclusion encloses the main findings of this work.

2   CHAPTER 2: LITERATURE REVIEW

2.1   THE ROLE OF SUSTAINABILITY IN NANOTECHNOLOGY

Accelerated human progress demands considerable action to solve struggles like natural resource depletion and living beings' welfare. Global and local strategies are proposed to develop technologies to monitor and control pollution, improve energy efficiency, and preserve ecosystems to attain environmental-related challenges. Some of these strategies are the sustainable development goals (AXON; JAMES, 2018), the European Green Deal (GOTTARDO et al., 2021), the United Nations 2030 Agenda for Sustainable Development (LEE et al., 2016), and the Brazilian National Strategy for the Conservation and Sustainable Use of Biodiversity (BUSTAMANTE et al., 2019). Nevertheless, there is still room for improvement in innovation and technology solutions that can contribute to accomplishing these strategies (Axon and James, 2018).

The novel trends in science propose smart and nanoengineered materials as "materials of the future" since their enhanced chemical and physical properties related to size (1-100 nm) allow to boost a multitude of applications, including those related to environmental protection (energy conversion, pollution control, smart catalysts, water treatment, etc.) (DE MELLO DONEGÁ, 2014; WILLIAM D. CALLISTER; DAVID G. RETHWISCH, 2015). Remarkably, nanomaterials can be designed as individual building blocks by defining their chemical composition, size, and shape (DE MELLO DONEGÁ, 2014), which provides an opening to design sustainable nanomaterials.

One way to achieve sustainable nanomaterials production is to adopt the green chemistry principles proposed by Anastas and Warner in 1998 (listed below), which were thought of as "chemistry guidelines for the development of safe, cheap, and environmentally friendly methodologies, including the reaction conditions, reagents, and solvents, as well as the use of renewable natural materials and energy". Thereby, green chemistry can be referred to as processes or products with controlled environmental production (FANTONI; TOLOMELLI; CABRI, 2022; LENOIR; SCHRAMM; LALAH, 2020); when applied to nanotechnology, is usually called 'sustainable nanotechnology' or "green nanotechnology" (GOTTARDO et al., 2021).

The twelve principles of green chemistry (ANASTAS; WARNER, 1998)*:*

I.   **Prevention.** *It is better to prevent waste than to treat or clean up waste after it has been created.*

II. **Atom Economy.** *Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.*

III. **Less Hazardous Chemical Synthesis.** *Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.*

IV. **Designing Safer Chemicals**. *Chemical products should be prepared to preserve the efficacy of function while reducing toxicity.*

V.   **Safer Solvents & Auxiliary.** *Auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.*

VI. **Design for Energy Efficiency.** *Energy requirements should be recognized for their environmental and economic impacts and minimized. Synthetic methods should be conducted at ambient temperature and pressure.*

VII. **Use of Renewable Feedstocks.** *A raw material or feedstock should be renewable rather than depleted whenever technically and economically practicable.*

VIII. **Reduce Derivatives.** *Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided because such steps require additional reagents and can generate waste.*

IX. **Catalysis.** *Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.*

X.   **Design for Degradation.** *Chemical products should be designed so that at the end of their function, they break down into innocuous degradation products and do not persist in the environment.*

XI. **Real-Time Analysis for Pollution Prevention**. *Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control before the formation of hazardous substances.*

XII. ***Inherently Safer Chemistry for Accident Prevention***. *Substances used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.*

García-Quintero and Palencia 2021 summarized some of the most significant events regarding green chemistry and nanotechnology (Table 1). Both areas have had their heyday in parallel for nearly 50 years. Nevertheless, they still need to integrate more to make way for the production and use of environmentally friendly nanomaterials.

Table 1. Historical events related to green chemistry and nanotechnology.

Year	Historical fact	Reference
1959	Physicist Richard Feynman suggested potential applications of manipulating objects in nanoscales at the California Institute of Technology through his work "There's Plenty of Room at the Bottom."	(ZEKIĆ; VUKOVIĆ; HALKIJEVIĆ, 2018)
1962	Rachel Carson published her book Silent Spring about the scientific divulgation of the long-term adverse effects of pesticides on the environment.	(ALBINI; PROTTI, 2016)
1969	The Coca-Cola Company and the Midwest Research Institute in Kansas City analyzed two different beverage containers' environmental releases, an initial initiative of the Life Cycle Analysis.	(SHELDON, 2017, 2018)
1970	The US Environmental Protection Agency (EPA) was founded.	(PAULL, 2013)
1974	Norio Taniguchi defines the concept 'Nanotechnology'.	(SOHAIL et al., 2019)
1981	Observation and manipulation of nanostructures with the International Business Machines Corporation (IBM) Scanning Tunneling Microscope.	(ZEKIĆ; VUKOVIĆ; HALKIJEVIĆ, 2018)
1987	The World Commission on Environment and Development (Brundtland Commission) established the' Sustainable Development' concept.	(CONSTABLE; JIMENEZ-GONZALEZ; LAPKIN, 2009)
1988	Office of Pollution Prevention and Toxics at the EPA was founded.	(ALBINI; PROTTI, 2016)
1990	The Pollution Prevention Act in the American Congress approves it.	(SHELDON, 2017, 2018)
1990	Life Cycle Analysis is implemented.	(KRALISCH, 2009)
1991	"Green Chemistry" was proposed by Paul Anastas in the EPA.	(DICKS; HENT, 2015)
1991	Barry Trost proposed the "Atom Economy" metric.	(CONSTABLE, 2018)

1992	Roger Sheldon proposed the "Ecological factor" or E-factor.	(SHELDON, 2017, 2018)
1993	The first Green Chemistry Symposium was held: "Benign by Design: Alternative Synthetic Design for Pollution Prevention."	(ALBINI; PROTTI, 2016)
1995	The Green Chemistry Challenge Awards were established.	(MULVIHILL et al., 2011)
1996	The ISO 14001 emerged as an international standard for environmental management.	(JINDAL; JAIN, 2018)
1997	Green Chemistry Institute of the American Chemical Society was founded.	(MULVIHILL et al., 2011)
1998	Paul Anastas and John Warner established the 12 principles of green chemistry.	(DICKS; HENT, 2015)
1999	It launched the first publication of the Green Chemistry Journal in the Royal Society of Chemistry.	(DICKS; HENT, 2015)
1999	The metric "Effective Mass Yield" is proposed.	(HUDLICKY et al., 1999)
2001	Neil Winterton presents twelve additional principles of Green Chemistry.	(WINTERTON, 2001)
Early years of the 21st century	"Green Nano" emerges as a working line in the Green Chemistry Institute of the American Chemical Society and the Oregon Nanoscience and Microtechnologies Institute.	(KHAN, 2020)
2005	Professor John Andraos established that the Atom Economy can encompass all the chemical substances involved in the synthetic process.	(DICKS; HENT, 2015)

Reprinted with permission from Elsevier (GARCÍA-QUINTERO; PALENCIA, 2021).

Some of the resulting efforts to incorporate sustainability and nanotechnology are reflected in the formation of the NanoSafety Cluster (BNN, 2023), which encourages projects and discussions to promote environmental health and safety in nanotechnology innovations. The caLIBRAte project (European Commission 2019) presents a risk governance framework for assessing and managing human and environmental risk modeling, capable of reflecting the heterogenic and dynamic nature of nanomaterials and environmental systems. The Project on Emerging Nanotechnologies- PEN (PROJECT ON EMERGING NANOTECHNOLOGIES - PEN, 2011) identifies the relationship between knowledge and regulatory processes to provide objective information for the commercialization of nanomaterials, ensuring the protection of human health. The Technical Committee, 352 of the European Committee for Standardization (CEN/TC352 2001) adopted a preliminary work entitled "Nanotechnologies - Safe-by-Design concept dedicated for nanoscale materials and

products containing nanomaterials," which includes standards for classification, terminology, and nomenclature; metrology and instrumentation, science-based health, safety, and environmental practices; and nanotechnology products and processes (GOTTARDO et al., 2021).

Despite the efforts to conceive nanotechnology with a sustainable approach, they must be strengthened since they are in an initial stage. There must be a clear consensus on how sustainability should be measured for nano products currently on the market (food, food packaging, cosmetics, and agricultural products) and those in the research process (DUTTA; DAS, 2021; ROSE et al., 2021). The design of nanomaterials assessed under sustainable metrics would allow them to obtain their benefits in technological applications with security for health and resource protection.

2.2 SUSTAINABILITY ASSESSMENT METHODS IN NANOTECHNOLOGY

Nanomaterials obtained through bio-mediated synthesis (additional information in section 2.3.2) are commonly called green nanomaterials. Nevertheless, this denomination might need to be clarified since most studies do not consider determining the environmental impacts involved (DUTTA; DAS, 2021; GARCÍA-QUINTERO; PALENCIA, 2021; HISCHIER; WALSER, 2012; JANKOVIĆ; PLATA, 2019; SALIERI et al., 2018). For example, synthesizing bio-mediated gold nanoparticles (AuNPs) can present more environmental impact than chemically synthesized AuNPs. The energy requirement to form the AuNPs was a significant contribution factor in the environmental assessment, with a cumulative energy demand of 0.85 MJ/mg AuNPs using sugar beet pulp and 0.4 MJ/mg AuNPs using borohydride (PATI; MCGINNIS; VIKESLAND, 2014). A similar situation occurs with Titanium dioxide nanoparticle synthesis (TiO_2 NPs) in which the energy demand plays a vital role in the environmental impacts generated. In this case, bio-mediated synthesis with microorganisms (0.019 MJ/mg TiO_2 NPs) presents higher cumulative energy demands than sol-gel (0.001 MJ/mg TiO_2 NPs), solvothermal (0.002 MJ/mg TiO_2 NPs) and flame spray pyrolysis synthesis (0.011 MJ/mg TiO_2 NPs), only surpassed by radio frequency thermal plasma synthesis (0.032 MJ/mg TiO_2 NPs) (WU; ZHOU; HICKS, 2019).

Thus, "green nanomaterial" or "sustainable nanomaterial" is usually taken lightly. Green metrics (atom economy, E-Factor, mass-based metrics, energy-based metrics, life cycle assessment) can be used to avoid the mentioned problem as a strategy to measure the sustainability of nanomaterials (GARCÍA-QUINTERO; PALENCIA, 2021; HISCHIER; WALSER, 2012; SALIERI et al., 2018).

2.2.1 Atom economy

Atom economy is related to the second principle of green chemistry and stands for minimizing waste to the molecular level (PARENT, 2002). Atom economy establishes conversion efficiency in a chemical reaction regarding all the atoms involved and the desired products expressed in a balanced chemical reaction. The expression to determine atom economy is described as follows:

$$Atom\ Economy = (SCP \times MWP) / \sum (SCR \times MWR) \tag{1}$$

Where SCP and SCR are stoichiometric coefficients of products and reactants, MWP and MWR are the product and reactant molecular weights, respectively. Atom economy enables the comparison of molar efficiency in synthesis with a corresponding target nanomaterial, though most of the reactions of nanomaterials synthesis do not have fixed element stoichiometry and become a parameter challenging to quantify. Besides, it disregards aspects like energy consumption, using solvents and catalysts, and even the effect on the planetary health of reactants, products, and byproducts (GARCÍA-QUINTERO; PALENCIA, 2021).

To solve this gap, multifunctional efficiency was later proposed as a specific metric to design nanomaterials with the highest incorporation of functional units and the minimum number of inactive components (GARCÍA-QUINTERO; PALENCIA, 2021). It is defined as follows:

$$Multifunctional\ efficiency = FR \times PE = \frac{n_{FU2}}{m_{BU} \times r_{PRS}} \tag{2}$$

FR is the functionality ratio, which refers to a building unit of the nanomaterial that provides properties for a specific task in the final application (drug delivery,

antimicrobial activity, electric transport, etc.). PE is process efficiency; n_{FU} is the number of functional units; m_{BU} is the total number of building units of the nanocarrier; and r_{PRS} is the number of process steps involved in the production process (Freund et al., 2018).

2.2.2 E-Factor

The e-Factor or Ecological-Factor is related to green chemistry's first and second principles. E-Factor establishes the relationship between the mass of waste generated in the synthetic process and the product mass, allowing the identification of partial and global perspectives on waste production in one-step and multi-step synthetic methods (GARCÍA-QUINTERO; PALENCIA, 2021; SHELDON; BODE; AKAKIOS, 2022). E-factor is defined as follows:

$$E - Factor = \frac{Mass\ of\ waste\ (kg)}{Mass\ of\ product\ (kg)} \tag{3}$$

Although the E-factor is similar to the atom economy, it stands apart due to its independence in requiring the molecular formula. Besides, the E-factor can consider the actual performance of the reaction and the inclusion of solvents. Some examples of recommended E-Values in industries are shown in Table 2. Nanosynthesis presents a high E-factor value among other productive processes because it implies the principle of dematerialization (REID; REED, 2016). This metric helps compare different synthesis processes; moreover, a flaw in E-Factor is that the potential hazard of the waste needs to be considered. For instance, each analysis must be evaluated according to its context with an objectively delimited scope (GARCÍA-QUINTERO; PALENCIA, 2021; JANKOVIĆ; PLATA, 2019).

Table 2. Recommended E-Values in different industries.

Productive sector	E-Factor recommended (kg waste/kg product)
Oil refining industry	0.1
Bulk chemicals	1.0 – 5.0
Fine chemicals	25.0 – 100.0
Pharmaceuticals	25.0 – 100.0
Nanosynthesis	100.0 – 100,000.0

Adapted from García-Quintero and Palencia 2021 and Sheldon, Bode, and Akakios 2022.

2.2.3 Mass-based metrics

Mass-based metrics are related to the first, second, fifth, eighth, and ninth principles and allow for calculation and interpretation regarding the efficiency of the material conversion for a specific procedure. Some mass metrics are the Process Mass Intensity (PMI), Effective Mass Yield (EMY), and Reaction Mass Efficiency (RME) (GARCÍA-QUINTERO; PALENCIA, 2021; SHELDON, 2017).

PMI includes the combined mass of all substances employed in both the synthesis and purification stages, along with the actual yield of the chemical reaction (CONSTABLE, 2018). PMI considers the E-Factor in its expression and allows it to involve material efficiency, use of resources, and generation of waste. Nevertheless, it presents difficulties when used in polydisperse systems since the particle distribution might be nonuniform, and incomplete reactions occur, leading to inexact selectivity (GARCÍA-QUINTERO; PALENCIA, 2021; REID; REED, 2016). PMI is defined as follows:

$$PMI = \frac{Mass\ of\ waste(kg) + Mass\ of\ product(kg)}{Mass\ of\ product(kg)} = E - factor + 1 \qquad (4)$$

EMY considers the mass of the products but also the non-benign reactants involved, thereby is closer to guaranteeing more safety in the evaluated processes. Nevertheless, there is no established parameter to decide which is a non-benign reagent, leaving the decision to the researcher's subjectivity. EMY is defined as follows:

$$EMY = \frac{Mass\ of\ products \times 100}{Mass\ of\ non-benign\ reagents} \qquad (5)$$

RME is a metric that involves the reactants to produce desired products and can integrate EMY and Atom economy metrics as well as the Stoichiometric Factor (SF). Thereby, RME can consider the chemical transformation during a reaction, although it is difficult to use when numerous byproducts exist (GARCÍA-QUINTERO; PALENCIA, 2021). The basic RME is defined as follows:

$$RME = \frac{Mass\ of\ products(kg)}{Mass\ of\ reagents(kg)} \qquad (6)$$

When integrated into EMY, atom efficiency and SF is defined as:

$$RME = \frac{EMY \times Atom\ economy}{SF} \tag{7}$$

Being SF is defined as:

$$SF = 1 + \frac{\sum mass\ of\ excess\ reagent}{\sum mass\ of\ stoichiometric\ reagents} \tag{8}$$

2.2.4 Energy-based metrics

Energy-based metrics apply the sixth principle of green chemistry and determine the energy demand required in a process. Generally, it is simple to calculate and can be measured through Energy Efficiency, Specific Productivity, and Energy Intensity (GARCÍA-QUINTERO; PALENCIA, 2021). The last one is a more suitable metric for nanomaterial synthesis by considering the total energy used to obtain a determined product mass. Nevertheless, energy intensity omits aspects related to material conversion and potential environmental risk (ALBINI; PROTTI, 2016). Energy intensity is defined as:

$$Energy\ Intensity = \left(\frac{Total\ process\ energy\ (MJ)}{Mass\ of\ the\ final\ product(kg)}\right) \tag{9}$$

2.2.5 Life cycle analysis (LCA)

LCA is a complete parameter to estimate the potential environmental impacts of products, services, and processes across their entire life cycles. It is based on the concept of life cycle thinking. It uses a systematic and iterative approach consisting of four axes: goal and scope, life cycle inventory, life cycle impact, and life cycle assessment (GARCÍA-QUINTERO; PALENCIA, 2021; SALIERI et al., 2018).

The goal and scope (boundaries) of an LCA define a target product or process in a functional area (functional unit) and the analysis framework. It can be defined under different approaches:

- Cradle-to-grave: obtainment of raw materials until final disposal.
- Cradle-to-gate: obtaining the raw materials and manufacturing.
- Gate-to-gate: manufacturing.
- Gate-to-grave: manufacturing and final disposal.

- Cradle-to-cradle: There are no final products or processes, but they are reintegrated into the studied system; this approach is considered for circular production processes.

The life cycle inventory consists of collecting, validating, and quantifying necessary information regarding energy and materials from the phases established in the goal and scope (input and output flows), such as precursors, techniques, waste generation, potential destination, emissions, etc. Different databases exist (Ecoinvent, SimaPro, GABI, Agribalyse, among others) that compile this information for additional resources, easing the inventory analysis (HISCHIER; WALSER, 2012; SALIERI et al., 2018).

The life cycle impact assessment (LCIA) consists of calculating the potential environmental and human health impacts through indicators quantified through impact scores (IS) that allow equivalences and comparisons of results against reference compounds. The most relevant impact categories are Global Warming (GW), Land Use (LU), Abiotic Resource Depletion (ADP), Eutrophication (EU), Acidification (AC), Photochemical Ozone Creation (POCP), Ozone Depletion (OD), Human Toxicity (HH), Ecotoxicity (EC), Respiratory Effects (RE), Fossil Fuel Depletion (FF), and Cumulative Energy Demand (CED) (GARCÍA-QUINTERO; PALENCIA, 2021; HAUSCHILD; HUIJBREGTS, 1997). Then, the IS for the potential environmental impacts is calculated as the summary of the individual flows from the inventory for each impact category, defined as:

$$IS_j = \sum_i \sum_k \sum_l IS_{j,i,k,l} \tag{10}$$

Where j is the impact category, i is the contribution of the elementary flow, k is the location of the product or process under study, and l is the environmental compartment (atmosphere, soil, water, biota, etc.).

The elementary flows of the impact categories are determined under impact scores:

$$IS_{j,i,k,l} = Q_{i,k,l} \times CF_{j,i,k,l} \tag{11}$$

Where $Q_{i,k,l}$ is the quantity of elementary flow i extracted at location k or emitted to compartment l at location k, in simplified words, it can be understood as the quantity of emission or expended resources in a determined place.

$CF_{j,i,k,l}$ is the characterization factor under each impact category j for elementary flow i extracted at location k or emitted to compartment l at location k. CF quantifies the potency of the emitted substances for the specific impact category and is expressed as:

$$CF = FF \times XF \times EF \tag{12}$$

Where FF is the product of the fate factor, XF is the exposure factor, and EF is the effect factor. FF represents the persistence of a substance in a matrix (water, air, soil); XF represents the exposure of sensitive targets (living beings) in the receiving environment; EF represents the effects of the exposure on the targets for the impact category (HAUSCHILD; HUIJBREGTS, 1997; SALIERI et al., 2018).

The life cycle interpretation consists of comprehending the results given in the previous axes, including factors like the uncertainty of the data, comparisons, context, and relevance of the results since these might vary according to the geographic area, type of manufacturing, cultural and temporal aspects (HISCHIER; WALSER, 2012; SALIERI et al., 2018).

Even though LCA is conceived as the completest tool to evaluate the sustainability of processes in general and is the most suitable metric to analyze nanomaterials, it still needs to be more accurate. Currently, there is insufficient inventory information and gaps in the characterization factors, environmental release accounting, and nanomaterials modeling (GARCÍA-QUINTERO; PALENCIA, 2021; HISCHIER; WALSER, 2012; SALIERI et al., 2018).

Additionally, some of the future challenges for sustainability assessment for nanomaterials are integrating risk assessments and economic assessments and applying regulatory frameworks to metrics to analyze, like LCA, to develop and

produce safe and competitive nanomaterials (DENG et al., 2017; GOTTARDO et al., 2021; HORGAN et al., 2023; PEIJNENBURG et al., 2021; SALIERI et al., 2021).

2.3 CARBON QUANTUM DOTS: TOWARDS GREENER NANOMATERIALS

The enforcement of greener approaches to design nanomaterials is achievable depending on the chemical nature of the precursor and the desired structure (DEVATHA; THALLA, 2018; KHARISSOVA et al., 2019). Specific nanomaterials, such as Carbon Quantum Dots (CQDs), can be obtained by adopting nearly all 12 green chemistry principles and, thus, are better suited for minimizing environmental consequences (Table 3).

Table 3. Green chemistry principles embraced by CQDs.

Green chemistry principle		Green attribute of CQDs	Ref.
I	Prevention	Subproducts can be reduced through high-yield production synthesis. For example, reports using carbon sources such as Chinese ink (61%) and bee pollen (30.8%) have allowed production yields.	(YANG et al., 2014; ZHANG; YU, 2016)
II	Atom Economy	Further exploration and study are still needed to establish the molecular formula of CQDs and some carbon precursors. However, EDS and XPS analysis are some approaches to address the elemental composition of CQDs.	(HIMAJA; KARTHIK; SINGH, 2015; SINGH et al., 2020)
III	Less Hazardous Chemical Synthesis	The primary reagents for CQDs can be water and non-toxic carbon sources at neutral pH.	(Shi et al., 2019)
IV	Designing Safer Chemicals	CQDs were shown to be the least toxic quantum dot. CQDs can promote plant cell proliferation and root growth depending on the surface properties and concentration (<0.25 mg/ml).	(LI et al., 2020b; RANI et al., 2020)
V	Safer Solvents & Auxiliary	CQDs can be produced using water as a solvent in hydrothermal and microwave synthesis methodologies.	(BORUAH et al., 2020; KURIAN; PAUL, 2021)
VI	Design For Energy Efficiency	The time and temperature of the reaction can be diminished using methodologies like microwave and sonochemical assisted.	(HUANG et al., 2020b; JING et al., 2019)
VII	Use Of Renewable Feedstocks	It is possible to adopt waste management of organic residues in the obtention of CQDs using various carbon sources (fruit and vegetable peels, husks, paper, soot, etc.).	(ARIAS et al., 2021; HAN et al., 2022)

| VIII	Reduce Derivatives	Some methodologies for CQD obtention present simple procedures (one-step process) with reduced derivatives.	(DOSHI; MUNGRAY, 2020; WANG et al., 2016)
IX	Catalysis	Reagents like H_2O_2 and ethanol are good assistants in CQD synthesis, reducing the reaction time and promoting oxidation.	(KUMARI; KUMARI; DAS, 2018; LIU et al., 2016)
X	Design For Degradation	CQDs can be autophagous since they can oxidize to CO_2 under natural light.	(LIU et al., 2021)
XI	Real-Time Analysis for Pollution Prevention	Although no reports study a real-time analysis in CQD formation, they can be used as sensors for real-time monitoring of contaminants like heavy metals, dyes, radioactive substances, etc.	(JOHN; ABRAHAM; MATHEW, 2022; WANG; HU, 2014)
XII	Inherently Safer Chemistry for Accident Prevention	It is possible to synthesize CQDs without using dangerous substances or, when necessary, replace reagents (H_3PO_4 instead of H_2SO_4) to carry out a safer process.	(GUPTA et al., 2020; ZHANG; SUN; WU, 2015)

Elaborated by the author.

CQDs are zero-dimensional nanomaterials with a size ranging from 1 to 10 nm. This small size involves the incidence of quantum confinement effects, which give rise to optical characteristics and electronic properties like broad and continuous absorption spectra, fluorescence, narrow emission, and high light stability (ARIAS et al., 2021; NAMDARI; NEGAHDARI; EATEMADI, 2017; RANI et al., 2020). As another kind of quantum dots, CQDs have more atoms on the surface due to 3-dimensional truncation (RANI et al., 2020), allowing high functionality. Depending on the type of synthesis and functionalization, the carbon-based skeleton's surface possesses various functional groups, including amino, amide, epoxy, oxygen, and hydroxyl functional groups (LIU; WANG; DU, 2020; LIU et al., 2020; TRAVLOU et al., 2018; WANG et al., 2019).

Additionally, CQDs are biocompatible, chemically stable, and can be obtained at low cost from diverse carbon sources (HUANG et al., 2020a; MOLAEI, 2019). As a result, CQDs have varied features that make them useful in different fields, including optoelectronics, medical, energy, and environmental applications (SADAT et al., 2022; TANG et al., 2021b; WU et al., 2020). Notably, the use of CQDs in environmental applications aids in the development of more sustainable technology, with good performance reported in research related to

wastewater treatment, pollutant detection, solar cells, and hydrogen production, among others (SADAT et al., 2022; SYED et al., 2019; WANG et al., 2019).

The described characteristics of CQDs have turned the material into an exciting research topic. According to the Scopus database, the bibliometric assessment performed in this work to synthesize CQDs (Figure 1) depicts how the number of publications presents a growing tendency in the last ten years. The publications considering green or sustainable synthesis also show an increasing trend, representing 26% of all publications related to the synthesis of CQDs.

Figure 1. Research published annually on CQDs synthesis.
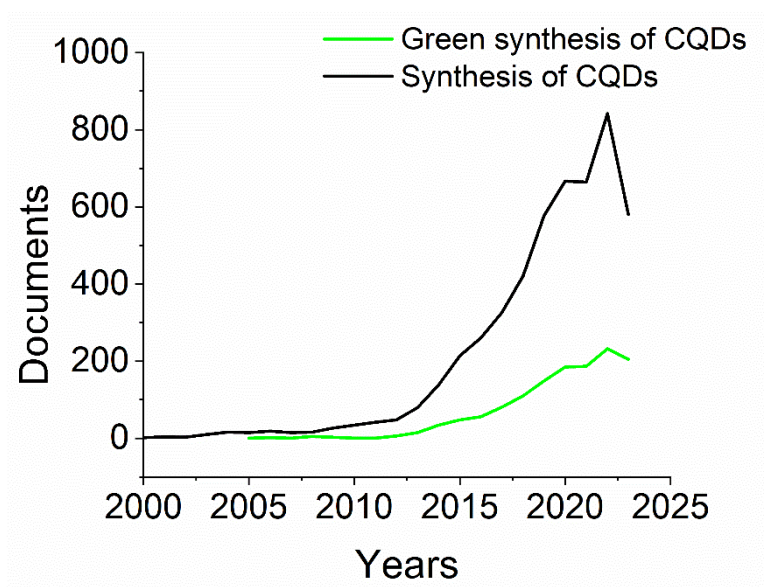
Elaborated by the author.

The topics associated with green and sustainable synthesis are shown through a network visualization of the keywords in the last years (Figure 2) using a minimum occurrence of ten words for the analysis. The main interests of research are clustered into four main topics: carbon, semiconductor carbon dots, fluorescence, and chemistry. Figure 2 indicates that the research on this topic prioritizes aspects of the material in which the clusters interconnect, forming attached networks. Additionally, the most isolated cases are recently published research of applications with CQDs related to photocatalysis, antibacterial activity, and medicine (synthesis and release of drugs, cancer cell studies, and bioimaging).

Figure 2. Document network visualization based on keywords for green (sustainable) CQDs.
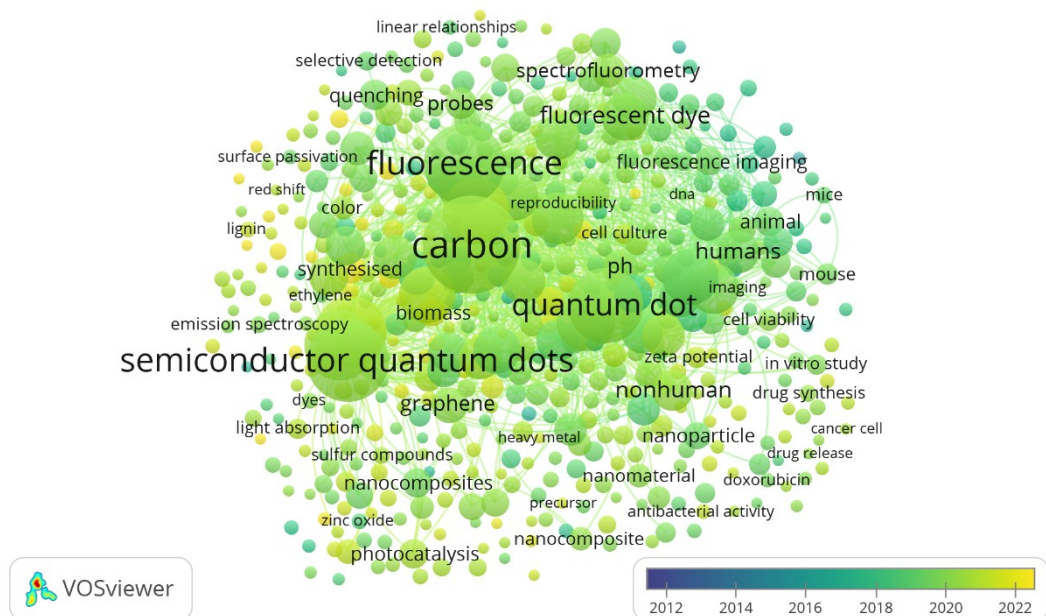
Elaborated by the author.

2.3.1 Main features of CQDs

Quantum dots (QDs) are semiconductor microcrystals with quantum confinement effects (with size between 1-10 nm), in which a short-wavelength shift appears in the absorption edge due to a separation increase between energy levels. The absorption of the photons produces excited states that are followed by optical deexcitation through light emission. This phenomenon gives place to different forms of luminescence, such as fluorescence, phosphorescence, bioluminescence, or chemiluminescence (ARIAS et al., 2021; DYES, 2008). CQDs are among the most recent types of quantum-sized nanoparticles discovered. In 2004, the group XU et al., 2004 accidentally discovered CQDs when they performed a purification test of a single-wall carbon nanotube. Using gel electrophoresis, the researchers found impurities that were carbon nanoparticles. To their surprise, these particles were highly fluorescent and would attract the interest of further studies (ARIAS VELASCO et al., 2023).

By these means, recognizing the properties of nanomaterials like CQDs allows us to determine their utility and aptness for a specific application, such as a wide range of visible light absorption for photocatalysis or low toxicity for drug release. CQDs' most

studied features are morphology, crystalline structure, optical properties, surface composition, and toxicity.

a) Morphology

The characterization techniques to identify the morphology characteristics of CQDs are Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), and Atom Force Microscopy (AFM). Given the size of CQDs, equipment is required to reach the scale of 1 to 10 nm (HIMAJA; KARTHIK; SINGH, 2015; JOHN; ABRAHAM; MATHEW, 2022). CQDs obtained through different green synthesis processes (hydrothermal, chemical oxidation, microwave, etc.) and carbon sources (vegetables, commercial reactants, fungi, etc.) tend to present a uniform size, spherical morphology, and homogeneous distribution (DEVI et al., 2018; JIA et al., 2020; LI et al., 2020a; PARK et al., 2020; THULASI; KATHIRAVAN; ASHA JHONSI, 2020). Nevertheless, some report evidence of the obtention of particles with larger sizes and aggregation, attributed to the synthesis parameters such as pretreatment methods and insufficient temperature or time of reaction (DOSHI; MUNGRAY, 2020; MÄKINEN et al., 2018; SABET; MAHDAVI, 2019).

b) Crystalline structure

The characterization techniques to identify the crystalline structure of CQDs are X-ray diffraction (XRD) and Resolution Transmission Electron Microscopy (HR-TEM) (John, Abraham, and Mathew, 2022). CQDs are mainly amorphous, and their crystallinity varies depending on the carbon source used in the synthesis. Nevertheless, CQDs present small graphitic or graphitic-like domains within their structure with a prominent 2θ peak around 22° and another less intense around 44°C (KHAN et al., 2019; PARK et al., 2020; SABET; MAHDAVI, 2019). CQDs commonly present lattice spacings close to 0.21 nm, related to the graphite carbon's diffraction facets (100) (JIA et al., 2020; KAILASA et al., 2019).

c) Optical properties

The primary characterization techniques to identify the optical properties of CQDs are Ultraviolet-Visible (UV-Vis) spectrophotometry and fluorescence spectrophotometry. To a minor extent, photoluminescence, electrochemiluminescence, and time-resolved fluorescence spectroscopy (JELINEK, 2017; JOHN; ABRAHAM; MATHEW, 2022; ZHAO et al., 2020). The optical attributes of CQDs likely represent their most remarkable and distinguishing characteristics since they are responsible for most of the known applications for CQDs (photo-responsive applications like sensors, light sensitizers, and photocatalysts) (ARIAS VELASCO et al., 2023). CQDs exhibit strong optical absorption within the UV spectrum, featuring a long tail that extends into the visible range and even to the near-infrared (NIR) region (LIU, 2020).

CQDs present excitation-dependent photoluminescence (excitation-dependent fluorescence emission), wide spectral range, and high emission intensities. These attributes are accountable for the multicolor color properties of CQDs upon exposure to ultraviolet light (JELINEK, 2017).

The fluorescence origin observed in CQDs is still under discussion but is possibly attributed to quantum confinement effects by conjugated π-domains and surface defects (JELINEK, 2017; MOLAEI, 2019). When conjugated π-domains cause fluorescence, the large sp^2 domain decreases the band gap, increasing the conjugated structure (LIU, 2020). On the other hand, surface defects formed by surface oxidation capture spots of excitons, causing surface-state-related fluorescence. This particular feature can be modulated by the synthesis method (JELINEK, 2017; LIU, 2020).

d) Surface composition

The characterization techniques to identify the surface composition of CQDs are Raman scattering, X-ray Photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy (JELINEK, 2017). CQDs comprise a carbon core with different surface atoms attached, like nitrogen-, oxygen-, and carbon-bonded units. In FTIR analysis, it is expected to find

a spectrum for CQDs with bands at 3378 cm^{-1} (attributed to O-H groups stretching vibration), 1608 cm^{-1} (attributed to C=O stretching), and 1130 cm^{-1} (attributed to CO stretching) (JELINEK, 2017; RANI et al., 2020). As a result, CQDs can contain abundant functional groups on the surface, facilitating their surface modification (passivation and functionalization) and heteroatom doping. These modifications on the CQDs surface bring advantages like increasing chemical and physical stability, extending life function, enhancing water dispersion, and increasing catalytic activity (DIMOS, 2016; LIM; SHEN; GAO, 2015; WU et al., 2020).

e) Toxicity

Different techniques identify a material's toxicity depending on the tested living being (cell, plant, mammal). Essentially, toxicity is established as the damage caused by a given dose or substance exposure, and it is measured as LD$_{50}$, the average toxin that kills 50% of the population analyzed (EU, 2011). CQDs have exhibited low toxicity. Nevertheless, aspects like concentration, heteroatom doping, and surface charge cause alteration in their contact behavior (HAVRDOVA et al., 2016; USMAN et al., 2020; YANG et al., 2009). Some of the adverse effects reported for CQDs are growth decrease for yeast cells (concentration > 25 mg/ml) (BAGHERI et al., 2018), inhibition of *E.coli* (concentration > 0.0034 mg/ml) (GAGIC et al., 2020), abnormalities in the cell cycle causing reduction of 50% of the HEL293 cell viability (concentration > 0.5 mg/ml) (MAROUZI et al., 2021), LD$_{50}$ in 96 h for the microalgae C*. Pyrenoidosa* (concentration > 0.232 mg/ml) (XIAO et al., 2016). But also promotes root growth for mung beans (concentration < 0.5 mg/ml) (ZHANG et al., 2018) and wheat (concentration <0.15 mg/ml) (TRIPATHI; SARKAR, 2015). The extent of these effects may differ based on the biodistribution of CQDs within the biological system, so a comprehensive understanding of this topic is still under study.

2.3.2 Synthesis routes of CQDs

Different methods are suitable for synthesizing CQDs in the top-down and bottom-up approaches. In the top-down process, the macromolecule undergoes

disintegration or dispersion into smaller-sized CQDs through physical or chemical means. The most used methods in this approach are arc discharge, laser ablation, and acidic oxidation). Conversely, the bottom-up process primarily involves the chemical reaction-driven polymerization and carbonization of small molecules to form CQDs. The most used methods in this approach are the combustion routes, the microwave, hydrothermal, and solvothermal methods (JELINEK, 2017; WANG et al., 2019).

The **arc discharge** technique involves the reorganization of carbon atoms, which are broken down from bulk carbon precursors, within the anodic electrode. This reorganization is facilitated by the gas plasma generated in a sealed reactor. The temperature within the reactor can soar to as high as 3700°C due to the electric current, leading to the creation of a high-energy plasma. Within the cathode, carbon vapor assembles to give rise to CQDs (WANG et al., 2019). This synthesis method was first used to obtain CQDs when a single-wall carbon nanotube purification test was performed (XU et al., 2004). The CQDs obtained by arc discharge present good dispersion in water, but the particle distribution tends to be heterogeneous (DAS; BANDYOPADHYAY; PRAMANIK, 2018; RASAL et al., 2021; WANG et al., 2019).

The **laser ablation** technique employs a high-energy laser pulse to irradiate the target's surface, inducing a thermodynamic state marked by elevated temperature and pressure. Therefore, laser ablation leads to rapid heating and evaporation, transitioning the material into a plasma state. Subsequently, the vapor crystallizes to yield nanoparticles (WANG et al., 2019). The CQDs obtained by laser ablation allow a homogeneous distribution of the particles and distinct fluorescence properties. Nevertheless, the operational requirements are complex and expensive (BAKER; BAKER, 2010; DAS; BANDYOPADHYAY; PRAMANIK, 2018; WANG et al., 2019).

The **chemical oxidation (acid oxidation)** technique is extensively used to exfoliate and disintegrate bulk carbon into nanoparticles. This process also facilitates introducing hydrophilic groups, such as hydroxyl or carboxyl, onto the surface. These modifications lead to CQDs forming, enhancing their water dispersibility and fluorescence properties and promoting high mass production yields (61%) (WANG et al., 2019; YANG et al., 2014). Nevertheless, chemical oxidation requires the use of hazardous reagents like HNO_3 and H_2SO_4 (GUPTA et al., 2020; WANG et al., 2019).

The **combustion** technique includes pyrolysis, thermal oxidation, and electrothermal carbonization. In the synthesis process, the CQDs are formed by raising the temperature of the reaction mixture, leading to decomposition and carbonization processes that culminate in the formation of quantum particles (Goswami et al., 2021). This method is simple and versatile, although it might give place to forming CQDs with heterogeneous distribution and aggregated particles (GOSWAMI et al., 2021; RANI et al., 2020; WANG et al., 2019).

The **microwave** technique involves subjecting a carbon source to microwave radiation of synchronized perpendicular oscillations of electric and magnetic fields. This specific energy penetrates the carbon material uniformly, triggering swift and efficient heating. Consequently, the carbon material absorbs electromagnetic radiation and transforms it into thermal energy (SINGH et al., 2019). Notably, the microwave method has emerged as a well-established technique, owing to its ability to achieve rapid synthesis. Mainly, microwave-hydrothermal is a variation of the process that improves the heating speed and eliminates the effects of temperature gradients. In addition, obtaining temperatures above the boiling point by working at increased pressure leads to the fast preparation of monodisperse, small-sized carbon particles. CQDs obtained by this variation usually present higher quantum yields and smaller particles than those obtained using the standard microwave method. In conclusion, this technique is simple, fast, and eco-friendly, making it a preferred choice for preparing CQDs abundant in oxygen-containing groups. Nevertheless, the microwave method still presents challenges for high-scale production (SCHWENKE; HOEPPENER; SCHUBERT, 2015).

The **hydrothermal** technique involves the exposure of an organic precursor solution within water in a Teflon-lined stainless-steel autoclave with pressures exceeding 1 atmosphere and temperatures superior to 200°C. These reaction parameters allow the deoxidization of water molecules, and H^+ and OH^- ions are produced, creating repulsions between the carbon layers and allowing their oxidation, which also contributes to forming oxygen-containing functional groups. In hydrothermal synthesis, the carbon source undergoes a series of transformative stages, including dehydration, polymerization, carbonization, and passivation (Einarsrud and Grande,

2014; Y. Wang and Hu, 2014). This technique is the most used method due to the formation of particles with homogeneous distribution and intense fluorescence. Nevertheless, hydrothermal might imply a long reaction time and high energy consumption (PANG et al., 2014; RANI et al., 2020).

Additionally, when the solvent in the reaction is different from water, the method is known as solvothermal; some solvents include ethanol, toluene, ethylene glycol, dimethylformamide, etc. As an advantage, the fluorescence intensity can be increased. Nevertheless, undesired subproducts can be formed (OTTEN et al., 2022; WANG et al., 2019).

2.3.3 Carbon precursors for CQD synthesis

The bottom-up strategies for the synthesis of CQDs have gained attention due to their straightforward procedures, potential for easy scalability in production, precise control over initial molecule design, affordability, and overall because this allow the adaption of sustainable practices using carbon sources like minerals, residues, commercial reactants, forestry biomass, food, organic waste, and fungus (DAS et al., 2021; DIMOS, 2016; JAMALUDIN; RASHID; TAN, 2018; KHAN; PATIL, 2020; KURIAN; PAUL, 2021). The resulting size and fluorescence quantum yield of CQDs from different carbon sources are shown in Figure 3.

Figure 3. Characteristics of CQDs obtained from different carbon precursors.
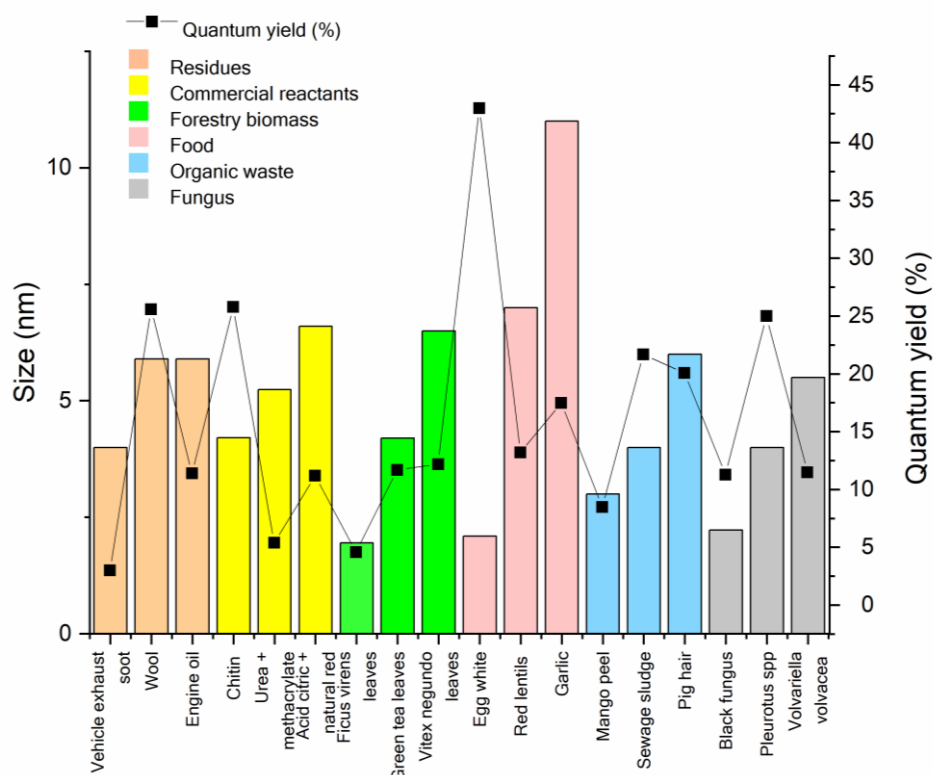
Elaborated by the author. (Residues: (THULASI; KATHIRAVAN; ASHA JHONSI, 2020), (WANG et al., 2016), (K; V; P, 2022).Commercial reactants: (JIANG et al., 2020), (ZHAO et al., 2023), (CHANG et al., 2023). Forestry biomass: (PEI et al., 2023),(Khan et al., 2023),(Korah and Mathew, 2023). Food: (ZHANG; SUN; WU, 2015), (KHAN et al., 2019), (ZHAO et al., 2015). Organic waste: (JIAO et al., 2019), (HU; GAO, 2020), (WANG et al., 2016). Fungus: (QIN et al., 2021), (VENKATESWARLU et al., 2018), (ZULFAJRI et al., 2020).)

The use of organic waste products is beneficial cause it involves waste management, is cost-effective, and has wide availability. This type of carbon source can achieve zero discharge wastes in the agroindustry (ARIAS et al., 2021; FAN et al., 2020). Besides, the production of CQDs with a desired quantum size and optical features (excitation-dependent fluorescent emission) can be obtained with an adequate synthesis method and a correct characterization of the carbon source (RANI et al., 2021) since different reports using the same precursor indicated the obtention of CQDs with dissimilar characteristics. For example, the obtention CQDs from lemon juice obtained with the hydrothermal method (3 hours under 200°C) can form particles with an average size of 5.8 nm and a fluorescence quantum yield (QY) of 10.20% (TADESSE et al., 2018), while using the solvothermal method (10 hours under 190°C) produces particles with 4.8 nm of average size and a QY of 28% (DING et al., 2017).

CQDs obtained from biomass carbon sources also present a promising performance as other nanomaterials (including non-biomass-derived CQDs) in applications like cellular labeling and imaging, wound healing, gene detection, sensing of pollutants, photocatalysis, solar cells design, and hydrogen production (FAN et al., 2020; RANI et al., 2020). Nevertheless, the diverse synthesis methods and their abundant variations complicated the standardization process for CQDs, hindering the efforts to unveil aspects like the formation mechanisms, fluorescence mechanisms, costs of production, and environmental impacts and associated risks (KURIAN; PAUL, 2021; SADAT et al., 2022; SHI et al., 2019; SRIVASTAVA; DEV; KARMAKAR, 2018).

Some interesting carbon sources with potential for CQDs' production derived from agricultural waste are banana peel, orange peel, and pinion shell. For example, the global production of bananas was 116 million tons in 2019 and 6.8 million tons in Brazil in 2022. From this production, 30–40% of the total banana cropped is rejected for not meeting quality standards. The residual banana waste can be discarded as municipal waste, used as animal food (although there are some concerns about the effect of tannin in the husks on the animals that consume it), or used to manufacture many biochemical products (HIKAL et al., 2022; IBGE, 2022). The use of banana peels is advantageous since they contain a variety of phytochemicals like phenols, carbohydrates, proteins, amino acids, fiber, etc., that can be extracted to obtain high-value products (HIKAL et al., 2022). Banana peels have also been previously used as the carbon source for CQDs synthesis bringing reproductively fluorescent particles of 5.33 nm (LIVIA E. DA SILVA; ORLANDO LUCAS DE L. CALADO; CINTYA D. A. DO E. S. BARBOSA, 2023), 3-6 nm (HJORTH et al., 2017) , and 5 nm (ATCHUDAN et al., 2020).

The global orange production is around 47.8 million tons, and Brazil produced 16.8 million tons in 2022, making it the second largest producer of oranges after the United States (SERVICE, 2023). From this production, about 50-65% of the total weights of the fruits correspond to the peel. The orange peel waste can become a very serious environmental pollutant. Still, it can produce valuable added subproducts since it contains alkaloids, flavonoids, phenolic compounds, saponins, steroids, tannins, terpenoids, etc (WAGUE, 2017). Orange peels have also been previously used as a carbon source for CQDs synthesis, obtaining particles of average diameter 2.34 nm

(WANG et al., 2020), 2-7 nm (PRASANNAN; IMAE, 2013), and 4.2 nm (HU et al., 2021) used to detect heavy metals and microorganisms thanks to their optical properties.

Another agricultural organic waste of local interest is the pinion (or pine nut) shell, which is a regional product found in the southern regions of Brazil, Argentina, and Paraguay. The production in Brazil was 9.342 tons in 2019, and the shell appears as the primary food residue generated, corresponding to around 22% of the total mass. Pinion nut shells are generally discarded in landfills and on empty land and sometimes applied as fertilizer. In this context, the disposal of pine nut shells can be re-signified from the collection and appropriate final destination, being treated as a valuable subproduct since it is compound up of polysaccharides (cellulose and hemicellulose) and lignin, with smaller amounts of extractives and substances inorganic (KLOSOSKI, 2021). Pinion shells have not been extensively explored; some studies have centered on their potential as adsorbent or bio-fuel (pyrolysis) (CLADERA-OLIVERA et al., 2008; KLOSOSKI, 2021; ROYER et al., 2009). Therefore, their use in producing materials like CQDs seems very promising.

3   CHAPTER 3: MATERIALS AND METHODS

3.1   TRENDS OF CARBON QUANTUM DOTS SYNTHESIS AND SUSTAINABLE ASSESSMENT

3.1.1   Scope and System Boundaries

This work consists of a cradle-to-gate LCA that aims to evaluate the potential environmental impacts of the synthesis process for CQDs' obtention. The assessment was carried out first by identifying the synthesis parameters trends for pristine particles at a laboratory scale obtained from biomass as carbon sources, according to reported research found in the Scopus database. The most common synthesis techniques were selected (chemical oxidation, hydrothermal treatment, microwave, and pyrolysis), and a total of 70 studies were considered. The frequency modal parameters were identified from each synthesis technique to define the life cycle inventory.

Additionally, three scenarios for the carbon source were considered. The first scenario assumes the use of raw organic matter, the second scenario considers using a dry carbon source, and the third scenario replaces using biomass for citric acid, a typical commercial reactant used to obtain CQDs.

This study focused on the production phase of nanoparticles on a laboratory scale. It encompassed both the immediate emissions from CQD production and the consequential effects stemming from the extraction of resources and energy generation upstream. The environmental consequences were assessed using a functional unit based on mass, where 1 gram of produced CQDs was the reference. This approach enables a comparison of equivalent nanomaterial quantities based on their synthesis yield. The scope and system boundaries are shown in Figure 4.

Figure 4. Scope and boundaries for LCA.

Life cycle assesment

Scope and system limits for each CQD synthesis method.

Cradle-to-gate assessment – Laboratory scale – Functional unit 1 g
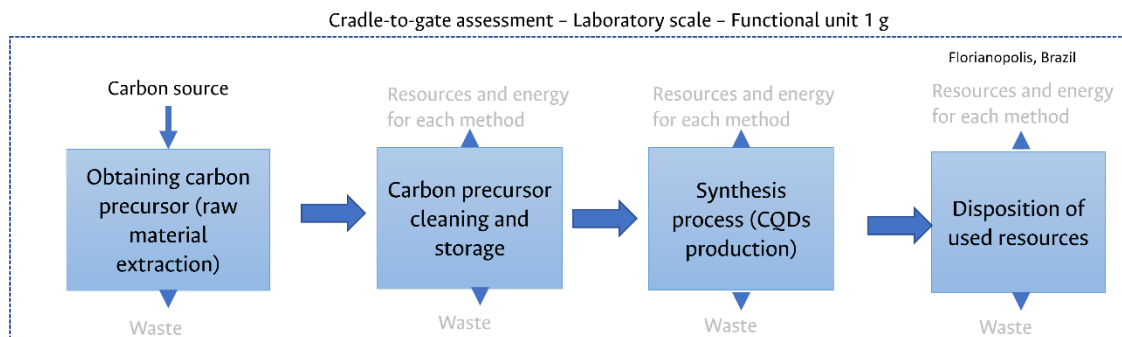
General considerations
Dry biomass was created in the database as a new product, considering biomass washing (40 ml water/g biomass).Electric drying and grinding, and final disposal in landfill, assuming 30% product loss.For all reactions, a 450 W centrifuge was considered.

Elaborated by the author.

3.1.2 Life Cycle Inventory Data

The evaluation of the environmental impacts of CQD syntheses was based on inventory data from the tendency analysis for laboratory-scale synthesis procedures, which consists of raw materials (carbon sources and solvents), electricity (heating plate, oven, microwave, and centrifuge), and subproducts involved in the synthesis procedures (primary data).

The foreground system included in this study was modeled from the data in the Ecoinvent® 3.7 database using information from Brazil (BR) providers and, when necessary, Rest-of-World (RoW). The electricity inputs used corresponded to high voltage hydropower levels, and the disposal of solid subproducts was destined for landfills, while gaseous subproducts for evaporation were considered greenhouse gases.

The biomass carbon sources correspond to residual biomass from local products (second and third-generation bioproducts). Acquiring a first-generation carbon source to produce CQDs will increase the manufacturing costs and environmental impacts of crop production. The dried biomass was created on the database as a new product, considering the washing of the biomass (40 ml of water/g

biomass), the electrical drying and grounding, and the final disposal in landfill, assuming 30% of product loss. In each synthesis technique, the materials required are a standard heating plate of 650 W, deionized water, and HNO_3 for the chemical oxidation synthesis. An electric convection oven of 5 kW and deionized water are used for hydrothermal synthesis. Microwave reactor of 850 W and deionized water for microwave synthesis. And inert atmosphere oven of 9 kW and deionized water. For all reactions, a centrifuge of 450 W was considered.

3.1.3 Environmental impact assessment

The Environmental impacts were modeled using the ReCiPe 2016 endpoint method H (Hierarchist version). This method prioritizes the hierarchy of effects by considering the most critical environmental concerns first. It follows a structured approach where impacts are categorized into hierarchies, and the impacts with higher relevance or potential to cause significant harm are given more weight in the assessment (HISCHIER; WALSER, 2012; HORNE; GRANT; VERGHESE, 2010). The impact potentials evaluated according to the ReCiPe method are shown in Table 4.

Table 4. Impact categories of ReCiPe 2016

Impact category	Abbreviation	Units
Fine particulate matter formation	FPM	kg PM2.5 eq
Fossil resource scarcity	FRS	kg oil eq
Freshwater ecotoxicity	FEX	kg 1,4-DCB
Freshwater eutrophication	FET	kg P eq
Global warming	GW	kg CO_2 eq
Human carcinogenic toxicity	HCT	kg 1,4-DCB
Human non-carcinogenic toxicity	HNCT	kg 1,4-DCB
Ionizing radiation	IRAD	kBq Co-60 eq
Land use	LU	m^2a crop eq
Marine ecotoxicity	MEX	kg 1,4-DCB
Marine eutrophication	MET	kg N eq
Mineral resource scarcity	MRS	kg Cu eq
Ozone formation, Human health	OZH	kg NOx eq
Ozone formation, Terrestrial ecosystems	OCT	kg NOx eq
Stratospheric ozone depletion	SOD	kg CFC11 eq
Terrestrial acidification	TER	kg SO2 eq
Terrestrial ecotoxicity	TEO	kg 1,4-DCB
Water consumption	WC	m^3

Elaborated by the author.

3.2 SYNTHESIS OF CQDS

The synthesis reaction proposed for CQDs intends to encourage sustainability by minimizing procedure steps and avoiding the use hazardous reagents, considering the findings of the LCA described in Section 3.1. Banana peel (BP), Orange peel (OP), and Pinion Shell (PS) were used as carbon sources to synthesize CQDs since these organic wastes are abundant in the southern region of Brazil and can present an opportunity for waste management in the agroindustry sector.

The carbon sources were oven-dried under 60°C for 16 hours (until reaching constant weight) and manually ground to powder. The reaction was carried out with a microwave reactor Antoon Par Monowave 300. 1 g of each carbon source was mixed with deionized water as a solvent in a concentration of 100 g/L. Each sample was heated to 150°C, 165°C, and 180°C for 10, 20, and 30 min, as shown in table 4. Then, samples were purified with centrifugation of 4,500 RPM under 15 minutes and further filtration with filter paper (2 μm porosity). The samples were stored and protected from light sources for further analysis.

Table 5. Operational parameters for CQDs synthesis for each carbon source.

Sample	Temperature (°C)	Time (min)
1	150	10
2	150	20
3	150	30
4	165	10
5	165	20
6	165	30
7	180	10
8	180	20
9	180	30

Elaborated by the author.

3.2.1 Characterization of CQDs

3.2.1.1   Optical properties analysis

The optical characteristics of the samples were studied with the UV-Vis response and the fluorescence response, carried out through spectroscopy analysis. In the UV-Vis analysis, a Spectrometer UV-Vis-Femto 80 was used in a data sweep from 220 to 750 nm. The fluorescence spectrum was determined using a Plate reader Infinite 200 PRO with a data sweep from 270 to 700 nm with an excitation of 360 nm.

Additionally, the bandgap energy was calculated for all samples using the Tauc plot by extrapolating to zero the linear fit. The following equation was used:

$$\alpha = A(hv - Eg)^n/hv \tag{13}$$

Where α is the absorption coefficient, A is a proportionality constant, hv is the light energy, and n was assumed as 2 for indirect transitions.

3.2.1.2   Surface analysis

The surface functional groups of the eighth sample for each carbon precursor (BP, OP, PS: 180°C – 20 min) were determined with a spectrometer Cary 660 FTIR mixed in *KBr* powder in a data sweep from 400 to 4,000 cm^{-1} with 1869 scans.

3.2.1.3   Crystallographic analysis

The crystal structure of the CQDs' samples and the carbon precursors was determined with a Rigaku MiniFlex600 DRX from 5 to 70° with a step size of 0.02°.

4 CHAPTER 4: RESULTS AND DISCUSSION

4.1 TRENDS OF CARBON QUANTUM DOTS GREEN SYNTHESIS

The reaction practical areas (synthesis parameters) of CQDs synthesis for the methods of chemical oxidation (CO), hydrothermal (H), microwave (M), and pyrolysis (P) are shown in Figure 5. These areas were established according to reported synthesis determined as "green synthesis" of pristine CQDs. The selected methodologies studied considered synthesis that used biomass as a carbon source and did not include functionalization or doping of the particles. Various carbon sources were included, like palm kernel shells, salvia, cabbage leaves, red lentils, cinnamon, mango peel, and sugarcane bagasse.

Determining the practical areas of synthesis for CQDs from biomass allows the identification of the synthesis trends in terms of temperature and time of reaction. Methods like chemical oxidation and microwave allow a faster reaction than hydrothermal and pyrolysis.

Figure 5. Practical areas of CQDs synthesis from biomass.
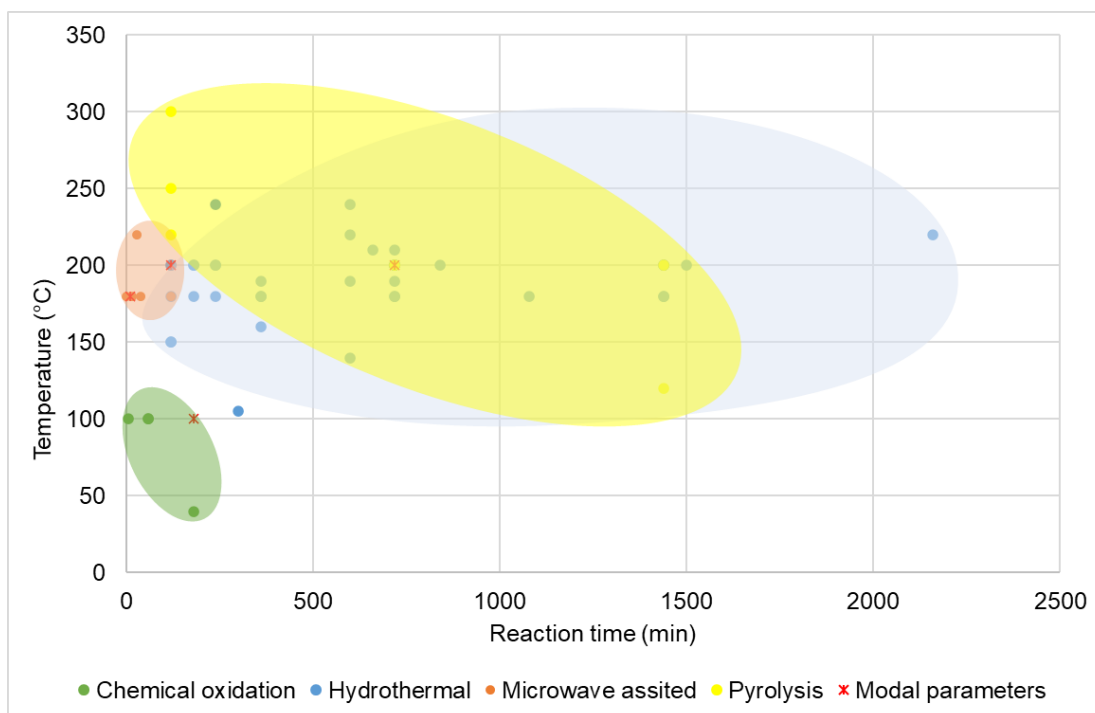
Elaborated by the author.

The most used synthesis parameters were determined from the practical areas, finding the following modal frequency parameters: for chemical oxidation 3 hours - 100°C, hydrothermal 12 hours – 200 °C, microwave 10 min – 180 °C, and pyrolysis 2 hours – 200°C that were used for the LCA. This result indicates room for improvement in sustainability terms in the green CQDs synthesis procedures since the most common parameters do not correspond to those consuming fewer resources. Analyzing practical areas to identify synthesis parameters can be valuable in the experimental planning stage and decision-making process for manufacturing materials like CQDs.

The effect of the time and temperature of the synthesis was contrasted with the medium-size distribution (Figure 6) and the quantum yield (Figure 7). The size distribution presents variation, considering that the range of interest is from 1 nm to 10 nm. In general, the size diameter synthesized places in 4 ± 2 nm. The more independent method from the reaction conditions corresponds to the microwave method (3 to 4.25 nm), which might be caused by the heating process's rapid and efficient energy distribution (KHARISSOVA et al., 2019; PANG et al., 2014). In contrast, the other methods (CO, H, P) can modify the particle medium size by tuning the reaction conditions and the carbon source.

Figure 6. Effect of the synthesis reaction on the particle size.
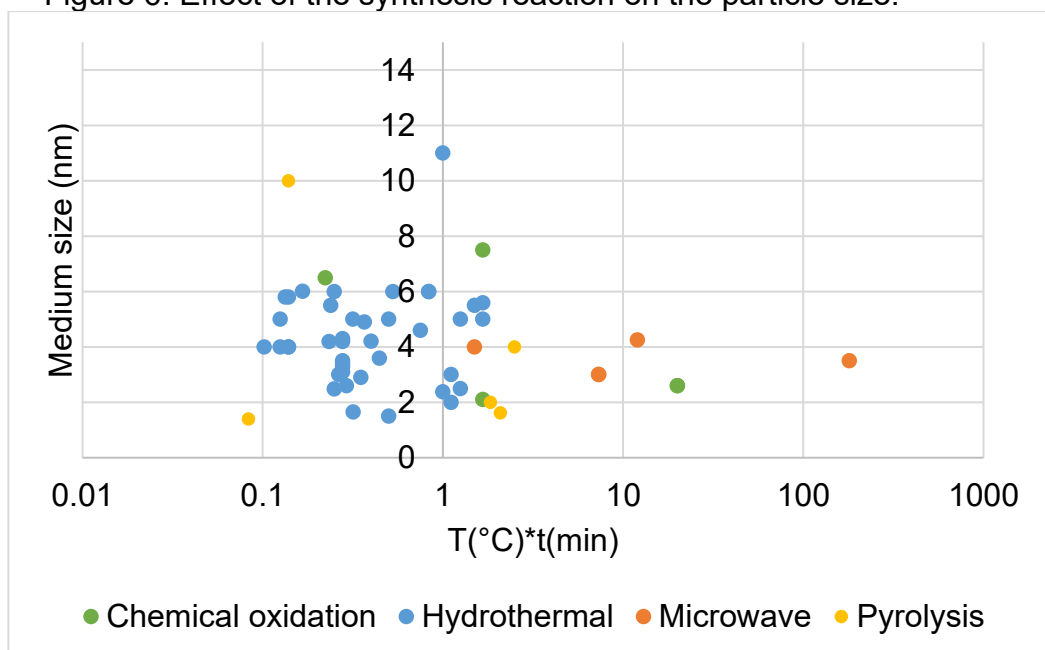
Elaborated by the author.

The sole effect of temperature and time reaction does not represent a triggering factor to modify the fluorescence QY. The chemical oxidation method is the synthesis technique less affected by changes in the condition reactions with QY ranging from 3 to 9 %. This result points out that the carbon source plays a more significant role in the fluorescence behavior of the CQDs than the method itself.

One of the main contributors to modifying fluorescence behavior is possibly the carbon/nitrogen relationship of the biomass source in conjunction with the temperature (Chen, Zhang, et al., 2023). Nevertheless, recent machine learning algorithms with an accuracy of 80% and 94% indicate that CQDs synthesized from commercial reactants (citric acid, ethylenediamine, and phenylenediamine) can tune their optic properties like the color, fluorescence, and emission wavelength by modifying the solvent, purification method, and precursors. These parameters correlate more with the optic properties than reaction temperature and time (Chen, Luo, et al., 2023; Senanayake et al., 2022). These results support the idea that changing critical parameters of the synthesis process, like time and temperature, is suitable for reaching a greener method without affecting the properties of the CQDs.

Figure 7. Effect of the synthesis reaction in the quantum yield.
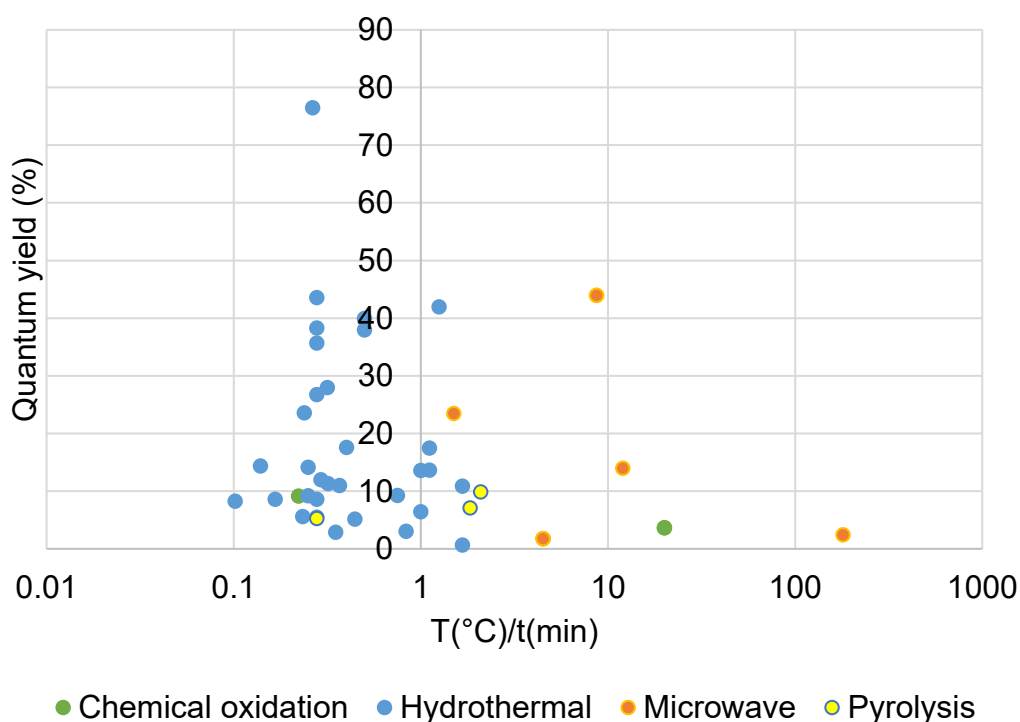
Elaborated by the author.

4.2 LIFE CYCLE ASSESSMENT

The effect of the particular environmental impact category on the overall performance of the evaluated CQDs synthesis methods is shown in Figure 8. All the processes in the first and second scenarios present a tendency in the contribution of the generated impact. GW, TEO, HNCT, and WC are the environmental factors that are more detrimental when producing CQDs. The synthesis methods have an approximately GW contribution of 51 to 54%, TEO contribution of 18%, WC contribution of 18%, and HNCT contribution of 5 %. While in the third scenario, the contributions are approximately 12% for GW, 63% for TEO, 16% for HNTC, and 4% for FRS.

Figure 8. Impact contributions for each synthesis method.
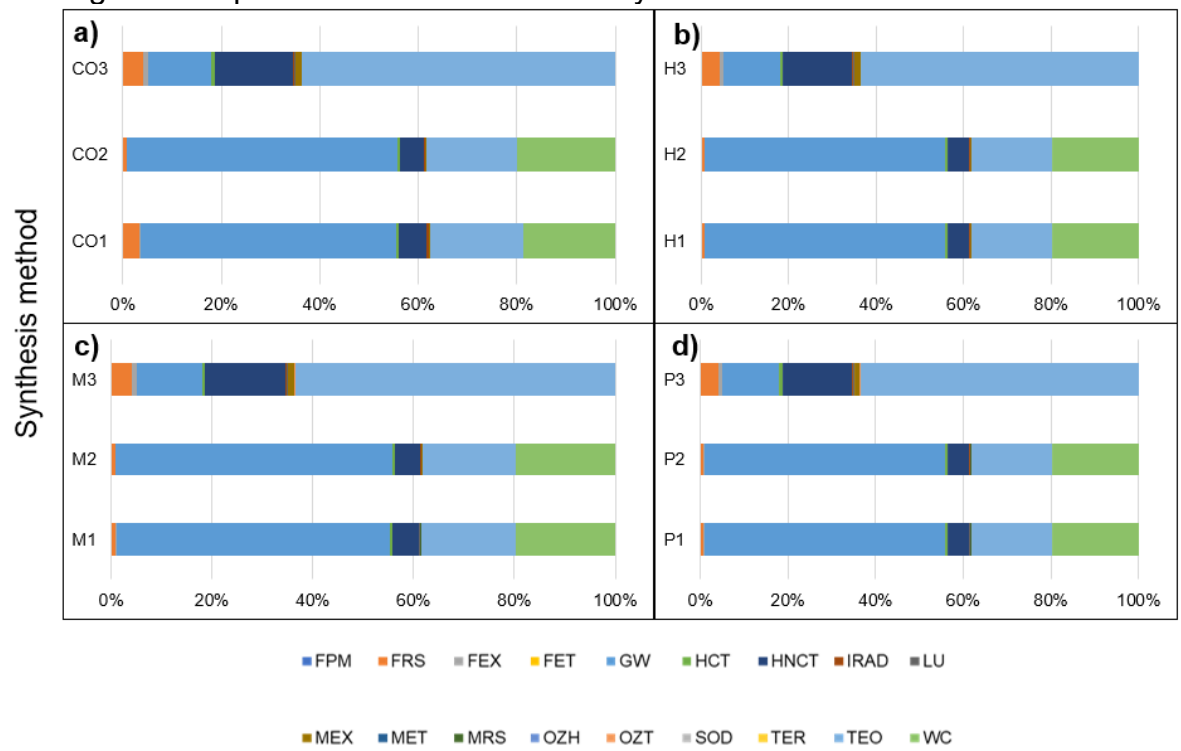
Elaborated by the author.

The predominance of the GW impact in the first and second scenarios is related to the heating procedures of the synthesis methods; thereby, modifying the energy consumption can significantly diminish the overall environmental damage of the process when using biomass as a carbon source. This result agrees with the previous report analyzing CQDs from commercial coffee grounds in which electricity

consumption is the most contributing process (CRISTA et al., 2020). On the other hand, when the carbon source is modified to citric acid, the contribution of GW diminishes by 23% since the effects of producing the reagent present a contribution of 28% higher in TEO.

While the impact factors are uniformly influenced across all synthesis methods, their specific contributions vary based on the respective scenarios, as depicted in Figure 9.

Figure 9. GB, TEO, HNCT, and WC in the synthesis methods.
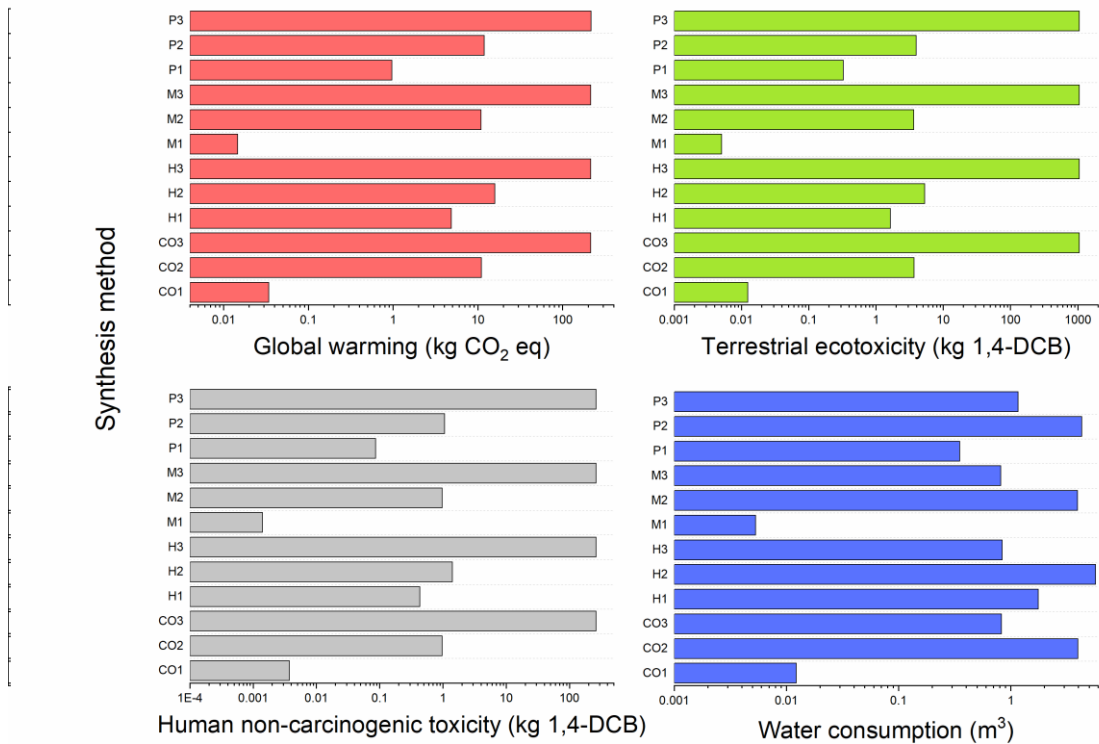
Elaborated by the author.

The three scenarios indicate that using a biomass carbon source is more sustainable than using a chemical commercial reactant like citric acid. Although using raw biomass would be the more sustainable option, it can present disadvantages in the manufacturing processes related to storage and stability. Dried biomass can solve

these obstacles and still have a lower impact than a reagent like citric acid. The second scenario is the more technical and sustainable option for CQDs synthesis (Figure 10).

Figure 10. Main impact categories in the second LCA scenario.
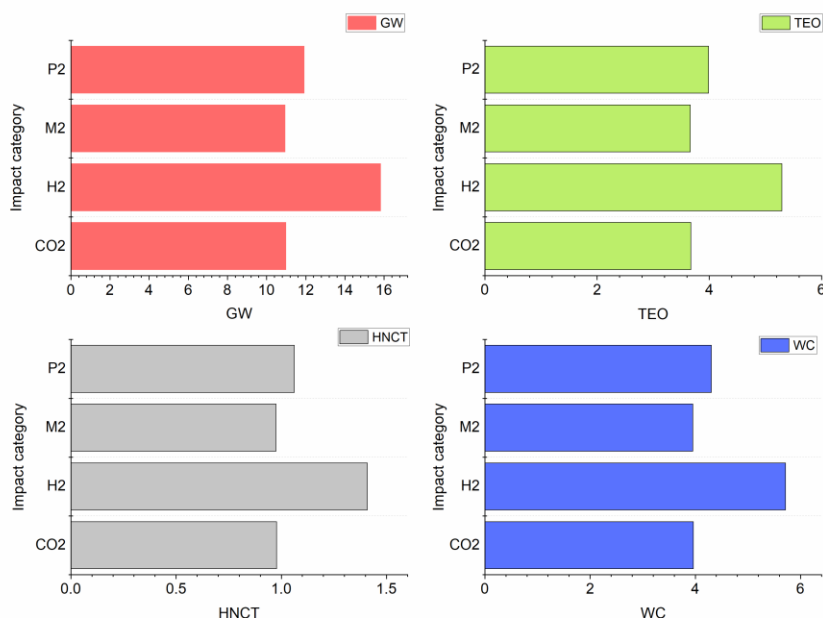
Elaborated by the author.

The more sustainable option is microwave synthesis, compared to the techniques in the second scenario, followed by the chemical oxidation process. Lastly, pyrolysis methods and hydrothermal are less sustainable. Regarding GW, the microwave method represents a generation of 10.1 kg CO_2 eq, the chemical oxidation of 11 kg CO_2 eq, the pyrolysis of 12 kg CO_2 eq, and the hydrothermal of 16 kg CO_2 eq.

4.3   SYNTHESIS AND CHARACTERIZATION OF CQDS

4.3.1.1   Optical properties analysis

The UV-Vis spectrums of the BP CQDs samples are shown in Figure 11, which presents strong optical absorption in the UV region and weaker absorption in the visible region. Generally, carbon nanomaterials like carbon nanotubes, graphene, graphene

oxide, etc., also present strong absorption in the UV region (LIU, 2020; SON; PARK, 2018; WAZIR; KUNDI, 2016).

The changes in temperature and time of reaction of CQDs did not modify the region of absorption but changed the intensity of the absorption. Higher absorptions were identified at 150°C and 180°C. Increasing the reaction time caused a decrease in the absorption intensity; therefore, it is more convenient to carry out the synthesis process of up to 20 min with the microwave-assisted method when using BP as a carbon source.

Figure 11. UV-Vis spectrum of BS CQDs.
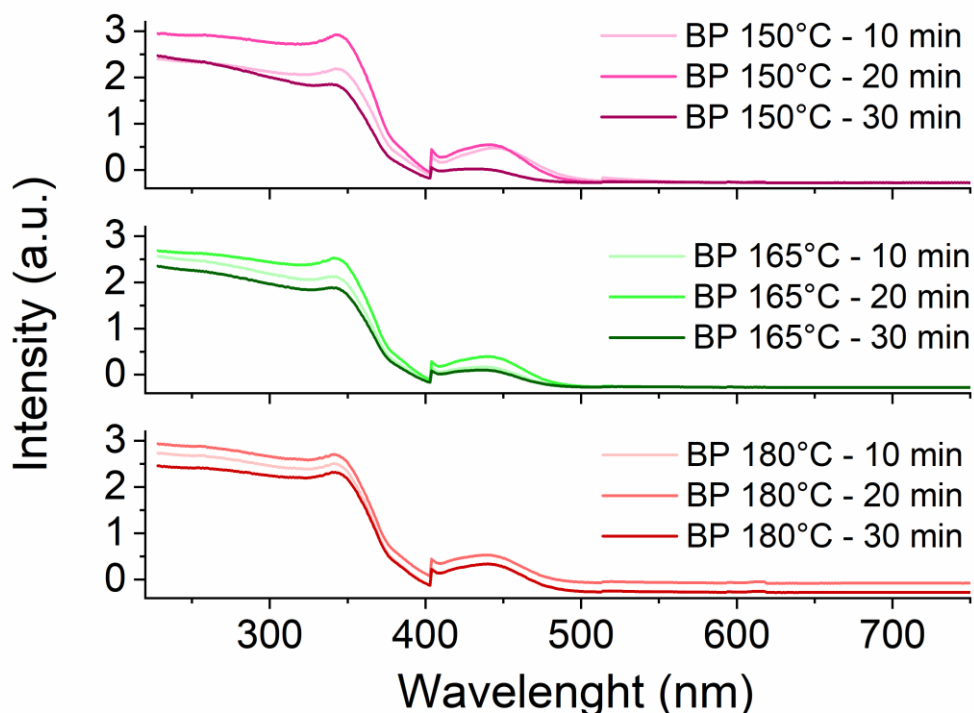
Elaborated by the author.

The UV-Vis spectrums of the OP CQDs samples are shown in Figure 12. OP CQDs samples present absorption in the same regions as BP CQDs. Nevertheless, the effect of time and temperature reactions differs. In this case, higher energy and time of reaction results in stronger absorption. Additionally, increasing the temperature to 180°C causes almost no effects on the residence time since the samples of 10, 20, and 30 min of reaction present nearly the same absorption intensity.
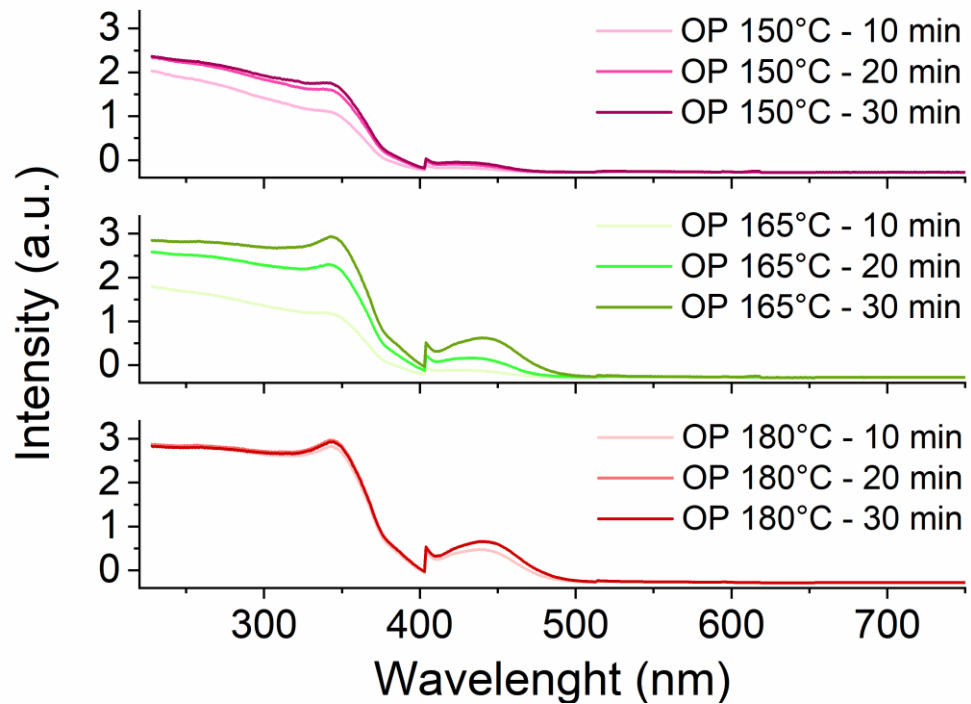
Figure 12. UV-Vis spectrum of OP CQDs.

Elaborated by the author.

The UV-Vis spectrums of the PS CQDs samples are shown in Figure 13. In which PS samples present strong absorption in the UV region as BP and OP CQDs. In contrast, it gives an additional absorption peak in the visible region. The effect of time and temperature reaction in PS CQDs shows a more remarkable change in the absorbance spectrum. The lower temperature and time cause a diminution of the absorbance in the UV region and tend to disappear in the visible region. Increasing the time and temperature of the reaction for PS CQDs contributes to the absorption of both UV and visible light.

Figure 13. UV-Vis spectrum of PS CQDs.
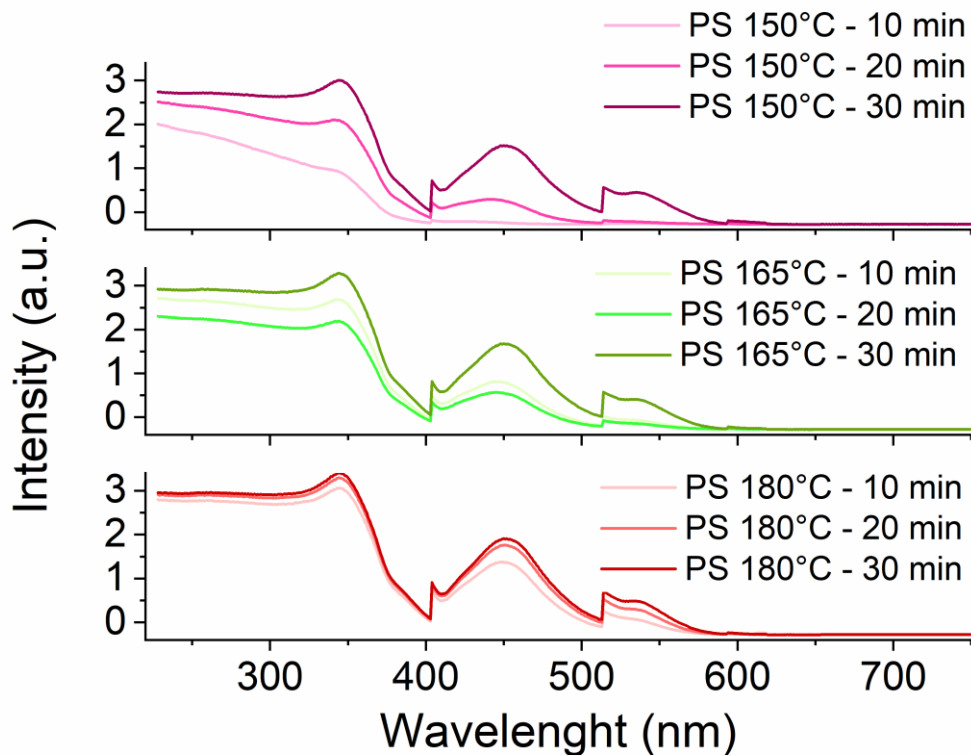
Elaborated by the author.

The different absorption peaks in the UV-Vis spectrum for CQDs from BP, OP, and PS (Figure 13) indicate their relationship with the electron transition of CQDs' core and shell. When the electron transition is attributed to the core of the CQD's particle, the absorption is present in the short wavelength bands below 300 nm (Band I), which correspond to a $p \rightarrow p^*$ transition involving aromatic sp^2 carbons (aromatic C=C bonds); and when there is strong absorption from 300 nm to 400 nm (Band II) correspond to $n \rightarrow p^*$ transition of the C=O bond in carbon cores (LIU, 2020). The three different CQDs (BP, OP, and PS) present electron transition attributed to the core of the particles with a prominence of the $n \rightarrow p^*$ transition of the C=O bond.

When the electron transition is attributed to the shell, the absorption bands above 400 nm (Band III-V) originate from the surface state transition with electron-alone pairs (LIU, 2020) (Figure 14). The CQDs (BP, OP, and PS) also present electron transitions caused by the surrounding functional groups of the particles related to C=O bonding, like hydroxyl, carboxyl, and epoxy groups.

Additionally, the PS CQDs present absorption in band IV, which is directly attributed to the addition of graphitic nitrogen into the carbon sp^2 lattice since the graphitic nitrogen centers can insert excess electrons into the unoccupied π* orbitals and reduce the HOMO−LUMO (highest occupied molecular orbital - lowest unoccupied molecular orbital) gap and the energies of the corresponding optical transitions (LIU, 2020). Smaller HOMO-LUMO gaps ease the charge transfer between molecules, making the CQDs more conductive or suitable for charge transport, which is advantageous for application in electronic devices or chemical reactions driven by light energy (KATERIS; JAYARAMAN; WANG, 2023; ZAIATS et al., 2017).

Figure 14. Electron transition scheme for CQDs from BP, OP, and PS.
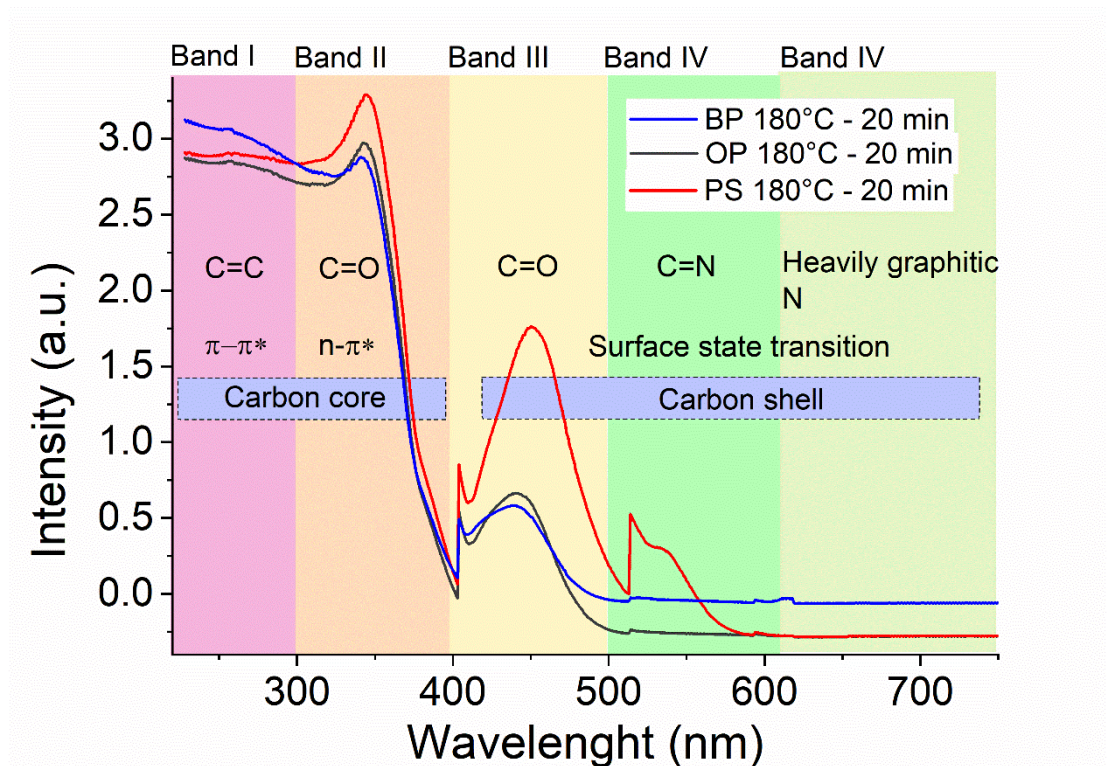
Elaborated by the author.

The Band Gap energy of the CQDs samples presents variations according to the carbon sources and reaction conditions, as shown in Figure 15. Increasing the reaction temperature decreases the variation in the bandgap energy, independent of time; for each carbon source, the reaction at 180°C allowed closer energy values.

The QDs generally present optical properties dependent on size, in which the nanocrystal size directly relates to the band gap. In this relation, the energy bandgap

increases with a decrease in quantum dot particle size (JIN et al., 2013; RANI et al., 2020). Therefore, the CQDs (BP: 3.4 eV, OP: 3.7 eV, and PS: 3.7) synthesized at 150°C present the smallest particle size, although no relation with reaction time is identified. Also, more homogeneous size distributions can be obtained at increasing temperature reactions. The obtained band gap energy values agree with previous reports of CQDs synthesized by different methodologies with ranges of 2 to 4 eV (AL-DOURI; BADI; VOON, 2018; KARATUTLU et al., 2018; YUAN et al., 2017).

Figure 15. Band gap energy of CQDs from BP, OP, and PS.
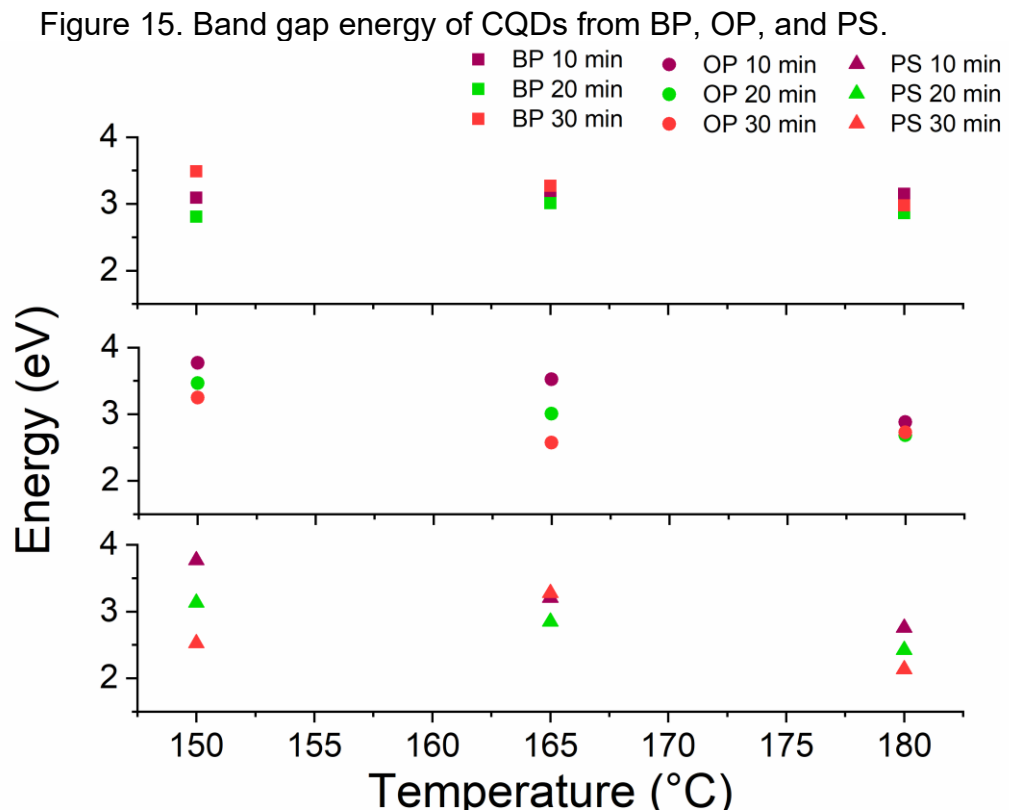
Elaborated by the author.

The three different carbon precursors present a typical characteristic of CQD materials, as shown in Figure 16. There is a visible difference in the color of the samples in daylight and ultraviolet light. The BP and OP CQDs presented a green fluorescence, while the PS differed lightly with a yellow color. Besides, the synthesized CQDs give stability in the fluorescence after several months of preparation and storage.

Figure 16. Pictures of the CQDs synthesis samples.
16.a) BP CQDs and PS CQDs in daylight. 16.b) BP CQDs and PS CQDs under ultraviolet lamp irradiation. 16.c) OP CQDs under an ultraviolet lamp irradiation (7 months storage).
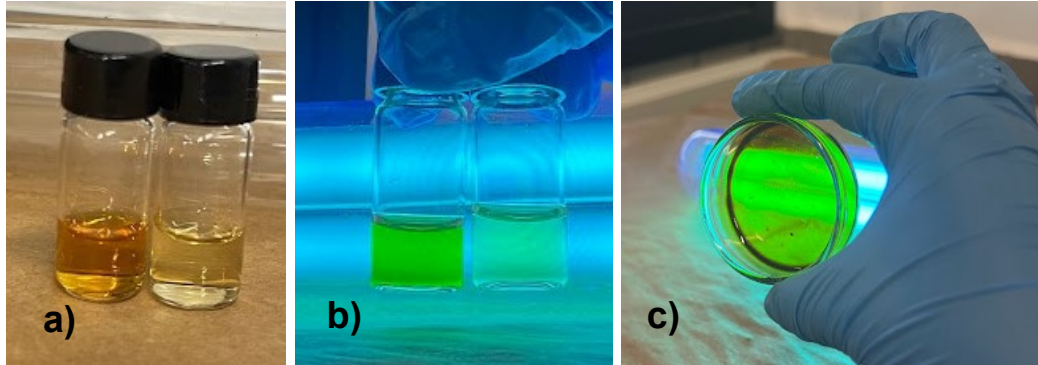
Elaborated by the author.

The behavior of the fluorescence of BP CQDs is shown in the spectrum of Figure 17. There is a higher intensity at 328 nm, although this intensity varies according to the synthesis reaction conditions. In this case, decreasing the residence times and temperature caused an increase in the fluorescence intensity, with 20 minutes and 150°C the optimal reaction time.

Figure 17. Fluorescence spectrum of BP CQDs.
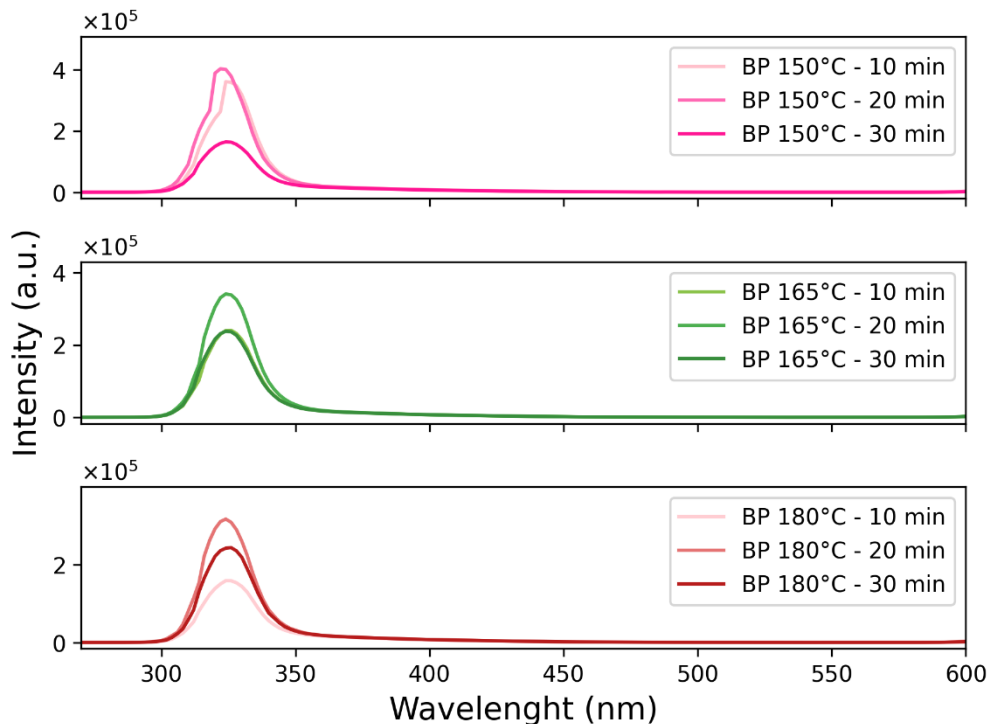
Elaborated by the author.

The OP CQDs did not present substantial changes in the fluorescence intensity related to the variation of the synthesis reaction conditions (Figure 18). Similarly to BP CQDs, the better residence time for the synthesis was 20 minutes, although the change in the temperature reaction does not present a significant influence.

Figure 18. Fluorescence spectrum of OP CQDs.
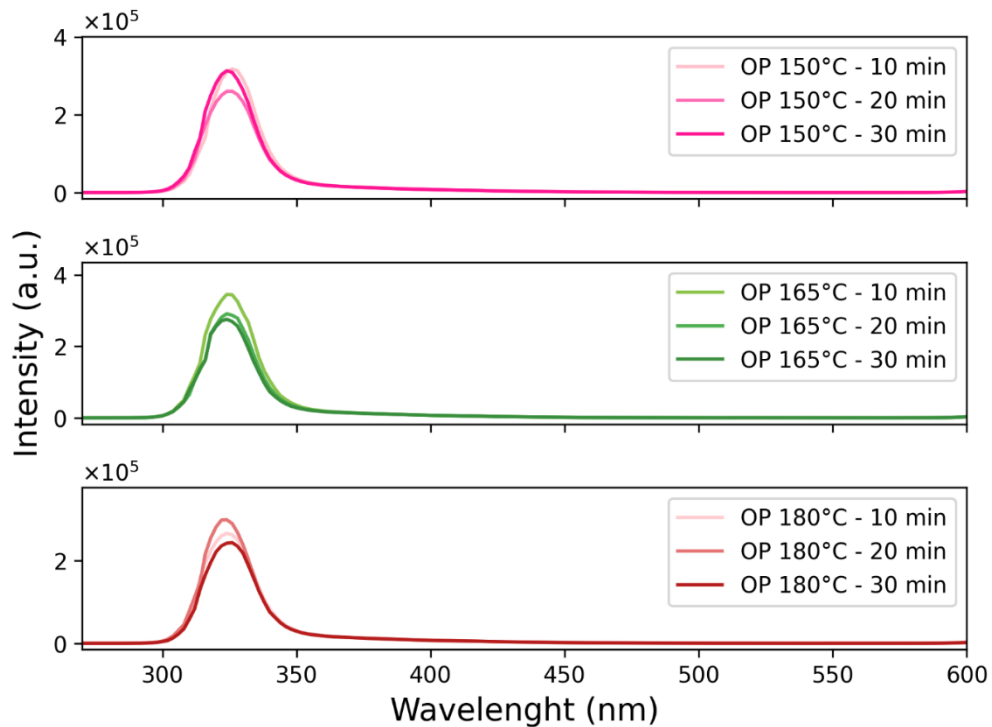
Elaborated by the author.

PS CQD samples presented higher fluorescence intensity than BP and OP CQDs (Figure 19). As in BP CQDs, the variation of the reaction conditions resulted in changes in the fluorescence behavior; the residence time did not show a relation with the intensity, although increasing the reaction temperature was beneficial in this respect.

Previous reports indicate that the fluorescence spectra of CQDs are influenced by carbon and nitrogen contents and related impurity levels in the carbon core and surface (LIU, 2020; YU et al., 2018). The nitrogen bonds present in PS may be the main attributions for the fluorescence behavior, in which the extrinsic emission mode (caused by CQD defects) plays a significant role (JIA et al., 2020).

Figure 19. Fluorescence spectrum of PS CQDs.
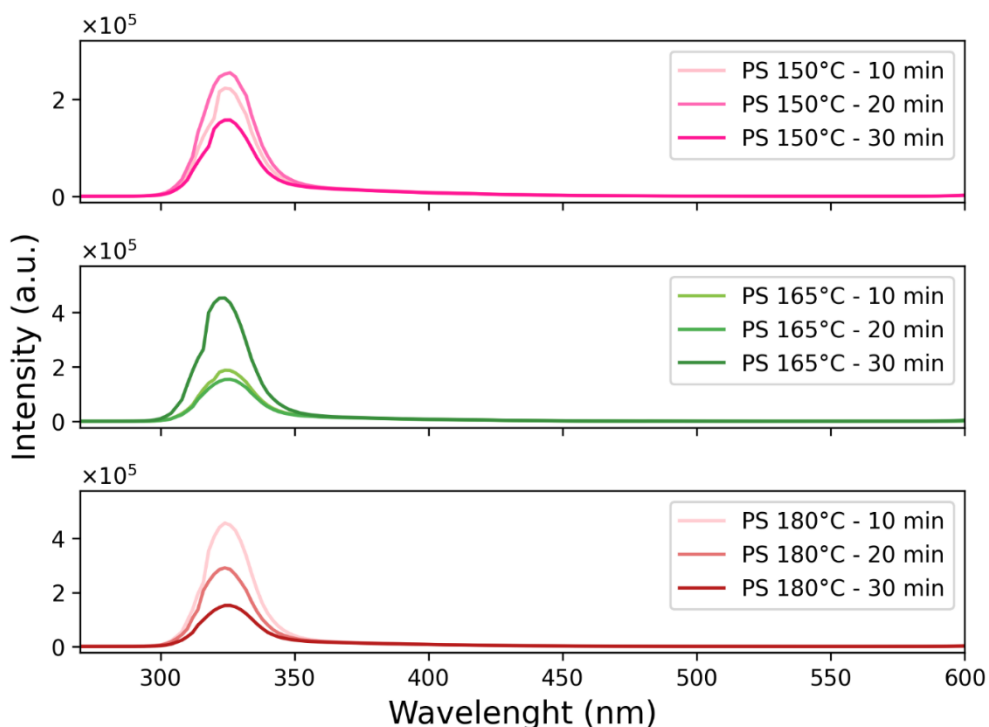
Elaborated by the author.

The different CQDs' fluorescence spectrums followed previous reports from carbon sources like *Eleusine coracana* (MURUGAN et al., 2019)*, polyethyleneimine (DENG et al., 2020), and sucrose (ZHANG et al., 2019). The intensity and emission characteristics are variables affected by external factors like excitation-emission, temperature, and pH (BRACHI, 2020; MURUGAN et al., 2019; QIANG et al., 2019).

Based on the UV-Vis and fluorescence characteristics of all CQD's samples, the reaction conditions of 180°C and 20 minutes were selected for characterization of the surface and crystallographic properties of the CQDs. Since the synthesis at 180°C presented more homogeneous properties, 20 minutes of reaction is the best time to ensure higher light absorption and fluorescence intensity in most samples.

4.3.1.2   Surface analysis

The functional groups on the raw carbon source and the CQDs surface were identified, as shown in Figure 20. There is a clear relationship between the carbon

source and the resulting CQD since they present almost the same absorption bands, thereby present strong similarities in the functional groups of the materials; analyzing the functional groups of a carbon source can be a crucial aspect of anticipating the features in CQDs.

In the FTIR spectra, the absorption bands at 3428 cm^{-1} correspond to the stretching vibrations of O-H (oxygen-hydrogen) in all samples, indicating good affinity with water. The absorption in the resulting CQDs (BP, OP, and PS) is similar despite the carbon sources presenting a larger quantity of O-H bonds (TANG et al., 2018). The absorption peak at approximately 2925 cm^{-1} indicates the stretching vibrations of C-H (carbon-hydrogen) bonds. This region is often called the "CH stretch" region of the IR spectrum. It is associated with organic compounds like hydrocarbons, alkanes, alkenes, and alkynes. The absorption peak located at approximately 1740 cm^{-1} indicates the stretching vibration of the carbonyl (C=O) functional group. This region is often called the "C=O stretch" region of the IR spectrum. The C=O functional group is commonly found in aldehydes, ketones, carboxylic acids, esters, and amides. The C=O stretching vibration involves the periodic stretching and contraction of the double bond between the carbon and oxygen atoms in the carbonyl group. The absorption peak at approximately 1623 cm^{-1} corresponds to the amide I band, a characteristic vibrational mode in peptides and proteins. The amide I band is associated with the stretching vibrations of the C=O (carbonyl) bond within the peptide backbone (LARKIN, 2017; STUART, 2004).

From the region of 1630 cm^{-1} to 400 cm^{-1}, more variations are present among the different CQDs. For example, OP and PS CQDs have absorption in 1520 cm^{-1}, corresponding to the amide II band, another important vibrational mode in peptides and proteins. The amide II band is associated with bending vibrations involving the peptide backbone's N-H (amide) and C-N bonds. Corresponding to the asymmetric bending vibration of the methyl (CH$_3$) groups in organic compounds. This region is also related to the "CH$_3$ deformation" region of the IR spectrum (LARKIN, 2017; STUART, 2004).

The absorption peak located at approximately 1385 cm^{-1} is present in all samples. It corresponds to the asymmetric bending vibration of methyl groups,

involving the bending motion of the hydrogen atoms in the methyl group, with hydrogen atoms moving more asynchronously. The absorption peak located at approximately 1230 cm^{-1} corresponds to the stretching vibration of the C-N bond ("C-N stretch" region), indicating the presence of amine groups (NH_2 or NH) or amide groups ($CONH_2$), in which the PS CQDs present more contribution. The absorption peak located at approximately 1055 cm^{-1} corresponds to the stretching vibration of the C-O bond ("C-O stretch" region), indicating compounds containing ester groups (RCOOR'). Finally, the absorption peak at approximately 664 cm^{-1} corresponds to the out-of-plane bending vibration of the hydrogen atoms (H) in compounds containing aromatic rings, such as benzene rings (LARKIN, 2017; STUART, 2004).

The most important difference between the carbon precursors and the CQDs was the intensity of the absorption bands, which indicate that the OP and PS samples presented higher concentration of the OH- functional groups due to the size, formation of more surface defects and oxygen-containing groups. In contrast the BP CQDs preserve the concentration of the main functional groups (OH- and C-H) when compared to the BP carbon source. For instance, OP and PS CQDs can be more hydrophilic and reactive than BP CQDs. From all the samples, PS CQDs presented more chemical reactions in the synthesis process, since there is presence of slight shifting in the fingerprint zone compared to the bulk carbon source, that can be linked with the presence of nitrogen functional groups, which involves auto-doping of the particles.

Figure 20. FTIR spectra of the BP, OP, and PS carbon sources and synthesized CQDs.
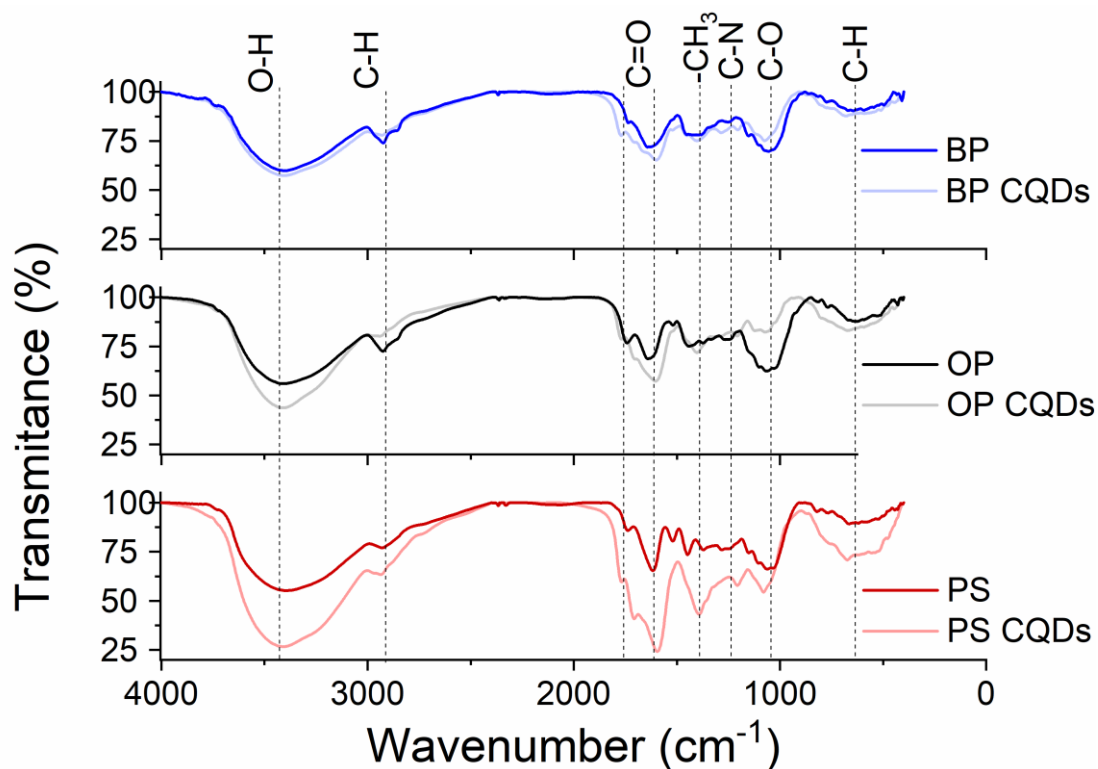
Elaborated by the author.

4.3.1.3   Crystallographic analysis

The XRD patterns of the carbon sources and their CQD counterparts differ since all the carbon sources present stronger crystallinity, and the CQDs have a more amorphous structure (Figure 21). The peak broadening can be caused by the size of the CQDs particles, in which the presence of small crystalline domains contributes to an overall more amorphous appearance.

The CQDs show a single broad peak at 26.5°, 26.1°, and 27° for BP, OP, and PS, respectively. This result can be attributed to an interlayer spacing of d = 3.29 Å and the (002) diffraction patterns of graphitic carbon materials with the turbostratic disorder (carbon atoms arranged in a disordered and non-aligned manner, resulting in a lack of long-range crystalline order). Additionally, there is also presence of the graphitic carbon crystallographic planes (004), (006), and (008) regard to the peaks formed in 56.6°, 62.4°, and 68.1° (MURUGAN et al., 2019; RAMAR; MOOTHATTU; BALASUBRAMANIAN, 2018; TANG et al., 2021a). Since the synthesis procedure was equal for the samples it can be concluded that the carbon sources OP and PS

presented inherent graphitic structures or higher degree of order may result in CQDs with increased crystallinity compared to BP.

Figure 21. XRD patterns of the BP, OP, and PS carbon sources and synthesized CQDs.
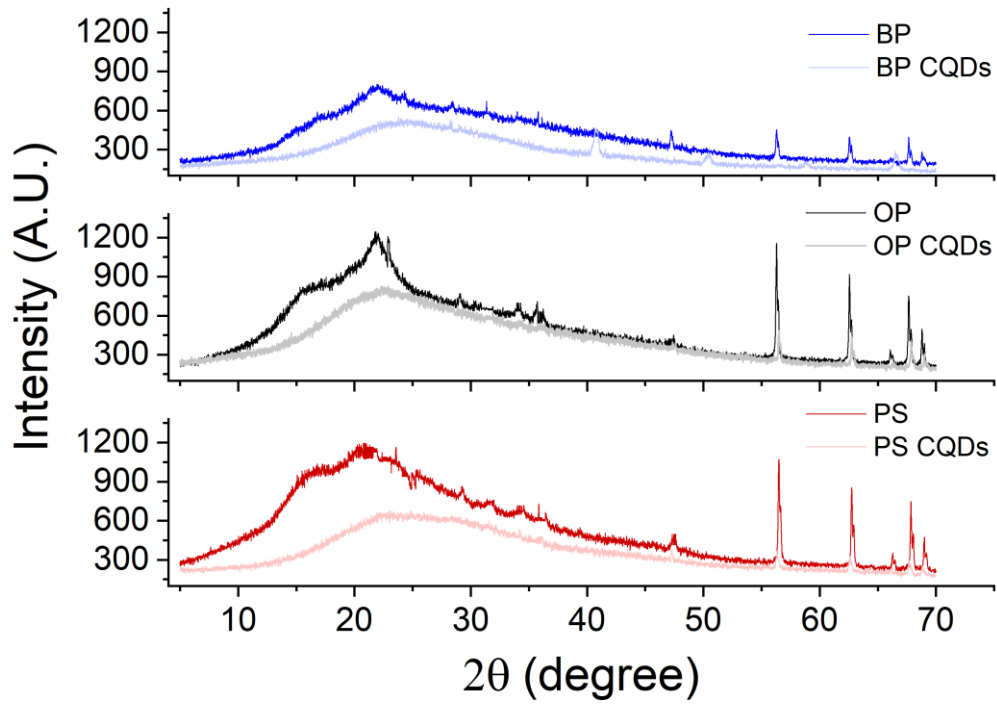
Elaborated by the author.

5   CONCLUSION

The predominant synthesis parameters employed in widely used green synthesis methods for CQDs were systematically analyzed, delineating the practical reaction zones based on varying time and temperature parameters. This investigation revealed noteworthy trends, indicating that certain green methodologies can be optimized for enhanced sustainability by reducing both reaction time and temperature. Notably, microwave-assisted, and chemical oxidation methods emerged as particularly eco-friendly approaches within the spectrum of CQD synthesis. This discernment contributes valuable insights to the development of more sustainable and efficient protocols for CQD fabrication.

The impact of specific environmental categories on the overall environmental performance of the evaluated CQD synthesis is consistent in the first and second scenarios, in which a trend emerges in the contribution to environmental impact. GW (global warming), TEO (terrestrial ecotoxicity), HNCT (human non-carcinogenic toxicity), and WC (water consumption) are the most impacted factors in CQD production. Contributions to GW account for around 51% to 54%, TEO about 18%, WC about 18%, and HNCT around 5% for all synthesis methods. In the third scenario, contributions shift to approximately 12% for GHG, 63% for TEO, 16% for HNCT, and 4% for WC. The prominence of GW impact in the first and second scenarios is attributed to the heating procedures of the synthesis methods. Modifying energy consumption could notably reduce environmental damage by adopting biomass as a carbon source. When transitioning to citric acid as a carbon source, GW contributions decrease by 23%, as effects of reagent production present a 28% higher contribution to TEO.

The three scenarios indicate that using biomass as a carbon source is more sustainable than chemical reagents like citric acid. While raw biomass is a greener option, challenges related to storage and stability are addressed by using dried biomass, still yielding a lower impact than citric acid. The second scenario emerges as the more technically and sustainably viable option for CQD synthesis.

In the synthesis and characterization of CQDs from BP (banana peel), OP (orange peel), and PS (pinion shell) obtained by following a greener approach the optical properties analysis revealed significant absorption in the UV region and weaker absorption in the visible region. The different synthesis conditions evaluated influenced absorption intensity but did not change absorption region, from which the better reaction parameters were 180°C during 20 minutes, these conditions contribute to provide homogeneous samples with the lowest energy consumption. UV-Vis spectra indicated electron transitions in the core and shell of CQDs, with specific emission characteristics related to surrounding functional groups. Fluorescence spectra further revealed varying fluorescence intensities and behaviors among different CQD samples, influenced by factors like temperature and time of reaction. Nitrogen bonds, in specific instances, played a role in fluorescence behavior, contributing to charge transfer and potential applications in electronic devices. Surface analysis through FTIR spectra identified functional groups, showing a consistent relationship between carbon source, and resulting CQDs. Amide and carbonyl functional groups were detected, along with specific vibrations indicating the presence of various bonds. Additionally, XRD patterns revealed an amorphous structure in CQDs, with single broad peaks suggesting graphitic carbon materials with turbostratic disorder. The three CQDs were obtained successfully presenting slight differences inherited by their respective carbon sources, being the PS CQDs the sample with more distinctive features, which are attributed to a possible higher nitrogen content in the carbon source.

In conclusion, the evaluated synthesis methods underscore the significance of environmental impacts, and adopting biomass as a carbon source proves to be more sustainable. Among techniques, microwave synthesis and chemical oxidation stand out as greener options. The synthesized CQDs exhibit distinct optical and fluorescence properties, reflecting their carbon sources and production conditions. These findings contribute to a better understanding of the synthesis and characterization of CQDs and their potential applications in various fields.

Future work perspectives

This job leaves the doors open for new research related to the exploration of high-scale synthesis and identifying the toxicity levels of CQDs. Also, the reported CQDs can be integrated into nanomaterial assemblies to implement in photo-dependent applications like sensing, photocatalysis, and solar cell devices. Lastly, integrating theoretical modeling and machine learning strategies can be crucial to predicting the particle's synthesis product properties and contact behavior, ensuring the custom production of CQDs.

Data availability

Data will be made available on request.

REFERENCES

AL-DOURI, Y.; BADI, N.; VOON, C. H. Synthesis of carbon-based quantum dots from starch extracts: Optical investigations. **Luminescence**, v. 33, n. 2, p. 260–266, 2018.

ALBINI, A.; PROTTI, S. Paradigms in Green Chemistry and Technology. **Paradigms in Green Chemistry and Technology**, 2016.

ANASTAS, P. T.; WARNER, J. C. **Green chemistry : theory and practice**. Oxford [England] SE -: Oxford University Press Oxford [England], 1998.

ARIAS, V. et al. Carbon Quantum Dots Based on Carbohydrates as Nano Sensors for Food Quality and Safety. **Starch/Staerke**, v. 73, n. 11–12, p. 1–9, 2021.

ARIAS VELASCO, V. et al. Context and prospects of carbon quantum dots applied to environmental solutions. **Environmental Nanotechnology, Monitoring and Management**, v. 20, n. September, 2023.

ASHOURI, R. et al. Synthesis of Carbon Quantum Dots from Olive Stones for Efficient Adsorption of Benzene from the Ambient Air. **Journal of Nanostructures**, v. 11, n. 3, p. 480–497, 2021.

ATCHUDAN, R. et al. Hydrophilic nitrogen-doped carbon dots from biowaste using dwarf banana peel for environmental and biological applications. **Fuel**, v. 275, n. April, p. 117821, 2020.

AXON, S.; JAMES, D. The UN Sustainable Development Goals: How can sustainable chemistry contribute? A view from the chemical industry. **Current Opinion in Green and Sustainable Chemistry**, v. 13, p. 140–145, 2018.

BAGHERI, Z. et al. Investigation the cytotoxicity and photo-induced toxicity of carbon dot on yeast cell. **Ecotoxicology and Environmental Safety**, v. 161, n. January, p. 245–250, 2018.

BAKER, S. N.; BAKER, G. A. Luminescent carbon nanodots: Emergent nanolights. **Angewandte Chemie - International Edition**, v. 49, n. 38, p. 6726–6744, 2010.

BNN, B. **Home**. Disponível em: <https://www.nanosafetycluster.eu/>. Acesso em: 30 jul. 2023.

BORUAH, A. et al. Blue-emitting fluorescent carbon quantum dots from waste biomass sources and their application in fluoride ion detection in water. **Journal of**

Photochemistry and Photobiology B: Biology, v. 209, n. April, p. 111940, 2020.

BRACHI, P. Synthesis of fluorescent carbon quantum dots (CQDs) through the mild thermal treatment of agro-industrial residues assisted by γ-alumina. **Biomass Conversion and Biorefinery**, v. 10, n. 4, p. 1301–1312, 2020.

BUSTAMANTE, M. M. C. et al. Ecological restoration as a strategy for mitigating and adapting to climate change: lessons and challenges from Brazil. **Mitigation and Adaptation Strategies for Global Change**, v. 24, n. 7, p. 1249–1270, 2019.

CEN/TC352. **Nanotechnology iTeh Standards**.

CHANG, D. et al. Dual photoluminescence emission carbon dots for ratiometric optical dual-mode and smartphone-integrated visual detection of mercury ion. **Journal of Environmental Chemical Engineering**, v. 11, n. 2, p. 109425, 2023.

CHAUDHARY, P. et al. Nanoparticle-mediated bioremediation as a powerful weapon in the removal of environmental pollutants. **Journal of Environmental Chemical Engineering**, v. 11, n. 2, p. 109591, 2023.

CHEN, J. et al. Machine-learning analysis to predict the fluorescence quantum yield of carbon quantum dots in biochar. **Science of The Total Environment**, v. 896, n. April, p. 165136, 2023a.

CHEN, J. et al. Controlled Synthesis of Multicolor Carbon Dots Assisted by Machine Learning. **Advanced Functional Materials**, v. 33, n. 2, 2023b.

CHRISTÉ, S.; DA SILVA, J. C. G. E.; DA SILVA, L. P. Evaluation of the environmental impact and efficiency of N-doping strategies in the synthesis of carbon dots. **Materials**, v. 13, n. 3, p. 23–26, 2020.

CIAMBELLI, P.; LA GUARDIA, G.; VITALE, L. **Nanotechnology for green materials and processes**. **Studies in Surface Science and Catalysis**, 2019.

CLADERA-OLIVERA, F. et al. Thermodynamic properties of moisture desorption of raw pinhão (Araucaria angustifolia seeds). **International Journal of Food Science & Technology**, v. 43, n. 5, p. 900–907, 1 maio 2008.

CONSTABLE, D. J. C. Green chemistry metrics. **Green metrics**, p. 1–27, 2018.

CONSTABLE, D. J. C.; JIMENEZ-GONZALEZ, C.; LAPKIN, A. Process Metrics. In: **Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes**. [s.l: s.n.]. p. 228–247.

CRISTA, D. M. A. et al. Turning spent coffee grounds into sustainable

precursors for the fabrication of carbon dots. **Nanomaterials**, v. 10, n. 6, p. 1–17, 2020.

CRISTA, D. M. A.; DA SILVA, J. C. G. E.; DA SILVA, L. P. Evaluation of different bottom-up routes for the fabrication of carbon dots. **Nanomaterials**, v. 10, n. 7, p. 1–15, 2020.

DAS, P. et al. Acoustic cavitation assisted synthesis and characterization of photoluminescent carbon quantum dots for biological applications and their future prospective. **Nano-Structures and Nano-Objects**, v. 25, p. 100641, 2021.

DAS, R.; BANDYOPADHYAY, R.; PRAMANIK, P. Carbon quantum dots from natural resource: A review. **Materials Today Chemistry**, v. 8, p. 96–109, 2018.

DE MELLO DONEGÁ, C. The Nanoscience Paradigm: "Size Matters!" BT - Nanoparticles: Workhorses of Nanoscience. In: DE MELLO DONEGÁ, C. (Ed.). Berlin, Heidelberg: Springer Berlin Heidelberg, 2014. p. 1–12.

DENG, X. Y. et al. Synthesis of Functionalized Carbon Quantum Dots as Fluorescent Probes for Detection of Cu2+. **Chinese Journal of Analytical Chemistry**, v. 48, n. 10, p. e20126–e20133, 2020.

DENG, Y. et al. Deriving characterization factors on freshwater ecotoxicity of graphene oxide nanomaterial for life cycle impact assessment. **International Journal of Life Cycle Assessment**, v. 22, n. 2, p. 222–236, 2017.

DEVATHA, C. P.; THALLA, A. K. Green Synthesis of Nanomaterials. In: **Synthesis of Inorganic Nanomaterials: Advances and Key Technologies**. [s.l: s.n.]. p. 169–184.

DEVI, S. et al. Ethylenediamine mediated luminescence enhancement of pollutant derivatized carbon quantum dots for intracellular trinitrotoluene detection: Soot to shine. **RSC Advances**, v. 8, n. 57, p. 32684–32694, 2018.

DICKS, A. P.; HENT, A. Atom Economy and Reaction Mass Efficiency. **Green Chemistry Metrics: A Guide to Determining and Evaluating Process Greenness**, p. 17–44, 2015.

DIMOS, K. Carbon Quantum Dots: Surface Passivation and Functionalization. **Current Organic Chemistry**, v. 20, p. 682–695, 2016.

DING, H. et al. Facile synthesis of red-emitting carbon dots from pulp-free lemon juice for bioimaging. **Journal of Materials Chemistry B**, v. 5, n. 26, p. 5272–5277, 2017.

DOSHI, K.; MUNGRAY, A. A. Bio-route synthesis of carbon quantum dots from tulsi leaves and its application as a draw solution in forward osmosis. **Journal of**

Environmental Chemical Engineering, v. 8, n. 5, p. 104174, 2020.

DULGER, M. et al. Leaching potential of nano-scale titanium dioxide in fresh municipal solid waste. **Chemosphere**, v. 144, p. 1567–1572, 1 fev. 2016.

DUTTA, D.; DAS, B. M. Scope of green nanotechnology towards amalgamation of green chemistry for cleaner environment: A review on synthesis and applications of green nanoparticles. **Environmental Nanotechnology, Monitoring and Management**, v. 15, n. December 2020, p. 100418, 2021.

DYES, O. Design and Properties of Fluorescence Reporters. **Introduction to Fluorescence Sensing**, p. 119–196, 2008.

EINARSRUD, M. A.; GRANDE, T. 1D oxide nanostructures from chemical solutions. **Chemical Society Reviews**, v. 43, n. 7, p. 2187–2199, 2014.

EU. Scientific Committee on Health and Environmental Risks SCHER Scientific Committee on Emerging and Newly Identified Health Risks SCENIHR Scientific Committee on Consumer Safety SCCS Toxicity and Assessment of Chemical Mixtures. **European commision for the toxicity and assessment of chemical mixture**, n. November, p. 1–50, 2011.

EUROPEAN COMMISION. **Performance testing, calibration and implementation of a next generation system-of-systems Risk Governance Framework for nanomaterials**. Disponível em: <https://cordis.europa.eu/project/id/686239>. Acesso em: 30 jul. 2023.

FAN, H. et al. Food waste as a carbon source in carbon quantum dots technology and their applications in food safety detection. **Trends in Food Science and Technology**, v. 95, n. July 2019, p. 86–96, 2020.

FANTONI, T.; TOLOMELLI, A.; CABRI, W. A translation of the twelve principles of green chemistry to guide the development of cross-coupling reactions. **Catalysis Today**, v. 397–399, n. July 2021, p. 265–271, 2022.

FERNANDES, S.; DA SILVA, J. C. G. E.; DA SILVA, L. P. Life Cycle Assessment-Based Comparative Study between High-Yield and "Standard" Bottom-Up Procedures for the Fabrication of Carbon Dots. **Materials**, v. 15, n. 10, 2022.

FERNANDES, S.; ESTEVES DA SILVA, J. C. G.; PINTO DA SILVA, L. Comparative life cycle assessment of high-yield synthesis routes for carbon dots. **NanoImpact**, v. 23, n. March, 2021.

FOJTŮ, M.; TEO, W. Z.; PUMERA, M. Environmental impact and potential health risks of 2D nanomaterials. **Environmental Science: Nano**, v. 4, n. 8, p. 1617–

1633, 2017.

FREUND, R. et al. Multifunctional Efficiency: Extending the Concept of Atom Economy to Functional Nanomaterials. **ACS Nano**, v. 12, n. 3, p. 2094–2105, 2018.

GAGIC, M. et al. One-pot synthesis of natural amine-modified biocompatible carbon quantum dots with antibacterial activity. **Journal of Colloid and Interface Science**, v. 580, p. 30–48, 2020.

GARCÍA-QUINTERO, A.; PALENCIA, M. A critical analysis of environmental sustainability metrics applied to green synthesis of nanomaterials and the assessment of environmental risks associated with the nanotechnology. **Science of the Total Environment**, v. 793, p. 148524, 2021.

GIROUX, M. S. et al. Assessing the environmental effects related to quantum dot structure, function, synthesis and exposure†‡. **Environmental Science: Nano**, v. 9, n. 3, p. 867–910, 2021.

GOSWAMI, A. D. et al. Sustainable and green synthesis of carbon nanomaterials: A review. **Journal of Environmental Chemical Engineering**, v. 9, n. 5, p. 106118, 2021.

GOTTARDO, S. et al. Towards safe and sustainable innovation in nanotechnology: State-of-play for smart nanomaterials. **NanoImpact**, v. 21, n. November 2020, 2021.

GUPTA, D. A. et al. Fluorescence detection of Fe3+ ion using ultra-small fluorescent carbon dots derived from pineapple (Ananas comosus): Development of miniaturized analytical method. **Journal of Molecular Structure**, v. 1216, p. 128343, 2020.

HAN, Y. et al. Green conversion of excess sludge to N-Ca self-doping sustainable carbon quantum dots with remarkable fluorescence enhancement and residual heavy metal reduction. **Journal of Environmental Chemical Engineering**, v. 10, n. 6, p. 108934, 2022.

HAUSCHILD, M. Z.; HUIJBREGTS, M. A. J. **Life Cycle Impact Assessment**. [s.l: s.n.]. v. 2

HAVRDOVA, M. et al. Toxicity of carbon dots-Effect of surface functionalization on the cell viability, reactive oxygen species generation and cell cycle. **Carbon**, v. 99, p. 238–248, 2016.

HIKAL, W. M. et al. Banana Peels: A Waste Treasure for Human Being. **Evidence-based Complementary and Alternative Medicine**, v. 2022, 2022.

HIMAJA, A. L.; KARTHIK, P. S.; SINGH, S. P. Carbon Dots: The Newest Member of the Carbon Nanomaterials Family. **Chemical Record**, v. 15, n. 3, p. 595–615, 2015.

HISCHIER, R.; WALSER, T. Life cycle assessment of engineered nanomaterials: State of the art and strategies to overcome existing gaps. **Science of the Total Environment**, v. 425, p. 271–282, 2012.

HJORTH, R. et al. Ecotoxicity testing and environmental risk assessment of iron nanomaterials for sub-surface remediation – Recommendations from the FP7 project NanoRem. **Chemosphere**, v. 182, p. 525–531, 2017.

HONGMEI, X.; YIZHEN, H. Study on Organic Dye Removal in Wastewater Treatment and Purification Technology Using MgWO4@Carbon Quantum Dot Composite Photocatalyst. **Russian Journal of Physical Chemistry A**, v. 95, n. 6, p. 1247–1254, 2021.

HORGAN, M. D. et al. Development and application of screening-level risk analysis for emerging materials. **Sustainable Materials and Technologies**, v. 35, n. October 2022, p. e00524, 2023.

HORNE, R.; GRANT, T.; VERGHESE, K. Life Cycle Assessment - Principles, Practice and Prospects. **Austral Ecology**, v. 35, n. 1, p. 117–118, 2010.

HU, X. et al. Green one-step synthesis of carbon quantum dots from orange peel for fluorescent detection of Escherichia coli in milk. **Food Chemistry**, v. 339, n. August 2020, p. 127775, 2021.

HU, Y.; GAO, Z. Sewage sludge in microwave oven: A sustainable synthetic approach toward carbon dots for fluorescent sensing of para-Nitrophenol. **Journal of Hazardous Materials**, v. 382, n. August 2019, p. 121048, 2020.

HUANG, H. T. et al. Synthesis and evaluation of polyamine carbon quantum dots (CQDs) in Litopenaeus vannamei as a therapeutic agent against WSSV. **Scientific Reports**, v. 10, n. 1, p. 1–11, 2020a.

HUANG, J. et al. Broad spectrum response flower spherical-like composites CQDs@CdIn2S4/CdS modified by CQDs with up-conversion property for photocatalytic degradation and water splitting. **International Journal of Hydrogen Energy**, v. 45, n. 3, p. 1822–1836, 2020b.

HUDLICKY, T. et al. Toward a "reagent-free" synthesis: Tandem enzymatic and electrochemical methods for increased effective mass yield (EMY). **Green Chemistry**, v. 1, n. 2, p. 57–59, 1999.

IBGE. **Produção de Banana**. Disponível em: <https://www.ibge.gov.br/explica/producao-agropecuaria/banana/br>. Acesso em: 1 out. 2023.

JAMALUDIN, N.; RASHID, S. A.; TAN, T. **Natural biomass as carbon sources for the synthesis of photoluminescent carbon dots**. [s.l.] Elsevier Inc., 2018.

JANKOVIĆ, N. Z.; PLATA, D. L. Engineered nanomaterials in the context of global element cycles. **Environmental Science: Nano**, v. 6, n. 9, p. 2697–2711, 2019.

JELINEK, R. **Carbon Quantum Dots. Synthesis, Properties and Applicatons**. [s.l: s.n.].

JIA, J. et al. Facile and Efficient Fabrication of Bandgap Tunable Carbon Quantum Dots Derived From Anthracite and Their Photoluminescence Properties. **Frontiers in Chemistry**, v. 8, n. February, p. 1–10, 2020.

JIANG, Q. et al. Potentiality of carbon quantum dots derived from chitin as a fluorescent sensor for detection of ClO−. **Microchemical Journal**, v. 157, n. June, p. 105111, 2020.

JIAO, X. Y. et al. The synthesis of fluorescent carbon dots from mango peel and their multiple applications. **Colloids and Surfaces A: Physicochemical and Engineering Aspects**, v. 577, n. April, p. 306–314, 2019.

JIN, S. H. et al. Tuning the photoluminescence of graphene quantum dots through the charge transfer effect of functional groups. **ACS Nano**, v. 7, n. 2, p. 1239–1245, 2013.

JINDAL, D.; JAIN, I. Role of companies in environmental management through corporate social responsibility and sustainability policy. **Green Chemistry in Environmental Sustainability and Chemical Education**, p. 23–42, 2018.

JING, S. et al. Facile and High-Yield Synthesis of Carbon Quantum Dots from Biomass-Derived Carbons at Mild Condition. **ACS Sustainable Chemistry and Engineering**, v. 7, n. 8, p. 7833–7843, 2019.

JOHN, B. K.; ABRAHAM, T.; MATHEW, B. A Review on Characterization Techniques for Carbon Quantum Dots and Their Applications in Agrochemical Residue Detection. **Journal of Fluorescence**, p. 449–471, 2022.

K, K.; V, B. M.; P, N. A green approach for synthesis of highly fluorescent carbon dots from waste engine oil: A strategy for waste to value added products. **Diamond and Related Materials**, v. 121, n. September 2021, p. 108724, 2022.

KAILASA, S. K. et al. Tuning of carbon dots emission color for sensing of Fe 3+ ion and bioimaging applications. **Materials Science and Engineering C**, v. 98, n. January, p. 834–842, 2019.

KAKAEI, K. High efficiency platinum nanoparticles based on carbon quantum dot and its application for oxygen reduction reaction. **International Journal of Hydrogen Energy**, v. 42, n. 16, p. 11605–11613, 2017.

KARATUTLU, A. et al. Structural, Optical, Electrical and Electrocatalytic Activity Properties Of Luminescent Organic Carbon Quantum Dots. **ChemistrySelect**, v. 3, n. 17, p. 4730–4737, 2018.

KATERIS, N.; JAYARAMAN, A. S.; WANG, H. HOMO-LUMO gaps of large polycyclic aromatic hydrocarbons and their implication on the quantum confinement behavior of flame-formed carbon nanoparticles. **Proceedings of the Combustion Institute**, v. 39, n. 1, p. 1069–1077, 2023.

KHAN, A. et al. pH-sensitive green tea-derived carbon quantum dots for real-time monitoring of shrimp freshness. **Colloids and Surfaces A: Physicochemical and Engineering Aspects**, v. 666, n. January, p. 131242, 2023.

KHAN, S. H. Green nanotechnology for the environment and sustainable development. **Green Materials for Wastewater Treatment**, p. 13–46, 2020.

KHAN, Z. G.; PATIL, P. O. A comprehensive review on carbon dots and graphene quantum dots based fluorescent sensor for biothiols. **Microchemical Journal**, v. 157, n. May, p. 105011, 2020.

KHAN, Z. M. S. H. et al. Hydrothermal treatment of red lentils for the synthesis of fluorescent carbon quantum dots and its application for sensing Fe3+. **Optical Materials**, v. 91, n. January, p. 386–395, 2019.

KHARISSOVA, O. V. et al. **Greener synthesis of chemical compounds and materials**. [s.l: s.n.]. v. 6

KLOSOSKI, L. **POTENCIAL DE APROVEITAMENTO DA CASCA DE PINHÃO (Araucaria angustifolia) NO PROCESSO DE PIRÓLISE EM TERMOS DE SUAS PROPRIEDADES FÍSICO-QUÍMICAS E PARÂMETROS CINÉTICOS**. [s.l.] Universidade Tecnológica Federal do Paraná, 2021.

KORAH, B. K.; MATHEW, B. Sustainable carbon quantum dots from Vitex negundo leaves as a synergistic nanoplatform for triple object sensing and anticounterfeiting applications. **Materials Today Sustainability**, v. 21, p. 100273, 2023.

KRALISCH, D. Application of LCA in Process Development. In: **Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes**. [s.l: s.n.]. p. 248–271.

KUMAR, P. et al. A review on advancements in carbon quantum dots and their application in photovoltaics. n. IIII, p. 4714–4759, 2022.

KUMARI, B.; KUMARI, R.; DAS, P. Journal of Pharmaceutical and Biomedical Analysis Visual detection of G-quadruplex with mushroom derived highly fluorescent carbon quantum dots. **Journal of Pharmaceutical and Biomedical Analysis**, v. 157, p. 137–144, 2018.

KURIAN, M.; PAUL, A. Recent trends in the use of green sources for carbon dot synthesis–A short review. **Carbon Trends**, v. 3, p. 100032, 2021.

LARKIN, P. J. **Infrared and Raman Spectroscopy: Principles and Spectral Interpretation**. [s.l: s.n.].

LEE, B. X. et al. Transforming Our World: Implementing the 2030 Agenda Through Sustainable Development Goal Indicators. **Journal of Public Health Policy**, v. 37, n. 1, p. S13–S31, 2016.

LENOIR, D.; SCHRAMM, K. W.; LALAH, J. O. Green Chemistry: Some important forerunners and current issues. **Sustainable Chemistry and Pharmacy**, v. 18, n. March, p. 100313, 2020.

LI, D. Y. et al. Single-step synthesis of polychromatic carbon quantum dots for macroscopic detection of Hg2+. **Ecotoxicology and Environmental Safety**, v. 190, n. December 2019, 2020a.

LI, P. et al. Carbon quantum dots derived from lysine and arginine simultaneously scavenge bacteria and promote tissue repair. **Applied Materials Today**, v. 19, p. 100601, 2020b.

LIM, S. Y.; SHEN, W.; GAO, Z. Carbon quantum dots and their applications. **Chemical Society Reviews**, v. 44, n. 1, p. 362–381, 2015.

LIU, F.; WANG, X. DI; DU, S. YU. Production of gold/silver doped carbon nanocomposites for effective photothermal therapy of colon cancer. **Scientific Reports**, v. 10, n. 1, p. 1–9, 2020.

LIU, M. et al. Carbon quantum dots directly generated from electrochemical oxidation of graphite electrodes in alkaline alcohols and the applications for specific ferric ion detection and cell imaging. **Analyst**, v. 141, n. 9, p. 2657–2664, 2016.

LIU, M. Optical Properties of Carbon Dots: A Review. **Nanoarchitectonics**, v.

1, n. 1, p. 1–12, 2020.

LIU, Y. et al. Barium charge transferred doped carbon dots with ultra-high quantum yield photoluminescence of 99.6% and applications. **Chinese Chemical Letters**, n. 2019, 2020.

LIU, Y. Y. et al. Photodegradation of carbon dots cause cytotoxicity. **Nature Communications**, v. 12, n. 1, p. 1–12, 2021.

LIVIA E. DA SILVA; ORLANDO LUCAS DE L. CALADO; CINTYA D. A. DO E. S. BARBOSA. Study of the Photophysical Properties of Carbon Dots Derived from Banana Peels From Different Cities Used to Produce Ink and Film Fluorescence. **Journal of Bioengineering, Technologies and Health**, v. 5, n. 4, p. 250–256, 2023.

MÄKINEN, M. A. et al. Transcription of lignocellulose-decomposition associated genes, enzyme activities and production of ethanol upon bioconversion of waste substrate by Phlebia radiata. **Applied Microbiology and Biotechnology**, v. 102, n. 13, p. 5657–5672, 2018.

MAROUZI, S. et al. One-pot hydrothermal synthesis of carbon quantum dots from Salvia hispanica L. seeds and investigation of their biodistribution, and cytotoxicity effects. **Journal of Environmental Chemical Engineering**, v. 9, n. 4, p. 105461, 2021.

MOLAEI, M. J. A review on nanostructured carbon quantum dots and their applications in biotechnology, sensors, and chemiluminescence. **Talanta**, v. 196, p. 456–478, 2019.

MULVIHILL, M. J. et al. Green chemistry and green engineering: A framework for sustainable technology development. **Annual Review of Environment and Resources**, v. 36, p. 271–293, 2011.

MURATOGLU, A.; YUCE, M. I. World Energy Outlook and Place of Renewable Resources. **International Journal of Scientific and Technological Research www.iiste.org ISSN**, v. 1, n. 7, 2015.

MURUGAN, N. et al. Applied Surface Science Green synthesis of fl uorescent carbon quantum dots from Eleusine coracana and their application as a fl uorescence ' turn-o ff ' sensor probe for selective detection of Cu 2 +. **Applied Surface Science**, v. 476, n. December 2018, p. 468–480, 2019.

NAMDARI, P.; NEGAHDARI, B.; EATEMADI, A. Synthesis, properties and biomedical applications of carbon-based quantum dots: An updated review. **Biomedicine and Pharmacotherapy**, v. 87, n. 88, p. 209–222, 2017.

NATIONS, U. Global environment outlook – GEO-6: Healthy Planet-Healthy People. 2019.

OTTEN, M. et al. Pyrolysis and Solvothermal Synthesis for Carbon Dots: Role of Purification and Molecular Fluorophores. **Langmuir**, 2022.

PANG, Y. L. et al. A critical review on the recent progress of synthesizing techniques and fabrication of TiO2-based nanotubes photocatalysts. **Applied Catalysis A: General**, v. 481, p. 127–142, 2014.

PARENT, K. Green Chemistry Principle : Atom Economy. **Cleaning Up With Atom Economy**, v. 1991, n. 4, p. 1–11, 2002.

PARK, S. J. et al. Color tunable carbon quantum dots from wasted paper by different solvents for anti-counterfeiting and fluorescent flexible film. **Chemical Engineering Journal**, v. 383, n. July 2019, 2020.

PATI, P.; MCGINNIS, S.; VIKESLAND, P. J. Life Cycle Assessment of "green" Nanoparticle Synthesis Methods. **Environmental Engineering Science**, v. 31, n. 7, p. 410–420, 2014.

PAULL, J. The Rachel Carson Letters and the Making of Silent Spring. **SAGE Open**, v. 3, n. 3, p. 2158244013494861, 1 jul. 2013.

PEI, S. et al. Green preparation of silanized carbon dots with ficus virens leaves as a potent antibacterial agent and an effective fluorescent sensor of iron ion. **Journal of Luminescence**, v. 260, n. March, p. 119837, 2023.

PEIJNENBURG, W. et al. Identification of emerging safety and sustainability issues of advanced materials: Proposal for a systematic approach. **NanoImpact**, v. 23, n. April, 2021.

PRASANNAN, A.; IMAE, T. One-pot synthesis of fluorescent carbon dots from orange waste peels. **Industrial and Engineering Chemistry Research**, v. 52, n. 44, p. 15673–15678, 2013.

PROJECT ON EMERGING NANOTECHNOLOGIES - PEN. **Nanotechnology - Project on Emerging Nanotechnologies**. , fev. 2011. Disponível em: <http://www.nanotechproject.tech>

QIANG, R. et al. Synthesis of carbon quantum dots with green luminescence from potato starch. **New Journal of Chemistry**, v. 43, n. 27, p. 10826–10833, 2019.

QIN, J. et al. PH sensing and bioimaging using green synthesized carbon dots from black fungus. **RSC Advances**, v. 11, n. 50, p. 31791–31794, 2021.

RAMAR, V.; MOOTHATTU, S.; BALASUBRAMANIAN, K. Metal free, sunlight

and white light based photocatalysis using carbon quantum dots from Citrus grandis: A green way to remove pollution. **Solar Energy**, v. 169, n. February, p. 120–127, 2018.

RANI, U. A. et al. A review of carbon quantum dots and their applications in wastewater treatment. **Advances in Colloid and Interface Science**, v. 278, p. 102124, 2020.

RANI, U. A. et al. Sustainable production of nitrogen-doped carbon quantum dots for photocatalytic degradation of methylene blue and malachite green. **Journal of Water Process Engineering**, v. 40, n. November 2020, p. 101816, 2021.

RASAL, A. S. et al. Carbon Quantum Dots for Energy Applications: A Review. **ACS Applied Nano Materials**, v. 4, n. 7, p. 6515–6541, 2021.

RATNAYAKE, S. P. et al. Carbon quantum dots-decorated nano-zirconia: A highly efficient photocatalyst. **Applied Catalysis A: General**, v. 570, n. September 2018, p. 23–30, 2019.

REID, B. T.; REED, S. M. Improved methods for evaluating the environmental impact of nanoparticle synthesis. **Green Chemistry**, v. 18, n. 15, p. 4263–4269, 2016.

ROCO, M. C.; HERSAM, M. C.; MIRKIN, C. A. **Nanotechnology Research Directions for Societal Needs in 2020**. [s.l: s.n.].

ROSE, J. et al. The SERENADE project – A step forward in the Safe by Design process of nanomaterials: Moving towards a product-oriented approach. **Nano Today**, v. 39, p. 101238, 2021.

ROYER, B. et al. Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions—Kinetic and equilibrium study. **Journal of Hazardous Materials**, v. 164, n. 2, p. 1213–1222, 2009.

SABET, M.; MAHDAVI, K. Green synthesis of high photoluminescence nitrogen-doped carbon quantum dots from grass via a simple hydrothermal method for removing organic and inorganic water pollutions. **Applied Surface Science**, v. 463, n. August 2018, p. 283–291, 2019.

SADAT, H. et al. Recent advances in photochemical-based nanomaterial processes for mitigation of emerging contaminants from aqueous solutions. **Applied Nanoscience (Switzerland)**, n. 0123456789, 2022.

SALIERI, B. et al. Life cycle assessment of manufactured nanomaterials: Where are we? **NanoImpact**, v. 10, n. December 2017, p. 108–120, 2018.

SALIERI, B. et al. Integrative approach in a safe by design context combining

risk, life cycle and socio-economic assessment for safer and sustainable nanomaterials. **NanoImpact**, v. 23, n. December 2020, 2021.

SCHWENKE, A. M.; HOEPPENER, S.; SCHUBERT, U. S. Synthesis and Modification of Carbon Nanomaterials utilizing Microwave Heating. **Advanced Materials**, v. 27, n. 28, p. 4113–4141, 2015.

SENANAYAKE, R. D. et al. Machine Learning-Assisted Carbon Dot Synthesis: Prediction of Emission Color and Wavelength. **Journal of Chemical Information and Modeling**, v. 62, n. 23, p. 5918–5928, 2022.

SENDÃO, R. et al. Comparative life cycle assessment of bottom-up synthesis routes for carbon dots derived from citric acid and urea. **Journal of Cleaner Production**, v. 254, p. 1–10, 2020.

SERVICE, F. A. Citrus : World Markets and Trade. **United States**, n. July, p. 1–4, 2023.

SHELDON, R. A. The: E factor 25 years on: The rise of green chemistry and sustainability. **Green Chemistry**, v. 19, n. 1, p. 18–43, 2017.

SHELDON, R. A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. **ACS Sustainable Chemistry and Engineering**, v. 6, n. 1, p. 32–48, 2018.

SHELDON, R. A.; BODE, M. L.; AKAKIOS, S. G. Metrics of green chemistry: Waste minimization. **Current Opinion in Green and Sustainable Chemistry**, v. 33, p. 100569, 2022.

SHI, X. et al. Review on carbon dots in food safety applications. **Talanta**, v. 194, n. August 2018, p. 809–821, 2019.

SINGH, H. et al. One-pot hydrothermal synthesis and characterization of carbon quantum dots (CQDs). **Materials Today: Proceedings**, v. 28, p. 1891–1894, 2020.

SINGH, R. K. et al. Progress in microwave-assisted synthesis of quantum dots (graphene/carbon/semiconducting) for bioapplications: a review. **Materials Today Chemistry**, v. 12, p. 282–314, 2019.

SOHAIL, M. I. et al. Chapter One - Environmental application of nanomaterials: A promise to sustainable future. In: VERMA, S. K.; DAS, A. K. B. T.-C. A. C. (Eds.). **Engineered Nanomaterials and Phytonanotechnology: Challenges for Plant Sustainability**. [s.l.] Elsevier, 2019. v. 87p. 1–54.

SON, Y. R.; PARK, S. J. Green preparation and characterization of graphene

oxide/carbon nanotubes-loaded carboxymethyl cellulose nanocomposites. **Scientific Reports**, v. 8, n. 1, p. 2–11, 2018.

SRIVASTAVA, A. K.; DEV, A.; KARMAKAR, S. Nanosensors and nanobiosensors in food and agriculture. **Environmental Chemistry Letters**, v. 16, n. 1, p. 161–182, 2018.

STUART, B. H. Spectral Analysis. In: **Infrared Spectroscopy: Fundamentals and Applications**. Analytical Techniques in the Sciences. [s.l: s.n.]. p. 45–70.

SYED, N. et al. Carbon-Based Nanomaterials via Heterojunction Serving as Photocatalyst. **Frontiers in Chemistry**, v. 7, n. October, p. 1–7, 2019.

TADESSE, A. et al. Facile Green Synthesis of Fluorescent Carbon Quantum Dots from Citrus Lemon Juice for Live Cell Imaging. **Asian Journal of Nanoscience and Materials**, v. 1, n. 1, p. 36–46, 2018.

TANG, J. et al. Modulation of red-light emission from carbon quantum dots in acid-based environment and the detection of chromium (Ⅲ) ions. **Journal of Materials Science and Technology**, v. 83, p. 58–65, 2021a.

TANG, X. et al. Nitrogen-doped fluorescence carbon dots as multi-mechanism detection for iodide and curcumin in biological and food samples. **Bioactive Materials**, v. 6, n. 6, p. 1541–1554, 2021b.

TANG, Y. et al. Rapid synthesis of highly photoluminescent nitrogen-doped carbon quantum dots via a microreactor with foamy copper for the detection of Hg2+ ions. **Sensors and Actuators, B: Chemical**, v. 258, p. 637–647, 2018.

THANGARAJ, B.; SOLOMON, P. R.; RANGANATHAN, S. Synthesis of Carbon Quantum Dots with Special Reference to Biomass as a Source - A Review. **Current Pharmaceutical Design**, v. 25, n. 13, p. 1455–1476, 2019.

THULASI, S.; KATHIRAVAN, A.; ASHA JHONSI, M. Fluorescent Carbon Dots Derived from Vehicle Exhaust Soot and Sensing of Tartrazine in Soft Drinks. **ACS Omega**, v. 5, n. 12, p. 7025–7031, 2020.

TRAVLOU, N. A. et al. S- and N-doped carbon quantum dots: Surface chemistry dependent antibacterial activity. **Carbon**, v. 135, p. 104–111, 2018.

TRIPATHI, S.; SARKAR, S. Influence of water soluble carbon dots on the growth of wheat plant. **Applied Nanoscience (Switzerland)**, v. 5, n. 5, p. 609–616, 2015.

ÜNLÜSAYIN, M. et al. Nano-encapsulation competitiveness of omega-3 fatty acids and correlations of thermal analysis and Karl Fischer water titration for European

anchovy (Engraulis encrasicolus L.) oil/β-cyclodextrin complexes. **LWT - Food Science and Technology**, v. 68, p. 135–144, 2016.

USMAN, M. et al. The effect of surface charge on cellular uptake and inflammatory behavior of carbon dots. **Colloids and Interface Science Communications**, v. 35, n. January, p. 100243, 2020.

VENKATESWARLU, S. et al. Fungus-derived photoluminescent carbon nanodots for ultrasensitive detection of Hg2+ ions and photoinduced bactericidal activity. **Sensors and Actuators, B: Chemical**, v. 258, p. 172–183, 2018.

WAGUE, A. Phytochemical Screening and Proximate Analysis of Sweet Orange (Citrus Sinesis) Fruit Wastes. **Ijsrst.**, v. 3, n. 7, p. 48–53, 2017.

WANG, M. et al. Sensitivity fluorescent switching sensor for Cr (VI) and ascorbic acid detection based on orange peels-derived carbon dots modified with EDTA. **Food Chemistry**, v. 318, n. February, p. 126506, 2020.

WANG, S. et al. One-step fabrication of high quantum yield sulfur- and nitrogen-doped carbon dots for sensitive and selective detection of Cr(VI). **RSC Advances**, v. 6, n. 109, p. 107717–107722, 2016.

WANG, X. et al. A Mini Review on Carbon Quantum Dots: Preparation, Properties, and Electrocatalytic Application. **Frontiers in Chemistry**, v. 7, n. October, p. 1–9, 2019.

WANG, Y.; HU, A. Carbon quantum dots: synthesis, properties and applications. **Journal of Materials Chemistry C**, v. 2, n. 34, p. 6921–6939, 2014.

WAZIR, A. H.; KUNDI, I. W. Synthesis of graphene nano sheets by the rapid reduction of electrochemically exfoliated graphene oxide induced by microwaves. **Journal of the Chemical Society of Pakistan**, v. 38, n. 1, p. 11–16, 2016.

WILLIAM D. CALLISTER; DAVID G. RETHWISCH. Fundamentals of Materials Science and Engineering: An Integrated Approach (Fifth Edition). **Wiley**, p. 964, 2015.

WINTERTON, N. Twelve more green chemistry principles. **Green Chemistry**, v. 3, n. 6, p. 73–81, 2001.

WU, F.; ZHOU, Z.; HICKS, A. L. Life Cycle Impact of Titanium Dioxide Nanoparticle Synthesis through Physical, Chemical, and Biological Routes. **Environmental Science and Technology**, v. 53, n. 8, p. 4078–4087, 2019.

WU, H. et al. Recent Advance in Carbon Dots: From Properties to Applications. **Chinese Journal of Chemistry**, 2020.

XIAO, A. et al. Carbon and Metal Quantum Dots toxicity on the microalgae

Chlorella pyrenoidosa. **Ecotoxicology and Environmental Safety**, v. 133, p. 211–217, 2016.

XU, X. et al. Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. **Journal of the American Chemical Society**, v. 126, n. 40, p. 12736–12737, 2004.

YANG, S. et al. Large-scale fabrication of heavy doped carbon quantum dots with tunable-photoluminescence and sensitive fluorescence detection. **Journal of Materials Chemistry A**, v. 2, n. 23, p. 8660–8667, 2014.

YANG, S. T. et al. Carbon dots as nontoxic and high-performance fluorescence imaging agents. **Journal of Physical Chemistry C**, v. 113, n. 42, p. 18110–18114, 2009.

YETISEN, A. K. et al. Nanotechnology in Textiles. **ACS Nano**, v. 10, n. 3, p. 3042–3068, 22 mar. 2016.

YU, J. et al. Luminescence mechanism of carbon dots by tailoring functional groups for sensing Fe3+ ions. **Nanomaterials**, v. 8, n. 4, p. 1–12, 2018.

YUAN, F. et al. Bright Multicolor Bandgap Fluorescent Carbon Quantum Dots for Electroluminescent Light-Emitting Diodes. **Advanced Materials**, v. 29, n. 3, 2017.

ZAIATS, G. et al. Quantum Dot Light-Emitting Devices: Beyond Alignment of Energy Levels. **ACS Applied Materials and Interfaces**, v. 9, n. 36, p. 30741–30745, 2017.

ZEKIĆ, E.; VUKOVIĆ, Ž.; HALKIJEVIĆ, I. Application of nanotechnology in wastewater treatment. **Gradjevinar**, v. 70, n. 4, p. 315–323, 2018.

ZHANG, J.; YU, S. H. Carbon dots: large-scale synthesis, sensing and bioimaging. **Materials Today**, v. 19, n. 7, p. 382–393, 2016.

ZHANG, L. et al. Carbon quantum dots doped with phosphorus and nitrogen are a viable fluorescent nanoprobe for determination and cellular imaging of vitamin B12 and cobalt(II). **Microchimica Acta**, v. 186, n. 8, 2019.

ZHANG, M. et al. One-step hydrothermal synthesis of chiral carbon dots and their effects on mung bean plant growth. **Nanoscale**, v. 10, n. 26, p. 12734–12742, 2018.

ZHANG, Z.; SUN, W.; WU, P. Highly Photoluminescent Carbon Dots Derived from Egg White: Facile and Green Synthesis, Photoluminescence Properties, and Multiple Applications. **ACS Sustainable Chemistry and Engineering**, v. 3, n. 7, p. 1412–1418, 2015.

ZHAO, L. et al. One-pot synthesis of nitrogen-doped carbonized polymer dots with tunable emission for multicolor light-emitting diodes. **Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy**, v. 299, n. February, p. 122815, 2023.

ZHAO, Q. et al. Spectroscopic studies of the optical properties of carbon dots: Recent advances and future prospects. **Materials Chemistry Frontiers**, v. 4, n. 2, p. 472–488, 2020.

ZHAO, S. et al. Green Synthesis of Bifunctional Fluorescent Carbon Dots from Garlic for Cellular Imaging and Free Radical Scavenging. **ACS Applied Materials and Interfaces**, v. 7, n. 31, p. 17054–17060, 2015.

ZHOU, Q. et al. Applications of TiO_2 nanotube arrays in environmental and energy fields: A review. **Microporous and Mesoporous Materials**, v. 202, p. 22–35, 2015.

ZULFAJRI, M. et al. Utilization of carbon dots derived from Volvariella volvacea mushroom for a highly sensitive detection of Fe^{3+} and Pb^{2+} ions in aqueous solutions. **Chemosensors**, v. 8, n. 3, p. 1–14, 2020.