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**Green Synthesis of Carbon Dots from Rice Husks Doped with Rare Earths for  
Agrochemical Detection Sensors**

Florianópolis – SC  
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Juliana De Gregori da Rocha

**Green Synthesis of Carbon Dots from Rice Husks Doped with Rare Earths for  
Agrochemical Detection**

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I dedicate this work to my parents, Julio Cezar Paim da Rocha and Leonete Raquel De Gregori da Rocha, the greatest blessing in my life, whose love goes beyond words, and who are the foundation of my life.

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"Keep the crucified Jesus in your heart, and  
all the crosses of the world will seem like  
roses to you"

*St. Padre Pio*

## RESUMO

*Carbon dots* (CDs) são nanomateriais fluorescentes promissores, caracterizados por sua elevada biocompatibilidade, propriedades ópticas ajustáveis e potencial para aplicações ambientais e analíticas. Neste trabalho, foi explorada uma rota de síntese verde via tratamento hidrotérmico, utilizando resíduos de casca de arroz como fonte de carbono, visando a produção de *carbon dots* de forma sustentável e alinhada aos princípios da economia circular. A dopagem com elementos de terras raras, especificamente cério (Ce) e gadolínio (Gd), foi realizada para avaliar seu impacto no rendimento quântico e nas propriedades fotoluminescentes. As amostras foram caracterizadas por espectroscopia no infravermelho com transformada de Fourier (FTIR), microscopia eletrônica de transmissão (TEM), espectroscopia de fotoelétrons excitados por raios X (XPS) e espectroscopia de fluorescência, para confirmar a dopagem e compreender suas implicações estruturais e ópticas. Um planejamento experimental do tipo delineamento composto central rotacional (DCCR) foi conduzido, variando a temperatura da reação e a carga de sólidos, com o objetivo de otimizar as condições de degradação da biomassa. As condições ótimas de síntese foram determinadas em 220 °C e 3% m/v de carga sólida. A partir desses parâmetros, realizou-se um estudo cinético variando o tempo de reação (0 h a 12 h), no qual foram avaliados o teor de açúcares totais, o rendimento quântico e a formação de compostos intermediários, permitindo estabelecer inferências sobre o mecanismo de formação dos *carbon dots*. Posteriormente, os *carbon dots* foram dopados com cério e gadolínio visando aplicações como sensores ópticos fluorescentes para a detecção de agroquímicos. Os *carbon dots* dopados com cério (Ce-CDs) apresentaram rendimento quântico de 23,77% e limite de detecção de 1,78 µmol/L para glifosato, enquanto os CDs dopados com gadolínio (Gd-CDs) exibiram rendimento quântico de 15,93% e elevada sensibilidade para mesotriona, com limite de detecção de 4,3 µmol/L. A aplicação dos sensores em amostras reais de água evidenciou boa eficiência analítica, com recuperações de 72,7% – 93,4% para Ce-CDs e 66,7% – 89,3% para Gd-CDs, associadas a baixos desvios relativos, demonstrando a robustez dos *carbon dots* dopados em matrizes ambientais.

**Palavras-chave:** *carbon dots*, síntese verde, casca de arroz, dopagem com terras raras, sensores ópticos fluorescentes.

## ABSTRACT

Carbon dots (CDs) are promising fluorescent nanomaterials characterized by their high biocompatibility, tunable optical properties, and strong potential for environmental and analytical applications. In this study, a green synthesis route based on hydrothermal treatment was explored using rice husk residues as a carbon source, aiming at the sustainable production of carbon dots aligned with the principles of circular economy. Doping with rare-earth elements, specifically cerium (Ce) and gadolinium (Gd), was performed to evaluate its impact on the quantum yield and photoluminescent properties. The samples were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and fluorescence spectroscopy to confirm dopant incorporation and to elucidate their structural and optical implications. A central composite rotational design (CCRD) was applied by varying reaction temperature and solid loading in order to optimize biomass degradation conditions. Optimal synthesis conditions were determined at 220 °C and 3% w/v solid loading. Based on these parameters, a kinetic study was conducted by varying the reaction time (0–12 h), in which total sugar content, quantum yield, and the formation of intermediate compounds were evaluated, allowing inferences regarding the carbon dot formation mechanism. Subsequently, the carbon dots were doped with cerium and gadolinium for application as fluorescent optical sensors for agrochemical detection. Cerium-doped carbon dots (Ce-CDs) exhibited a quantum yield of 23.77% and a detection limit of 1.78  $\mu\text{mol/L}$  for glyphosate, whereas gadolinium-doped carbon dots (Gd-CDs) showed a quantum yield of 15.93% and high sensitivity toward mesotrione, with a detection limit of 4.3  $\mu\text{mol/L}$ . The application of the sensors in real water samples demonstrated good analytical efficiency, with recoveries ranging from 72.7% to 93.4% for Ce-CDs and from 66.7% to 89.3% for Gd-CDs, associated with low relative deviations, confirming the robustness of rare-earth-doped carbon dots in environmental matrices.

**Keywords:** carbon dots, green synthesis, rice husk, rare-earth doping, fluorescent optical sensors.

## RESUMO EXPANDIDO

### Introdução

Os *carbon dots* (CDs) constituem uma classe emergente de nanomateriais carbonáceos quase esféricos, com dimensões tipicamente inferiores a 10 nm, que vêm despertando grande interesse científico devido às suas propriedades ópticas singulares, especialmente a fluorescência ajustável, alta estabilidade fotoquímica, boa solubilidade em meio aquoso e baixa toxicidade (Wan *et al.*, 2021). Diferentemente dos *quantum dots* semicondutores tradicionais, os CDs apresentam composição predominantemente orgânica, podendo ser obtidos a partir de fontes abundantes e renováveis, o que amplia significativamente seu potencial de aplicação em contextos sustentáveis. Essas características tornam os *carbon dots* materiais promissores para uso em sensores ópticos, bioimagem, dispositivos optoeletrônicos, fotocatalise e aplicações ambientais, destacando-se como alternativas mais seguras e ambientalmente compatíveis em comparação a nanomateriais metálicos ou semicondutores convencionais (Kumar *et al.*, 2022).

Nos últimos anos, esforços significativos têm sido direcionados ao desenvolvimento de rotas de síntese mais sustentáveis para *carbon dots*, especialmente aquelas baseadas em biomassa residual e resíduos agroindustriais (Thongsai *et al.*, 2019). Estratégias de síntese *bottom-up*, como os métodos hidrotermais, permitem a conversão de precursores ricos em carbono em nanomateriais fluorescentes por meio de processos relativamente simples, com baixo consumo de reagentes tóxicos e possibilidade de controle das propriedades estruturais e ópticas (Perumal *et al.*, 2021). Nesse contexto, a utilização de resíduos agroindustriais, como a casca de arroz, representa uma abordagem alinhada aos princípios da economia circular e da química verde, agregando valor a materiais de descarte e reduzindo impactos ambientais associados ao acúmulo desses resíduos (Dhongde *et al.*, 2024). Além disso, a compreensão dos mecanismos de formação dos CDs a partir da biomassa é fundamental para o aprimoramento das rotas sintéticas e para o controle reprodutível de suas propriedades funcionais.

Uma estratégia amplamente investigada para ampliar o desempenho óptico e funcional dos *carbon dots* consiste na dopagem com heteroátomos ou elementos metálicos, com destaque para as terras raras, como cério e gadolínio (Baranovskaya *et al.*, 2021). A incorporação desses dopantes pode introduzir novos estados eletrônicos, modificar defeitos superficiais e alterar a densidade de grupos funcionais, impactando diretamente o rendimento quântico, o comportamento fotoluminescente e a seletividade em aplicações sensoras (Chen *et al.*, 2016; Jiao *et al.*, 2022; Orhan *et al.*, 2023). No contexto ambiental, *carbon dots* dopados têm se mostrado particularmente promissores para a detecção fluorescente de contaminantes emergentes em matrizes aquosas reais, como pesticidas e herbicidas amplamente utilizados na agricultura (Meng *et al.*, 2022). Assim, o desenvolvimento de CDs dopados a partir de fontes renováveis combina avanços em nanociência, sustentabilidade e monitoramento ambiental, estabelecendo uma base sólida para aplicações tecnológicas de alto impacto científico e socioambiental.

## Objetivos

Este trabalho tem como objetivo investigar se *carbon dots* sintetizados a partir de casca de arroz podem atuar como sensores fluorescentes seletivos para a detecção de agroquímicos em meio aquoso, contribuindo simultaneamente para a valorização de um resíduo agroindustrial abundante e de baixo valor agregado na geração de nanomateriais sustentáveis. Para isso, busca-se avaliar se parâmetros de síntese, como temperatura, carga sólida e tempo de reação, influenciam o grau de carbonização da biomassa, a conversão de compostos orgânicos em *carbon dots* e suas propriedades ópticas, especialmente o rendimento quântico. Adicionalmente, investiga-se se a composição química da biomassa exerce influência direta na formação, na estrutura e nas características superficiais dos nanomateriais obtidos, bem como se é possível propor um mecanismo de formação dos *carbon dots* com base nos constituintes presentes no precursor utilizado. Por fim, examina-se se a dopagem com terras raras, especificamente cério e gadolínio, modifica as propriedades físico-químicas, morfológicas e de superfície dos *carbon dots* e se essa estratégia resulta em maior sensibilidade e desempenho analítico na detecção fluorescente de agroquímicos em amostras de água.

## Metodologia

A síntese dos *carbon dots* foi realizada por rota hidrotérmica, utilizando água como solvente e casca de arroz como precursor orgânico renovável. Inicialmente, a biomassa foi submetida a procedimentos de preparo e caracterização, com o objetivo de compreender sua composição química e sua influência na formação dos nanomateriais. A síntese foi conduzida sob diferentes condições experimentais, visando promover a carbonização controlada da matéria orgânica e a conversão dos compostos presentes na biomassa em estruturas carbonáceas fluorescentes. Após a reação, os sistemas obtidos foram submetidos a etapas de separação, purificação, filtração e diálise, assegurando a remoção de resíduos sólidos e espécies moleculares de baixo peso molecular, com posterior caracterização dos materiais obtidos.

Com o intuito de investigar os fatores que governam a formação dos *carbon dots*, foi realizado um estudo sistemático dos parâmetros de síntese, avaliando-se o efeito da temperatura e da carga de sólidos alimentada no reator sobre o grau de carbonização da matéria orgânica. A partir da determinação da condição ótima de síntese em termos de temperatura e carga de sólidos, conduziu-se um estudo cinético para avaliar a influência do tempo de reação na liberação de compostos de degradação, na formação e liberação de açúcares derivados da quebra dos polissacarídeos da biomassa e no rendimento quântico dos *carbon dots*. Paralelamente, as transformações químicas ocorridas ao longo da reação foram monitoradas, buscando correlacionar a conversão dos constituintes orgânicos da biomassa com a geração das estruturas fluorescentes, o que possibilitou a proposição de um mecanismo de formação dos *carbon dots* com base nos constituintes presentes no precursor utilizado.

Após a obtenção da condição ótima de síntese, considerando temperatura, carga de sólidos e tempo de reação, realizou-se a dopagem dos *carbon dots* com elementos terras raras, especificamente cério e gadolínio, empregando a rota hidrotérmica. Os nanomateriais dopados e não dopados foram caracterizados por um

conjunto de técnicas físico-químicas e espectroscópicas, incluindo métodos para a avaliação da morfologia, estrutura cristalina, composição química superficial e propriedades ópticas. As características de absorção e emissão foram investigadas, com ênfase na determinação do rendimento quântico e na análise do efeito da dopagem sobre o comportamento fotoluminescente dos *carbon dots*.

Por fim, a aplicação dos *carbon dots* como sensores fluorescentes foi avaliada por meio de ensaios de detecção de agroquímicos em meio aquoso. Foram investigados oito agroquímicos de interesse ambiental e agrícola, incluindo atrazina, imidacloprida, glifosato, mesotriona, dicamba, diuron, amicarbazona e acefato, analisando-se parâmetros como sensibilidade, seletividade e resposta fluorescente frente aos analitos de interesse. Adicionalmente, foram realizados testes em amostras de água real, a fim de verificar o potencial de aplicação ambiental dos nanomateriais desenvolvidos. Essa etapa permitiu correlacionar as modificações estruturais e ópticas induzidas pela dopagem com o desempenho dos *carbon dots* na detecção fluorescente de contaminantes, reforçando sua aplicabilidade como sensores sustentáveis.

## Resultados e Discussão

Os parâmetros de síntese exerceram influência significativa sobre a formação e as propriedades dos *carbon dots* produzidos a partir da casca de arroz. A variação da temperatura e da carga de sólidos alimentada no reator afetou diretamente o grau de carbonização da biomassa, refletindo-se tanto no rendimento do processo quanto no comportamento óptico dos nanomateriais obtidos. Observou-se que condições inadequadas de síntese resultaram em sistemas com baixa fluorescência, enquanto condições mais severas favoreceram a formação de estruturas carbonáceas mais organizadas, com melhor desempenho fotoluminescente. Esses resultados evidenciam que o controle dos parâmetros de síntese é fundamental para a obtenção de *carbon dots* com propriedades ópticas adequadas para aplicações sensoras.

O estudo cinético revelou que o tempo de reação desempenha papel fundamental na conversão dos constituintes orgânicos da biomassa em *carbon dots*. Verificou-se que a evolução temporal da reação está associada à liberação de compostos de degradação e de açúcares provenientes da quebra dos polissacarídeos presentes na casca de arroz, os quais atuam como precursores intermediários na formação das estruturas fluorescentes. A correlação entre a diminuição desses compostos solúveis e o aumento do rendimento quântico dos *carbon dots* permitiu compreender a progressiva carbonização e reorganização das espécies orgânicas ao longo do processo. Esses achados forneceram subsídios para a proposição de um mecanismo de formação dos *carbon dots* baseado na composição química da biomassa utilizada.

A dopagem dos *carbon dots* com terras raras, especificamente cério e gadolínio, promoveu modificações em suas propriedades físico-químicas, estruturais e ópticas. A incorporação efetiva dos dopantes foi confirmada por espectroscopia de fotoemissão de raios X, evidenciando a presença de cério e gadolínio na composição superficial dos nanomateriais. Os *carbon dots* dopados apresentaram alterações no comportamento fotoluminescente, associadas à introdução de novos estados eletrônicos e defeitos estruturais, o que se refletiu em um aumento do rendimento

quântico em comparação aos *carbon dots* não dopados. Esses resultados demonstram que a dopagem com terras raras constitui uma estratégia eficaz para modular as propriedades dos nanomateriais e potencializar seu desempenho em aplicações analíticas.

Nos ensaios de aplicação como sensores fluorescentes, os *carbon dots* dopados demonstraram capacidade de detectar diferentes agroquímicos em meio aquoso. A resposta fluorescente apresentou variações dependentes do tipo de analito e do sistema avaliado, indicando seletividade e sensibilidade diferenciadas frente aos agroquímicos investigados. Os testes realizados em amostras de água real confirmaram a aplicabilidade dos *carbon dots* em matrizes ambientais complexas, evidenciando seu potencial como sensores sustentáveis para o monitoramento de contaminantes emergentes.

### **Considerações Finais**

Este trabalho demonstrou que a casca de arroz pode ser eficientemente valorizada como precursor para a síntese de *carbon dots* fluorescentes por rota hidrotérmica, estabelecendo uma abordagem integrada para compreender os mecanismos de formação desses nanomateriais a partir da biomassa. A análise combinada da composição química do precursor, das transformações ocorridas durante a síntese e das propriedades dos *carbon dots* obtidos permitiu elucidar a relação entre os constituintes da biomassa, o grau de carbonização e o desempenho óptico dos nanomateriais. Os resultados evidenciam que o controle criterioso dos parâmetros de síntese é fundamental para maximizar a conversão da matéria orgânica em estruturas carbonáceas fluorescentes com propriedades ajustadas para aplicações analíticas.

A introdução da dopagem com terras raras, especificamente cério e gadolínio, mostrou-se uma estratégia eficaz para a modulação das propriedades estruturais, superficiais e ópticas dos *carbon dots*. A incorporação dos dopantes, confirmada por técnicas espectroscópicas, promoveu a formação de novos estados eletrônicos e defeitos superficiais, resultando em melhorias no comportamento fotoluminescente e no rendimento quântico dos materiais.

Por fim, a aplicação dos *carbon dots* dopados como sensores fluorescentes para a detecção de agroquímicos em meio aquoso evidenciou elevado potencial analítico, mesmo em matrizes ambientais reais. A sensibilidade e a seletividade observadas confirmam a robustez dos nanomateriais desenvolvidos e sua adequação para o monitoramento de contaminantes emergentes. De forma geral, este estudo consolida a integração entre valorização de resíduos agroindustriais, síntese verde e engenharia de nanomateriais, oferecendo uma base sólida para o desenvolvimento futuro de sensores fluorescentes sustentáveis e para a expansão das aplicações de nanomateriais carbonáceos nas áreas ambiental e analítica.

**Palavras-chave:** *carbon dots*; síntese verde; casca de arroz; dopagem com terras raras; sensores ópticos fluorescentes.

## FIGURES LIST

|                                                                                                                                                                                                                                                                               |     |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 1 – Classification of different types of CDs includes crystalline GQDs with anisotropic shape, crystalline CQDs with spherical shape, amorphous CNPs with spherical shape, and PDs with crosslinked monomers .....                                                     | 31  |
| Figure 2 – Representative illustration of the effect of the solvent on the mechanism of growth and photoluminescence of CDs in water, glycerol, and DMF, respectively, resulting in an increase in the degree of carbonization during the solvothermal synthesis method ..... | 36  |
| Figure 3 – Description of the two approaches to obtaining carbon dots (bottom-up and top-down) mentioning the main methods and sources of raw material.....                                                                                                                   | 37  |
| Figure 4 – Schematic illustration summarizing the hydrothermal method for synthesizing CDs.....                                                                                                                                                                               | 40  |
| Figure 5 – Schematic illustration of the chemical transformation of rice husk residue into CDs.....                                                                                                                                                                           | 53  |
| Figure 6 – Summarized flowchart for obtaining RE-CDs by the hydrothermal method .....                                                                                                                                                                                         | 59  |
| Figure 7 – Schematic illustration summarizing the different steps included in the green R-CDs synthesis methodology, study of the kinetics associated with the synthesis parameters, as well as their characterization .....                                                  | 69  |
| Figure 8 – Chemical composition of the raw RH .....                                                                                                                                                                                                                           | 85  |
| Figure 9 – Response surface generated from the CCRD as a function of temperature and solids charge for degradation compounds .....                                                                                                                                            | 94  |
| Figure 10 – Response surface generated from the CCRD as a function of temperature and solids charge for removal of organic compounds .....                                                                                                                                    | 95  |
| Figure 11 – Analysis of a) total sugars; b) yields of degradation compounds; c) kinetic behavior of quantum yield as a function of reaction time; and d) severity factor .....                                                                                                | 98  |
| Figure 12 – Characterization of R-CDs: a) IR spectra and b) XRD patterns.....                                                                                                                                                                                                 | 101 |

|                                                                                                                                                                                                                                        |     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 13 – Optical characterization of R-CDs: a) UV-visible absorption spectrum; b) fluorescence spectra at different excitation wavelengths from 320 nm to 500 nm; and c) emission and excitation spectra of synthesized R-CDs ..... | 102 |
| Figure 14 – Morphological and surface characterization of R-CDs: a-c) TEM images; d) histogram of particle size distribution, and e) zeta potential of R-CDs .....                                                                     | 104 |
| Figure 15 – The XPS spectrum of R-CDS: a) XPS survey spectrum; b) high-resolution C 1s; c) high-resolution O 1s peaks; and d) high-resolution Si 2p.....                                                                               | 105 |
| Figure 16 – Visual appearance of freeze-dried R-CDs synthesized under different hydrothermal temperatures .....                                                                                                                        | 107 |
| Figure 17 – Mechanistic insights in CDs formation.....                                                                                                                                                                                 | 109 |
| Figure 18 – Characterization of Ce-CDs: a) IR spectra; and b) XRD patterns.....                                                                                                                                                        | 113 |
| Figure 19 – Optical analysis of Ce-CDs: a) UV–visible absorption spectrum; b) fluorescence spectra at different excitation wavelengths from 320 nm to 460 nm; and c) emission and excitation spectrum of synthesized Ce-CDs .....      | 115 |
| Figure 20 – Fluorescence intensity of Ce-CDs as a function of pH .....                                                                                                                                                                 | 117 |
| Figure 21 – Morphological analysis of Ce-CDs: a) TEM image and b) Histogram of particle size distribution .....                                                                                                                        | 119 |
| Figure 22 – The XPS spectrum of Ce-CDS: a) XPS survey spectrum; b) high-resolution C 1s; c) high-resolution O 1s peaks; d) high-resolution Si 2p and e) high-resolution of Ce 3d.....                                                  | 121 |
| Figure 23 – Study of the selectivity of Ce-CDs concerning different agrochemicals                                                                                                                                                      | 122 |
| Figure 24 – Emission spectra of Ce-CDs with increasing concentrations of glyphosate 0.5 $\mu\text{mol/L}$ – 20 $\mu\text{mol/L}$ .....                                                                                                 | 123 |
| Figure 25 – Linear band of increasing intensity and concentration of glyphosate (0.5 $\mu\text{mol/L}$ – 20 $\mu\text{mol/L}$ ).....                                                                                                   | 124 |
| Figure 26 – Characterization of Gd-CDs: a) IR spectra; and b) XRD patterns .....                                                                                                                                                       | 128 |
| Figure 27 – Optical analysis of Gd-CDs: a) UV–visible absorption spectrum; b) fluorescence spectra at different excitation wavelengths from 320 nm to 460 nm; and c) emission and excitation spectrum of synthesized Ce-CDs .....      | 129 |

|                                                                                                                                                                                                                                                                                |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 28 – Fluorescence intensity of Gd-CDs as a function of pH .....                                                                                                                                                                                                         | 131 |
| Figure 29 – Morphological analysis of Gd-CDs: a) TEM image; and b) histogram of particle size distribution .....                                                                                                                                                               | 132 |
| Figure 30 – The XPS spectrum of Gd-CDS: a) XPS survey spectrum; b) high-resolution C 1s; c) high-resolution O 1s peaks; d) high-resolution Si 2p; and e) high-resolution of Gd 4d.....                                                                                         | 133 |
| Figure 31 – Study of the selectivity of Gd-CDs concerning different agrochemicals                                                                                                                                                                                              | 135 |
| Figure 32 – Fluorescence emission spectra of Gd-CDs recorded with increasing mesotrione concentrations up to 20 $\mu\text{mol/L}$ .....                                                                                                                                        | 136 |
| Figure 33 – Linear band of increasing intensity and concentration of mesotrione (0.5 $\mu\text{mol/L}$ to 20 $\mu\text{mol/L}$ ).....                                                                                                                                          | 137 |
| Figure 34 – Emission spectra of rare-earth-doped carbon dots (Ce-CDs and Gd-CDs) in different aqueous media: a) emission spectra of Ce-CDs in ultrapure water and lagoon water, compared with the spectrum of lagoon water without CDs; and b) emission spectra of Gd-CD ..... | 139 |
| Figure 35 – a) Photoluminescence spectra of Ce-CDs dispersed in lagoon water without contaminant (red), lagoon water containing glyphosate (green), ultrapure water with Ce-CDs (blue), and lagoon water alone (black); and .....                                              | 140 |

## TABLES LIST

|                                                                                                                                                                          |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources. ....                                               | 45  |
| Table 2 – Summary of some studies involving the use of rice husks in the hydrothermal synthesis of CDs .....                                                             | 54  |
| Table 3 – Summary of some studies involving doping Ce-CDs and Gd-CDs via hydrothermal synthesis.....                                                                     | 62  |
| Table 4 – Experimental design of the variables used in the synthesis of CDs .....                                                                                        | 72  |
| Table 5 – Chemical characterization of the solid fraction in all runs and the subsequent recovery of solids and polysaccharides .....                                    | 87  |
| Table 6 – Analyzing the chemical composition of the liquid fraction in terms of sugar content, degradation compounds, quantum yield, and severity factor for each run... | 91  |
| Table 7 – Influences of the independent variables temperature ( $X_1$ ) and solid load ( $X_2$ ) on quantum yield in hydrothermal processing .....                       | 93  |
| Table 8 – Chemical composition of the liquid fraction in terms of sugar content, degradation compounds, quantum yield, and severity factor for each run .....            | 99  |
| Table 9 – Performance of cerium-doped CDs in real samples for glyphosate detection .....                                                                                 | 141 |
| Table 10 – Performance of gadolinium-doped CDs in real samples for mesotrione detection.....                                                                             | 142 |

## LIST OF ABBREVIATIONS

**CCRD** – Central Composite Rotational Design

**CDs** – Carbon Dots

**Ce** – Cerium

**Ce-CDs** – Cerium-doped Carbon Dots

**CNDs** – Carbon Nanodots

**CNPs** – Carbon Nanoparticles

**DC** – Degradation Compounds

**DMF** – Dimethylformamide

**EDX** – Energy Dispersive X-Ray

**FTIR** – Fourier-Transform Infrared Spectroscopy

**Gd** – Gadolinium

**Gd-CDs** – Gadolinium-doped Carbon Dots

**GO** – Graphene Oxide

**GQDs** – Graphene Quantum Dots

**HPLC** - High-Performance Liquid Chromatography

**LC** – Lagoa da Conceição

**NMR** – Nuclear Magnetic Resonance

**PDs** – Polymer Dots

**PL** – Photoluminescence

**QCE** – Quantum Confinement Effect

**QY** – Quantum Yield

**RAMAN** - Raman Spectroscopy

**R-CDs** – Carbon Dots from Rice Husk Biomass

**RE** – Rare Earth

**RE-CDs** – Rare Earth Doped Carbon Dots

**RH** – Rice Husk

**SEM** – Scanning Electron Microscopy

**TEM** – Transmission Electron Microscopy

**TS** – Total Sugar

**UFLC** – Ultra-Fast Liquid Chromatography

**UV–Vis** – Ultraviolet–Visible Absorption Spectroscopy

**XPS** – X-Ray Photoelectron Spectroscopy

## **XRD** – X-Ray Diffraction

## SUMMARY

|              |                                                                                                                         |           |
|--------------|-------------------------------------------------------------------------------------------------------------------------|-----------|
| <b>1</b>     | <b>INTRODUCTION .....</b>                                                                                               | <b>26</b> |
| <b>2</b>     | <b>OBJECTIVES .....</b>                                                                                                 | <b>30</b> |
| 2.1          | GENERAL OBJECTIVE .....                                                                                                 | 30        |
| 2.2          | SPECIFIC OBJECTIVES .....                                                                                               | 30        |
| <b>3</b>     | <b>LITERATURE REVIEW .....</b>                                                                                          | <b>31</b> |
| 3.1          | WHAT ARE CARBON DOTS? .....                                                                                             | 31        |
| <b>3.1.1</b> | <b>Main properties of CDs .....</b>                                                                                     | <b>33</b> |
| 3.1.1.1      | <i>Physicochemical properties of CDs .....</i>                                                                          | <i>33</i> |
| 3.1.1.2      | <i>Electrochemical properties of CDs .....</i>                                                                          | <i>34</i> |
| 3.1.1.3      | <i>Optical and Photoluminescence Properties of CDs .....</i>                                                            | <i>34</i> |
| 3.2          | SYNTHESIS OF CDS .....                                                                                                  | 36        |
| <b>3.2.1</b> | <b>The hydrothermal method for CD synthesis .....</b>                                                                   | <b>38</b> |
| <b>3.2.2</b> | <b>Green synthesis of CDs (from natural resources) .....</b>                                                            | <b>41</b> |
| 3.2.2.1      | <i>Green synthesis of CDs by hydrothermal method .....</i>                                                              | <i>43</i> |
| 3.2.2.2      | <i>Rice husks as a carbon source for green synthesis of CDs .....</i>                                                   | <i>52</i> |
| 3.3          | RARE EARTH DOPED CARBON DOTS (RE-CDS) .....                                                                             | 57        |
| <b>3.3.1</b> | <b>Hydrothermal synthesis of CDs doped with Gd and Ce .....</b>                                                         | <b>59</b> |
| 3.4          | APPLICATION OF RE-DOPED CARBON DOTS IN THE DETECTION OF AGROCHEMICAL RESIDUES .....                                     | 64        |
| <b>4</b>     | <b>STATE-OF-THE-ART CONSIDERATIONS AND JUSTIFICATION .....</b>                                                          | <b>67</b> |
| <b>5</b>     | <b>MATERIALS AND METHODS .....</b>                                                                                      | <b>69</b> |
| 5.1          | RAW MATERIAL .....                                                                                                      | 70        |
| 5.2          | GREEN SYNTHESIS OF CDS AND EXPERIMENTAL DESIGN .....                                                                    | 71        |
| <b>5.2.1</b> | <b>Hydrothermal synthesis of CDs .....</b>                                                                              | <b>71</b> |
| <b>5.2.2</b> | <b>Experimental design for the optimized removal of organic compounds and degradation products from rice husk .....</b> | <b>71</b> |

|                                                                                               |           |
|-----------------------------------------------------------------------------------------------|-----------|
| 5.2.3 Kinetics of carbon dots from rice husk biomass (R-CDs) .....                            | 73        |
| 5.2.4 Severity factor.....                                                                    | 74        |
| 5.2.5 Chemical characterization of lignocellulosic biomass .....                              | 74        |
| 5.2.6 Quantum yield determination and quantification of sugars and degradation compounds..... | 76        |
| 5.2.7 Statistical analysis of hydrothermal of R-CDs .....                                     | 77        |
| 5.3 CHARACTERIZATION OF CARBON DOTS .....                                                     | 77        |
| 5.3.1 Transmission electron microscopy (TEM) .....                                            | 77        |
| 5.3.2 Fourier transform infrared spectroscopy (FTIR).....                                     | 78        |
| 5.3.3 X-ray diffraction (XRD) .....                                                           | 78        |
| 5.3.4 UV-VIS spectroscopy .....                                                               | 78        |
| 5.3.5 X-ray Photoelectron Spectroscopy and Zeta Potential .....                               | 78        |
| 5.4 DOPING CDS WITH RARE EARTHS .....                                                         | 79        |
| 5.4.1 Materials.....                                                                          | 79        |
| 5.4.2 Synthesis of Ce-CDs and Gd-CDs.....                                                     | 80        |
| 5.5 SENSITIVITY AND SELECTIVITY OF THE CDS .....                                              | 80        |
| 5.6 APPLICATION OF DOPED CDS IN REAL SAMPLES .....                                            | 83        |
| <b>6 RESULTS AND DISCUSSION .....</b>                                                         | <b>85</b> |
| 6.1 EFFECTS OF HYDROTHERMAL SYNTHESIS ON RICE HUSK COMPOSITION.....                           | 85        |
| 6.2 EFFECTS OF HYDROTHERMAL SYNTHESIS ON THE SOLUBILIZATION OF COMPOUNDS.....                 | 89        |
| 6.3 KINETICS OF HYDROTHERMAL SYNTHESIS FOR THE FORMATION OF R-CDs.....                        | 95        |
| 6.4 CHARACTERIZATION OF CDS.....                                                              | 100       |
| 6.4.1 Mechanistic Insights of R-CDs formation .....                                           | 106       |
| 6.5 CERIUM DOPED CARBON DOTS .....                                                            | 112       |

|       |                                                      |     |
|-------|------------------------------------------------------|-----|
| 6.5.1 | Characterizations of Ce-CDs .....                    | 113 |
| 6.5.2 | Application of Ce-CDs on Agrochemical Detection..... | 122 |
| 6.6   | GADOLINIUM-DOPED CARBON DOTS (GD-CDS) .....          | 125 |
| 6.6.1 | Characterization of Gd-CDs.....                      | 126 |
| 6.6.2 | Application Gd-CDs.....                              | 135 |
| 6.7   | DETECTION OF DOPED CDS IN REAL SAMPLES .....         | 138 |
| 6.7.1 | Sensor Performance .....                             | 141 |
| 7     | CONCLUSIONS .....                                    | 145 |
|       | REFERENCES .....                                     | 147 |

## CONCEPTUAL DIAGRAM OF THE STUDY

|                                           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
|-------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Why carry out this research?              | <p>The development of this research arises from the need to develop sustainable, effective and low-cost methods for detecting agrochemical contaminants in agricultural environments. Given the environmental and health impact caused by the extensive use of agrochemicals, there is an urgent need to create technologies that monitor these pollutants efficiently. The research seeks to take advantage of the agro-industrial residue of rice husks, promoting a circular economy approach and offering an innovative solution by using carbon dots doping with cerium and gadolinium as sensors, a strategy still unexplored in the literature.</p> |
| What has already been done?               | <p>Previous research has shown the potential of CDs as sensors due to their biocompatibility, optical properties and ease of production from renewable sources. In addition, recent advances have explored the doping of carbon dots with rare earth elements, such as cerium and gadolinium, to improve their fluorescence properties and stability. However, few studies have investigated the use of doped CDs specifically as agrochemical sensors, and even fewer have used green synthesis from waste such as rice husks, which makes this study a pioneer in exploring this sustainable approach to environmental monitoring.</p>                   |
| What are the hypotheses of this research? | <p>The green synthesis of CDs from rice husks will represent a viable and efficient strategy for generating sustainable fluorescent nanomaterials. Doping the CDs with cerium and gadolinium will enhance their optical and electronic properties, particularly fluorescence intensity, quantum yield, and detection sensitivity. The doped CDs will be sensitive and selective in detecting agrochemicals, highlighting their potential applicability in the development of environmentally relevant sensing platforms.</p>                                                                                                                               |

## CONCEPTUAL DIAGRAM OF THE STUDY

|                                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|---------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>What methodology will be used?</b> | <p><b>Biomass preparation and characterization:</b> Rice husks will be processed as raw material through cleaning, drying, and grinding, followed by sieving to a particle size of 30 mesh. The chemical characterization of the biomass will be carried out by acid hydrolysis, followed by quantification of the resulting monomeric sugars and degradation products using high-performance liquid chromatography (HPLC), to assess its structural components (cellulose, hemicellulose, and lignin), which influence the formation of CDs.</p> <p><b>Hydrothermal synthesis of CDs:</b> CDs will be synthesized using rice husk in hydrothermal reactors, controlling variables such as temperature, solid load and reaction time. This process will allow CDs to be formed in a sustainable and efficient way.</p> <p><b>Doping with cerium and gadolinium:</b> The CDs will be doped during hydrothermal synthesis, incorporating rare earth elements (cerium and gadolinium) to improve the optical and electronic properties of the CDs.</p> <p><b>Physico-chemical characterization of the doped CDs:</b> The CDs will be analyzed using techniques such as fluorescence spectroscopy, FTIR, TEM, XPS and UV-Vis, to confirm the doping, evaluate the structure and identify the functional groups, as well as measuring the luminescence and quantum yield.</p> <p><b>Sensitivity and selectivity tests for agrochemicals:</b> The efficiency of the doped CDs as sensors will be evaluated using different agrochemical compounds, assessing their ability to detect these contaminants with both sensitivity and selectivity through fluorescence spectroscopy.</p> |
|---------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

## CONCEPTUAL DIAGRAM OF THE STUDY

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|------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>What are the preliminary results?</b> | <p>The hydrothermal synthesis of CDs from rice husks is feasible and results in particles with fluorescent properties, confirming the potential of rice husk biomass as a sustainable carbon source to produce nanomaterials.</p> <p>Doping with cerium and gadolinium was successfully carried out, with an increase in the fluorescence intensity and quantum yield of doped CDs compared to undoped CDs. This enhancement suggests that the rare earth elements improved the optical properties, as expected.</p> <p>The doped CDs showed sensitivity in the presence of agrochemicals, especially in tests with model contaminants, indicating a specific fluorescent response when exposed to these compounds. This initial result is promising for the use of doped CDs as environmental sensors.</p> <p>The doped CDs showed good stability under different pH and temperature conditions, maintaining their fluorescent and colloidal properties, which points to their suitability for environmental monitoring applications.</p> |
|------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

## 1 INTRODUCTION

The growing global demand for food and the intensification of agricultural practices have driven the extensive use of agrochemicals to protect and increase crop productivity. Although these compounds are highly effective, they have generated relevant environmental impacts, mainly through the contamination of soil and water resources, as well as the permanence of toxic residues in agricultural products. For this reason, the search for methods to monitor and detect contaminants has become crucial for the sustainability of the agricultural sector. This allows for the control of contamination levels and the reduction of risks to human health and the environment (Carvalho, 2017; Khan *et al.*, 2024; Perumal *et al.*, 2021).

In recent years, important advancements in nanomaterial technologies have facilitated the development of increasingly precise devices and sensors for the detection of pollutants in environmental and biological matrices (John, Abraham e Mathew, 2022; Xu, H. *et al.*, 2015; Zhou *et al.*, 2019). Among these nanomaterials are carbon dots, a class of fluorescent carbon nanoparticles that have been recognized for their optical properties, biocompatibility, low production cost, and the possibility of synthesis from organic waste (Ge *et al.*, 2021; Khairul Anuar *et al.*, 2021; Li *et al.*, 2013). Given their considerable potential, carbon dots have been employed in a variety of applications, including bioimaging, photodynamic therapy, chemical sensing, and environmental monitoring. This has opened a promising avenue for the development of agricultural contaminant sensors (Ding *et al.*, 2017; Kang e Lee, 2019; Mauro *et al.*, 2023; Molaei, 2019; Sun, 2020).

CDs can be synthesized through different approaches, generally classified into top-down and bottom-up methods. Physical top-down techniques, such as laser ablation, arc discharge, and electrochemical exfoliation, can yield carbon dots with narrow size distributions and high crystallinity, but typically require high energy input, sophisticated instrumentation, and elevated operational costs. Bottom-up chemical routes, including thermal decomposition, solvothermal reactions, and microwave-assisted synthesis, allow greater control over surface chemistry and optical properties; however, they often involve organic solvents, chemical reagents, or complex

purification steps that may limit their environmental compatibility. In contrast, green synthesis strategies based on biomass-derived precursors emphasize sustainability and low toxicity, although they may present challenges related to longer synthesis times, moderate yields, and batch-to-batch variability due to the natural heterogeneity of raw materials. Despite these limitations, green routes offer advantages in terms of environmental impact and resource valorization, particularly when aligned with circular economy principles.

In this context, the development of analytical methods for environmental monitoring must not only focus on sensitivity and selectivity but also consider sustainability criteria. Concepts such as Green Analytical Chemistry and White Analytical Chemistry have emerged to guide the design of analytical methodologies that minimize environmental impact, reduce reagent consumption, simplify sample preparation, and improve overall safety throughout the analytical process (Nowak *et al.*, 2021). In this sense, fluorescence-based sensing platforms using carbon dots represent a promising strategy, as they combine low reagent demand, mild operating conditions, and rapid analysis, aligning analytical performance with sustainability principles.

However, to enhance the efficacy and utility of CDs as sensors, doping with rare earth elements has been demonstrated to be an advantageous approach, providing improvements in their electronic and optical properties (Rocha *et al.*, 2024). The incorporation of elements such as cerium and gadolinium into the structure of CDs has been demonstrated to optimize fluorescence, increase quantum yield, and favor the stability of the nanomaterial under different pH and temperature conditions. Cerium, with its ability to switch between oxidation states, and gadolinium, with its magnetic properties, have been identified as ideal dopants for CDs aimed at sensor applications (Molaei, 2022; Zhang *et al.*, 2021a). These elements offer versatility and improved sensitivity for the detection of pollutants (Popov *et al.*, 2022; Wang. *et al.*, 2021).

Another pertinent aspect of this study is the utilization of rice husk (RH) as a precursor in the synthesis of CDs, following the principles of green chemistry. Brazil, one of the largest producers and consumers of rice in the world, generates

approximately 10 million ton of this grain per year, resulting in a considerable quantity of rice husk as an agro-industrial byproduct (CONAB, 2023). This waste, which is typically discarded or underused, contains high cellulose, hemicellulose, and lignin content, rendering it an excellent raw material to obtain CDs. The synthesis of CDs from rice husks not only adds value to the waste, thereby promoting a circular economy approach, but also contributes to environmental sustainability by reducing the amount of wasted material (Muthayya *et al.*, 2014; Silva *et al.*, 2021).

Therefore, the central issue that this study seeks to address is the understanding and optimization of the green synthesis of CDs from rice husk biomass, with emphasis on the influence of its chemical constituents on the formation mechanism of the nanomaterials. Unlike many studies that focus primarily on the application of green-synthesized CDs, this work aims to elucidate how the composition of agro-industrial residues affects the carbonization process, the generation of intermediate compounds, and the resulting optical properties. This approach enables a more rational design of synthesis conditions and a deeper comprehension of the transformation of lignocellulosic biomass into functional carbon nanostructures. To achieve this goal, a green hydrothermal process was applied using rice husk as a carbon source, under controlled temperature and solid load conditions, to optimize the degradation of the biomass and the conversion of its organic components into fluorescent carbon cores. A systematic kinetic study was conducted to monitor sugar release, intermediate formation, and quantum yield evolution, establishing correlations that allowed for the proposal of a plausible formation mechanism for the CDs. This investigation bridges an important gap in literature, as few works have evaluated the direct relationship between the chemical composition of natural precursors and the efficiency of carbonization in the synthesis of CDs.

Once the optimal synthesis conditions were established and the influence of biomass constituents was elucidated, the study advanced toward assessing the functional performance of the resulting nanomaterials. To this end, cerium and gadolinium were selected as dopants due to their ability to introduce additional electronic states and modify the surface chemistry of CDs. The doped systems (Ce-CDs and Gd-CDs) were then evaluated for their potential in the detection of

agrochemicals, exploring how rare earth incorporation influences fluorescence behavior, quantum yield, and sensitivity toward environmental contaminants.

The originality of this research lies in the dual approach adopted. First, it provides a detailed mechanistic understanding of the formation of CDs derived from an abundant and underutilized agro-industrial residue, the rice husk, addressing a clear gap in green nanomaterial synthesis research. Second, it introduces the doping of CDs with cerium and gadolinium as a novel strategy for the development of functional nanomaterials with potential applications in agrochemical detection. Altogether, this work contributes to the advancement of sustainable nanotechnology by combining fundamental insights into biomass transformation with the creation of environmentally responsible materials capable of supporting innovation in agriculture, environmental monitoring, and the circular economy.

Lastly, this study aligns with key United Nations Sustainable Development Goals (SDGs), including SDG 6 (Clean Water and Sanitation), by enabling contaminant detection in water; SDG 12 (Responsible Consumption and Production), through waste valorization; and SDG 13 (Climate Action), by promoting environmentally conscious alternatives in materials science. Overall, the use of waste-derived functional nanomaterials addresses current demands for sustainable innovation, environmental protection, and circular economy strategies.

## 2 OBJECTIVES

### 2.1 GENERAL OBJECTIVE

Investigate whether carbon dots synthesized from rice husks are selective fluorescent sensors for detecting agrochemicals, to promote the valorization of this abundant and low-value-added agro-industrial waste in the generation of sustainable nanomaterials.

### 2.2 SPECIFIC OBJECTIVES

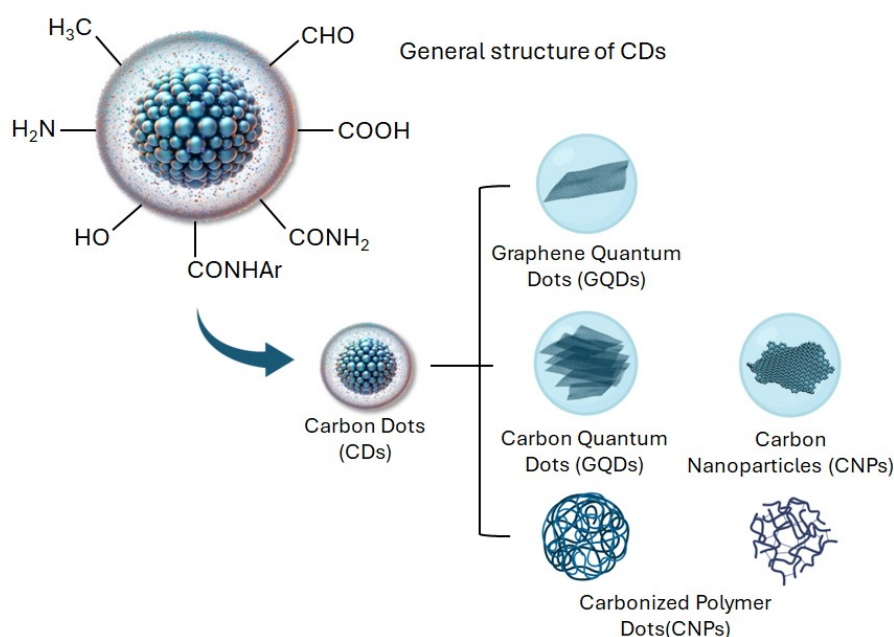
- evaluate whether synthesis parameters, such as temperature and solid loading, influence the degree of biomass carbonization;
- investigate whether the reaction time affects the conversion of organic compounds into carbon dots and influences their optical properties, such as quantum yield;
- analyze whether the chemical composition of the biomass directly affects the formation and structural characteristics of the carbon dots;
- assess whether it is possible to propose a formation mechanism for carbon dots based on the constituents present in the biomass used;
- examine whether doping with cerium and gadolinium alters the physicochemical, morphological, and surface properties of the carbon dots;
- evaluate whether rare-earth element doping modulates the photoluminescent behavior of carbon dots and may contribute to enhanced sensitivity for agrochemical detection in aqueous samples.

### 3 LITERATURE REVIEW

#### 3.1 WHAT ARE CARBON DOTS?

Carbon dots represent a class of fluorescent carbon-based nanomaterials that exhibit a range of sizes, chemical functionality, and photophysical properties (Wan *et al.*, 2021). Carbon dots can be classified into three categories: (1) graphene quantum dots (GQDs), (2) carbon nanodots (CNDs), and (3) polymer dots (PDs) (Ozyurt *et al.*, 2023; Tao *et al.*, 2019). Figure 1 shows a basic illustration of the main types of carbon dots. Spherical-shaped CNDs can be further classified into two subgroups: carbon nanoparticles (CNPs) and carbon quantum dots (CQDs). CNPs do not exhibit a crystal lattice or quantum confinement effect (QCE), while CQDs and GQDs do. CQDs consist of multiple graphene layers with surface groups, and GQDs are formed by one or a few  $\pi$ -conjugated graphene sheets with edge or interlayer defects. As a result, fluorescence mechanisms differ in CNPs, photoluminescence (PL) arises from molecular, subdomain, and surface states, whereas in CQDs and GQDs, it is primarily attributed to QCE (Kumar *et al.*, 2022).

Figure 1 – Classification of different types of CDs includes crystalline GQDs with anisotropic shape, crystalline CQDs with spherical shape, amorphous CNPs with spherical shape, and PDs with crosslinked monomers



Source: adapted from Ozyurt *et al.* (2023).

Considering the classification criteria discussed above, the carbon dots synthesized in this study can be classified as carbon quantum dots (CQDs). This classification is supported by several characterization results. Transmission electron microscopy (TEM) revealed well-dispersed, spherical nanoparticles with average diameters between 3 nm and 4 nm, which is typical of CQDs. Although the XRD patterns did not display sharp crystalline peaks, likely due to the small domain size and partially amorphous structure, the photoluminescence behavior, characterized by strong blue emission and excitation-dependent fluorescence, is indicative of quantum confinement effects, a hallmark of CQDs. Additionally, FTIR and XPS analyses confirmed the presence of abundant oxygen-containing functional groups on the surface, indicating the formation of a passivated amorphous shell. Together, these features are consistent with a hybrid core–shell structure typically attributed to CQDs synthesized via bottom-up methods from biomass precursors.

To further understand the structural organization and properties of CQDs, it is important to highlight their core–shell architecture and the mechanisms behind their formation. CQDs possess a core–shell structure that is formed through the nucleation process, which involves the gradual growth of the core and the formation of a "self-passivated" shell comprising functional groups (Figure 1) (Tang *et al.*, 2012). A detailed investigation revealed that the core (intrinsic states) can be either graphitic crystalline ( $sp^2$ ) or amorphous (mixed  $sp^2/sp^3$ ), depending on the degree of  $sp^2$  carbon presence in the core. Most researchers have reported the presence of graphitic crystalline cores, exhibiting  $sp^2$  hybridization (Dager *et al.*, 2019; Hola *et al.*, 2014; Schüpfer *et al.*, 2021; Sciortino *et al.*, 2016). The cores are relatively small in size, with a typical diameter of 2 nm – 3 nm and a lattice spacing of 0.2 nm (Ghorai *et al.*, 2022). The specific type of core depends on the synthesis technique, the precursors used, and other synthetic conditions, such as temperature, duration, and others. In general, reaction temperatures exceeding 300 °C result in exceptional graphitization ( $sp^2$ ), whereas lower temperatures yield an amorphous core, unless  $sp^2/sp^3$  hybridized carbon is present in the precursor (Martindale *et al.*, 2017; Yu *et al.*, 2018). The current understanding of the core is merely an outcome of the evidence derived from various characterization techniques, including transmission electron microscopy (TEM), high-

resolution TEM (HR-TEM), X-ray diffraction (XRD), and Raman Spectroscopy (John, Abraham e Mathew, 2022; Rooj e Mandal, 2023).

The shell of CQDs is typically amorphous, comprising functional groups (which result in surface states) such as oxygen, amino-based groups, or polymer chains, among others, which depend on the starting materials or dopant species. CQDs can be readily functionalized with a variety of functional groups on their surface, including hydroxyl, carboxyl, carbonyl, amino, epoxy, and others. This allows for the binding of both organic and inorganic moieties (Figure 1) (Han *et al.*, 2020; Molaei, 2019). The functionalities of CQDs determine whether their surfaces exhibit hydrophilic or hydrophobic properties. These properties ultimately influence the thermodynamic stabilities of CQDs in different solvents, particularly in water. In other words, the surface chemistry of the shell determines the stability of the CQDs in an aqueous solution (Kumar *et al.*, 2022; Wu *et al.*, 2021).

### **3.1.1 Main properties of CDs**

The excellent properties of CDs have made them widely used material in several different fields. This section will present a brief overview of the electrochemical and optical properties of CDs, which render them ideal candidates for applications in agrochemical sensing, bioimaging, drug/gene delivery, and photodynamic/photothermal therapy.

#### ***3.1.1.1 Physicochemical properties of CDs***

The photoluminescence and electronic properties of CDs are contingent upon electronic transitions across the band gap of the  $sp^2$  domains and are influenced by surface states, fluorophores, and element doping. The quantum confinement effect is an important characteristic of CDs, particularly GQDs and CQDs with a crystal lattice, where the dimensions of the CDs are less than the Bohr radius (Yan *et al.*, 2019). The Bohr radius is defined as the radius of a particle at which the separation between an electron and a hole becomes discrete (Ratnikov, 2020). Quantum confinement arises because of the reduction in size of the system, whereby the dimensions are less than

the Bohr radius of the exciton. This phenomenon becomes dominant when the radius approaches that of the Bohr radius. Quantum confinement effect (QCE) is the dominant phenomenon in CDs with large  $sp^2$  conjugated domains and fewer surface states. The valence and conduction bands are separated from each other by the  $sp^2$  conjugated domains, and the band gap is formed by the transition of electrons from the conduction band to the valence band (Ozyurt *et al.*, 2023).

Additionally, CDs possess oxygen-containing functionalities, namely carboxylic acid fractions, which provide a substrate for facile functionalization and dispersion in water. Moreover, CDs can be doped with heteroatoms, including nitrogen, phosphorus, sulfur, or rare earth elements, depending on the desired properties (Chandra *et al.*, 2013; Das *et al.*, 2021; Yang *et al.*, 2019).

#### 3.1.1.2 Electrochemical properties of CDs

CDs possess distinctive electrochemical characteristics, namely electron transfer, which render them a promising class of materials for electrochemical applications (Cheng *et al.*, 2021; Zhai *et al.*, 2022). The following characteristics of CDs offer advantages in electrochemistry: (a) a large surface area increases electrical conductivity due to electron-hole pair formation; (b) low cost and low toxicity; (c) abundant surface functionalities, including carboxyl, amino, and hydroxyl groups, which permit surface modification to enhance particle stability and modify their chemical and physical properties, and; (d) doping of heteroatoms can augment the electronic properties of CDs by promoting intramolecular charge transfer and providing reactive sites in electrocatalysis (Cheng *et al.*, 2021; Guin *et al.*, 2018; Mansuriya e Altintas, 2021; Ozyurt *et al.*, 2023; Wang *et al.*, 2019).

#### 3.1.1.3 Optical and Photoluminescence Properties of CDs

Carbon dots, despite structural variations among different types, share similar optical properties. These variations are primarily influenced by surface functionalities, synthesis methods, heteroatom doping, precursor selection, and the chemical environment during synthesis (Zhao *et al.*, 2020). Typically, CDs exhibit strong

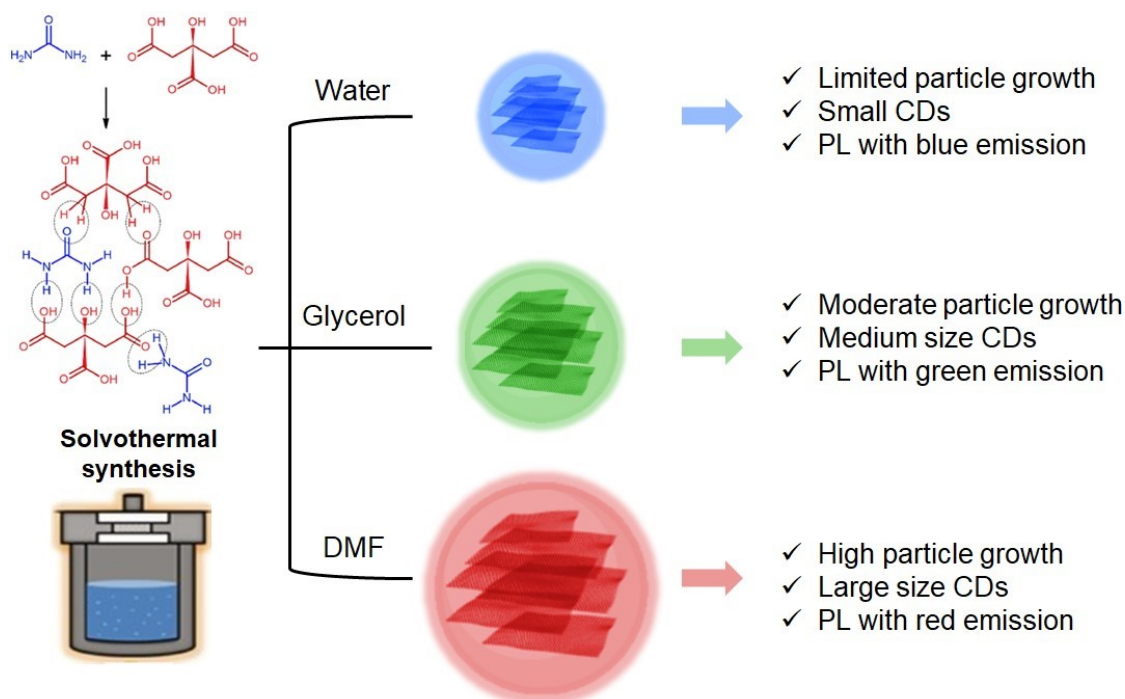
absorption in the ultraviolet (UV) region, which can extend into the visible and near-infrared (NIR) regions (Liu *et al.*, 2021). The optical absorption behavior of CDs typically shows two prominent bands: one between 200 nm – 280 nm, corresponding to  $\pi \rightarrow \pi^*$  transitions of aromatic C=C bonds, and another between 280 nm – 400 nm, associated with  $n \rightarrow \pi^*$  transitions of carbonyl (C=O) groups (Das, Ngashangva, and Goswami, 2021; Rajender, Goswami, and Giri, 2019; Zhang *et al.*, 2012). Additional absorption bands beyond 400 nm are often attributed to surface states containing lone pair electrons, which may overlap with  $n \rightarrow \pi^*$  transitions (Liu, 2020). Variations in the absorption profiles of CDs are closely related to differences in their electronic structures and chemical compositions (Tam *et al.*, 2014; Tang *et al.*, 2013).

In addition to absorption properties, the photoluminescence (PL) behavior of CDs has attracted notable interest due to their tunable emission across the visible spectrum. The PL characteristics are strongly dependent on factors such as size, composition, surface states, morphology, and synthesis routes (Das, Ngashangva, and Goswami, 2021; Ozyurt *et al.*, 2023). The emission mechanism is primarily attributed to the quantum confinement effect (QCE) and surface-related emissive traps, which include functional groups, defects, heteroatom doping, and edge states (Ai *et al.*, 2021; Sk *et al.*, 2014). However, the exact origin of PL remains not fully understood (Liu, 2020). Most CDs exhibit excitation-dependent blue and green emissions due to heterogeneity in size and surface chemistry (Diao *et al.*, 2018; Lu *et al.*, 2021; Wei *et al.*, 2018).

Recent studies have focused on controlling synthesis parameters to tune PL emissions by modulating particle size, surface states, and environmental factors such as solvent, pH, and concentration, opening applications in bioimaging, light-emitting devices (LEDs), and chemical sensing (Chen *et al.*, 2018; Lei, Hsieh, and Liu, 2019; Sun *et al.*, 2020; Yuan *et al.*, 2017). The role of QCE is particularly notable, as it alters the electronic structure by influencing the density and distribution of electronic states within  $sp^2$ -hybridized and  $\pi$ -conjugated domains in the CD core (Choppadandi *et al.*, 2021). For instance, Tian *et al.* (2017) demonstrated that the  $sp^2$  domain size in CDs can be tuned by selecting different solvents during synthesis.

Using citric acid and urea as precursors in a one-pot solvothermal process, they produced multicolored CDs in water, glycerol, dimethylformamide (DMF), and mixed solvents. Among these, DMF led to the formation of CDs with the largest  $sp^2$  domains and red-shifted emissions, evidencing the influence of solvent polarity on the degree of dehydration, carbonization, and resulting optical properties. Figure 2 summarizes these results, showing how solvent choice affects CD size, color, and photoluminescent behavior.

Figure 2 – Representative illustration of the effect of the solvent on the mechanism of growth and photoluminescence of CDs in water, glycerol, and DMF, respectively, resulting in an increase in the degree of carbonization during the solvothermal synthesis method



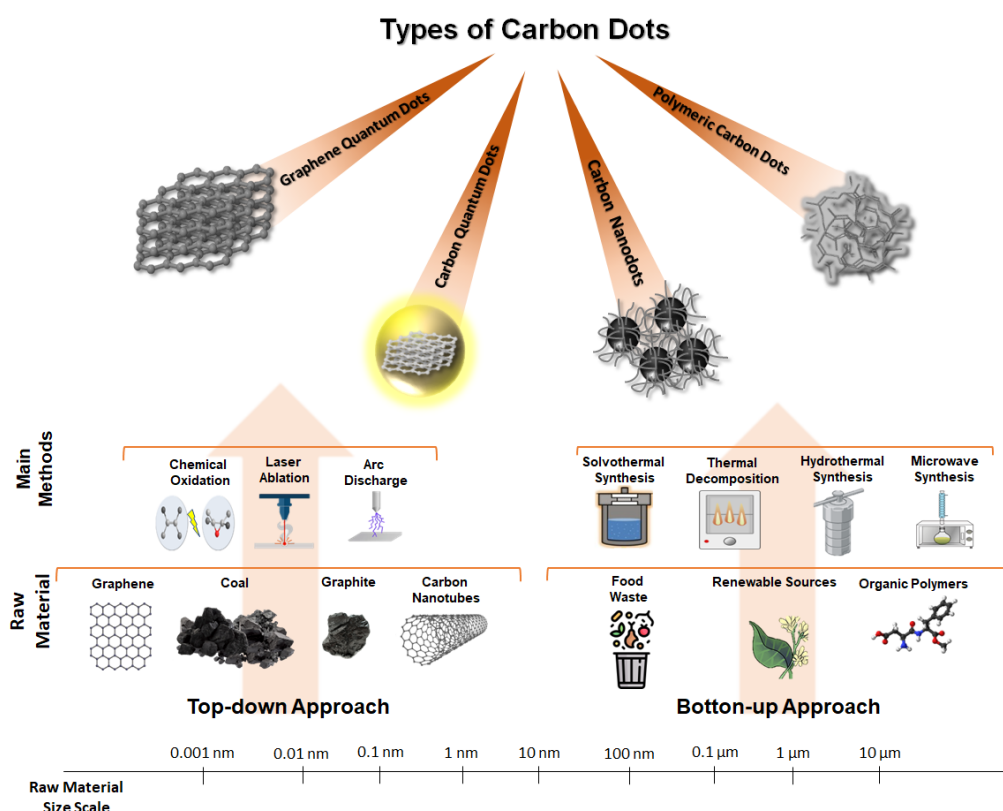
Source: adapted from Tian *et al.* (2017).

### 3.2 SYNTHESIS OF CDS

CDs can be synthesized via bottom-up or top-down approaches using carbon-based or organic precursors (Figure 3). Although the synthesis is relatively simple, challenges remain, such as nanoparticle aggregation during carbonization, controlling particle size and uniformity, and tuning surface properties (Liu *et al.*, 2020). The bottom-up approach builds CDs from small organic or polymer precursors using

methods like hydrothermal, microwave, or pyrolysis. In contrast, the top-down approach breaks down larger carbon structures into nanoparticles through techniques such as laser ablation, arc discharge, or electrochemical methods (Liu *et al.*, 2020; Paulo; Palomares; Martinez-Ferrero, 2016). In general, the top-down approaches facilitate the synthesis of crystalline CDs with relatively intact structures. However, this typically requires several steps for the decomposition of carbon materials in harsh conditions, which involve strong oxidants, concentrated acids, and elevated temperatures. Additionally, the size distribution and morphology of CDs produced with this approach cannot be precisely controlled (Kang e Lee, 2019; Kumar *et al.*, 2022). In contrast, the bottom-up approach has been shown to yield amorphous CDs (amorphous carbon cores) with a high density of doping sites and functional groups. However, the synthesis of crystalline CDs has also been reported by some researchers (Liu *et al.*, 2019; Sharma e Das, 2019).

Figure 3 – Description of the two approaches to obtaining carbon dots (bottom-up and top-down) mentioning the main methods and sources of raw material



Source: Rocha *et al.* (2024).

In the bottom-up approach, the structure and size of CDs are dependent on several factors, including the molecular structures of the precursors, the solvent used, and the reaction conditions (such as reaction time, temperature, and pressure). The reaction conditions are of paramount importance, as they exert a profound influence on the reactants and the highly random nucleation and growth processes that are intrinsic to the synthesis of CDs. Despite the inherent difficulties, some research groups have achieved the synthesis of size- and composition-controlled CQDs through the meticulous optimization of reaction parameters (Kumar *et al.*, 2022; Liu *et al.*, 2020).

While both approaches have been employed in the synthesis of CDs, the bottom-up approach is cost-effective and environmentally friendly and is, therefore, the most utilized. In both approaches, post-treatment can be employed to modify the surface functional groups and enhance the performance of CDs. Additionally, CDs can be modified during synthesis. The surface passivation of CDs removes emissive traps from the surface, thereby enhancing the quantum yield (QY). Similarly, doping with heteroatoms such as N<sub>2</sub> and P or metals such as Au or Mg can be employed to improve their electrical conductivity and solubility (Molaei, 2019; Rooj e Mandal, 2023; Wei *et al.*, 2018).

### **3.2.1 The hydrothermal method for CDs synthesis**

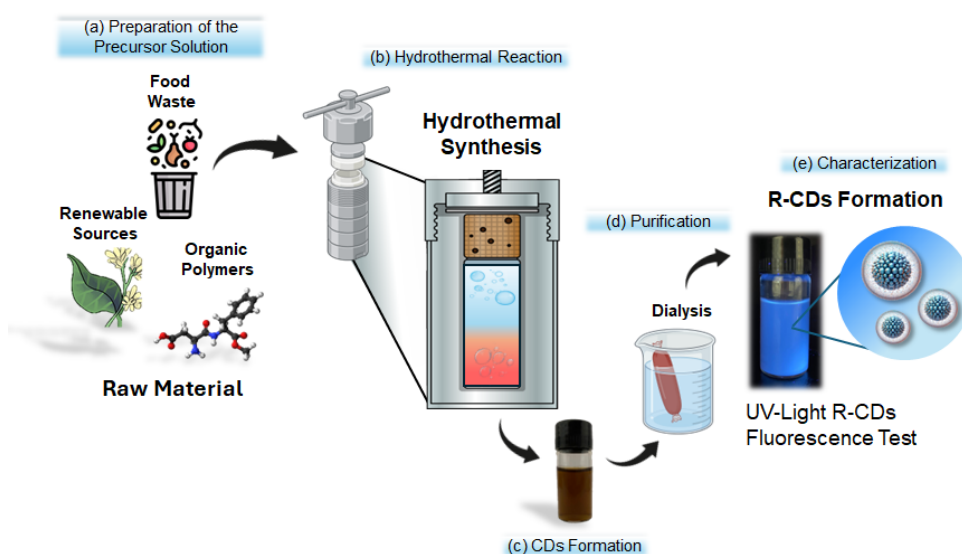
Hydrothermal synthesis is a one-step, cost-effective, non-toxic, and environmentally friendly synthetic technique for the synthesis of carbon dots via chemical reactions. In this process, the use of a hydrothermal reactor simplifies the synthesis process, eliminating the need for complex equipment and expensive reagents. In this method, the chemical species and solvent are placed in a Teflon-lined stainless-steel chamber, known as an autoclave, where the solution is heated to temperatures and pressures above ambient conditions. The optical and electronic properties of these carbon dots can be tuned by varying the organic precursors and altering the temperature; however, the size of the CDs remains poorly controlled (Paulo; Palomares; Martinez-Ferrero, 2016). The main steps in the hydrothermal synthesis of CDs can be briefly listed according to Sun (2020) and Vishneratina *et al.* (2022):

- a) **Preparation of the precursor solution:** the raw material is pre-treated (by grinding or drying, if necessary) and dispersed in an aqueous solution, usually deionized water, with the pH adjusted as necessary. Adjusting the pH is important to control the size and properties of the CDs.
- b) **Hydrothermal reaction:** the precursor solution is placed in a closed reactor (autoclave) and subjected to temperatures ranging from 150 °C – 250 °C, with reaction times ranging from a few hours to up to a day. The pressure generated in the closed system facilitates the carbonization of the organic precursors of the raw material, leading to the formation of CDs.
- c) **Formation of CDs:** under these conditions, thermal degradation of the raw material takes place, leading to the formation of carbon nuclei and surface passivation, which generates the characteristic fluorescence of CDs.
- d) **Purification:** after the reaction, the mixture is cooled, and the CDs are separated by centrifugation or filtration to remove by-products and impurities. In some cases, additional techniques such as dialysis or solvent extraction can be used to improve the purity of the CDs.
- e) **Characterization:** the CDs are then characterized using techniques such as fluorescence spectroscopy, FTIR, TEM (Transmission Electron Microscopy), and XPS (X-Ray Photoelectron Spectroscopy) to analyze their structural properties, composition and optical performance.

Some studies involving the hydrothermal synthesis of CDs can be mentioned. Zhang *et al.* (2022) reported the hydrothermal synthesis of carbon dots from Siberian elm (*Ulmus pumila* L.) seeds, highlighting an eco-friendly, biomass-based approach. The produced CDs exhibited a near-spherical shape (average diameter 3.83 nm), with blue fluorescence under UV light and robust stability across varying pH and light conditions. The CDs showed selective quenching by Fe<sup>3+</sup> ions, suggesting their utility

for  $\text{Fe}^{3+}$  detection in polluted water, and demonstrated biocompatibility, proving effective in labeling HepG2 cells with blue fluorescence. Figure 4 shows a brief schematic illustration of the hydrothermal method for synthesizing CDs via a green route, utilizing sustainable feed stocks such as food waste, renewable sources, and organic polymers. Initially, a precursor solution is prepared and subjected to reaction within a hydrothermal reactor under controlled temperature and pressure conditions. Following the formation of the crude CDs, the sample undergoes a purification process through dialysis to remove unreacted species and by-products. The process yields purified CDs, whose formation and optical quality are verified by fluorescence emission under ultraviolet (UV) light, confirming the characteristic properties of these nanomaterials.

Figure 4 – Schematic illustration summarizing the hydrothermal method for synthesizing CDs



Source: adapted from Visheratina *et al.* (2022).

Similarly, Prathap *et al.* (2023) employed an eco-friendly hydrothermal method to synthesize highly fluorescent, plant-derived carbon dots (PJ-CDs) from *Prosopis juliflora* leaf extract for biomedical purposes. Characterized by fluorescence spectroscopy, SEM, TEM, EDX, XRD, FTIR, and UV-Vis, the PJ-CDs displayed an absorption peak at 270 nm ( $n \rightarrow \pi^*$  transitions) and a quantum yield of 7.88%. Stable across various ionic strengths and pH gradients, these spherical PJ-CDs (~ 8 nm) exhibited selective antimicrobial efficacy against *Staphylococcus aureus*, and proved

useful for bioimaging in *Caenorhabditis elegans*, indicating potential pharmaceutical applications.

Finally, more recently Watcharamongkol *et al.* (2024) developed carbon dots and nitrogen-doped CDs from cassava pulp, utilizing a one-step hydrothermal process at 200 °C. With tunable fluorescence, high quantum yield, and photostability, the CDs were effective as fluorescent sensors for  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  detection and mercury detoxification in plants. Enhanced antioxidant activity and metal ion detection on test strips were also achieved. The study revealed dynamic and static quenching mechanisms and notable DPPH radical scavenging activity, demonstrating the CDs' potential in environmental and agricultural applications.

### **3.2.2 Green synthesis of CDs (from natural resources)**

What characteristics define a synthesis process as environmentally friendly? In order to respond to this question, it is necessary to consider certain principles of green chemistry as set forth by Anastas and Warner (2000). These include the following: (a) the use of less hazardous chemical synthesis; (b) the design of safer chemicals; (c) the use of safer solvents and auxiliaries; (d) the design of processes that are more energy efficient; (e) the use of renewable feedstocks; and (f) the implementation of inherently safer chemistry for the purpose of accident prevention.

In summary, the principles can be applied to the synthesis of CDs using non-toxic, renewable precursors and solvents, ensuring a safe and secure process. Moreover, the synthesized CDs themselves should be non-toxic and chemically stable. Although the synthesis of CDs is typically an energy-intensive process, it is advisable to prioritize the use of lower-energy synthesis methods. Furthermore, given the potential for the formation of numerous side products and intermediates, it is essential to assess their safety profile to guarantee their appropriate disposal (Chahal *et al.*, 2021).

The synthesis of carbon dots from natural sources, particularly plant-based materials, is crucial due to their applications in health and electronic technologies. This

approach also mitigates the reliance on harmful and expensive raw materials like metals. Furthermore, utilizing natural resources for carbon dots production plays an essential role in environmental pollution management, offering innovative strategies for ecological remediation. Employing agricultural waste not only reduces environmental concerns linked to its accumulation in cultivation areas but also leverages the therapeutic properties of various non-toxic medicinal plants that exhibit both *in vitro* and *in vivo* health benefits. However, plant extracts are seldom utilized as final products, since their phytochemical composition may vary significantly depending on the extraction method (Jing *et al.*, 2023a; Perumal *et al.*, 2021).

From a pharmacological perspective, utilizing crude extracts or fractions rather than single isolated compounds offers advantages due to the multi-target effects of the diverse phytochemicals present in medicinal plants. However, challenges such as the identification of active compounds, understanding synergistic interactions, instability, solvent toxicity, and low solubility of bioactive compounds must be overcome for the development of viable products. In this context, nanotechnology-based approaches emerge as promising solutions. Particularly, the synthesis of carbon dots from medicinal plants with proven biological activity is an area of considerable interest. Once optimized, these sustainably synthesized carbon dots can represent an accessible final product, leveraging the therapeutic properties of medicinal plants. Furthermore, the application of sustainably synthesized carbon dots may reduce dependence on traditional healthcare practices or medicinal plant sources, as reported by Jing *et al.* (2023) and Khan *et al.* (2024).

Additionally, the selection of specific agricultural waste and medicinal plants for the green synthesis of carbon dots is economically advantageous, as it can enhance farmers' incomes and bolster the agricultural sector. Furthermore, non-dimensional fluorescent semiconductor dots are crucial for a variety of electronic applications, being derived from non-toxic, low-cost natural materials like plants. These distinctive characteristics address health benefits and environmental issues, such as transforming agricultural waste into valuable products and generating non-toxic fluorescent semiconductor dots through green synthesis methods, underscoring the

significance of utilizing natural resources for carbon dots production (Khairul Anuar *et al.*, 2021; Omran, Whitehead e Baek, 2021; Perumal *et al.*, 2021).

As previously described, carbon dots synthesis can be achieved through top-down and bottom-up approaches, encompassing chemical, electrochemical, and physical methods. These include modification functionalization, nanohybrids, ultrasonic treatment, chemical oxidation, microwave irradiation, solvothermal techniques, and hydrothermal techniques, as well as doping during preparation or post-treatment of the CDs. To align the literature review with the objectives of this study, emphasis will be placed on the hydrothermal method for the green synthesis of CDs.

#### *3.2.2.1 Green synthesis of CDs by hydrothermal method*

As previously outlined, hydrothermal synthesis of CDs is a bottom-up approach that requires high temperatures and pressures. Researchers consider it an effective, environmentally friendly, cost-effective, non-toxic, and simple-to-operate method.

In summary, the green synthesis of carbon dots via the hydrothermal method, an environmentally friendly process, involves four sequential and interconnected processes. Firstly, polymerization occurs, where organic precursor molecules, such as sugars, citric acids, or plant extracts, are subjected to high temperatures and pressures in the presence of water, inducing these molecules to combine and form larger, more complex structures. Secondly, the polymeric structures formed undergo aromatization, involving dehydration and cyclization, leading to the formation of aromatic rings, which are stable carbon structures fundamental to the properties of CDs. Following this, nucleation takes place, the process where the initial nuclei of the CDs are formed as the aromatic rings aggregate and organize into small carbon nanoparticles.

Finally, growth occurs, where the CD nuclei gradually grow by incorporating more carbon molecules from the solution. Precise control of reaction conditions, like temperature, time, and precursor concentration, allows for adjusting the size and properties of the synthesized CDs. These four processes occur simultaneously and interdependently within the hydrothermal method, resulting in the formation of CDs with

unique characteristics and desirable properties for various applications (Khan *et al.*, 2024; Wareing, Gentile e Phan, 2021).

A variety of biomass sources have been employed to synthesize CDs via the hydrothermal method, including papaya juice (Kasibabu, D'souza, Jha e Kailasa, 2015), bell pepper (De e Karak, 2013), banana (*Musa acuminata*) juice (De e Karak, 2013), garlic (Zhao *et al.*, 2015), citrus pectin hydrogel (Zhao, Zhang e Zhou, 2014), walnut shells (Yang, Shimanouchi e Kimura, 2015), sugar cane juice (Mehta, Jha e Kailasa, 2014), pomegranate (Kasibabu *et al.*, 2015), apple (Mehta *et al.*, 2015), pomace (Liu *et al.*, 2013), and other green sources. Table 1 summarizes studies that have employed the hydrothermal method for synthesizing CDs from diverse biological precursors.

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources.

(to be continued)

| Carbon Source           | Temperature (°C) | Heating Time (h) | Size (nm) | QY (%) | Excitation/Emission (nm) | Fluorescence  | Application                                                  | References                               |
|-------------------------|------------------|------------------|-----------|--------|--------------------------|---------------|--------------------------------------------------------------|------------------------------------------|
| Aloe                    | 180              | 11               | 5.0       | 10.3   | 441 / 503                | Yellow        | Detection of Tartrazine                                      | (Xu, H. <i>et al.</i> , 2015)            |
| Apple juice             | 150              | 12               | 4.5       | 4.27   | 365 / 475                | Blue          | Antimicrobial                                                | (Mehta <i>et al.</i> , 2015)             |
| Azadirachta indica      | 150              | 4                | 3.2       | 27.0   | 340 / 467                | Blue          | Detection of H <sub>2</sub> O <sub>2</sub> and Ascorbic Acid | (Yadav <i>et al.</i> , 2019)             |
| Bagasse                 | 180              | 3                | 1.8       | 12.3   | 360 / 475                | Blue          | Biomedical                                                   | (Du <i>et al.</i> , 2014)                |
| Bamboo                  | 300              | 3                | 11.0      | 5.0    | 313 / 419                | Blue          | --                                                           | (Yang <i>et al.</i> , 2020)              |
| Banana juice            | 150              | 4                | 3.0       | 8.95   | 360 / 460                | Green         | --                                                           | (De e Karak, 2013)                       |
| Bee pollens             | 180              | 24               | 2.1       | 12.8   | 340 / 505                | Blue          | Bioimaging                                                   | (Zhang <i>et al.</i> , 2015)             |
| Black tea               | 200              | 5                | 4.6       | 7.0    | 383 / 461                | Green and Red | Bioimaging                                                   | (Kasibabu, D'Souza, Jha e Kailasa, 2015) |
| <i>Bombyx mori</i> silk | 190              | 3                | 5.0       | 13.9   | 370 / 450                | Blue          | Bioimaging                                                   | (Wu <i>et al.</i> , 2013)                |
| Cabbage                 | 140              | 5                | 2.0 - 6.0 | 16.5   | 365 / 405                | Blue          | Biomedical                                                   | (Alam <i>et al.</i> , 2015)              |
| Carica papaya juice     | 170              | 12               | 3.0       | 7.0    | 383 / 461                | Green         | Bioimaging                                                   | (Kasibabu, D'Souza, Jha e Kailasa, 2015) |

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources  
(continuation)

| Carbon Source                 | Temperature (°C) | Heating Time (h) | Size (nm)   | QY (%) | Excitation/Emission (nm) | Fluorescence        | Application                   | References                      |
|-------------------------------|------------------|------------------|-------------|--------|--------------------------|---------------------|-------------------------------|---------------------------------|
| Carrot                        | 160              | 6                | 8.00        | 5.16   | 360 / 442                | Blue, Green and Red | Bioimaging                    | (Liu <i>et al.</i> , 2017)      |
| Cocoon silk                   | 200              | 48               | 70.0        | 38.00  | 330 / 475                | Blue                | Bioimaging                    | (Li <i>et al.</i> , 2013)       |
| Coriander Leaves              | 240              | 4                | 2.98        | 6.48   | 360 / 447                | Green               | Biosensor                     | (Sachdev e Gopinath, 2015)      |
| Cucumber juice                | 120              | 6                | > 10.00     | 3.25   | 370 / 450                | Green               | Detection of Hg <sup>2+</sup> | (Wang, C. <i>et al.</i> , 2014) |
| Dragon fruit                  | 180              | 12               | 2.50        | --     | 320 / 380                | Blue                | Dye degradation               | (Arul <i>et al.</i> , 2017)     |
| Dried shrimp                  | 170              | 12               | 6.00        | 54.00  | 360 / 430                | Blue                | Bioimaging                    | (D'Souza <i>et al.</i> , 2016)  |
| Durian                        | 150              | 12               | 2.00 – 6.00 | 79.00  | 400 / 601                | Orange              | Bioimaging                    | (Wang <i>et al.</i> , 2018)     |
| Egg white                     | 220              | 48               | 2.10        | 64.00  | 315 / 420                | Blue                | Bioimaging                    | (Zhang, Sun e Wu, 2015)         |
| <i>Eleocharis dulcis</i>      | 120              | 5                | 3.00        | 11.00  | 380 / 458                | Blue                | Biosensor                     | (Bao <i>et al.</i> , 2018)      |
| <i>Enteromorpha prolifera</i> | 180              | 10               | 2.75        | 8.00   | 460 / 517                | Green               | Removal of Fe <sup>3+</sup>   | (Xu <i>et al.</i> , 2017)       |
| Fish scale                    | 200              | 20               | 9.00        | 9.00   | 360 / 440                | Multi-Colored       | Biosensor                     | (Zhang <i>et al.</i> , 2018)    |
| Garlic                        | 200              | 3                | 11.00       | 17.50  | 320 / 580                | Blue                | Bioimaging                    | (Zhao <i>et al.</i> , 2015)     |

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources  
(continuation)

| Carbon Source        | Temperature<br>(°C) | Heating Time<br>(h) | Size<br>(nm)  | QY<br>(%) | Excitation/Emission<br>(nm) | Fluorescence | Application                   | References                    |
|----------------------|---------------------|---------------------|---------------|-----------|-----------------------------|--------------|-------------------------------|-------------------------------|
| Ginger               | 300                 | 2                   | 4.30          | 13.40     | 545 / 590                   | Blue         | Cytotoxicity                  | (Li <i>et al.</i> , 2014)     |
| <i>Ginkgo biloba</i> | 200                 | 8                   | 4.11          | 21.70     | 360 / 427                   | Blue         | Electrocatalyst               | (Li <i>et al.</i> , 2018)     |
| Grape juice          | 180                 | 12                  | 2.70          | 13.50     | 331 / 419                   | Blue         | Bioimaging                    | (Huang <i>et al.</i> , 2014)  |
| Grape peel           | 180                 | 6                   | 3.00          | 3.10      | 355 / 435                   | --           | Detection of Fe <sup>3+</sup> | (Xu, J. <i>et al.</i> , 2015) |
| Grass                | 200                 | 3                   | 5.00          | 6.20      | 360 / 443                   | Blue         | Detection of Cu(II)           | (Liu <i>et al.</i> , 2012)    |
| Hair                 | 200                 | 6                   | 29.00 - 80.00 | 24.80     | 340 / 443                   | Blue         | Detection of Hg <sup>2+</sup> | (Hou <i>et al.</i> , 2014)    |
| Honey                | 100                 | 2                   | 2.00          | 19.80     | 338 / 420                   | Blue         | Bioimaging                    | (Yang <i>et al.</i> , 2014)   |
| Jinhua bergamot      | 200                 | 5                   | 10.00         | 50.70     | 330 / 440                   | Blue         | Detection of Hg <sup>2+</sup> | (Yu, J. <i>et al.</i> , 2015) |
| Kitchen waste        | 150                 | 2                   | 50.00         | --        | 300 / 440                   | Green        | --                            | (Himaja <i>et al.</i> , 2014) |
| Lemon juice          | 190                 | 10                  | 4.60          | 28.00     | 533 / 850                   | Red          | Bioimaging                    | (Ding <i>et al.</i> , 2017)   |
| Lemon peel           | 20                  | 12                  | 3.00          | 14.00     | 300 / 540                   | Green        | Photocatalysis                | (Tyagi <i>et al.</i> , 2016)  |

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources (continuation)

| Carbon Source        | Temperature (°C) | Heating Time (h) | Size (nm) | QY (%)      | Excitation/Emission (nm) | Fluorescence | Application                   | References                      |
|----------------------|------------------|------------------|-----------|-------------|--------------------------|--------------|-------------------------------|---------------------------------|
| Mango peel           | 300              | 2.0              | 3.0       | 8.50        | 360 / 425                | Blue         | Detection of Fe <sup>3+</sup> | (Jiao <i>et al.</i> , 2019)     |
| Milk                 | 180              | 2.0 – 8.0        | 3.0 – 5.0 | 5.86 – 7.55 | 330 / 420                | Blue         | --                            | (Wang, D. <i>et al.</i> , 2014) |
| Oatmeal              | 220              | 7.0              | 40.0      | 37.40       | 360 / 460                | Blue         | Bioimaging                    | (Yu. <i>et al.</i> , 2015)      |
| Onion waste          | 120              | 2.0              | 25.0      | 28.00       | 320 / 426                | Blue         | Bioimaging                    | (Bandi <i>et al.</i> , 2016)    |
| Orange juice         | 20               | 2.5              | 4.5       | 26.00       | 360 / 455                | Blue         | Bioimaging                    | (Sahu <i>et al.</i> , 2012)     |
| Passion fruit shells | 180              | 3.0              | 5.0       | 1.80        | 450 / 553                | --           | Biomedical                    | (Yang <i>et al.</i> , 2021)     |
| Peach gum            | 180              | 16.0             | 5.0       | 28.46       | 450 / 505                | Multicolor   | Bioimaging                    | (Liao, Cheng e Zhou, 2016)      |

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources (continuation)

| Carbon Source             | Temperature (°C) | Heating Time (h) | Size (nm) | QY (%) | Excitation/Emission (nm) | Fluorescence | Application                   | References                         |
|---------------------------|------------------|------------------|-----------|--------|--------------------------|--------------|-------------------------------|------------------------------------|
| Pigskin                   | 250              | 2                | 7.0       | 24.10  | 460 / 521                | Green        | Bioimaging                    | (Wen <i>et al.</i> , 2016)         |
| Pipe tobacco              | 180              | 8                | 5.0       | 3.20   | 369 / 450                | Blue         | Detection of Cu <sup>2+</sup> | (Sha <i>et al.</i> , 2013)         |
| Pomegranate peels         | 180              | 36               | 2.0 – 5.0 | 7.20   | --                       | --           | Bioimaging                    | (Amith Yadav <i>et al.</i> , 2018) |
| Pomelo peels              | 200              | 3                | 2.0 – 4.0 | 6.90   | 365 / 444                | Blue         | Detection of Hg(II)           | (Lu <i>et al.</i> , 2012)          |
| Potato                    | 170              | 12               | 0.2 - 2.2 | 6.14   | 374 / 455                | Blue         | Bioimaging                    | (Mehta <i>et al.</i> , 2014)       |
| Prawn shell               | 25               | 5                | 6.0       | 54.00  | 390 / 405                | Blue         | Detection of Cu               | (Gedda <i>et al.</i> , 2016)       |
| <i>Prunus avium</i> fruit | 180              | 5                | 7.0       | 13.00  | 360 / 411                | Blue         | Bioimaging                    | (Edison <i>et al.</i> , 2016)      |
| <i>Shiitake</i> mushrooms | 200              | 12               | 2.0 – 6.0 | 5.50   | 450 / 500                | Blue         | Bioimaging                    | (Wang, W.-J. <i>et al.</i> , 2016) |

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources  
(continuation)

| Carbon Source         | Temperature<br>(°C) | Heating Time<br>(h) | Size<br>(nm)     | QY<br>(%) | Excitation/Emission<br>(nm) | Fluorescence | Application     | References                      |
|-----------------------|---------------------|---------------------|------------------|-----------|-----------------------------|--------------|-----------------|---------------------------------|
| Soy milk              | 180                 | 3                   | 13.00 –<br>40.00 | 2.60      | 330 / 525                   | Blue         | Bioimaging      | (Li <i>et al.</i> , 2013)       |
| Starch                | 190                 | 2                   | 2.25 - 3.50      | 21.70     | 298 / 534                   | Blue         | Bioimaging      | (Chen <i>et al.</i> ,<br>2018)  |
| Strawberry juice      | 180                 | 12                  | 5.20             | 6.30      | 283 / 427                   | Blue         | Detection of Hg | (Huang <i>et al.</i> ,<br>2013) |
| Sugar cane<br>bagasse | 180                 | 3                   | 1.80             | 54.00     | 360 / 550                   | Blue         | Biomedical      | (Du <i>et al.</i> ,<br>2014)    |
| Sugar cane juice      | 120                 | 3                   | 2.71             | 5.76      | 254 / 370                   | Blue         | Bioimaging      | (Mehta, Jha e<br>Kailasa, 2014) |
| Sugarcane<br>molasses | 150                 | 12                  | --               | 5.80      | 305 / 390                   | Blue         | Citotoxicity    | (Huang <i>et al.</i> ,<br>2017) |
| Sweet pepper          | 180                 | 5                   | 2.00 – 7.00      | 19.30     | 365 / 500                   | --           | Biosensor       | (Yin <i>et al.</i> ,<br>2013)   |

Table 1 – Summary of different studies involving the hydrothermal synthesis of CDs from various green carbon sources  
(conclusion)

| Carbon Source        | Temperature (°C) | Heating Time (h) | Size (nm) | QY (%) | Excitation/Emission (nm) | Fluorescence | Application                   | References                    |
|----------------------|------------------|------------------|-----------|--------|--------------------------|--------------|-------------------------------|-------------------------------|
| Sweet potato         | 180              | 3                | 1.0 - 3.0 | 2.80   | 365 / 442                | Blue         | Detection of Hg <sup>2+</sup> | (Lu <i>et al.</i> , 2013)     |
| Tender coconut waste | 180              | 4                | 2.5       | 60.18  | 320 / 430                | Blue         | Bioimaging                    | (Gunjal <i>et al.</i> , 2019) |
| Watermelon           | 220              | 2                | 2.0       | 7.10   | 360 / 580                | Blue         | Bioimaging                    | (Zhou <i>et al.</i> , 2012)   |
| Wheat straw          | 180              | 2                | 2.1       | 20.00  | 370 / 500                | Blue         | Bioimaging                    | (Liu <i>et al.</i> , 2021)    |
| Willow bark          | 200              | 3                | 1.0 – 4.0 | 6.00   | 340 / 431                | --           | --                            | (Prasannan e Imae, 2013)      |
| Willow leaves        | 180              | 24               | 2.0 – 4.0 | --     | 300 / 520                | Blue         | Electrocatalyst               | (Gao <i>et al.</i> , 2014)    |
| Winter melon         | 180              | 2                | 4.5       | 7.51   | 360 / 448                | Blue         | Bioimaging                    | (Feng <i>et al.</i> , 2015)   |
| Yam                  | 200              | 2                | 2.7       | 9.30   | 320 / 420                | Blue         | Detection of Hg <sup>2+</sup> | (Li, Ni e Kokot, 2015)        |

-- Unavailable Information

Source: elaborated by the author (2024).

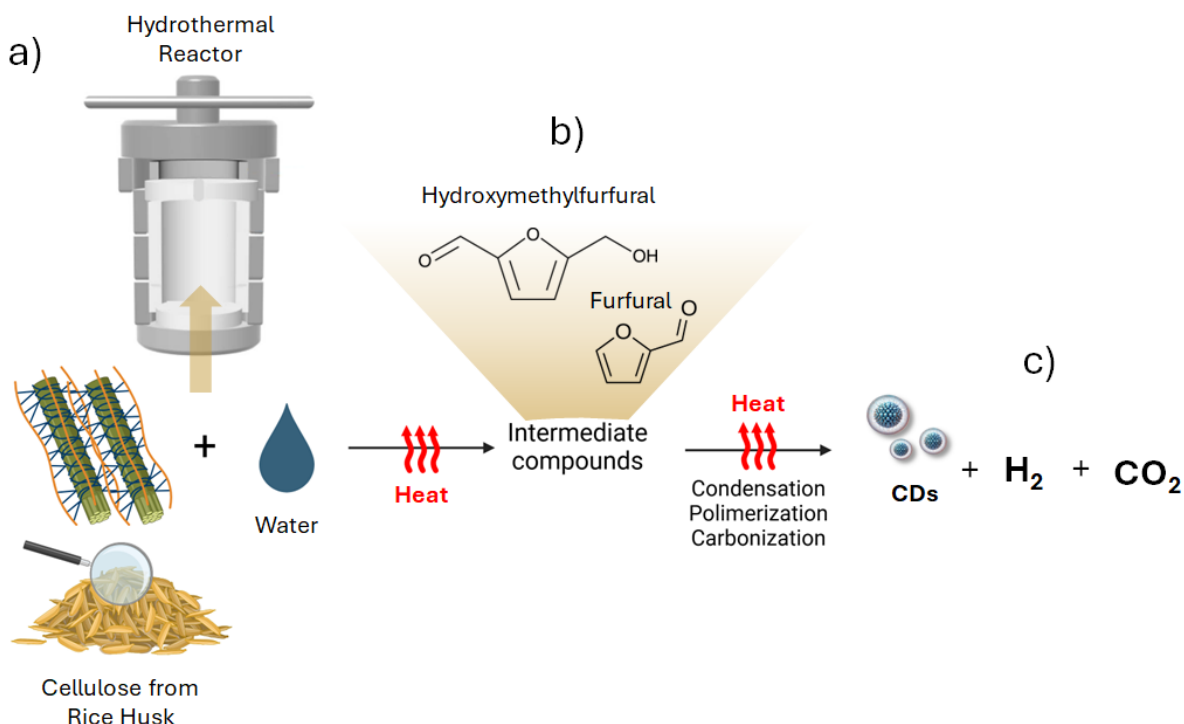
### 3.2.2.2 Rice husks as a carbon source for green synthesis of CDs

Brazil is one of the largest producers and consumers of rice in the world, with annual production exceeding 10 million ton (Silva *et al.*, 2021). According to data from the National Supply Company (CONAB), in 2022 the country produced approximately 10.8 million ton of paddy rice, consolidating its position as the largest producer and consumer in Latin America. Although rice production represents a relatively small share of Brazil's Gross Domestic Product (GDP) the sector plays a crucial role in food security and income generation for millions of Brazilians, especially in the South and Midwest regions (CONAB, 2023; Muthayya *et al.*, 2014). In addition, Brazil occupies a prominent position in the international rice trade, exporting part of its production to various countries, mainly in Latin America and Africa (Burkholz and Schweitzer, 2019).

The biochemical composition of rice husks is rich in cellulose, hemicellulose and lignin, natural polymers that give this material unique structural and chemical properties. Cellulose, for example, is a linear polymer of glucose, which can be converted into elemental carbon under suitable pyrolysis or hydrothermal reaction conditions (Gunaratne *et al.*, 2019; Rosado *et al.*, 2021). A schematic summary of the chemical conversion of rice husks into CDs is illustrated in Figure 5.

In short, during the hydrothermal reaction, the cellulose in rice husks undergoes hydrolysis, i.e. the breaking of its bonds by the action of water, resulting in simple sugars such as glucose. These sugars, in turn, undergo a dehydration process, losing water molecules and forming intermediate compounds such as furfural and hydroxymethylfurfural. These intermediate compounds then reorganize and bond, forming aromatic and heterocyclic structures, which are the basic building blocks of elemental carbon for the formation of CDs. As the temperature and reaction time increase, these structures condense further, forming an increasingly complex carbon network, resulting in the formation of CDs (Borrero-López *et al.*, 2018; Hossain *et al.*, 2020; Wongso *et al.*, 2021). In addition, high pressure and high temperature conditions favor the formation of well-defined crystalline structures and the obtaining of CDs with controlled properties (Visheratina *et al.*, 2022). These characteristics make rice husks an interesting precursor for the synthesis of carbon dots.

Figure 5 – Schematic illustration of the chemical transformation of rice husk residue into CDs



Source: elaborated by the author (2024).

The use of rice husks as a substrate for the green synthesis of CDs has several advantages. In addition to contributing to the valorization of agro-industrial waste, this approach reduces the environmental impact associated with the inappropriate disposal of rice husks and promotes the circular economy. The abundance of this material in Brazil, together with the simplicity of the synthesis process, makes this technology promising for the large-scale production of CDs. Table 2 summarizes the use of rice husk residue as a precursor in the hydrothermal synthesis of CDs.

Some recent studies include the use of rice husks as a precursor in the hydrothermal synthesis of CDs. One such study was carried out by Mercy *et al.* (2023), that developed a green and simple one-pot synthesis method to produce water-soluble carbon quantum dots (CQDs) from rice husk. The CQDs were characterized using various techniques, including UV-vis spectroscopy, SEM, XPS, and FTIR, and their optical properties were investigated. The CQDs exhibited excellent stability under different pH, temperature, and time conditions, as well as excitation wavelength-

dependent fluorescence. The CQDs were successfully applied as a sensor for amoxicillin, demonstrating high sensitivity with a detection limit in the nanomolar range.

Table 2 – Summary of some studies involving the use of rice husks in the hydrothermal synthesis of CDs

| Pre-Treatment of Rice        | Synthesis Conditions | Size (nm)  | Characterization                              | Application                       | References                                  |
|------------------------------|----------------------|------------|-----------------------------------------------|-----------------------------------|---------------------------------------------|
| Washing, drying and grinding | 200 °C, 10 h         | 6.0 – 13.0 | TEM, XRD, UV-Vis, EDX and FTIR                | --                                | (Wongso <i>et al.</i> , 2019)               |
| Washing and drying           | 200 °C, 12 h         | 6.3        | FTIR, TEM, SEM, RAMAN, AFM and UV-Vis         | Anti-corrosive                    | (Dhongde <i>et al.</i> , 2024)              |
| Washing and drying           | 315 °C, 4 h          | 143.0      | TEM, SEM, FTIR, XPS and UV-Vis                | Detection of amoxicillin in water | (Jessy Mercy <i>et al.</i> , 2023)          |
| Washing and drying           | 200 °C, 10 h         | 8.3        | UV-Vis, TEM, EDS, XPS and FTIR                | Biosensor                         | (Kundu, Maity e Basu, 2022)                 |
| Washing, drying and grinding | 140 °C, 24 h         | 2.4        | TEM, XRD, UV-Vis, EDX and FTIR                | RE probe                          | (Chu e Cao, 2021)                           |
| Washing and drying           | 200 °C, 12 h         | --         | SEM, FTIR and UV-Vis                          | Solar cells                       | (Paramitha <i>et al.</i> , 2024)            |
| Washing and drying           | 190 °C, 4 h          | 8.3        | FTIR, UV-Vis, XPS and TEM                     | Metal removal                     | (Chung Hui, Lun Ang e Soraya Sambudi, 2021) |
| Washing and drying           | 190 °C, 12 h         | > 10.0     | FTIR, UV-Vis, XPS and TEM                     | Metal removal                     | (Zainal Abidin <i>et al.</i> , 2020)        |
| Washing and drying           | 200, 12 h            | 2.7        | FTIR, UV-Vis, XPS and TEM                     | Detection of Fe <sup>+3</sup>     | (Qi <i>et al.</i> , 2019)                   |
| Washing and drying           | 175 °C, 5 h          | 10.0       | FTIR, XRD, EDX and SEM                        | Dye removal                       | (Heng <i>et al.</i> , 2021)                 |
| Washing and drying           | 200 °C, 10 h         | 3.6        | HRTEM, XRD, FTIR, XPS, UV-Vis, PL, Raman, EDX | Photocatalysis                    | (Wongso <i>et al.</i> , 2021)               |
| Washing and drying           | 200 °C, 6 h          | 4.0 – 5.0  | TEM, HR-TEM, DLS, FTIR, XPS, Raman, UV-Vis,   | Sensor                            | (Thongsai <i>et al.</i> , 2019)             |
| Washing, drying and grinding | 200 °C, 10 h         | 3.0 – 6.0  | TEM, HRTEM, AFM, XRD, EDX, Raman, UV-Vis      | Cell imaging                      | (Wang <i>et al.</i> , 2016)                 |

-- Unavailable Information

Abbreviations: (TEM) Transmission Electron Microscopy; (SEM) Scanning Electron Microscopy; (FTIR) Fourier Transform Infrared Spectroscopy; (EDX) Energy Dispersive X-ray; (XRD) X-Ray diffraction; (AFM) Atomic Force Microscopy and (RAMAN) Raman Spectroscopy.

Source: elaborated by the author (2024).

Several studies have explored rice husks as a sustainable carbon precursor for the synthesis of CDs, taking advantage of its high availability and lignocellulosic composition. Most investigations rely on hydrothermal or thermal routes, employing rice husk in various forms: raw, carbonized, or chemically treated. Although these

studies have advanced promising applications such as chemical sensors, bioimaging, and optoelectronic devices, a recurring limitation lies in the lack of comprehensive analysis regarding the biomass composition, synthesis yield, and characterization of solid by-products.

Dhongde *et al.* (2024) investigated the use of carbon quantum dots (RH-QDs) synthesized from rice husk via hydrothermal synthesis as an anti-corrosive agent in epoxy coatings. The incorporation of 0.1 wt% and 0.5 wt% RH-QDs into epoxy coatings improved the corrosion protection performance of carbon steel substrates in 3.5 wt% NaCl solution, as evaluated by electrochemical impedance spectroscopy, potentiodynamic polarization, and salt spray tests. Additionally, the adhesion strength of the epoxy coating was enhanced due to the strong interaction between the RH-QDs and the epoxy matrix. Density functional theory calculations further supported the experimental findings, revealing that the RH-QDs strengthen the interface between the epoxy-hardener system, thereby hindering the electrochemical corrosion process.

Furthermore, Qi *et al.* (2019) synthesized N-doped CDs using a one-step hydrothermal process with glycine as a nitrogen source. The resulting CDs were applied in  $\text{Fe}^{3+}$  and tetracycline detection and in bioimaging. However, the study was limited to a single synthesis condition and did not assess process yield or the composition of solid residues. Similarly, Thongsai *et al.* (2019) adopted a green strategy to synthesize undoped CDs as pH sensors without experimental variations or discussion of lignocellulosic transformation.

Wang *et al.* (2016) focused on scalable production by controlling rice husk carbonization time prior to acid treatment, aiming to fine-tune morphology and optical properties. Nonetheless, the study did not provide mass balance data or characterize solid by-products. In Heng *et al.* (2021), microwave-assisted CDs were synthesized for  $\text{Cr}^{6+}$  detection, but no information was provided on biomass conversion efficiency. Hui *et al.* (2021) emphasized the optical characterization of hydrothermally synthesized undoped CDs, without addressing optimization or quantitative transformation. Abidin *et al.* (2020) used urea as a nitrogen dopant and explored the impact of reaction time on quantum yield but did not quantify the biomass constituents or the resulting hydrochar.

Other studies focused on functionalization and sensing applications. Chu *et al.* (2021) developed a dual-mode (fluorescence and colorimetric)  $\text{Cu}^{2+}$  sensor using polyethyleneimine-passivated CDs. However, biomass composition and by-product analysis were not included. In the study by Dhongde *et al.* (2024), CDs were incorporated into epoxy matrices for anticorrosive coatings, with different loading concentrations tested; however, no characterization of the precursor or analysis of synthesis yield was performed.

Paramitha *et al.* (2024) proposed an innovative use of rice husk-derived CDs and carbon residue in dye-sensitized solar cells (DSSCs) as sensitizers and counter electrodes, respectively. Despite the creative approach, low efficiency and the absence of biomass conversion data limited the study. Similarly, Kundu *et al.* (2022) and Mercy *et al.* (2023) applied CDs in  $\text{Fe}^{3+}$ /PPi and amoxicillin detection, respectively, achieving good analytical performance without addressing key synthesis parameters or residue quantification.

Chu and Cao (2021) demonstrated effective  $\text{Cu}^{2+}$  detection using pyrolyzed CDs yet provided no insights into the conversion of the biomass. Finally, Wongso *et al.* (2019) systematically investigated the effect of synthesis pH on photoluminescent properties but again failed to quantify synthesis efficiency or mass distribution. Considering this landscape, the present thesis advances the state of the art by systematically addressing critical aspects that are overlooked in most rice husk-based CD studies. While prior research often emphasizes material application or operational parameters (e.g., temperature, time), few, if any attempt to elucidate how biomass is converted into CDs, how much of the organic matter is solubilized during reaction, or what the composition of the remaining solid fraction (hydrochar) is.

Here, rice husk is not merely treated as a carbon source but as a complex and variable system, whose transformation must be understood to optimize CD formation. This work provides a complete mass balance, quantifying the yield of the liquid fraction (CDs), the release of reducing sugars, the quantum yield, and the degradation products formed during the reaction. The solid residue was also fully characterized, allowing for a deeper understanding of the process and possible reuse of the hydrochar.

Another key innovation is the kinetic study of CD formation, which is rarely explored in literature. This allowed for the identification of the optimal reaction time, avoiding unnecessarily long synthesis periods frequently reported, such as 10 h (Wongso *et al.*, 2019), 12 h (Dhongde *et al.*, 2024), and up to 24 h (Chu and Cao, 2021), which lead to increased energy consumption. By optimizing reaction time, the process becomes not only more efficient but also aligned with the principles of green chemistry.

In summary, by integrating biomass compositional analysis, reaction parameter optimization, kinetic evaluation, yield quantification, and subsequent rare-earth doping for environmental sensing, this thesis offers a comprehensive and unprecedented contribution to the green synthesis of nanomaterials. It establishes a robust methodological framework for the rational and sustainable valorization of agro-industrial residues, such as rice husk, in the development of functional carbon-based nanostructures.

### 3.3 RARE EARTH DOPED CARBON DOTS (RE-CDs)

Rare earth (RE) is the collective designation for the 17 metallic elements that comprise the lanthanide series (La–Lu), scandium (Sc) and yttrium (Y) within the periodic table. The gradual occupation of  $4f$  orbitals renders them promising materials with distinctive mechanical, chemical, optical, and magnetic properties, exhibiting various applications in industrial and technological domains (Balaram, 2019; Leal Filho *et al.*, 2023). In the present context, the emergence of nanoscience and nanotechnology has led to a heightened significance of RE-doped nanomaterials in modern science. They are regarded as a particularly promising material in a range of fields, including nanophysics, nano chemistry, and nanomedicine (Su e Kang, 2020).

RE-doped nanomaterials exhibit distinctive physicochemical properties while maintaining their intra-configurational transitions and line-type spectra irrespective of alterations in their size and shape. These properties are superior to those observed in their bulk counterparts. Since the development of rare earth (RE) elements following their discovery approximately 2 centuries ago, RE nanomaterials have become integral

components of high-tech products and advanced materials, representing a valuable strategic resource on a global scale (Zhang *et al.*, 2020).

Rare earth (RE) luminescent and magnetic materials have received extensive attention from researchers in recent decades due to their unique properties stemming from their  $4f$  electron configuration. These materials exhibit distinctive line-like emission spectra, excellent photostability, long luminescent lifetimes, and substantial Stokes/anti-Stokes shifts. However, the parity-forbidden nature of  $4f-4f$  transitions in RE ions often leads to low absorption coefficients and narrow absorption bands, limiting their luminescent intensity. To address this limitation, the synthesis of RE complexes has emerged as a promising approach to enhance luminescence efficiency. Nevertheless, these complexes may suffer from poor thermal stability and photobleaching. In contrast, carbon dots from green synthesis offer superior photostability, thermal stability, chemical resistance, and resistance to photobleaching and blinking. These advantages make RE-CDs hybrids a compelling option for achieving improved luminescent stability and processability compared to pure molecular RE complexes (Baranovskaya *et al.*, 2021; Li; Wei; Gao, 2021).

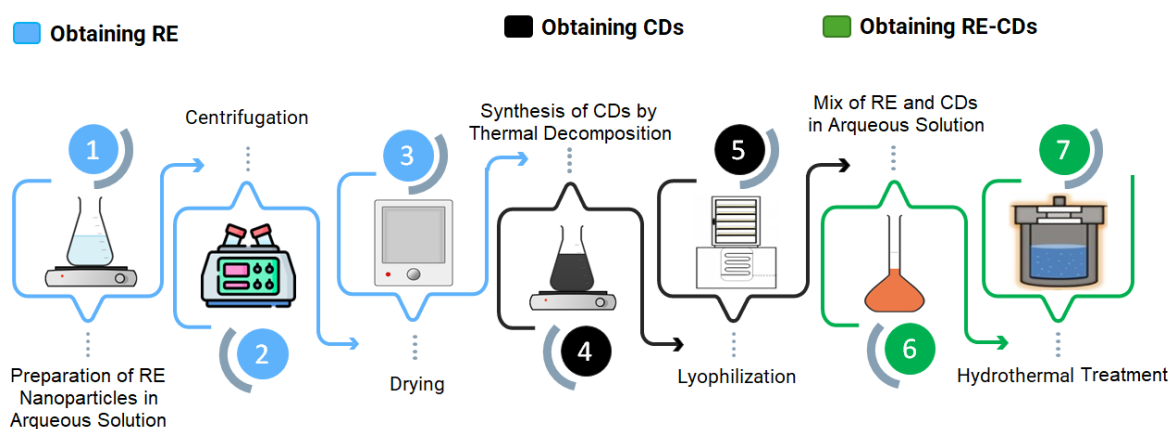
The main advantage of luminescent RE-CDs is the combination of the properties of luminescence from both RE and CDs, which enhances their performance and extends the duration of luminescence. The intensive attention on CDs for luminescence applications is attributed to their prominent features, including facile preparation, high chemical stability and photostability, remarkable water solubility, and biocompatibility. However, the luminescence properties of CDs are relatively limited to blue-green emission, and they exhibit strong self-absorption-induced quenching, which represents a notable challenge (Xu *et al.*, 2021). The RE ions display distinctive luminescence characteristics, including a sharp emission spectrum, a long lifetime, a high quantum yield, and tunability. It is therefore anticipated that the combination of RE and CDs will result in the realization of strong and tunable emission, which will in turn facilitate the extension of the mode of luminescence probes. This combination enhances the potential functions of RE-CDs, facilitating the provision of more comprehensive and accurate diagnostic information beyond that which is achievable through conventional magnetic resonance imaging (MRI) /fluorescence imaging

(Zhang et al., 2020). To illustrate,  $\text{Eu}^{3+}$  complexes with a distinctive  $5d-4f$  transition exhibit enhanced fluorescent characteristics, characterized by red-shifted emissions. The excellent ability of europium complexes to detect citrate at extracellular concentrations of up to 500  $\mu\text{M}$  has been demonstrated by De Rosa *et al.* (2021). Furthermore, RE elements possess remarkable magnetic properties, exemplified by gadolinium, rendering them suitable for magnetic detection and as contrast agents with excellent biocompatibility and data storage (Chen *et al.*, 2016; Jiao *et al.*, 2022; Orhan *et al.*, 2023). Therefore, the integration of RE and CDs enables a synergistic effect, whereby the properties of both components are enhanced, thus creating new and improved material with a range of potential applications.

### 3.3.1 Hydrothermal synthesis of CDs doped with Gd and Ce

As previously documented, the hydrothermal method allows for the synthesis of CDs and RE (or other RE-derived materials) to be conducted in a single pot or through the implementation of multi-step approaches. One such approach involves the preparation of CDs and RE (or other RE-derived materials) in separate stages, subsequently combining them to form RE-CDs composite materials. Figure 6 shows a summarized flowchart for obtaining RE-CDs by the hydrothermal method.

Figure 6 – Summarized flowchart for obtaining RE-CDs by the hydrothermal method



Source: adapted from Thakur *et al.* (2022).

As already described, doping CDs with RE is promising because it increases their quantum yield and stability under different pH and temperature conditions,

enabling applications in environmental sensors, biological markers and bioimaging. Cerium (Ce) is a rare earth element that stands out as a promising dopant for carbon dots (CDs) due to its unique oxidation-reduction properties and its ability to form stable complexes with ligands on the surface of CDs. This element has two main oxidation states,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ , which allows cerium to act as a regulator in the electronic behavior of CDs, facilitating charge transfer processes and improving the fluorescence quantum yield. Ce's ability to switch between oxidation states, especially in controlled environments, makes it ideal for applications in sensors and bioimaging devices, where stability and fluorescence intensity are key (Popov *et al.*, 2022; Zhang *et al.*, 2020).

In addition, cerium provides antioxidant and photoprotective properties to CDs, due to its ability to effectively neutralize reactive oxygen species (ROS). This is especially valuable in biomedical and environmental contexts, where the presence of ROS can be harmful. The electronic structure of Ce allows it to interact strongly with functional groups on the surface of CDs, such as carboxylic and hydroxyl groups, facilitating adsorption and improving the colloidal stability of CDs (Zou *et al.*, 2020).

To address the challenge of sensitive detection of the anticancer drug doxorubicin (DOX), Thakur *et al.* (2022) developed a novel sensor using carbon dots/cerium oxide nanocomposites ( $\text{CDs/CeO}_2$ ) on a screen-printed carbon electrode (SPCE). Synthesized via a hydrothermal process with taurine-based CDs, the optimized 5 wt%  $\text{CDs/CeO}_2$  nanocomposite demonstrated superior electrochemical performance, enhancing electron transfer and sensitivity. The sensor showed high selectivity for DOX, even in the presence of interferents, offering potential applications for pharmaceutical and biological sample analysis.

Zeng *et al.* (2022) developed an eco-friendly corrosion inhibitor, Ce and N co-doped carbon dots ( $\text{Ce@N-CDs}$ ), synthesized via a hydrothermal approach. Characterization through FTIR, XPS, and TEM revealed their structure, while electrochemical testing indicated a high inhibition efficiency of 98% for Ce-10% on copper. Analyses suggest the formation of a passivation layer, combining N-CDs and cerium oxides, which effectively prevents corrosive medium penetration on copper surfaces.

Zhang *et al.* (2019) explored the synthesis of cerium-doped carbon quantum dots (Ce-doped CQDs) as effective antioxidants, addressing issues of oxidative stress in biomedical applications. Using a one-step hydrothermal method, they produced Ce-doped CQDs with a particle size of approximately 2.5 nm, which exhibited properties like strong fluorescence, stability in solution, and biocompatibility. Notably, the Ce-doped CQDs demonstrated a high  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio, contributing to their ROS-scavenging abilities. The study found that these nanoparticles could effectively neutralize hydroxyl radicals and protect cells from hydrogen peroxide-induced oxidative damage, suggesting therapeutic potential for diseases linked to oxidative stress.

Gadolinium (Gd) is a rare earth element that exhibits distinctive magnetic and optical characteristics, rendering it a promising candidate for doping carbon dots (CDs). As stated by Zhang *et al.* (2020, 2024), gadolinium is one of the rare earth elements with the highest electron spin magnetic moment, which enables it to enhance the signal intensity of magnetic resonance imaging (MRI) contrast agents by shortening the relaxation period of T1-weighted images. Moreover, due to its extensive transition number, which encompasses a broad spectrum of wavelengths from ultraviolet to infrared, gadolinium's elevated atomic number and considerable ionic radius increase the luminescence and stability of CDs when doped with this element, thereby enhancing their performance in applications such as bioimaging and drug delivery (Wang *et al.*, 2021; Zheng *et al.*, 2019). Additionally, gadolinium's capacity to exist in multiple oxidation states ( $\text{Gd}^{3+}$  and  $\text{Gd}^{2+}$ ) endows it with tunable electronic properties, thereby enabling efficient energy transfer processes (Demireva, Kim e Armentrout, 2016). This versatility positions gadolinium-doped CDs as advanced materials in nanotechnology, chemical sensors, and biomedicine (Cardo *et al.*, 2023; Gong *et al.*, 2014; Mauro *et al.*, 2023). In view of the wide range of applications aimed at doping CDs with the elements Ce and Gd, Table 4 presents a summary of some studies involving doping Ce-CDs and Gd-CDs via hydrothermal synthesis.

Table 3 – Summary of some studies involving doping Ce-CDs and Gd-CDs via hydrothermal synthesis  
(to be continued)

| Rare Earth Element | Precursor of Carbon             | Particle Size (nm) | Quantum Yield (%) | Color of Emission | Applications                                         | Emission Range (nm) | References                                        |
|--------------------|---------------------------------|--------------------|-------------------|-------------------|------------------------------------------------------|---------------------|---------------------------------------------------|
| Ce                 | Citric acid                     | 5.25               | --                | Blue              | Protection crops from abiotic stress                 | 320 - 380           | Dong, Gong e Zhao, 2022                           |
| Ce                 | Citric acid and urea            | 5.00               | --                | Blue              | Growth and development in wheat                      | 310 - 434           | Gong e Dong, 2021                                 |
| Ce                 | Citric acid                     | 2.00 – 4.00        | --                | Blue              | Wound healing                                        | 359 - 433           | Zhang, Zhai, Ma, Huang, Yan, <i>et al.</i> , 2021 |
| Ce                 | Ethylenediaminetetraacetic acid | 2.80               | --                | Blue              | Enhanced antioxidant for hydroxyl radical scavenging | 380 - 520           | Zou <i>et al.</i> , 2020                          |
| Ce                 | Urea and carbon nitride         | 5.00               | --                | Red               | Photocatalytic activity                              | 360 - 460           | Sun <i>et al.</i> , 2022                          |
| Ce                 | Citric acid                     | 5.25               | --                | Blue              | Protection crops from abiotic stress                 | 320 - 380           | Dong, Gong e Zhao, 2022                           |
| Ce                 | Tannic acid                     | 40.00 – 50.00      | --                | Blue              | Detection of fluoride                                | 340 - 495           | Meng <i>et al.</i> , 2022                         |
| Ce                 | Citric acid                     | 4.16               | 93.14             | Blue              | Detection of tetracyclines residues                  | 340 - 440           | Zhang e Fan, 2021                                 |
| Ce                 | Petal of cherry blossoms        | 3.00 – 5.00        | --                | Blue              | Hydrogen peroxide sensor                             | 320 - 415           | Wang, Y. <i>et al.</i> , 2019                     |
| Gd                 | Arginine                        | 5.38               | 57.78             | Blue              | Magnetic resonance                                   | 200 - 600           | Zheng <i>et al.</i> , 2019                        |

Table 3 – Summary of some studies involving doping Ce-CDs and Gd-CDs via hydrothermal synthesis  
(conclusion)

| Rare Earth Element | Precursor of Carbon             | Particle Size (nm) | Quantum Yield (%) | Color of Emission | Applications                                 | Emission Range (nm) | References                        |
|--------------------|---------------------------------|--------------------|-------------------|-------------------|----------------------------------------------|---------------------|-----------------------------------|
| Gd                 | Citric acid and urea            | 21.3 ± 3.10        | 5.60              | Red               | Cancer phototherapy                          | 470 - 550           | Jiao <i>et al.</i> , 2022         |
| Gd                 | 3-aminothiophenol               | 2.45 ± 0.91        | 3.32              | Blue              | Radiometric nano-sensor                      | 415 - 490           | Wang <i>et al.</i> , 2022         |
| Gd                 | Citric acid                     | 2.00 ± 0.5         | 49.94 to 83.67    | Blue              | Fluorescence/magnetic resonance              | 240 - 400           | Maghsoudinia <i>et al.</i> , 2021 |
| Gd                 | 3,4-dihydroxyhydrocinnamic acid | 3.13               | 26.84             | Blue              | Magnetic resonance imaging and drug delivery | 200 - 500           | Jiang <i>et al.</i> , 2021        |
| Gd                 | Starch                          | 3.00 – 8.00        | 54.00             | Blue              | Fluorescent probe                            | 365 - 600           | Molaei, 2022                      |
| Gd                 | Citrate acid                    | 2.25 ± 0.54        | 1.29 to 48.32     | Blue              | Fluorescence and magnetic resonance imaging  | 240 - 400           | Huang <i>et al.</i> , 2020        |

-- Unavailable Information

Source: elaborated by the author (2024).

### 3.4 APPLICATION OF RE-DOPED CARBON DOTS IN THE DETECTION OF AGROCHEMICAL RESIDUES

As the global population increases, achieving high agricultural yields becomes crucial. To combat crop threats such as pests, farmers use a variety of agrochemicals, including pesticides and herbicides, which have greatly increased agricultural productivity. However, unrestricted use of these chemicals leads to toxic, non-biodegradable residues contaminating soil, water, and air, raising serious ecological concerns. Such residues can cause health issues, including cancer, birth defects, hormonal disruptions, and drug resistance in organisms (Carvalho, 2017; Devi, Manjula e Bhavani, 2022).

Currently, various techniques for detecting agrochemical residues, such as chromatography, mass spectrometry, and enzyme-linked immunosorbent assays, exist but have drawbacks like being time-consuming and requiring expert handling. In contrast, carbon dots offer a simpler and more efficient fluorescence-based sensing method that is sensitive, specific, and cost-effective (Ashrafi Tafreshi *et al.*, 2020; John, Abraham e Mathew, 2022). Fluorescence quenching, a decrease in emission intensity due to molecular interactions, can result from various processes, including energy transfer and electron exchange, making CDs advantageous for real-time detection in agricultural settings. Research indicates that carbon dots sensors can detect metal ions, drugs, and pesticides at concentrations considerably below regulatory limits. While CDs typically exhibit lower quantum yields compared to semiconductor quantum dots, efforts to enhance their performance include doping with nitrogen and sulfur.

CDs can function directly as a signal source or be conjugated with materials like aptamers, molecularly imprinted polymers, and enzymes for specific applications. The fluorescence intensity of CDs can decrease due to electron transfer interactions with analytes, indicating detection (Cardoso *et al.*, 2019; Khairol Anuar *et al.*, 2021; Latief, Islam e Khan, 2023). Although there are few studies on the use of Ce-CDs or Gd-CDs nanohybrids for detecting agrochemical pollutants, particularly through green synthesis, scientific literature indicates that doping carbon dots with rare earth (RE) elements enhances their potential for such applications. The incorporation of RE elements, such as cerium or gadolinium, improves the optical properties of the CDs,

increasing their fluorescence intensity and stability. This hybridization facilitates enhanced sensitivity and selectivity toward target pollutants through mechanisms like efficient energy transfer and electron exchange. Consequently, CDs-RE hybrids exhibit superior detection limits and response times, making them promising candidates for real-time monitoring of hazardous agrochemicals in agricultural and environmental contexts (Omar *et al.*, 2022). In another more recent study, Zhang and Fan (2021) synthesized cerium and nitrogen co-doped carbon quantum dots (Ce-N-CDs) using a hydrothermal method. These Ce-N-CDs exhibited high quantum yield and were successfully applied as sensitive fluorescent probes for the detection of tetracycline residues in food samples.

About the doping of CDs with gadolinium for use in agrochemical substances, there is a scarcity of studies published in literature. However, recent research developed by Zhao *et al.* (2024) has provided insight into this area. The researchers developed a rapid one-step hydrothermal method to synthesize yellow-green carbon quantum dots (4-ASA/Gd-CDs) co-doped with gadolinium and 4-aminosalicylic acid (4-ASA). The CDs displayed dual enzyme-like activity, encompassing oxidase-like and superoxide dismutase-like activity. The authors demonstrated that the CDs could be employed for the colorimetric detection of  $\text{Cu}^{2+}$  ions, with a low detection limit of 0.38  $\mu\text{M}$ .

Despite significant progress in the synthesis and application of RE-CDs, most existing studies predominantly utilize synthetic carbon precursors such as citric acid, urea, and polyethylene glycol (Table 4). While these synthetic routes are effective, they often overlook the potential of green and sustainable alternatives that could minimize environmental impact and add value to otherwise low-value biomass residues. This work contributes to the field by employing a fully green synthesis methodology, using rice husks, an abundant agro-industrial residue, as a novel carbon precursor, which remains largely unexplored in the context of RE-CD synthesis. In this study, doping was carried out only after optimizing the reaction parameters, including time, temperature, and solid loading, to achieve the most efficient conversion of biomass into CDs.

This preliminary investigation of the biomass composition plays a key role in achieving a more efficient conversion of its constituents into the target carbon-based nanomaterial, contributing to shorter synthesis times and more sustainable production routes. Although RE-CDs have demonstrated versatile applications ranging from catalysis and magnetic resonance imaging to controlled drug release and cellular imaging, there is a notable gap concerning their use in detecting hazardous agrochemical residues in environmental matrices. This research addresses that gap by focusing on real-time fluorescence-based sensing of agrochemical contaminants, leveraging the enhanced fluorescence intensity and stability imparted by rare earth doping combined with an eco-friendly synthesis route. Therefore, the present work not only advances the sustainable production of high-performance RE-doped CDs but also expands their practical applicability toward urgent environmental monitoring challenges, offering a promising platform for sensitive and selective detection of agrochemical pollutants in water systems.

#### 4 STATE-OF-THE-ART CONSIDERATIONS AND JUSTIFICATION

The development of sustainable and environmentally friendly technologies for detecting agrochemical pollutants has become increasingly important due to the rising environmental contamination caused by the intensive use of pesticides, herbicides, and other chemicals. Green synthesis of carbon dots from agricultural waste, such as rice husks, is particularly promising, combining environmental sustainability with the conversion of waste materials into functional nanomaterials. This approach is economically viable, transforming biological waste into nanomaterials with tunable optical and electronic properties suitable for chemical sensor applications.

Recent literature highlights substantial progress in green CD synthesis, especially via hydrothermal methods, noted for their simplicity and low cost. However, studies on rare earth doped CDs are limited, especially those utilizing green synthesis approaches. Doping with RE elements, such as gadolinium and cerium, can enhance CDs' properties, including increased quantum yield and the formation of active sites for pollutant interaction. This enhancement is especially relevant for agrochemical detection, as RE elements modulate CDs' electronic and surface properties, improving their sensitivity and selectivity toward specific contaminants.

Beyond performance benefits, the development of RE-doped CDs from green synthesis represents a remarkable advancement in state-of-the-art technologies, merging eco-friendly approaches with high-functionality chemical sensors. Using rice husks, an abundant agricultural waste, highlights the economic and ecological significance of this project, creating high-value applications for an underutilized resource.

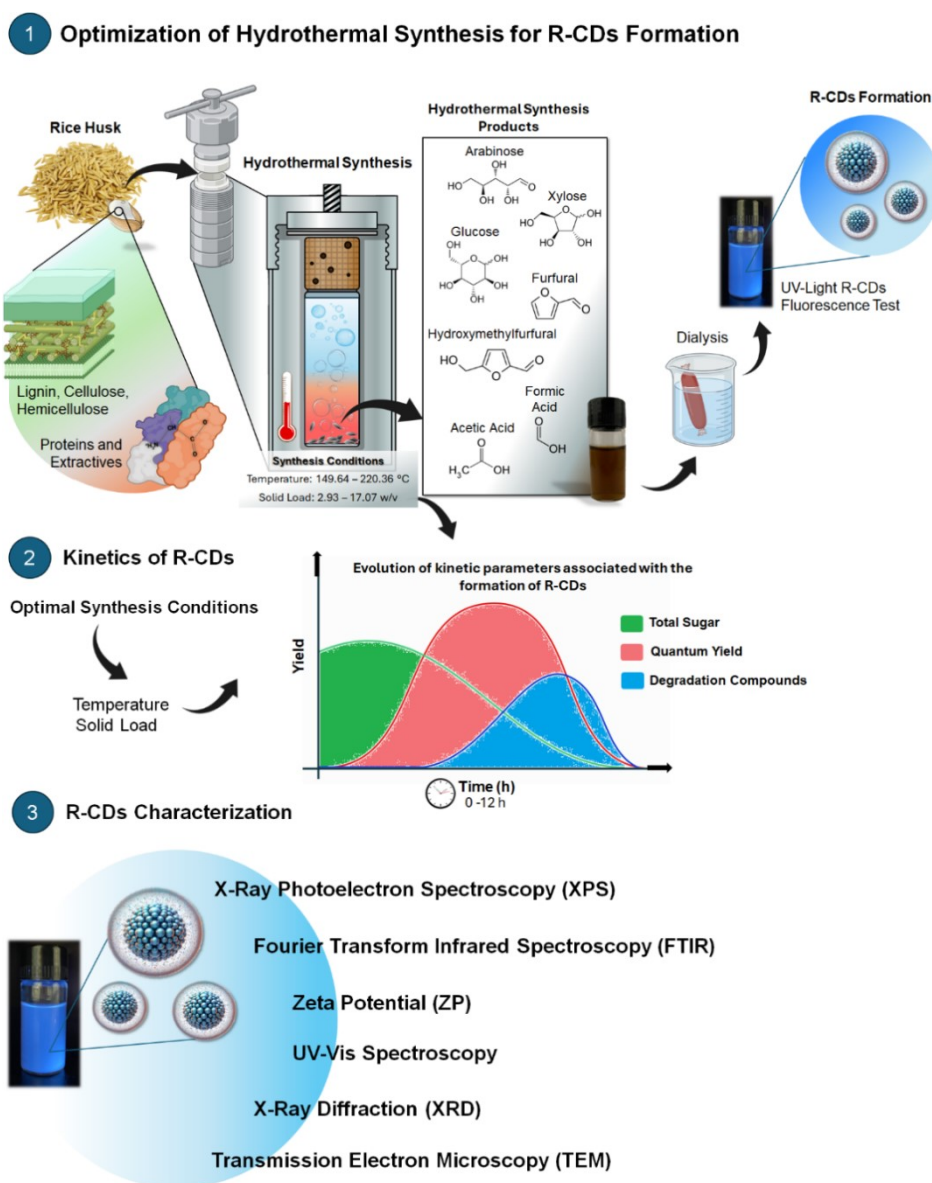
In summary, this research makes significant scientific and environmental contributions by proposing an innovative and sustainable approach to understanding the transformation of lignocellulosic biomass into carbon-based nanomaterials. The study focuses on elucidating how the chemical composition of rice husk influences the synthesis, structure, and optical behavior of carbon dots, addressing a major gap in the current literature on green nanomaterial production. The doped systems with rare earth elements (Ce and Gd) were subsequently explored as a complementary stage

to assess the potential application of the optimized CDs in agrochemical detection. To achieve these goals, a detailed methodology was established, encompassing biomass characterization, the optimization of hydrothermal synthesis parameters, kinetic evaluation of the conversion process, and the structural and optical characterization of the resulting nanomaterials. The following section describes the materials and experimental procedures employed in this study.

## 5 MATERIALS AND METHODS

This section presents the methodology used to develop this thesis. Figure 7 shows a schematic illustration summarizing the different steps included in the green CD synthesis methodology, the study of the kinetics associated with the synthesis parameters, as well as the characterization of the CDs from rice husk residues (R-CDs).

Figure 7 – Schematic illustration summarizing the different steps included in the green R-CDs synthesis methodology, study of the kinetics associated with the synthesis parameters, as well as their characterization



Source: elaborated by the author (2024).

Firstly, CDs were synthesized using rice husk as a precursor (R-CDs), following an experimental design of the Central Composite Rotational Design (CCRD) type to assess the optimum synthesis condition. Subsequently, a mechanistic study was carried out to assess which biomass constituents are responsible for the formation of R-CDs and how the synthesis conditions directly affect this process. All the experimental procedures were carried out at the Materials and Scientific Computing Laboratory (LabMAC) and the Biological Engineering Laboratory (LIEB) of the Chemical and Food Engineering Department at UFSC.

In the second part of the study, carbon dots synthesized under the optimized hydrothermal conditions were doped with rare-earth elements, gadolinium (Gd) and cerium (Ce), with the aim of enhancing their structural, optical, and sensing properties. The selection of these dopants was based on their known ability to modulate surface states and improve fluorescence stability in carbon-based nanomaterials. The doped CDs were extensively characterized using spectroscopic and microscopic techniques to investigate changes in morphology, surface chemistry, and photophysical behavior resulting from the doping process. Finally, their performance as fluorescent nanosensors was assessed through the detection of target agrochemicals, specifically glyphosate and mesotrione, in both ultrapure water and real environmental samples collected in the region of Lagoa da Conceição, located in the city of Florianópolis, Santa Catarina, Brazil (27°33'38" S; 48°27'13" W), aiming to evaluate selectivity, sensitivity, and robustness under realistic conditions.

## 5.1 RAW MATERIAL

The Rice Husk (RH) used in this study was obtained from the company Rofertil (Santo Antônio de Posse, São Paulo, Brazil), which was ground using a Willey knife mill (DeLeo, Porto Alegre, Brazil) to a particle size of 30 mesh, a granulometry commonly used in biomass processing due to its balance between surface area and processability (Kundu, Maity, and Basu, 2022). Distilled water was used for the preparation of the rice husk suspensions employed in the hydrothermal synthesis experiments.

## 5.2 GREEN SYNTHESIS OF CDS AND EXPERIMENTAL DESIGN

### 5.2.1 Hydrothermal synthesis of CDs

The hydrothermal synthesis from rice husk was conducted using a high-pressure stainless-steel reactor (Model RTA-BB-450-CM, METALQUIM, Brazil) with a 450 mL capacity, maximum operating temperature of 300 °C, a heating power of 1.0 kW, and a maximum working pressure of 138 bar.

### 5.2.2 Experimental design for the optimized removal of organic compounds and degradation products from rice husk

To investigate the release of compounds originating from the lignocellulosic structure of the rice husk for the reactional medium, it has been employed a 2<sup>2</sup> Central Composite Rotational Design (CCRD). This design consisted of 4 tests under axial conditions and three repetitions at the central point, resulting in 11 experimental runs. The independent variables considered were temperature (149.64 °C, 160 °C, 185 °C, 210 °C, and 220.36 °C), denoted as  $X_1$ , and solid load (2.93 w/v, 5.0 w/v, 10.0 w/v, 15.0 w/v, 17.07 w/v), represented as  $X_2$ . The selection of temperature and solid load as independent variables was based on their well-established influence on the hydrothermal conversion of lignocellulosic biomass. Santana *et al.* (2023) employed a similar central composite design to optimize oligosaccharide production from tobacco stems, using comparable ranges (temperature: 161.72 °C – 218.3 °C; SL: 2.93% – 17.07%). Accordingly, this study adopted equivalent conditions to assess their effects on rice husk degradation CDs formation, considering that both parameters significantly impact the release of degradation compounds essential for CD synthesis. Table 5 shows the experimental design of the variables used in the synthesis of CDs.

The dependent variables were: (1) the percentage of organic compound removal (ROC) from RH (% ,  $w[\text{cellulose} + \text{hemicellulose} + \text{lignin} + \text{protein} + \text{extractives}] / w[\text{total organic compounds}]$ ) to the liquid fraction during the hydrothermal reaction; and (2) the percentage of degradation compounds (% ,  $w[\text{xylose} + \text{glycose} +$

arabinose + cellobiose + acetic acid + formic acid + FF + HMF] / w[polysaccharides]) formed during the reaction according by Santana *et al.* (2024).

Table 4 – Experimental design of the variables used in the synthesis of CDs

| Tests | Reaction Temperature | Solids Load       |
|-------|----------------------|-------------------|
|       | (°C)                 | (w/v)             |
|       | (X <sub>1</sub> )    | (X <sub>2</sub> ) |
| 1     | 160.00 (-1)          | 5.00 (-1)         |
| 2     | 210.00 (+1)          | 5.00 (-1)         |
| 3     | 160.00 (-1)          | 15.00 (+1)        |
| 4     | 210.00 (+1)          | 15.00 (+1)        |
| 5     | 149.64 (-1.41)       | 10.00 (0)         |
| 6     | 220.36 (+1.41)       | 10.00 (0)         |
| 7     | 185.00 (0)           | 2.93 (-1.41)      |
| 8     | 185.00 (0)           | 17.07 (+1.41)     |
| 9     | 185.00 (0)           | 10.00 (0)         |
| 10    | 185.00 (0)           | 10.00 (0)         |
| 11    | 185.00 (0)           | 10.00 (0)         |

Source: elaborated by the author (2024).

The hydrothermal synthesis was done by feeding the reactor with biomass and distilled water in predetermined proportions, as specified in the experimental design. The reactions were conducted at 500 rpm and maintained for 4 h, counted from when the proposed temperature was reached under each condition (Jothi *et al.*, 2021). After the completion of the reaction, the reactor was cooled to room temperature (25 °C), and the dark brown mixture was centrifuged in a Centribio 80-2B centrifuge for 30 min at 5.000 g. Afterward, the supernatant was filtered through a 0.22 µm cellulose acetate membrane to quantification of degradation compounds and total sugar (TS) such as cellobiose, glucose, xylose, arabinose, furfural, HMF, acetic acid, and formic acid by high-performance liquid chromatography (HPLC).

The analysis was carried out in a Shimadzu Prominence LC-20A chromatograph equipped with a Bio-Rad® Aminex HPX-87H column (300 mm × 7.8 mm) and refractive index detector (RID-20A), employing a 10 µL sample injection, with 5 mmol/L H<sub>2</sub>SO<sub>4</sub> as the mobile phase at a flow rate of 0.6 mL/min, at 65 °C for 50 min. The retained material (solid residue) was subsequently dried in an oven at 105 °C for 24 h to

constant weight, and its lignocellulosic composition was characterized by cellulose, hemicellulose, lignin, and ash content.

The results were statistically analyzed by analysis of variance (ANOVA) using Statistica software (Statistica v.13.5, TIBCO Software Inc., Palo Alto, CA, USA), adopting a 5% significance level ( $p < 0.05$ ), in order to identify the optimal conditions that maximize the removal of organic compounds and the formation of rice husk degradation products, which are crucial factors in degradation compound (DC) formation (Wareing, Gentile and Phan, 2021). The statistical procedures are detailed in Section 5.2.7. Following the determination of temperature and solid load parameters, a kinetic analysis was conducted to assess the effect of time on the formation of total sugars (TS), degradation compounds (DC), and quantum yield (QY).

### 5.2.3 Kinetics of carbon dots from rice husk biomass (R-CDs)

The kinetics of R-CDs were carried out according to the methodology described by Santana *et al.* (2024) with a few modifications. An analysis was performed by varying the time (0 h, 2 h, 4 h, 6 h, 8 h, 10 h, and 12 h) under isothermal conditions, with the solid load and temperature (both optimized) kept constant, as well as the agitation (500 rpm). Time zero in the kinetic analysis corresponds to the moment the isothermal temperature is reached. The experiments were performed in duplicate, and after the synthesis was completed, the reaction medium was treated as specified in Section 5.2.2. The liquid fraction was analyzed, assessing the profile of DC formation ( $\%, w[\text{acetic acid} + \text{formic acid} + \text{FF} + \text{HMF}] / w[\text{polysaccharides}]$ ) and TS ( $\%, w[\text{xylose} + \text{glucose} + \text{arabinose} + \text{cellobiose}] / w[\text{polysaccharides}]$ ).

Quantum yield was also evaluated at each kinetic point to understand the mechanisms of R-CDs formation during hydrothermal synthesis. The results were statistically analyzed to select the time that provided the highest QY. The yield profile ( $\%w/w$ ) and concentration (g/L) of TS and DC were analyzed for each molecule individually, to establish correlations with the QY profile. This allowed for the identification of the relationship between R-CDs formation and the evolution of DC and TS over time. At the end of the kinetics study, an evaluation was conducted to identify the optimal conditions, considering the time, temperature, and optimized solid load to

maximize R-CDs production. The carbon dots obtained in the optimum reaction kinetics condition were subjected to dialysis with a cellulose acetate membrane (1000 Da, 1 kDa cut-off) in ultrapure water for 72 h according by Bian *et al.* (2023) to purify them. After this process, the carbon dots were characterized.

#### 5.2.4 Severity factor

The severity factor calculation was employed to assess the intensity of the hydrothermal synthesis process of R-CDs and to understand the impact of the combination of time and temperature on the structural alterations of raw RH in each run (Equation (1) and Equation (2)). This mathematical model can describe the behavior of the three phases of the hydrothermal process, which include heating, the isothermal period, and cooling (Santana *et al.*, 2023).

$$\log R_o = [R_o \text{ (Heating)}] + [R_o \text{ (Isothermal)}] + [R_o \text{ (Cooling)}] \quad (1)$$

$$\log R_o = \left[ \int_0^{t_m} \frac{T(t)-100}{w} \right] + \left[ \int_{c_i}^{c_f} \frac{T(t)-100}{w} \right] + \left[ \int_0^{t_m} \frac{T'(t)-100}{w} \right] \quad (2)$$

In this equation,  $\log R_o$  represents the severity factor,  $t_m$  denotes the time required to reach the maximum temperature, and  $T(t)$  and  $T'(t)$  describe the temperature profile ( $^{\circ}\text{C}$ ) as a function of time during the heating and cooling stages, respectively. The parameter  $w$  is an empirical value associated with the activation energy, which has been fixed at 14.75 for the specific raw material under investigation (Overend and Chornet, 1987). Furthermore,  $c_i$  and  $c_f$  represent the initial and final times of the isothermal treatment phase, respectively, measured in minutes.

#### 5.2.5 Chemical characterization of lignocellulosic biomass

The chemical composition of raw rice husk and the solid streams resulting from the hydrothermal synthesis in all runs were characterized. The content of extractives was determined through sequential extraction with ethanol and water, following the procedure outlined in the National Renewable Energy Laboratory (NREL/TP-510-

42619). Cellulose, hemicellulose, lignin, and ash were quantified using the method provided in NREL/TP-510-42618 (Sluiter *et al.*, 2012). Protein content was quantified using the Kjeldahl method, following the standard methodology established by AOAC (1995). The contents of solids (S), glucan (G), xylan (X), lignin (L), and organic compounds removed in the solid fraction after hydrothermal synthesis were calculated following Equations (3) to (7), as described in Ilanidis *et al.* (2021), Santana *et al.* (2024):

$$S_{\text{removal}}(\%) = \frac{S_{\text{RRH}}(\text{g})}{S_{\text{HRH}}(\text{g})} \times 100 \quad (3)$$

$$G_{\text{removal}}(\%) = \frac{G_{\text{RRH}}(\text{g})}{G_{\text{HRH}}(\text{g})} \times 100 \quad (4)$$

$$X_{\text{removal}}(\%) = \frac{X_{\text{RRH}}(\text{g})}{X_{\text{HRH}}(\text{g})} \times 100 \quad (5)$$

$$L_{\text{removal}}(\%) = \frac{L_{\text{RRH}}(\text{g})}{L_{\text{HRH}}(\text{g})} \times 100 \quad (6)$$

$$\text{OC}_{\text{removal}}(\%) = \frac{\text{OC}_{\text{RRH}}(\text{g})}{\text{OC}_{\text{HRH}}(\text{g})} \times 100 \quad (7)$$

where  $S_{\text{RRH}}$  represents the mass of rice husk removed after hydrothermal synthesis (g), and  $S_{\text{HRH}}$  is the mass of raw rice husk added in the hydrothermal synthesis process (g);  $G_{\text{RRH}}$ ,  $X_{\text{RRH}}$ ,  $L_{\text{RRH}}$ , and  $\text{OC}_{\text{RRH}}$  are the mass fractions of glucan, xylan, lignin and organic compounds removed in the rice husk after hydrothermal synthesis, respectively.  $G_{\text{HRH}}$  and  $X_{\text{HRH}}$ ,  $L_{\text{HRH}}$  and  $\text{OC}_{\text{HRH}}$  are the mass fractions of glucan, xylan, lignin, and organic compounds present in the raw rice husk added in the hydrothermal synthesis process (g), respectively.

### 5.2.6 Quantum yield determination and quantification of sugars and degradation compounds

For the analysis of the relative quantum yield in the kinetics stage, the R-CDs were dialyzed using a cellulose acetate membrane (cut-off 1000 Da, 1 kDa) in ultrapure water for 72 h according to Bian *et al.* (2023) and performed in triplicate. The liquid fraction obtained after the hydrothermal synthesis of RH was subjected to the analysis of fluorescence QY of R-CDs using a quinine sulfate solution in 0.1 M H<sub>2</sub>SO<sub>4</sub> (Q = 0.54%) as a reference due to the spectrum's similarity with the synthesized material according by Chaudhary *et al.* (2020) at an excitation wavelength of 360 nm as reported by Jothi *et al.* (2021), following Equation (8):

$$Q_x = Q_{st} \times \left( \frac{A_{st}}{A_x} \right) \times \left( \frac{I_x}{I_{st}} \right) \left( \frac{n_x}{n_{st}} \right)^2 \quad (8)$$

where Q is the quantum yield,  $n$  is the refractive index,  $A$  is the absorbance, and  $I$  is the measured integrated emission intensity. In addition, the indices  $st$  and  $x$  show the relative value of the standard material and the carbon dots, respectively.

Quinine sulphate ( $\Phi_R = 0.54$ ) was dissolved in 0.1 M H<sub>2</sub>SO<sub>4</sub> ( $n = 1.33$ ), while R-CDs were dissolved in distilled water ( $n = 1.33$ ) in preparation for the measurements. The absorbance in a 1 cm quartz cuvette was kept below 0.10 at the excitation wavelength of 360 nm to minimize the resorption effect (Shu *et al.*, 2020). Another aliquot of the liquid fraction was analyzed using ultra-fast liquid chromatography (UFLC) to identify and quantify major saccharides and degradation products, including glucose, xylose, arabinose, cellobiose, acetic acid, formic acid, and furfural.

The methodology was based on the work by Santana *et al.* (2023), utilizing a Shimadzu Prominence LC-20A chromatograph (Shimadzu, Tokyo, Japan) equipped with a Bio-rad® Aminex HPX-87H column (300 mm × 7.8 mm) and a refractive index detector RID-20A. A 10 µL sample injection was eluted with 5 mmol/L H<sub>2</sub>SO<sub>4</sub> at a 0.6 mL/min flow rate. The oven temperature was maintained at 65 °C, and the total run time was 50 min.

### 5.2.7 Statistical analysis of hydrothermal of R-CDs

A Response Surface Methodology (RSM) coupled with multiple regression was applied to model the synthesis of R-CDs in terms of QY. The statistical significance of the effects was verified through ANOVA, and non-significant effects were excluded from the initial model. Experimental data were re-adjusted only for significant parameters ( $p \leq 0.05$ ). The adequacy and quality of the fit were assessed using the lack of fit test, the coefficient of determination ( $R^2$ ), and its adjusted  $R^2$ . The generalized model utilized in the RSM is presented in Equation (9). In this equation,  $Y$  represents the predicted response, while  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  correspond to the regression coefficients for the intercept, linear, quadratic, and interaction terms, respectively.  $X_i$  and  $X_j$  denote the independent variables. Once the mathematical model was obtained, multi-response optimization using the desirability function was employed to maximize the highest QY condition according to Derringer and Suich (1980). The execution of the CCRD and data analysis were conducted using Statistica v.13.5 (T.I.B.C.O. Software Inc., Palo Alto, CA, USA).

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (9)$$

## 5.3 CHARACTERIZATION OF CARBON DOTS

### 5.3.1 Transmission electron microscopy (TEM)

Transmission electron microscopy micrographs were taken on a JEM-1011 electron microscope with 100 kV resolution. Sample preparation consisted of diluting a small amount of the material in 10 mL of isopropyl alcohol for deagglomeration in an ultrasonic bath. The supernatant was dripped using a precision pipette (100  $\mu$ L) onto copper grids covered with amorphous carbon film (GRIDS) suitable for TEM analysis. ImageJ® software was used to process the images and estimate particle size. The analysis was carried out at the Central Laboratory for Electron Microscopy (LCME) of the Federal University of Santa Catarina (UFSC).

### **5.3.2 Fourier transform infrared spectroscopy (FTIR)**

Fourier transform infrared spectroscopy (FTIR) was used to identify functional groups present in the samples. The analyses were performed on an Agilent Technologies Cary 660 FTIR spectrophotometer using the KBr pellet technique, with 2% (w/w) sample in potassium bromide, compressed into a transparent disk. Spectra were acquired in the range of  $4000\text{ cm}^{-1}$  –  $400\text{ cm}^{-1}$ , with a resolution of  $4\text{ cm}^{-1}$  and 32 scans. The measurements were conducted at the Central Analysis Laboratory of the Chemical and Food Engineering Department of Federal University of Santa Catarina (EQA-UFSC).

### **5.3.3 X-ray diffraction (XRD)**

The X-ray diffraction profiles of the materials were obtained using Rigaku MiniFlex600 XRD equipment under Cu-K $\alpha$  radiation ( $\lambda = 0.154\text{ nm}$ ) and angle  $2\theta$  ranging from  $10^\circ$  to  $60^\circ$ . The XRD analysis was carried out at the Interdisciplinary Laboratory for the Development of Nanostructures in the Chemical and Food Engineering Department of Federal University of Santa Catarina (EQA-UFSC).

### **5.3.4 UV-VIS spectroscopy**

Emission, excitation, and absorption spectra were collected using an Infinite M200 dual-beam UV–Vis microplate reader (Tecan) to investigate the optical properties of the synthesized R-CDs. UV–Vis absorption spectra were recorded in the wavelength range from 200 to 800 nm using quartz cuvettes with an optical path length of 1 cm. Ultrapure water was used as the blank for baseline correction. All measurements were performed at room temperature under identical experimental conditions. The UV–Vis analyses were carried out at the Multiuser Laboratory for Studies in Biology (LAMEB) of the Federal University of Santa Catarina (UFSC)

### **5.3.5 X-ray Photoelectron Spectroscopy and Zeta Potential**

X-ray photoelectron spectroscopy (XPS) was employed to identify elemental composition and chemical states on the surface of materials using a Thermo Scientific

K-alpha instrument with an Al K $\alpha$  monochromatic X-ray source and an energy step size of 0.025 eV. A C1s level of 284.8 eV was used as an internal standard. CasaXPS software was used to calculate elemental composition. A zeta potential analysis was carried out to investigate the particles' surface charge and colloidal stability (Malvern®Zetasizer Nano, ZS90). The analyses were carried out at the Multiuser Centre of the Centre for Technological Sciences at Santa Catarina State University (CMU/CCT/UDESC).

## 5.4 DOPING CDS WITH RARE EARTHS

### 5.4.1 Materials

The rare-earth dopants employed in this study were cerium(III) nitrate hexahydrate  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and gadolinium(III) nitrate hexahydrate  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Cerium nitrate was obtained from Neon Comercial Ltda. (Brazil) with a purity of  $\geq 99.0\%$  and appeared as a white crystalline solid, fully soluble in water. Gadolinium nitrate was purchased from Sigma-Aldrich (product code: 211591-100G) with a trace metal basis purity of 99.9%, supplied as colorless to pale-yellow crystals or lumps. Commercial buffer solutions covering a wide pH range (pH 2–11) were used to investigate the effect of pH on the fluorescence behavior of the doped carbon dots.

The buffers consisted of citric acid/disodium phosphate (pH 3 and 5), potassium biphthalate/sodium hydroxide (pH 4), disodium phosphate/monobasic potassium phosphate (pH 7), boric acid/potassium chloride (pH 9 and 10), and disodium phosphate/sodium hydroxide (pH 11), all purchased from Neon (Brazil). Analytical standards of the agrochemicals glyphosate, mesotrione, amicarbazone, atrazine, imidacloprid, dicamba, diuron, and acephate were obtained from Sigma-Aldrich (Pestanal® grade), each with a minimum purity of 98%. All experiments involving these compounds were carried out at room temperature (25 °C) under identical conditions and performed in triplicate.

#### 5.4.2 Synthesis of Ce-CDs and Gd-CDs

To dope the CDs with rare earth elements, cerium and gadolinium were introduced via a one-step hydrothermal method, adapted from the procedure reported by Zhang *et al.* (2021). The optimized kinetic condition was applied, with a solid loading of 3% w/v, while varying the amount of dopant relative to the biomass precursor (rice husk) at three different ratios: 1:1, 1:0.5, and 1:0.25. These ratios corresponded to 3.0 g, 1.5 g, and 0.75 g of gadolinium (III) nitrate hexahydrate ( $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and cerium (III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), respectively. This experimental design aimed to determine the optimal dopant-to-biomass ratio that maximizes quantum yield.

The chosen proportions were inspired by the study of Zhang *et al.* (2021), who applied a similar hydrothermal approach using cerium nitrate hexahydrate as the dopant and citric acid as the carbon source, employing a precursor-to-dopant mass ratio of approximately 1.33:1. Given that the same rare earth salt was used in the present study and considering that rice husk is a carbon-rich biomass, comparable dopant levels were adopted and extended. This gradient allowed us to evaluate the balance between effective doping and the potential for luminescence quenching or structural disruption at higher dopant concentrations, consistent with observations in other lanthanide-doped carbon dots systems.

Following dopant addition, the mixtures were transferred into a 100 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 220 °C for 4 h. After cooling to room temperature, the resulting suspensions were centrifuged at 2000 rpm for 15 min to remove white precipitates. The clear brown supernatants containing Ce-CDs or Gd-CDs were collected and purified by dialysis (MWCO 1.0 kDa) for 72 h against ultrapure water to remove unreacted small molecules. The purified solutions were then freeze-dried under vacuum for 48 h to obtain the Ce-CD and Gd-CD powders, which were stored in sealed containers for subsequent characterization.

#### 5.5 SENSITIVITY AND SELECTIVITY OF THE CDS

Prior to the sensitivity and selectivity assays, the fluorescence response of the doped carbon dots was evaluated as a function of pH using buffered solutions in the

range of pH 2–11. Both Ce-CDs and Gd-CDs exhibited maximum fluorescence intensity and signal stability under mildly basic conditions. Therefore, all subsequent detection experiments were conducted at the pH corresponding to the highest and most stable fluorescence response, ensuring optimal sensor performance, signal reproducibility, and analytical reliability.

The selectivity and sensitivity tests of the CDs for agrochemicals followed the methodology described by Wang *et al.* (2016), with a few modifications. The following agrochemicals were tested: atrazine, imidacloprid, glyphosate, mesotrione, dicamba, diuron, amicarbazone and acephate. Stock solutions of agrochemicals were freshly prepared in ultrapure water at appropriate concentrations and stored at 4 °C protected from light for short periods when necessary. Working standard solutions were obtained by serial dilution of the stock solutions immediately prior to each fluorescence measurement. This procedure was adopted to minimize potential degradation effects, particularly for glyphosate, which is known to exhibit limited stability in aqueous media. All standard solutions were prepared on the same day of analysis and used under identical experimental conditions.

First, the fluorescence spectrum of the synthesized CDs solution was measured. The emission and excitation wavelengths were set at 445 nm and 360 nm, respectively. Subsequently, 1 mL of a 500 µmol/L solution of each agrochemical was added to 1 mL of the diluted CDs solution, and the fluorescence spectrum of the resulting mixture was recorded to assess fluorescence quenching. All compounds were evaluated at the same concentration and under a 1:1 volumetric ratio, ensuring equimolar and comparable conditions. This approach enabled a direct assessment of the selective fluorescence quenching behavior of the CDs toward the target analyte. The agrochemical compound that showed the greatest effect on the fluorescence extinction of the CDs was selected to determine the detection limit at different concentrations. The fluorescence of each pure agrochemical compound was also evaluated using a Tecan Infinite M200 microplate reader.

The sensitivity of the doped carbon dots toward the selected agrochemical was assessed by constructing a calibration curve based on fluorescence quenching. A series of standard solutions of the analyte were prepared at concentrations ranging

from 0.5  $\mu\text{mol/L}$  to 20.0  $\mu\text{mol/L}$ . The concentration range adopted for the sensitivity tests was selected to assess the ability of the doped carbon dots to detect low pesticide concentrations with high sensitivity. This interval simulates real contamination levels typically observed in environmental water samples and challenges the fluorescence sensor to operate near its detection limits. Moreover, the selected range aligns with the methodology reported by Yuan *et al.* (2018), who successfully applied carbon dot-based probes to detect glyphosate within the same concentration interval, demonstrating excellent linearity and low detection limits.

Subsequently, the relative fluorescence intensity  $(F_0 - F)/F_0$ , where  $F_0$  and  $F$  represent the emission intensity in the absence and presence of the analyte, respectively, was measured and plotted against the analyte concentration. In this context, the blank signal ( $F_0$ ) corresponds to the fluorescence intensity of the CDs solution without the addition of agrochemicals, measured under identical experimental conditions. The linear regression equation and the correlation coefficient ( $R^2$ ) were determined to assess the quenching efficiency. The limit of detection (LOD) was calculated according to the Stern–Volmer approach (Sasikumar *et al.*, 2024) based on Equation (10):

$$\text{LOD} = \frac{3\sigma}{k} \quad (10)$$

where  $\sigma$  is the standard deviation of blank measurements ( $N = 10$ ), and  $k$  is the slope of the calibration curve. All measurements were performed in triplicate at room temperature using an excitation wavelength of 360 nm.

The analytical sensitivity of the proposed sensors was evaluated based on the slope of the calibration curve, the limit of detection, and the linear response range, which are standard parameters for comparing fluorescence-based analytical methods. The overall analytical performance was assessed using calibration curves, triplicate measurements, relative standard deviations, and limits of detection. Although post hoc tests such as Tukey's test are commonly applied to compare mean values among multiple treatments, in this study the objective was not to compare discrete groups, but rather to evaluate the linear dependence between fluorescence quenching and analyte

concentration. Therefore, regression analysis combined with triplicate measurements and standard deviation was considered sufficient to validate the analytical performance of the proposed sensors.

## 5.6 APPLICATION OF DOPED CDS IN REAL SAMPLES

Recovery experiments were conducted to evaluate the practical applicability of the rare-earth-doped carbon dots in complex environmental matrices. Real water samples were collected from Lagoa da Conceição, located in Florianópolis, Santa Catarina, Brazil (27°33'38" S; 48°27'13" W), a natural freshwater body of high ecological and socioeconomic relevance. The selected sample sites are representative areas previously reported to contain emerging contaminants, including pharmaceuticals and personal care products, as described by Silva *et al.* (2025). These findings highlight the lagoon's susceptibility to anthropogenic pollution, making it a relevant matrix for evaluating the performance of rare-earth-doped carbon dots under realistic environmental conditions. Water sampling was conducted following standardized procedures for surface water collection, as described in the literature (APHA, 2017; Silva *et al.*, 2025), including the collection of surface water in pre-cleaned amber glass bottles, transport under refrigerated conditions, and storage at 4 °C prior to analysis to preserve sample integrity and representativeness.

The sampling campaign was carried out by Professor Silvani Verruck, from the Department of Food Science and Technology at the Federal University of Santa Catarina (UFSC). The standard addition method was employed to minimize matrix effects and ensure analytical accuracy, as widely adopted in the literature for similar applications in real water systems (Hashemi *et al.*, 2021; Khaledian *et al.*, 2021). Samples were spiked with known concentrations of glyphosate and mesotrione at levels of 1 µmol/L, 2 µmol/L, 5 µmol/L, 10 µmol/L, 15 µmol/L, and 20 µmol/L, allowing for evaluation across a broad dynamic range, following the procedure reported by Khaledian *et al.* (2021). Water collection was carried out at five distinct sites within the lagoon: Bar do Boni, Barra da Lagoa, Centrinho da Lagoa, Costa da Lagoa, and Rio Vermelho, to account for spatial variability and compositional differences.

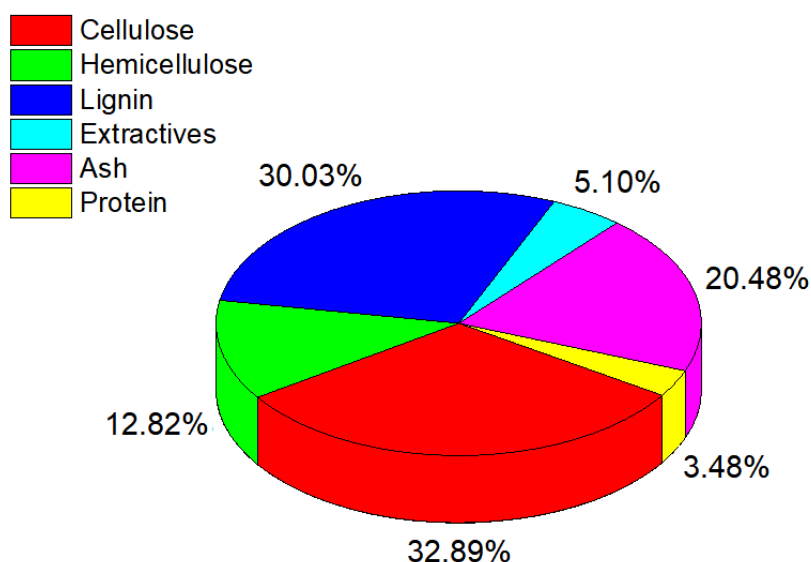
Subsequently, the samples were centrifuged at 4000 rpm for 30 min and filtered through 0.22  $\mu\text{m}$  cellulose acetate membranes, following the method used by Hashemi *et al.* (2021), to remove suspended solids and reduce background interference. The Ce-CDs and Gd-CDs were then dispersed into the enriched water samples and mixed. After a 1 min incubation at room temperature (25  $^{\circ}\text{C}$ ), the fluorescence emission was recorded at an excitation wavelength of 360 nm, following the detection methodology proposed by Chen *et al.* (2019). This procedure enabled a preliminary evaluation of the response of Ce-CDs and Gd-CDs in real water matrices, under controlled laboratory conditions. The recovery tests provided an initial indication of the behavior and analytical reliability of the doped CDs when exposed to complex environmental samples. Although performed under simulated conditions, these experiments represent an important step toward understanding the applicability of rare-earth-doped carbon dots in environmental analysis, particularly for the detection of agrochemical residues in natural waters.

## 6 RESULTS AND DISCUSSION

### 6.1 EFFECTS OF HYDROTHERMAL SYNTHESIS ON RICE HUSK COMPOSITION

This section presents and discusses the main experimental results obtained during the first stage of this study. Initially, the results of the experimental design and the kinetic study are addressed, highlighting the influence of synthesis parameters, such as temperature, solid loading, and reaction time, on biomass degradation and its conversion into CDs. Next, the CDs obtained under optimal conditions are thoroughly characterized using techniques such as XRD, FTIR, UV-Vis spectroscopy, fluorescence spectroscopy, TEM, and XPS. Finally, a plausible mechanism for CDs formation is proposed based on the chemical composition and degradation profile of the rice husk biomass. Before proceeding with the experimental design, the raw rice husk biomass was characterized in terms of its lignocellulosic composition, including cellulose, hemicellulose, lignin, and ash content (Figure 8).

Figure 8 – Chemical composition of the raw RH



Source: elaborated by the author (2025).

This initial analysis was essential for understanding the structural composition of the precursor and its potential influence on CDs formation. The composition was determined as follows:  $32.89\% \pm 0.52\%$  cellulose,  $12.82\% \pm 0.44\%$  hemicellulose

(comprising 12.4% arabinoxylan and 0.4% acetyl groups), 30.03%  $\pm$  0.54% lignin (comprising 22.3% insoluble lignin and 7.8% soluble lignin), 5.10%  $\pm$  0.64% extractives, 20.48%  $\pm$  0.50% total ash (comprising 2.9% acid-soluble ash and 17.6% acid-insoluble ash), and 3.48%  $\pm$  0.15% protein. These results are consistent with the findings of Wang *et al.* (2016), who reported that rice husks contain approximately 72% – 85% organic matter, including cellulose, hemicellulose, and lignin.

Table 5 shows the effects of hydrothermal synthesis on the chemical composition of the solid fraction under each experimental condition. Temperature notably influenced the structure of the biomass polysaccharides. When the temperature reached around 220.36 °C, only 19.01% of cellulose remained in the solid fraction, with no hemicellulose and a high concentration of residual lignin and ash. This indicated that 64% of the glucan and 100% of the xylan were solubilized into the liquid fraction. A similar trend is observed for temperatures exceeding 210 °C, resulting in higher polysaccharide removal yields in the solid fraction. On the other hand, there was a greater preservation of the polysaccharide structure of RH at lower temperatures. For instance, in run 5 (149.64 °C and 10% w/v), total preservation of glucan and low depolymerization of xylan was observed, resulting in percentages of 39.23% and 11.01% for cellulose and hemicellulose, respectively. At temperatures between 160 °C and 185 °C, cellulose ranged from 30% to 45%, while hemicellulose ranged from 2% - 11%. As expected, the hydrothermal reactions were the most effective at solubilizing the hemicellulose fraction, resulting in the lowest percentages of this fraction in the structural composition and achieving the highest removal yields.

According to Rosas Vega *et al.* (2023), water ionization occurs during high-temperature and high-pressure hydrothermal reactions, leading to the formation of hydronium ions. These ions are responsible for initiating the depolymerization of polysaccharides by selectively hydrolyzing heterocyclic ether linkages and cleaving acetyl groups. Furthermore, as noted by Santana *et al.* (2023), the organic acids released during this process catalyze the hydrolysis of polysaccharide fractions, particularly hemicellulose, and, depending on the severity factor, may also contribute to the hydrolysis of cellulose.

Table 5 – Chemical characterization of the solid fraction in all runs and the subsequent recovery of solids and polysaccharides

| Experimental Design |                  |                         | Contents in Recovered Solid (%) |               |              |              | Removal Yield (%) |        |        |        |       |
|---------------------|------------------|-------------------------|---------------------------------|---------------|--------------|--------------|-------------------|--------|--------|--------|-------|
| Run                 | Temperature (°C) | SL in dry basis % (w/w) | Cellulose                       | Hemicellulose | Lignin       | Ashes        | Solid             | Glucan | Xylan  | Lignin | ROC*  |
| 1                   | 160.00 (-1)      | 5.00 (-1)               | 45.72 ± 1.31                    | 6.79 ± 0.02   | 30.26 ± 1.87 | 20.30 ± 0.05 | 26.97             | 0.56   | 61.35  | 26.41  | 32.14 |
| 2                   | 210.00 (1)       | 5.00 (-1)               | 37.15 ± 1.64                    | 0.00 ± 0.00   | 39.66 ± 0.13 | 24.61 ± 0.90 | 38.80             | 33.04  | 100.00 | 16.15  | 46.90 |
| 3                   | 160.00 (-1)      | 15.00 (1)               | 43.43 ± 0.49                    | 7.29 ± 0.25   | 29.03 ± 1.04 | 22.55 ± 0.65 | 23.92             | 0.35   | 56.72  | 26.45  | 28.35 |
| 4                   | 210.00 (1)       | 15.00 (1)               | 28.29 ± 0.75                    | 0.00 ± 0.00   | 39.78 ± 0.40 | 33.11 ± 0.09 | 31.59             | 41.15  | 100.00 | 9.37   | 44.77 |
| 5                   | 149.64 (-α)      | 10.00 (0)               | 39.23 ± 1.33                    | 11.01 ± 0.55  | 27.30 ± 1.30 | 25.57 ± 0.10 | 20.34             | 4.98   | 31.61  | 27.59  | 26.75 |
| 6                   | 220.36 (α)       | 10.00 (0)               | 19.01 ± 1.29                    | 0.00 ± 0.00   | 48.56 ± 1.15 | 35.48 ± 1.22 | 37.72             | 64.00  | 100.00 | 0.00   | 50.38 |
| 7                   | 185.00 (0)       | 2.93 (-α)               | 32.47 ± 2.98                    | 2.33 ± 0.03   | 32.03 ± 3.11 | 38.96 ± 0.14 | 32.40             | 33.25  | 92.81  | 57.75  | 46.42 |
| 8                   | 185.00 (0)       | 17.07 (α)               | 44.89 ± 2.17                    | 2.37 ± 0.02   | 32.86 ± 1.38 | 23.22 ± 0.14 | 26.77             | 0.06   | 85.78  | 15.85  | 32.43 |
| 9                   | 185.00 (0)       | 10.00 (0)               | 30.77 ± 0.24                    | 1.91 ± 0.03   | 30.49 ± 1.34 | 38.03 ± 1.81 | 25.98             | 33.36  | 90.55  | 17.48  | 44.69 |
| 10                  | 185.00 (0)       | 10.00 (0)               | 31.07 ± 0.43                    | 1.87 ± 0.02   | 31.88 ± 0.73 | 38.72 ± 0.34 | 26.57             | 30.62  | 89.30  | 22.04  | 43.55 |
| 11                  | 185.00 (0)       | 10.00 (0)               | 29.61 ± 0.68                    | 1.64 ± 0.01   | 33.48 ± 2.31 | 38.00 ± 1.22 | 26.38             | 33.72  | 90.60  | 17.92  | 44.99 |

Notes: \*ROC (Removal of Organic Compounds) – Dependent variable used as a response in the experimental design.

Source: elaborated by the author (2024).

According to Santana *et al.* (2024), the resulting fragments undergo chemical transformations during hydrothermal reactions, evolving into simpler, low-molecular-weight molecules, including celooligosaccharides and arabino-xilooligosaccharides. These molecules can then be converted into glucose, xylose, and arabinose. Finally, these molecules may transform into hydroxymethylfurfural and furfural. These compounds can further dehydrate to form aromatic carbonaceous structures, constituting R-CDs' backbone as reported by Zhang *et al.* (2022).

With its high carbon content, lignin plays a crucial role in producing carbon dots. The hydrothermal syntheses demonstrated that a portion of the lignin solubilized into the liquid phase, with solubilization rates ranging from 0% to 58%. The highest lignin removal yield (57.75%) was achieved in Run 7, which used the lowest solid load, while the lowest removal was observed at temperatures above 200 °C. Interestingly, higher removal yields were recorded at lower temperatures (149.64 °C - 185 °C), likely due to the degradation of unstable lignin components into smaller, soluble molecules, facilitating quantification under milder conditions. In the case of rice husk (RH), unstable components represent 7.8% of the lignin (acid-soluble), which may be solubilized during hydrothermal synthesis. In contrast, at higher temperatures and pressures, the more stable regions of lignin (22.3% insoluble lignin), along with other organic molecules present in the biomass (such as proteins, extracts, cellulose, and hemicellulose), are converted into a thermally stable solid monolith, as reported by Jothi *et al.* (2021) and Park *et al.* (2018).

These monoliths are subsequently identified as "lignin" in the chemical characterization of the streams, which may influence the quantification of lignin removal, as described by Santana *et al.* (2024). Organic compounds present in the raw RH include the protein fraction (3.48%) and the extractives fraction (5.10%), which could have been converted into R-CDs since the presence of these compounds was not detected in the analyzed runs. According to Zhang *et al.* (2022), in hydrothermal synthesis, proteins can undergo amino acid decarboxylation, producing carbonic acids and amines. Furthermore, amino acid deamination generates ammonia and organic acids, which can be precursors in generating R-CDs.

## 6.2 EFFECTS OF HYDROTHERMAL SYNTHESIS ON THE SOLUBILIZATION OF COMPOUNDS

The results of the chemical composition of the liquid fraction, including total sugars (TS), degradation compounds (DC), and the severity factor after hydrothermal synthesis, are presented in Table 6. Quantified degradation compounds exhibited higher levels compared to sugars in most runs. The hemicellulose polysaccharide chain is more sensitive to hydrothermal synthesis and, therefore, more easily hydrolyzed. Due to this effect, the concentration of furfural showed higher levels than xylose in runs conducted at temperatures above 185 °C.

This phenomenon may be related to the severity level to which RH has been subjected and its positive impact on the formation of quantum compounds (Wareing, Gentile e Phan, 2021). According to Santana *et al.* (2024), under harsher conditions, xylan was degraded entirely, and over time, xylose underwent dehydration to form anhydrous xylose, which was subsequently oxidized to generate furfural. In parallel, condensation, chain fragmentation, and chain-forming reactions may occur to produce cyclic compounds. According to Jingmiao *et al.* (2022), these compounds subsequently undergo polymerization and condensation, forming aromatics with oxygen-containing functional groups, which can serve as precursors to carbon dots.

Low concentrations of glucose and cellobiose, derived from the cellulose structure of RH, were observed in the liquid fraction after hydrothermal synthesis. Cellulose experienced the least depolymerization among the polysaccharides, but as indicated in Table 6, considerable degradation of this polysaccharide occurred under more severe conditions. The phenomenon observed in the hemicellulose fraction may extend to the cellulose fraction, where low sugar concentrations can positively influence the production of carbon dots. Like what was observed with xylose, glucose units may have been converted into HMF, which was then further dehydrated into aromatic carbonaceous structures, contributing to the carbon backbone of carbon dots. According to Papaioannou *et al.* (2018), glucose is isomerized into fructose, which then undergoes dehydration through the elimination of three water molecules to form HMF. This compound is subsequently dehydrated and polymerized into small polymeric nano agglomerates, leading over time to the formation of carbonaceous spheres.

At the reaction temperature of 149 °C, the system exhibited the highest pH value among all tested conditions. This behavior can be attributed to the limited degradation of lignocellulosic components of the rice husk under milder thermal conditions. At lower temperatures, the hydrolysis and subsequent formation of low molecular weight carboxylic acids (such as acetic acid, formic acid, and lactic acid) is less pronounced. Consequently, there is reduced acidification of the reaction medium, which results in a higher final pH. In contrast, at higher reaction temperatures (e.g., 185 °C to 220 °C), the enhanced breakdown of cellulose and hemicellulose leads to a greater release of acidic degradation products, promoting acidification and lowering the pH of the system. Therefore, the higher pH at 149 °C reflects a system in which less thermal decomposition has occurred, indicating reduced solubilization of organic matter and minimal formation of acidic intermediates. This observation aligns with studies on hydrothermal processing of lignocellulosic biomass, where the extent of acid formation and medium acidification is strongly dependent on temperature and residence time (Li *et al.* 2017).

Table 6 – Analyzing the chemical composition of the liquid fraction in terms of sugar content, degradation compounds, quantum yield, and severity factor for each run

| Experimental Design |                     |                               | Compounds<br>(g/L) |             |             |             |             |                |             |             | Yield<br>(%, w/w) |       | Severity Factor |      |
|---------------------|---------------------|-------------------------------|--------------------|-------------|-------------|-------------|-------------|----------------|-------------|-------------|-------------------|-------|-----------------|------|
| Run                 | Temperature<br>(°C) | SL in Dry<br>Basis %<br>(w/v) | Cellobiose         | Glucose     | Xylose      | Arabinose   | Acetic acid | Formic<br>acid | HMF         | Furfural    | ST                | DC*   | ln (Ro)         | pH   |
| 1                   | 160.00 (-1)         | 5.00 (-1)                     | 0.86 ± 0.01        | 0.35 ± 0.00 | 2.68 ± 0.01 | 0.56 ± 0.00 | 1.52 ± 0.00 | 0.46 ± 0.01    | 0.07 ± 0.00 | 0.36 ± 0.01 | 10.54             | 10.54 | 4.22            | 3.65 |
| 2                   | 210.00 (1)          | 5.00 (-1)                     | 0.08 ± 0.00        | 0.19 ± 0.04 | 0.01 ± 0.00 | 0.56 ± 0.00 | 2.66 ± 0.01 | 0.77 ± 0.01    | 0.78 ± 0.01 | 0.34 ± 0.00 | 3.68              | 19.91 | 5.62            | 3.46 |
| 3                   | 160.00 (-1)         | 15.00 (1)                     | 2.29 ± 0.02        | 0.75 ± 0.00 | 5.17 ± 0.04 | 1.09 ± 0.01 | 4.38 ± 0.01 | 1.10 ± 0.01    | 0.18 ± 0.00 | 1.08 ± 0.00 | 13.56             | 9.83  | 4.23            | 3.78 |
| 4                   | 210.00 (1)          | 15.00 (1)                     | 0.17 ± 0.01        | 0.34 ± 0.02 | 0.17 ± 0.01 | 1.14 ± 0.03 | 7.29 ± 0.28 | 1.37 ± 0.09    | 1.31 ± 0.00 | 1.48 ± 0.00 | 2.65              | 16.70 | 5.63            | 3.54 |
| 5                   | 149.64 (-α)         | 10.00 (0)                     | 1.40 ± 0.01        | 0.33 ± 0.00 | 1.51 ± 0.00 | 1.10 ± 0.01 | 1.82 ± 0.00 | 0.56 ± 0.01    | 0.04 ± 0.00 | 0.24 ± 0.01 | 9.49              | 5.82  | 3.86            | 3.91 |
| 6                   | 220.36 (α)          | 10.00 (0)                     | 0.18 ± 0.07        | 0.38 ± 0.00 | 0.13 ± 0.03 | 1.62 ± 0.18 | 5.71 ± 0.24 | 1.07 ± 0.12    | 1.11 ± 0.00 | 1.27 ± 0.01 | 5.05              | 20.04 | 5.93            | 3.37 |
| 7                   | 185.00 (0)          | 2.93 (-α)                     | 0.06 ± 0.00        | 0.20 ± 0.00 | 0.14 ± 0.00 | 0.05 ± 0.00 | 0.94 ± 0.00 | 0.44 ± 0.00    | 0.53 ± 0.00 | 0.92 ± 0.00 | 3.36              | 21.13 | 4.91            | 3.46 |
| 8                   | 185.00 (0)          | 17.07 (α)                     | 0.20 ± 0.00        | 0.45 ± 0.00 | 0.56 ± 0.00 | 0.15 ± 0.00 | 7.45 ± 0.01 | 1.84 ± 0.00    | 0.97 ± 0.00 | 1.41 ± 0.02 | 1.74              | 14.96 | 4.92            | 3.55 |
| 9                   | 185.00 (0)          | 10.00 (0)                     | 0.27 ± 0.01        | 0.48 ± 0.01 | 0.56 ± 0.01 | 0.16 ± 0.00 | 4.49 ± 0.02 | 1.27 ± 0.01    | 0.74 ± 0.01 | 1.15 ± 0.00 | 3.22              | 16.74 | 4.91            | 3.56 |
| 10                  | 185.00 (0)          | 10.00 (0)                     | 0.26 ± 0.00        | 0.48 ± 0.00 | 0.56 ± 0.00 | 0.16 ± 0.00 | 4.41 ± 0.00 | 1.26 ± 0.00    | 0.74 ± 0.00 | 1.12 ± 0.01 | 3.19              | 16.47 | 4.93            | 3.58 |
| 11                  | 185.00 (0)          | 10.00 (0)                     | 0.24 ± 0.02        | 0.46 ± 0.02 | 0.56 ± 0.03 | 0.15 ± 0.01 | 4.00 ± 0.04 | 1.17 ± 0.04    | 0.70 ± 0.00 | 1.41 ± 0.00 | 3.08              | 15.93 | 4.94            | 3.55 |

Notes: \*DC (Degradation compounds) - Dependent variable used as a response in experimental design.

Source: elaborated by the author (2024).

During the synthesis of R-CDs from lignocellulosic biomass, the concentration of degradation compounds generated by the thermal decomposition of macromolecules (cellulose, hemicellulose, and lignin) is critical. Under high-temperature conditions, biomass is decomposed into smaller intermediates, such as sugars and degradation compounds, which serve as precursors for CD formation. The efficiency of CD nucleation and growth is directly related to the concentration of these intermediates, impacting the conversion of biomass into R-CDs. Therefore, understanding the phenomena involved in hydrothermal synthesis, such as organic compound removal (ROC) and degradation compound formation (DC), is essential for optimizing reaction parameters and maximizing the transformation of biomass into R-CDs.

Table 7 presents the effects of temperature and solid load on removing organic compounds (ROC) and forming degradation compounds (DC) during hydrothermal synthesis. It is observed that, for all analyzed models, the ROC and DC variables were highly significant ( $p < 0.001$ ) and did not exhibit a lack of fit ( $p \leq 0.05$ ). Furthermore, the model explained over 95% of the data variability, with an adjusted R-squared greater than 93%, indicating a good fit to the experimental data.

Regarding the model effects on ROC, temperature showed positive linear ( $X_1$ ) effects and negative quadratic effects ( $X_1^2$ ). Conversely, solid load had a notably negative effect on ROC, both linear ( $X_2$ ) and quadratic ( $X_2^2$ ). Overall, this indicates that higher temperatures can greatly enhance the removal of organic compounds from rice husks. In contrast, the model indicates that higher solid loads tend to decrease the efficiency of organic compound removal from rice husk. For the formation of degradation compounds (DC) in the reaction medium during hydrothermal synthesis, the model showed that the linear regression coefficient for temperature ( $X_1$ ) had significantly positive effects. In contrast, solid load exhibited negative linear and quadratic effects on DC formation, like its impact on ROC. The effects of temperature and solid load on ROC and DC are illustrated on the response surface presented in Figure 9.

Table 7 – Influences of the independent variables temperature ( $X_1$ ) and solid load ( $X_2$ ) on quantum yield in hydrothermal processing

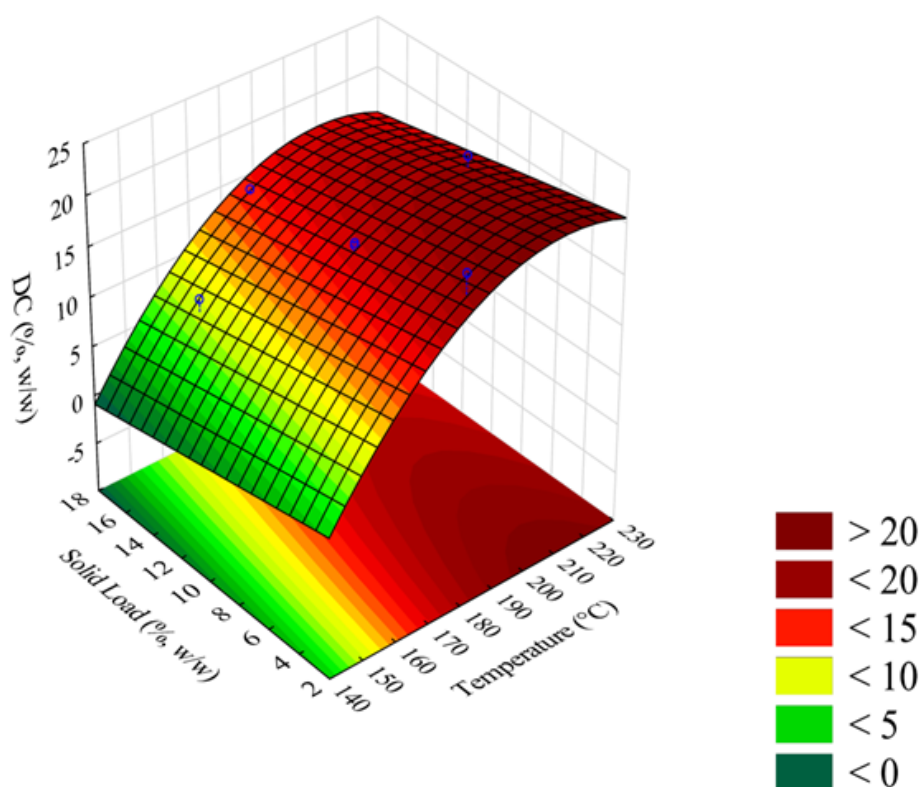
| Response Variable | Factors                      | Regression Coefficient | Standard Error | t-value | p-value | -95%  | 95%   |
|-------------------|------------------------------|------------------------|----------------|---------|---------|-------|-------|
| ROC<br>%, w/w     | Constant                     | 44.410                 | 1.25           | 35.40   | 0.000   | 41.34 | 47.48 |
|                   | $X_1$                        | 8.070                  | 0.77           | 10.51   | 0.000   | 6.20  | 9.95  |
|                   | $X_1^2$                      | -3.160                 | 0.91           | -3.46   | 0.014   | -5.40 | -0.92 |
|                   | $X_2$                        | -3.210                 | 0.77           | -4.18   | 0.006   | -5.09 | -1.33 |
|                   | $X_2^2$                      | -2.730                 | 0.91           | -2.99   | 0.024   | -4.97 | -0.49 |
|                   | $R^2$                        | 0.960                  |                |         |         |       |       |
|                   | $P - value$<br>(model)       | <0.001                 |                |         |         |       |       |
|                   | $P - value$<br>(lack of fit) | 0.080                  |                |         |         |       |       |
|                   |                              |                        |                |         |         |       |       |
| DC<br>%, w/w      | Constant                     | 16.870                 | 0.53           | 31.63   | 0.000   | 15.61 | 18.13 |
|                   | $X_1$                        | 4.540                  | 0.45           | 10.12   | 0.000   | 3.48  | 5.61  |
|                   | $X_1^2$                      | -2.190                 | 0.51           | -4.29   | 0.004   | -3.40 | -0.98 |
|                   | $X_2$                        | -1.580                 | 0.45           | -3.52   | 0.010   | -2.64 | -0.52 |
|                   | $R^2$                        | 0.950                  |                |         |         |       |       |
|                   | $P - value$ (model)          | <0.001                 |                |         |         |       |       |
|                   | $P - value$<br>(lack of fit) | 0.074                  |                |         |         |       |       |

Source: elaborated by the author (2024).

As reported by Santana *et al.* (2023), high solid loads can adversely affect removal of organic compounds and degradation compounds yields due to heat and mass transfer limitations, leading to medium saturation during hydrothermal synthesis,

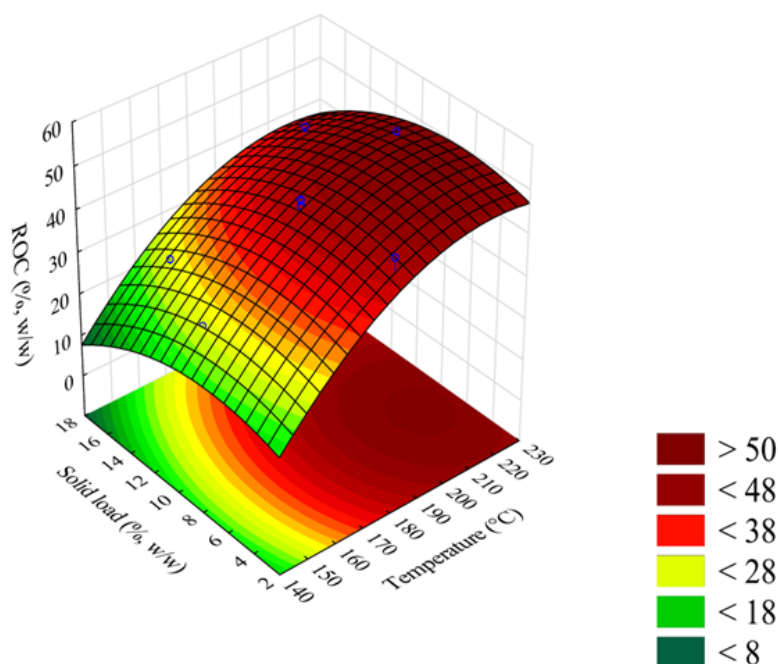
as demonstrated in Table 7. However, these limitations can be mitigated by increasing the temperature, which considerably enhances the decomposition of RH. Statistical analysis reveals that optimal conditions are achieved with low solid loads (3% w/v) and high temperatures (220 °C), maximizing the yields of the response variables in the reaction medium: degradation compounds (Figure 9) and removal of organic compounds (Figure 10). These results corroborate the findings of Wongso *et al.* (2021), who indicated that higher temperatures, up to 225 °C, are ideal for efficient carbonization, resulting in carbon dots with enhanced fluorescent properties. Thus, optimal conditions of high temperature and lower biomass load promote more uniform degradation, facilitating mass transfer and the formation and growth of R-CDs.

Figure 9 – Response surface generated from the CCRD as a function of temperature and solids charge for degradation compounds



Source: elaborated by the author (2024).

Figure 10 – Response surface generated from the CCRD as a function of temperature and solids charge for removal of organic compounds



Source: elaborated by the author (2024)

Following optimization, the ideal condition (220 °C – 3% w/v) was subjected to a kinetic study to evaluate the release profile of degradation compounds (DC), total solids (TS), and (quantum yield) QY over time. During this phase, the profile of sugars and degradation compounds was monitored regarding yield and concentration. Additionally, an analysis based on the severity factor was conducted to assess the impact of experimental conditions.

### 6.3 KINETICS OF HYDROTHERMAL SYNTHESIS FOR THE FORMATION OF R-CDS

The concentration and yield of total solids (TS) solubilized in the reaction medium during the kinetic study varied from 0.51 g/L and 3.72% w/w at 0 h (Figure 11a). As the exposure time at 220 °C increased, there was a gradual decrease in TS levels, reaching 0.11 g/L and 0.80% w/w by the end of the 12 h reaction period. Additionally, among all the sugars, xylose, derived from hemicellulose, was undetectable after 4 h. Similarly, cellobiose, a sugar derived from cellulose, was no longer detectable after 8 h. This trend can be attributed to the preferential degradation

of hemicellulose during hydrothermal synthesis, which solubilizes this polysaccharide into its monomers early in the reaction. Over time, xylose was further degraded, subsequently appearing as furfural. A similar trend of decreasing TS with time was observed by Santana *et al.* (2023) in the hydrothermal synthesis of tobacco stems.

The R-CDs showed no significant differences in their average concentrations throughout kinetic study, as shown in Table 8 and Figure 11b. This indicates that the R-CDs levels remained stable over the entire kinetic period. Acetic acid was the predominant compound, starting at 0.83 g/L and 6.02% w/w at 0 h, and increasing to 1.64 g/L and 11.96% w/w after 12 h. Acetic acid, like xylose, is derived from hemicellulose, which may explain its high concentration at all time points in the kinetics. The kinetics of R-CDs formation were investigated to assess how reaction time (ranging from 0 h to 12 h) affects the quantum yield. The analysis revealed a parabolic decreasing trend in the relationship between reaction time and QY, as shown in Figure 11c. Initially, the QY increases gradually, reaching a maximum value of  $19.28 \pm 0.28$  after 8 h of reaction (Table 8). However, a notable reduction is observed beyond this point, with the QY decreasing to  $4.95 \pm 1.31$  after 12 h of reaction. A series of interrelated factors can explain this pattern.

At the beginning of the reaction, the high temperature of 220 °C promotes the thermal degradation of the organic constituents present in rice husk, such as cellulose, hemicellulose, and lignin, breaking these macromolecules into smaller molecules and forming a carbonized material. According to CDs Luo *et al.* (2022), these carbonized molecules aggregate, giving rise to the initial R-. According to Kang *et al.* (2020), during this initial formation, functional groups such as hydroxyls (-OH) and carboxyls (-COOH) can attach to the CD structure, passivating its surface and enhancing its optical properties, which contributes to the increase in quantum yield (QY) and stability. The observed behavior is consistent with the findings of Li *et al.* (2024), where the biomass composition influenced the fluorescence properties of the carbon dots following hydrothermal treatment.

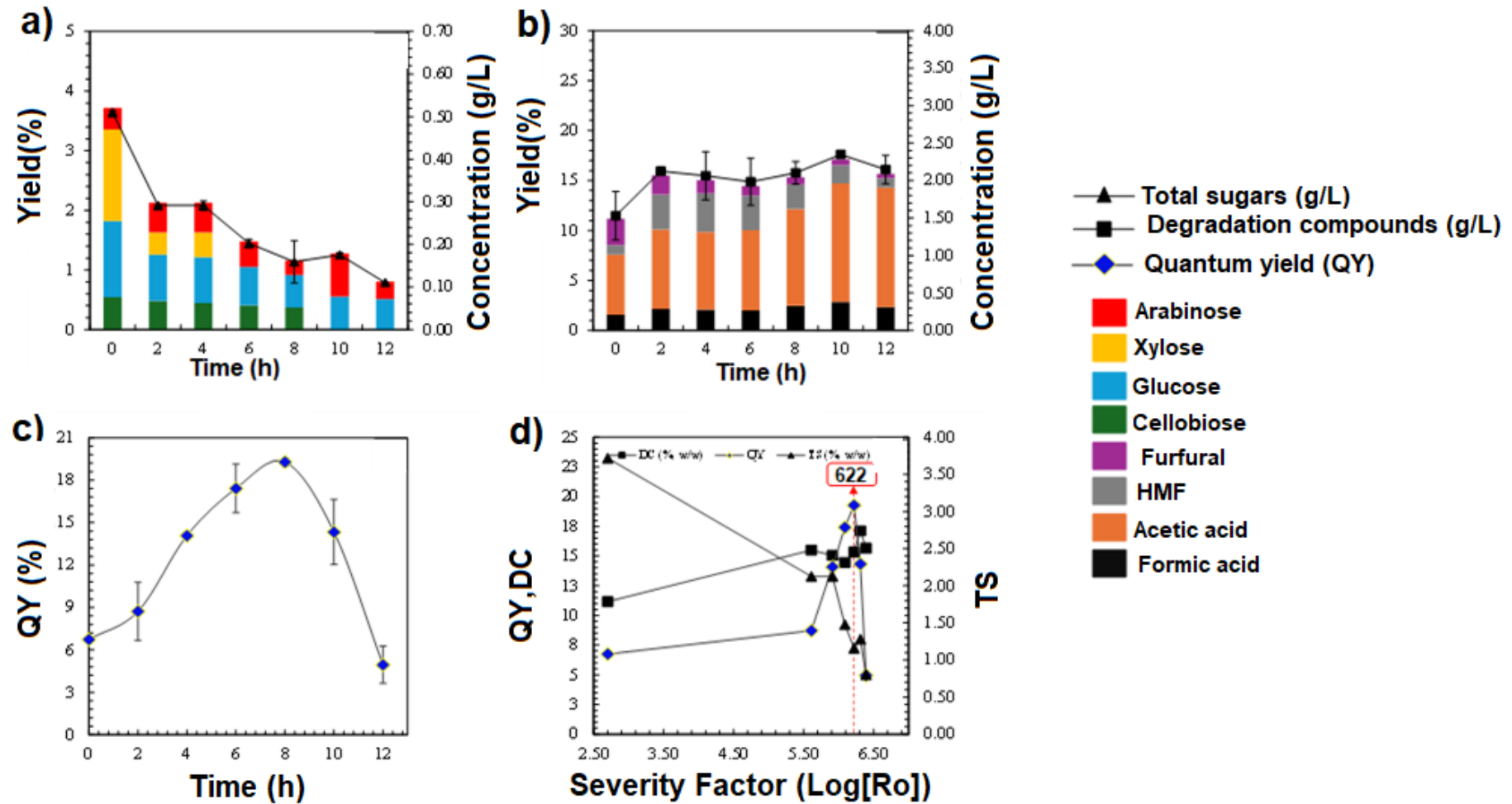
The decline in QY after 8 h of reaction can be attributed to the prolonged reaction time, which leads to the degradation of the formed R-CDs. Continuous exposure to high temperatures can cause bond rupture, resulting in the fragmentation

of the R-CDs and the loss of their luminescent properties as corroborated by Khavlyuk *et al.* (2021). The thermal degradation of R-CDs can lead to the formation of structural defects that act as trapping centers for excited electrons. As the size of the R-CDs increases, these defects become more prevalent, facilitating the trapping of non-radiative electrons. This process reduces the probability of photon emission, thereby decreasing both the particles' QY and the excited-state lifetime, as observed by Barman and Patra (2018).

Prolonged reaction times can also promote the aggregation of R-CDs, leading to the formation of larger aggregates. As highlighted by Zhou *et al.* (2017), these larger aggregates have a reduced surface area, which diminishes light interaction and, consequently, the QY of the R-CDs. QY for reaction times of 4 h, 6 h, 8 h, and 10 h did not show significant differences ( $p \leq 0.05$ ), suggesting that 4 h is the optimal synthesis condition (220 °C – 3% w/v), considering cost, practicality, and scalability. These findings are consistent with previous studies that achieved effective carbon dot synthesis under similar reaction times, as reported by De and Karak (2013) and Wang *et al.* (2017).

Therefore, based on the findings of Yang, Tao, and Wyman (2018), the severity factor is an important parameter for evaluating the intensity of hydrothermal synthesis processes, offering insights into how temperature and time conditions influence reactivity and efficiency. This parameter enables the determination of optimal conditions from a single variable, facilitating process scaling. As illustrated in Figure 11d, the concentration of TS decreases as the severity factor increases, while the levels of DC and QY increase correspondingly. When the severity factor reaches 6.22, indicating the optimal process conditions, the highest QY is observed, associated with a low concentration of TS and a plateau in DC levels. Therefore, the optimum kinetic condition was reached with 4 h of reaction, 220 °C and 3% w/v solid charge. The R-CDs obtained from this condition were dialyzed and subjected to characterization. Details of which will be presented in the following section.

Figure 11 – Analysis of a) total sugars; b) yields of degradation compounds; c) kinetic behavior of quantum yield as a function of reaction time; and d) severity factor



Source: elaborated by the author (2024).

Table 8 – Chemical composition of the liquid fraction in terms of sugar content, degradation compounds, quantum yield, and severity factor for each run

| Kinetic Condition |          | Compounds (g/L) |           |           |           |           |           |           |           | Yield                    |                        |                         | Severity Factor |           |
|-------------------|----------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--------------------------|------------------------|-------------------------|-----------------|-----------|
| Temperature (°C)  | Time (h) | Cellobiose      | Glucose   | Arabinose | Xylose    | Acetic    | Formic    | HMF       | FF        | QY                       | TS (% w/w)             | DC (% w/w)              | pH(Φ)           | ln(Ro)    |
| 220               | 0        | 0.07±0.01       | 0.18±0.00 | 0.05±0.00 | 0.21±0.01 | 0.83±0.19 | 0.22±0.05 | 0.13±0.02 | 0.36±0.06 | 6.74±0.17 <sup>a</sup>   | 3.73±0.03 <sup>a</sup> | 11.16±2.37 <sup>a</sup> | 3.49±0.01       | 2.70±0.03 |
|                   | 2        | 0.07±0.00       | 0.11±0.00 | 0.07±0.00 | 0.05±0.00 | 1.09±0.03 | 0.30±0.00 | 0.48±0.00 | 0.26±0.02 | 8.72±2.06 <sup>ac</sup>  | 2.13±0.01 <sup>b</sup> | 15.49±0.34 <sup>a</sup> | 3.48±0.02       | 5.61±0.02 |
|                   | 4        | 0.06±0.00       | 0.11±0.01 | 0.07±0.00 | 0.06±0.00 | 1.07±0.18 | 0.29±0.04 | 0.53±0.06 | 0.18±0.04 | 14.08±0.19 <sup>bc</sup> | 2.13±0.08 <sup>b</sup> | 15.05±2.34 <sup>a</sup> | 3.36±0.01       | 5.91±0.02 |
|                   | 6        | 0.06±0.00       | 0.09±0.00 | 0.06±0.00 | 0.00±0.00 | 1.10±0.20 | 0.27±0.04 | 0.48±0.06 | 0.13±0.01 | 17.41±1.70 <sup>b</sup>  | 1.48±0.07 <sup>c</sup> | 14.46±2.30 <sup>a</sup> | 3.32±0.01       | 6.09±0.01 |
|                   | 8        | 0.05±0.00       | 0.07±0.00 | 0.03±0.05 | 0.00±0.00 | 1.33±0.11 | 0.34±0.02 | 0.33±0.01 | 0.10±0.01 | 19.28±0.28 <sup>b</sup>  | 1.16±0.36 <sup>c</sup> | 15.35±1.10 <sup>a</sup> | 3.33±0.03       | 6.22±0.02 |
|                   | 10       | 0.00±0.00       | 0.08±0.00 | 0.10±0.00 | 0.00±0.00 | 1.63±0.04 | 0.39±0.00 | 0.25±0.00 | 0.08±0.00 | 14.33±2.30 <sup>bc</sup> | 1.28±0.04 <sup>c</sup> | 17.12±0.36 <sup>a</sup> | 3.33±0.01       | 6.31±0.01 |
|                   | 12       | 0.00±0.00       | 0.07±0.00 | 0.04±0.00 | 0.00±0.00 | 1.64±0.17 | 0.32±0.02 | 0.13±0.01 | 0.06±0.00 | 4.95±1.31 <sup>a</sup>   | 0.80±0.01 <sup>d</sup> | 15.66±1.37 <sup>a</sup> | 3.30±0.01       | 6.39±0.00 |

Notes: Data are expressed as mean ± SD (n = 3). Values followed by the same superscript letters do not differ (ANOVA, followed by Tukey's test;  $p \leq 0.05$ ).

Different superscript Note: letters indicate significant differences ( $p \leq 0.05$ ).

Source: elaborated by the author (2024).

## 6.4 CHARACTERIZATION OF CDs

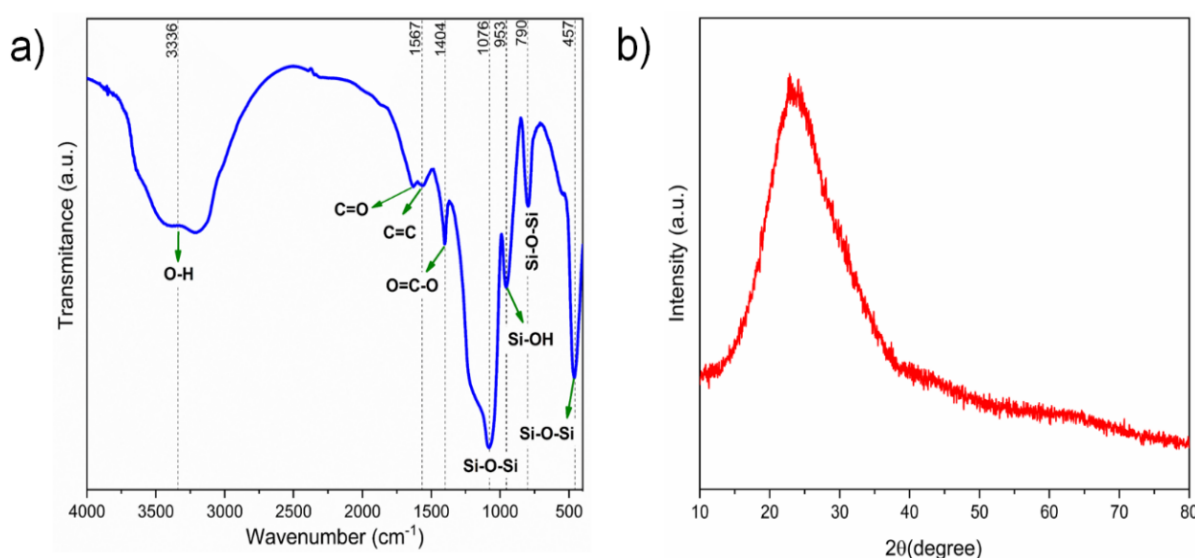
Figure 12a shows the infrared spectra of the R-CDs. The band around  $1567\text{ cm}^{-1}$  is characteristic of the stretching vibrations of non-conjugated linear alkenes ( $\text{C} = \text{C}$ ). According to Xu *et al.* (2015), the band in this spectrum region confirms the presence of graphitic carbon, of the  $sp^2$  domains of the carbon in the structure of R-CDs. The oxygen-containing functional groups were also identified in the region around  $1076\text{ cm}^{-1}$  spectra, related to the  $\text{C} - \text{O} - \text{C}$  stretching vibration in alcohols,  $1636\text{ cm}^{-1}$  related to the  $\text{C} = \text{O}$  bonds, and  $1404\text{ cm}^{-1}$  related to the  $\text{O} = \text{C} - \text{O}$  bonds. These results are in line with recent studies reported by Xu *et al.* (2015) and Xu *et al.* (2023).

In the study by Bose *et al.* (2018), it is mentioned that the thermal decomposition of rice husk may not eliminate the silicon content, allowing part of this element to be incorporated into the structure of the R-CDs. This is supported by the spectra recorded between  $1000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$ , which reveals evidence of the residual presence of silicon derived from the rice husk. For this reason, according to Basri *et al.* (2021); and Wang *et al.* (2017), the bands in  $790\text{ cm}^{-1}$  and  $457\text{ cm}^{-1}$  correspond to the asymmetric stretching vibration of the  $\text{Si} - \text{O} - \text{Si}$  bonds and the band in  $953\text{ cm}^{-1}$  refers to the  $\text{Si} - \text{OH}$  bond. As seen in the biomass characterization, the main constituents of rice husks are cellulose (28.59%), lignin (30.03%), and ash (20.48%). The main ash component is silicon dioxide ( $\text{SiO}_2$ ), which the band corroborates in this region, as reported by Feng *et al.* (2024) and Basri *et al.* (2021).

Figure 12b shows the diffractogram of the synthesized carbon dots, in which it is possible to confirm the amorphous nature using the broad peak at  $2\theta = 23.4^\circ$  attributed to reflection from the (0 0 2) plane and an interlayer spacing of 0.379 nm. As the interlayer distance of the carbon dots obtained (0.379 nm) is greater than that of graphite (0.335 nm), it can be inferred that the R-CDs do not have a typical graphitic structure and are not very crystalline *in nature*, as observed in the diffractogram. This difference in interplanar distance suggests that R-CDs have a different structural organization, with a lower degree of crystalline order than graphite. This behavior may be associated with the chemical composition of the rice husk used in the synthesis, as well as the formation of amorphous polymeric structures derived from carbohydrates and lignin during the hydrothermal reaction, as reported by Gomide *et al.* (2020) and

Pham *et al.* (2024). Similar interlayer distance values for R-CDs synthesized from rice husk biomass were obtained by Mahmoud, Fekry, and Abdelfattah (2020), and Pandey *et al.* (2014), with reported values of 0.377 nm, 0.370 nm, and 0.400 nm, respectively.

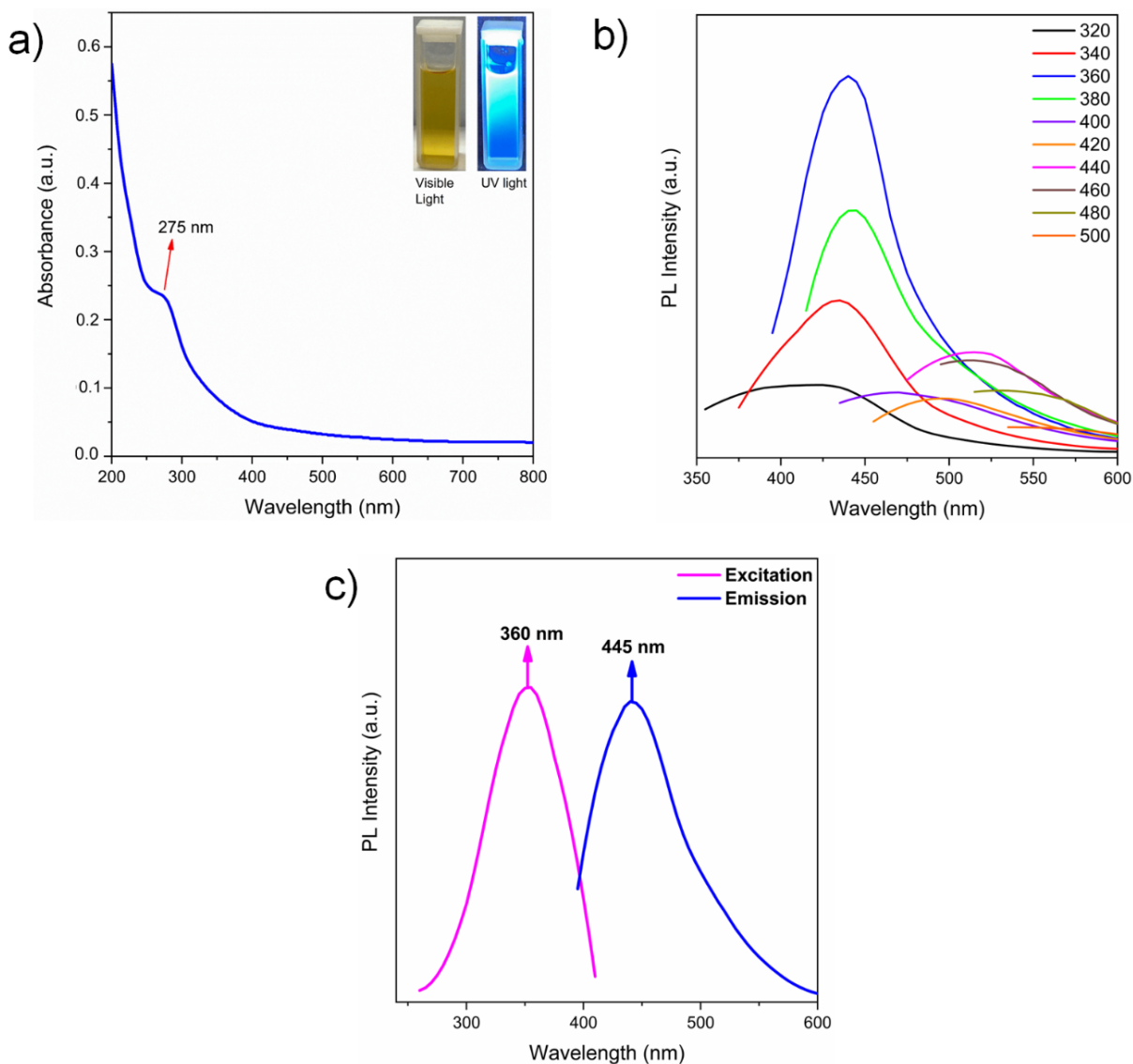
Figure 12 – Characterization of R-CDs: a) IR spectra and b) XRD patterns



Source: elaborated by the author (2024).

The optical properties were analyzed using the UV–visible absorption and fluorescence spectra of the synthesized carbon dots. Figure 13 shows the UV–Vis absorption spectrum of the synthesized carbon dots. The formation of the nanoparticles was confirmed by the color change from brown in visible light to blue under 365 nm UV irradiation (Figure 13). This optical response is consistent with the formation of surface emissive states and has also been observed in recent studies employing rice husk as a biomass precursor for CD synthesis, as described by Kundu, Maity and Basu (2022), Mogharbel *et al.* (2022), and Thongsai *et al.* (2019). These emissive states are commonly associated with oxygen- and nitrogen-containing functional groups generated during the hydrothermal carbonization of lignocellulosic components, such as cellulose, hemicellulose, and lignin. The presence of these surface functionalities contributes to the creation of localized energy levels that govern excitation-dependent photoluminescence behavior. These findings confirm that controlled carbonization of lignocellulosic residues yields CDs with well-defined luminescent properties, supporting their application in sustainable optical sensing and environmental monitoring.

Figure 13 – Optical characterization of R-CDs: a) UV-visible absorption spectrum; b) fluorescence spectra at different excitation wavelengths from 320 nm to 500 nm; and c) emission and excitation spectra of synthesized R-CDs



Source: elaborated by the author (2024).

The absorbance spectrum of the R-CDs (Figure 13a) showed a peak at 275 nm corresponding to the  $\pi$ - $\pi^*$  transitions of the  $sp^2$  domains of the carbon. Figure 13b shows the emission spectra of the R-CDs, where the nanoparticles were excited in a range from 320 nm to 500 nm. In the study by Yu *et al.* (2018), it was shown that the light intensity of the emission curves gradually increases as the excitation wavelength is varied, a behavior strongly related to the presence of functional groups on the surface of the R-CDs.

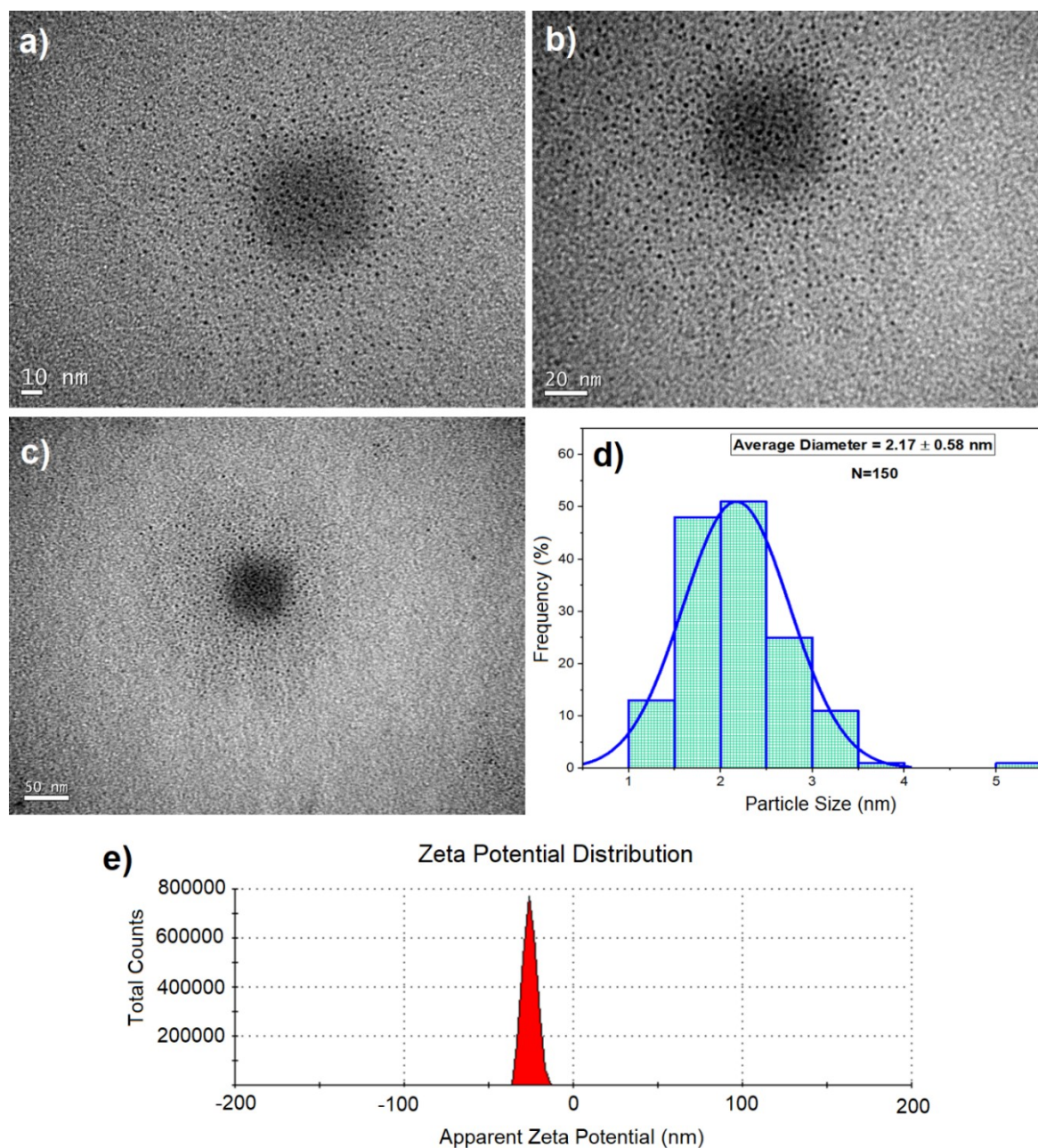
This contributes to the fluorescence emission of the synthesized R-CDs due to radiative recombination between holes and electrons mediated by photoinduced charge separation and trapping at surface sites as reported by Ding *et al.* (2016), Strauss *et al.* (2014) and Yu *et al.* (2021). The excitation wavelength at 360 nm showed the highest fluorescence, with maximum emission centered on 445 nm, corresponding to the blue emission wavelength (Figure 13c). The results are consistent with studies in the literature using rice husk as a precursor, with excitation wavelengths varying in the 320 nm - 360 nm range and maximum emission in the 430 nm - 466 nm range, as reported by Kundu, Maity and Basu (2022), Thongsai *et al.* (2019) and Wang *et al.* (2018).

Figure 14 shows TEM micrographs of the synthesized carbon dots, which are approximately spherical particles with good dispersion and an average diameter of 2.17 nm (Figure 14d). As reported by Chahal *et al.* (2021) and Yang *et al.* (2023), a defining characteristic of CDs is their size being below 10 nm, which aligns with the values obtained in this study. The uniform morphology and narrow size distribution indicate a controlled nucleation and growth process during hydrothermal synthesis, resulting in homogeneously dispersed nanoparticles. The absence of significant agglomeration further suggests that the surface of the CDs contains abundant oxygenated functional groups, which enhance electrostatic repulsion and colloidal stability. The nanometric dimensions are also consistent with the observed optical properties, as smaller particle sizes and surface passivation strongly influence the emission behavior of carbon dots.

In addition, zeta potential analysis was also performed to determine the surface electrical charge and colloidal stability of the nanoparticles (Figure 14e). The synthesized R-CDs exhibited a zeta potential value of -25.7 mV, indicating the presence of negatively charged ionizable functional groups, such as carboxyl (-COOH) and hydroxyl (-OH), on their surface, a result consistent with the findings of Radhakrishnan and Panneerselvam (2018). This interpretation is further supported by the FTIR spectrum, particularly in the 1400  $\text{cm}^{-1}$  to 3200  $\text{cm}^{-1}$  regions. This zeta potential value suggests, according by Xu, Wu and Xu (2007), that the carbon dots have strong electrostatic repulsion between them, preventing aggregation, which

results in a homogeneous and stable dispersion in the suspension, as seen in the TEM images.

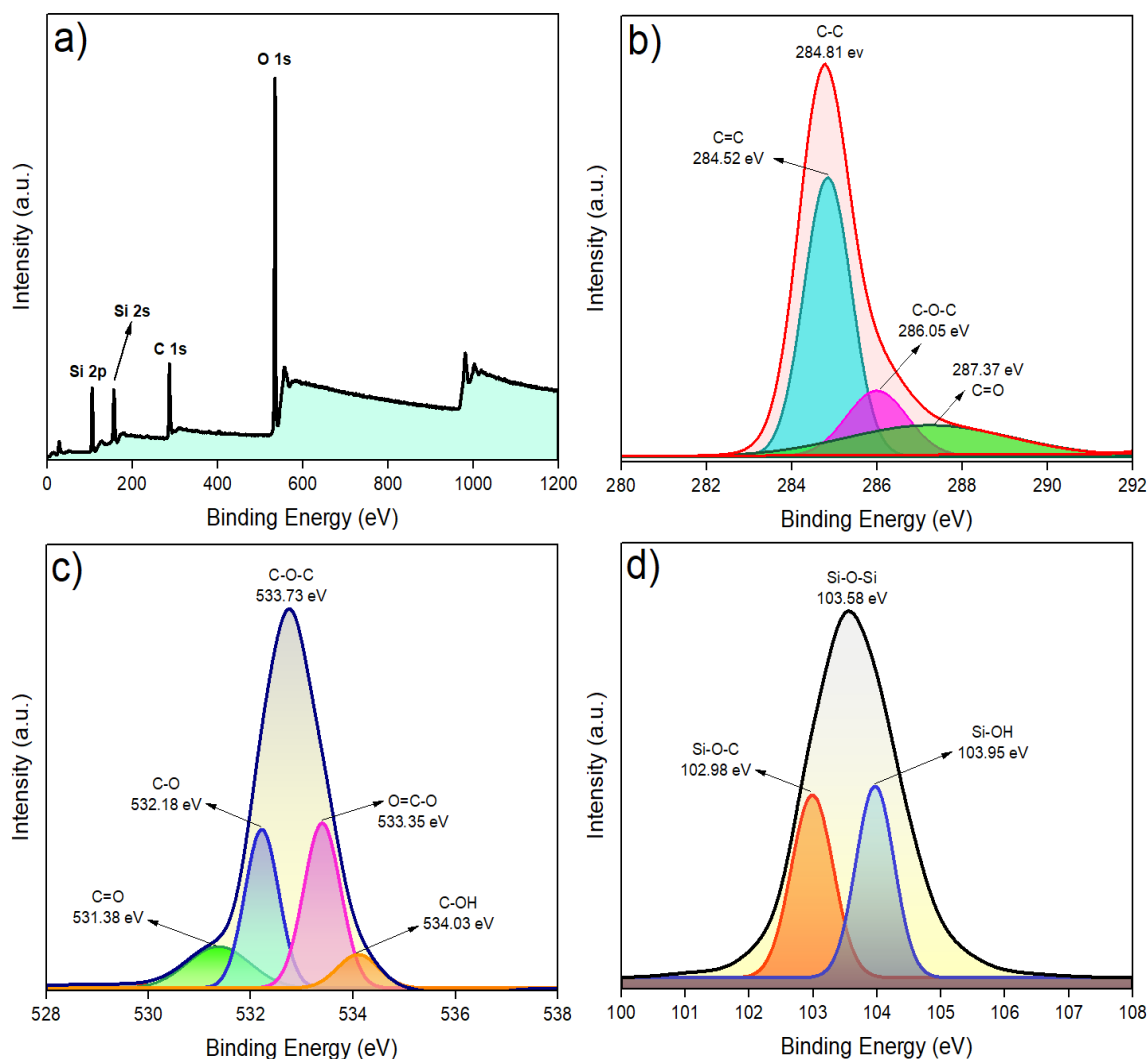
Figure 14 – Morphological and surface characterization of R-CDs: a-c) TEM images; d) histogram of particle size distribution, and e) zeta potential of R-CDs



Source: elaborated by the author (2024).

X-ray photoelectron spectroscopy (XPS) analysis was used to determine the chemical structure and electronic state of the elements present in the carbon dots synthesized from rice husk biomass, illustrated in Figure 15.

Figure 15 – The XPS spectrum of R-CDS: a) XPS survey spectrum; b) high-resolution C 1s; c) high-resolution O 1s peaks; and d) high-resolution Si 2p



Source: elaborated by the author (2024).

As can be seen from the full scan XPS spectra (Fig. 15a), the R-CDs showed 4 distinct peaks at binding energies of 103 eV, 150 eV, 285 eV and 533 eV, which correspond to Si 2p, Si 2s, C 1s and O 1s, respectively, as reported also by Wang *et al.* (2017). These peaks indicate the presence of silicon, carbon and oxygen elements in the R-CDs. Nitrogen had no visible peak in the spectrum due to its low atomic percentage (0.73%). Figure 15b shows the high-resolution deconvolution spectrum of C 1s in the range 280 eV - 292 eV. Different peaks appeared at 284.52 eV, 284.81 eV, 286.05 eV, and 287.37 eV, corresponding to C = C, C - C, C - C - O - C, and C = O bonds. Similarly, Fig. 15c shows that the deconvoluted spectrum of O 1s provides peaks at 531.38 eV, 532.18 eV, 533.35 eV, 533.73 eV, and 534.03 eV, corresponding

to C = O, C - O, O = C - O, C - O - C, and C - OH groups, respectively, as reported also by Ma *et al.* (2023) and Song *et al.* (2016).

The nitrogen content in the carbon dots was not detected in relevant quantities, which is attributed to the rice husk components. In the study by Zou and Yang (2019), rice husks were found to contain approximately 0.05% to 4.26% nitrogen in their overall elemental composition. The use of rice husks as biomass for synthesizing R-CDs leads to nitrogen in low concentrations in the material. This result is consistent with the characterization of the biomass composition with a low protein content in the rice husk (3.48%). The results are consistent with those of Zainal Abidin *et al.* (2020), who synthesized CDs via a hydrothermal process from rice husks, obtaining CDs with a nitrogen content of 1.52% - 1.92% without functionalization.

The high-resolution spectrum for Si 2p (Figure 15d) showed peaks at 102.98 eV, 103.58 eV, and 103.95 eV that correspond to Si - O - C, Si - O - Si, and Si - OH bonds, respectively. Therefore, the XPS results corroborate the bands identified in the FTIR spectrum, with a typical carbonaceous structure and surface groups containing oxygen and silicon from the biomass composition.

#### **6.4.1 Mechanistic Insights of R-CDs formation**

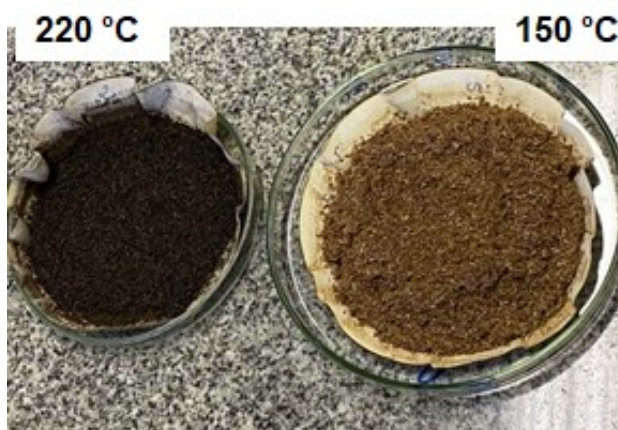
Proposing a mechanism for the formation of carbon dots from biomass that have several compounds with a high probability of generating R-CDs rich in functional groups is a major challenge. The process of forming R-CDs is intrinsically complex, involving multiple factors. Even so, the data presented shows consistent convergence and corroborates each other, reinforcing the validity of the observations. For this reason, an experimental design was first carried out to investigate the influence of the synthesis parameters, such as temperature and solids load, on the carbonization of the biomass, characterized by the release of the degradation compounds.

From the degradation profile of the biomass components, it can be inferred that polysaccharides, extractives, and proteins are the main carbon sources and that their degradation results in the formation of R-CDs. The increase in temperature favored the decomposition of polysaccharides into lower molecular weight molecules through

various condensation, depolymerization, and carbonization reactions that resulted in the formation of R-CDs. As the temperature increases, sugars such as glucose, arabinose, cellobiose, xylose, and cellobiose degrade further into lower molecular weight molecules and form R-CDs through various carbonization reactions inside the reactor. According to Table 6, tests 6 and 7, which used the highest temperature (220 °C) and the lowest solids load (3% w/v), generated the highest quantities of degradation compounds. These results show the influence of the reaction parameters on the formation of degradation products, which are directly related to the degree of carbonization of the biomass. The increase in the release of these compounds reflects more efficient carbonization, promoting more effective conversion of the organic precursor into R-CDs, the product of interest.

The reaction temperature is strongly associated with the carbonization process as described in the literature, since high temperatures intensify this process. According to Zhang *et al.* (2016), as the degree of carbonization increases, there is a tendency to form structures more similar to graphene, constituting R-CDs structure. During hydrothermal synthesis, the increase in temperature facilitates the thermal degradation of the lignocellulosic components of biomass (cellulose, hemicellulose, and lignin), forming carbon-rich molecular precursors. The data presented in Table 6 are consistent with the visual appearance of the R-CDs after the freeze-drying process (Figure 16).

Figure 16 – Visual appearance of freeze-dried R-CDs synthesized under different hydrothermal temperatures

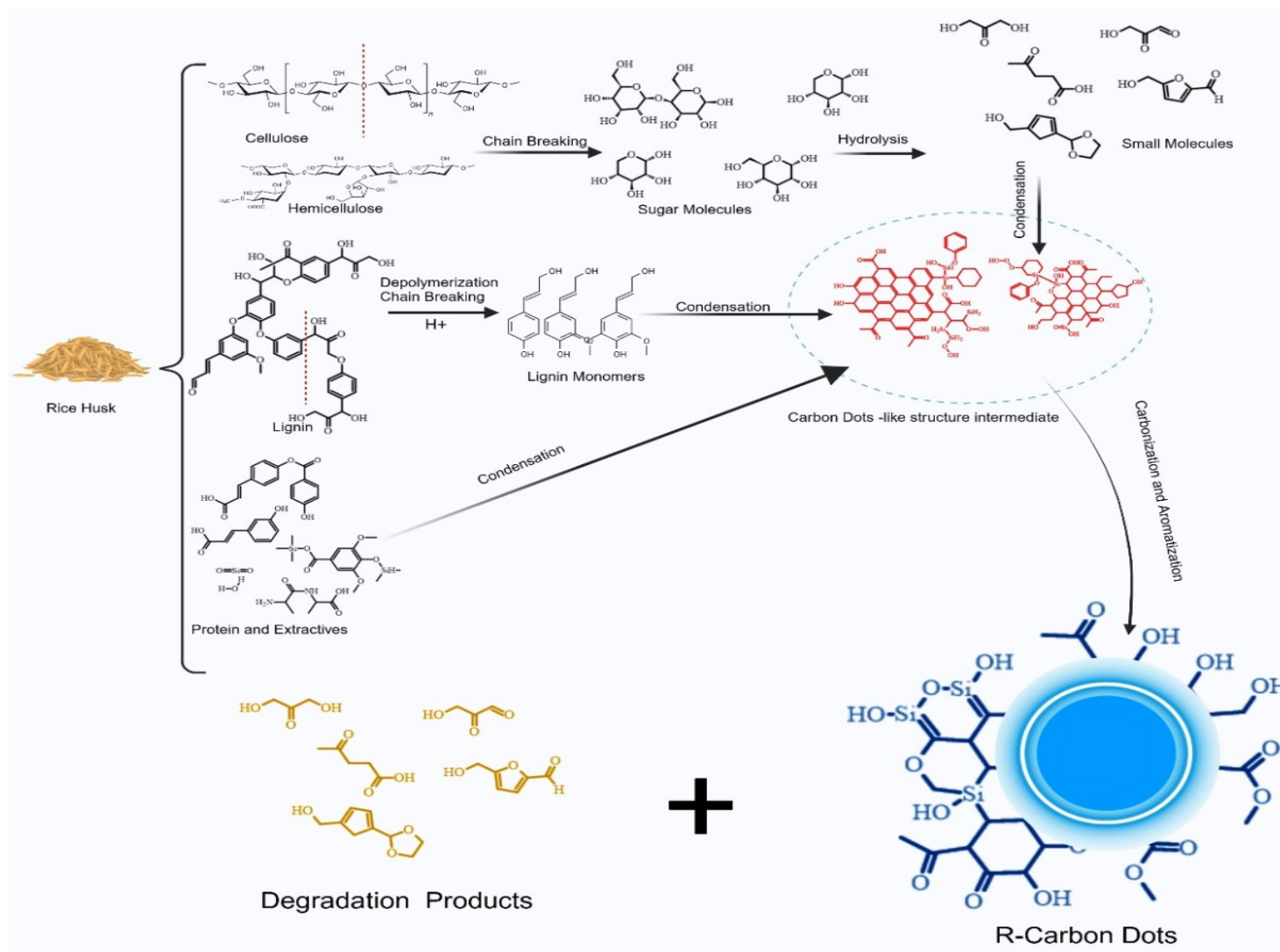


Source: elaborated by the author (2025).

The sample synthesized at the highest temperature (220 °C, condition 6 of the experimental design) exhibited a pronounced dark brown coloration, indicating a higher degree of carbonization. In contrast, the lighter brown color of the R-CDs obtained at the lowest synthesis temperature (149.64 °C, condition 5) reflects a milder degradation of the biomass and a lower extent of carbonization. However, very high temperatures can cause defects in carbon dots, thereby affecting their optical properties. Excessive heating leads to a decrease in fluorescence intensity due to an increase in non-radiative decay processes. This effect was also observed in the study by Yu *et al.* (2012), where high temperatures induced the formation of structural defects that act as trapping centers for excited electrons, favoring non-radiative emission and consequently reducing both the quantum yield and the optical performance of CDs. Wongso *et al.* (2021) verified this effect by observing that excessive carbonization of rice husk occurs at temperatures above 225 °C, reducing the performance of the optical properties of carbon dots. These findings are consistent with other studies that also employed rice husk as a biomass source, as reported by Jothi *et al.* (2021), Thongsai *et al.* (2019), and Wataniyakul *et al.* (2018).

In addition, the synthesis condition revealed the highest biomass conversion was at the lowest solid loading (3% w/v) with the highest amount of degradation products (Table 6), whose value was 21.13% w/w. This condition balances the availability of precursors for the formation of R-CDs while avoiding saturation of the reaction medium, promoting a homogeneous dispersion of the lignocellulosic components in the system. This improves heat and mass transfer, fundamental factors for thermal degradation reactions, aromatization, and carbonized structures' nucleation. In addition, the smaller mass in the reactor reduces the formation of large agglomerates, which could favor a higher surface-to-volume ratio. Thus, reaction interactions become more efficient, minimizing temperature gradients and the risk of aggregation and incomplete carbonization, promoting greater structural uniformity and superior optical properties in the R-CDs. The kinetic study made it possible to determine the ideal synthesis time under the optimized conditions. Based on the results obtained and the literature that covers in-depth studies of the components analyzed, a mechanism was proposed, and it is illustrated in Figure 17 that describes the potential route for converting cellulose and hemicellulose into CDs.

Figure 17 – Mechanistic insights in CDs formation



Source: elaborated by the author (2025).

Initially, it has been proposed that the cellulose and hemicellulose macromolecules undergo a depolymerization stage, during which the polymer chains break down into smaller sugars, as described by Zhu *et al.* (2024). The production of these sugars was proven by HPLC analysis, as shown in Table 6. Next, it has been suggested that these smaller sugars undergo a ring-opening process, forming even smaller molecules. Although not wholly identified in this study, these molecules may undergo condensation reactions, culminating in a complex macromolecular structure. This final stage involves carbonization and aromatization processes, resulting in the production of R-CDs.

Furthermore, lignin, a major structural component of the rice husk precursor, underwent transformation during the reaction. According to Zhu *et al.* (2024), lignin can be degraded under the experimental conditions used in this study, giving rise to monomers that potentially participate in the subsequent steps in forming R-CDs. These mechanistic insights offer an initial perspective on the possible reaction pathways involved in synthesizing carbon dots from lignocellulosic biomass, contributing to understanding the underlying processes. The monomers suggested in this mechanism were not detected at any stage of this work. The analyses did not identify the presence of these compounds, indicating that they may be consumed directly in the condensation process, contributing to the formation of the proposed macrostructure.

This macrostructure, in turn, undergoes subsequent stages of carbonization and aromatization, producing carbon dots. Rice husk, used as a precursor, is rich in minor compounds, including phenols, proteins, extractives, and hydrated silica, which is typical of this material. These compounds, especially phenolics, have similar chemical characteristics to lignin monomers and can also take part in condensation reactions, forming intermediate structures, as reported by Gan *et al.* (2023). These structures can evolve into macrostructures, forming R-CDs through carbonization and aromatization processes.

In addition, FTIR and XPS analysis showed that the R-CDs present silicon in their structure, suggesting that the silica from the rice husk was incorporated into the structure of the carbon dots. This result shows a process of self-doping, contributing to the structural and functional modification of the materials obtained. This indicates that

10% - 20% of silica in rice husks contributes to CDs formation and doping. Desai *et al.* (2019) obtained silica-doped CDs using (3-aminopropyl) triethoxysilane (APTES), while Kajani *et al.* (2023), Mo *et al.* (2021), and Wang *et al.* (2023) employed tetraethyl orthosilicate (TEOS). In contrast, Wang *et al.* (2017) reported more complex synthesis routes involving multiple steps and the use of corrosive acids, which made the process more intricate. However, this study demonstrates that silica incorporation into the R-CD structure is possible without additional silica sources, utilizing a green route with only rice husks. According to Desai *et al.* (2019) and Ornelas-Hernández, Garduno-Robles, and Zepeda-Moreno (2022), doping CDs with silica offers several advantages, including improved optical properties, enhanced thermal and chemical stability, better dispersibility, reduced toxicity, greater biocompatibility for biomedical applications, and increased sensitivity and selectivity for sensor applications. This opens new opportunities to explore silica doping using only rice husks.

It, therefore, remains a challenge for the scientific community to elucidate the formation of RCDs from complex biomass and to fully understand the mechanisms underlying their luminescence. Most studies on the green synthesis of carbon dots have primarily focused on their applications, with limited attention given to the influence of biomass composition and reaction parameters on the formation process. In this context, the present work sought to contribute to filling this gap by investigating how the degradation and conversion of biomass constituents evolve over time, providing kinetic insights into the formation pathway of carbon dots. This approach also enabled the determination of optimized synthesis conditions regarding solid load, reaction temperature, and reaction time, supporting the scalability of the production process.

Regarding lignocellulosic biomass, the direct conversion of constituents into R-CDs is laborious and requires more drastic reaction conditions. For this reason, obtaining a high degree of conversion remains a crucial concern. Furthermore, the mechanism proposed in this work is preliminary and does not consider the complex chemical interactions between the components in the reaction mixture. The complexity of these interactions represents a significant limitation to the precise identification of the processes involved. Future studies could address this limitation through the isolated investigation of monomers and the controlled addition of specific compounds, allowing for the validation and refinement of the mechanism suggested here. Finally,

using alternative green sources as precursors for forming CDs is highly encouraged, with numerous studies published in this area. However, it remains essential to investigate the composition of these sources to assess the conversion's feasibility.

## 6.5 CERIUM DOPED CARBON DOTS

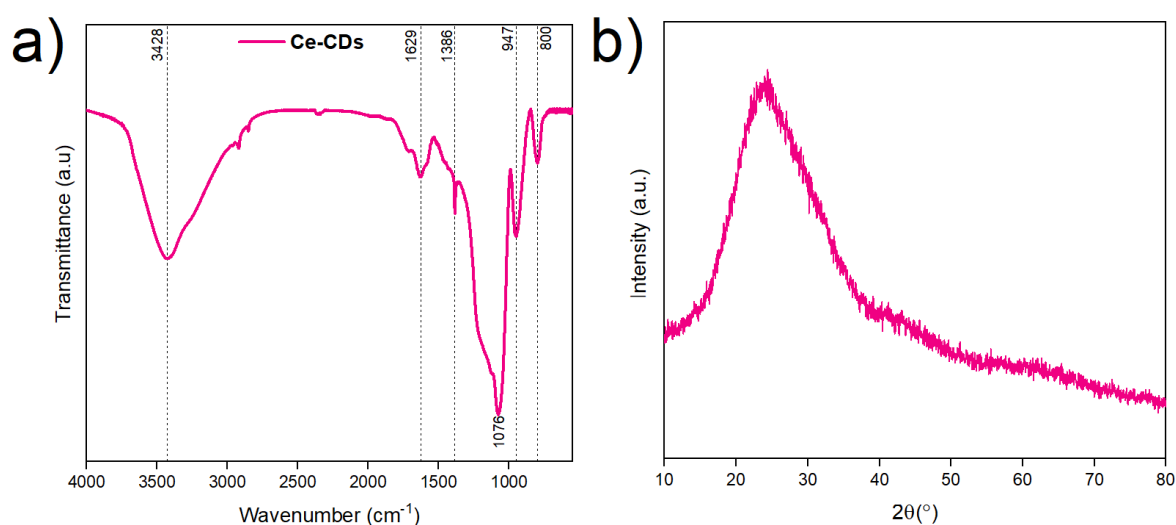
The Ce-CDs synthesized in this study presented QY of 20.16%, 19.82%, and 23.77% for dopant masses of 3.00 g, 1.50 g, and 0.75 g, respectively. Among these, the highest fluorescence efficiency was achieved with the lowest cerium mass (0.75 g), suggesting that excessive dopant concentration may lead to fluorescence quenching, possibly due to increased non-radiative recombination or surface defect saturation, according to Zhang *et al.* (2021). The QY of 23.77% stands out as a promising result when considering the use of a complex and sustainable carbon source, rice husk as the precursor. Compared to the literature, this value is higher than the 20% QY reported by Li *et al.* (2022) for Ce-CDs synthesized from folic acid and polyvinylpyrrolidone, but lower than the 93.14% reported by Zhang and Fan (2021) using citric acid as a precursor under hydrothermal conditions. Such discrepancies are expected, as the quantum yield of carbon dots depends strongly on precursor composition, synthesis conditions, surface passivation, and dopant interaction.

Unlike synthetic molecules like citric acid, rice husk is a lignocellulosic biomass rich in silica, which may influence energy transfer processes and limit passivation efficiency (Li *et al.*, 2022). Nevertheless, the QY values obtained here demonstrate that rice husk can be effectively converted into luminescent Ce-CDs with reasonable optical efficiency, supporting its use as a low-cost, renewable, and eco-friendly feedstock for advanced carbon nanomaterials. Based on its superior quantum yield, the Ce-CD synthesized with 0.75 g of dopant was selected for further characterization and application. Structural, morphological, and spectroscopic analyses confirmed successful doping and favorable surface chemistry. This sample was subsequently employed as a fluorescent probe for agrochemical detection, demonstrating high sensitivity toward glyphosate in aqueous systems.

### 6.5.1 Characterizations of Ce-CDs

The FTIR spectra of Ce-CDs (Figure 18a) revealed the presence of various oxygen-containing surface functional groups, as well as evidence of interactions between cerium and the carbon matrix.

Figure 18 – Characterization of Ce-CDs: a) IR spectra; and b) XRD patterns



Source: elaborated by the author (2025).

The broad band observed at 3428 cm<sup>-1</sup> is attributed to the stretching vibrations of O – H bonds, suggesting the presence of hydroxyl groups on the surface of the nanomaterials. These groups are typical of CDs synthesized via hydrothermal methods and confer high hydrophilicity and potential for further chemical modifications. According to Zhang *et al.* (2019), the presence of such functional groups may also contribute to the photoluminescent behavior and the ability of the material to anchor external species.

The band at 1629 cm<sup>-1</sup> corresponds to the bending vibrations of O – H bonds, often associated with adsorbed water or hydrogen-bonded carboxylic groups on the surface. In addition, this band may reflect the presence of C = C bonds within conjugated or aromatic domains in the graphitic core of the CDs, which is characteristic of carbon dots produced by bottom-up synthesis routes. The band observed at 1386 cm<sup>-1</sup> is related to the bending vibrations of C – H bonds. In cerium-doped materials, this region of the spectrum may also be influenced by interactions between surface

functional groups and active  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  sites, indicating the incorporation of the dopant into the carbonaceous network.

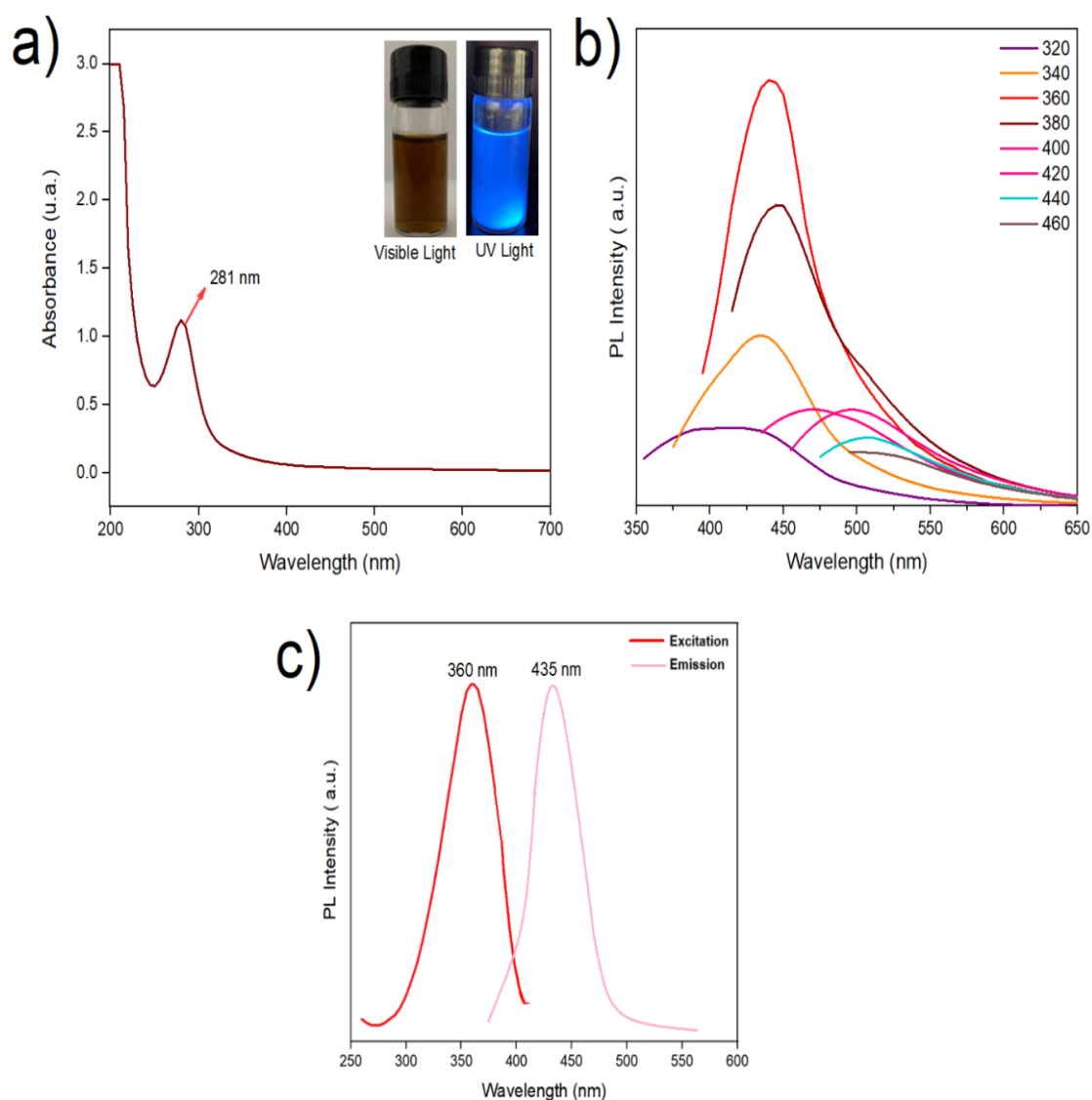
The absorption at  $1076\text{ cm}^{-1}$  is assigned to the asymmetric stretching vibrations of C – O – C or C – O bonds, characteristic of alcohol and ether groups present on the surface of the CDs. These oxygenated groups play a key role in colloidal stabilization in aqueous media and can promote chemical interactions with metal ions or target molecules in sensing applications. The band at  $947\text{ cm}^{-1}$ , although of lower intensity, may be associated with vibrational modes related to C – O bonds and possible Ce – O – C linkages formed during the doping process. This absorption suggests structural interactions between cerium atoms and the carbon matrix, reinforcing the evidence of successful doping.

Finally, the band identified at  $800\text{ cm}^{-1}$  is characteristic of Ce – O vibrations, typical of structures containing cerium oxide or Ce – O – C bonds within the doped network. The presence of this band supports the integration of cerium into the CD system and indicates the formation of hybrid structures between the metal oxide and the carbon-based nanomaterial. Together, these spectral assignments confirm the presence of oxygenated functionalities on the CDs, as well as the effective doping with cerium. These findings are consistent with those reported in the literature for similar systems, including the works of Li *et al.* (2022); Thakur *et al.* (2022); and Zhang *et al.* (2019), who described analogous FTIR spectra for cerium-doped CDs obtained via hydrothermal methods.

Figure 18b shows the XRD pattern of the Ce-CDs, displaying a broad diffraction peak centered around  $25^\circ$ , which is attributed to the (0 0 2) plane of graphitic carbon, indicating the presence of an amorphous or partially graphitized carbon structure. This broad feature is indicative of the presence of disordered graphitic layers or an amorphous carbon matrix, which is a common structural characteristic of carbon dots synthesized via hydrothermal routes. Such a pattern agrees with that reported by Li *et al.* (2022), who described similar XRD profiles for folic acid-modified Ce-CDs, confirming the existence of short-range graphitic ordering and the overall amorphous nature of the material.

The optical properties of Ce-CDs were evaluated by UV-Vis absorption and fluorescence spectroscopy, as shown in Figure 19. The UV-Vis absorption spectrum of the Ce-CDs exhibits an intense band centered at 281 nm, attributed to  $\pi$  -  $\pi$  transitions of electrons in aromatic or conjugated rings present in the graphitic domains of the Ce-CDs. This type of transition is typical for carbon dots with  $sp^2$  hybridized carbon-rich structures and has been similarly reported for Ce-doped carbon dots synthesized by hydrothermal methods also observed in studies of Zhang *et al.* (2019) and Li *et al.* (2022).

Figure 19 – Optical analysis of Ce-CDs: a) UV–visible absorption spectrum; b) fluorescence spectra at different excitation wavelengths from 320 nm to 460 nm; and c) emission and excitation spectrum of synthesized Ce-CDs



Source: elaborated by the author (2025)

Figure 19b shows the emission spectra of the Ce-CDs recorded at different excitation wavelengths ranging from 320 nm to 460 nm. The emission peaks exhibit excitation-dependent behavior, with variations in both position and intensity as the excitation wavelength increases. This characteristic is well known for carbon dots and is related to the presence of multiple surface trap states, heterogeneity of emissive sites, and variations in the size of the carbon core, according to Li *et al.* (2022). In addition, the doping with cerium is expected to introduce intermediate energy levels associated with  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ , which can facilitate additional electronic transitions or enhance charge separation and recombination, modulating the photoluminescence, as reported by Thakur *et al.* (2022).

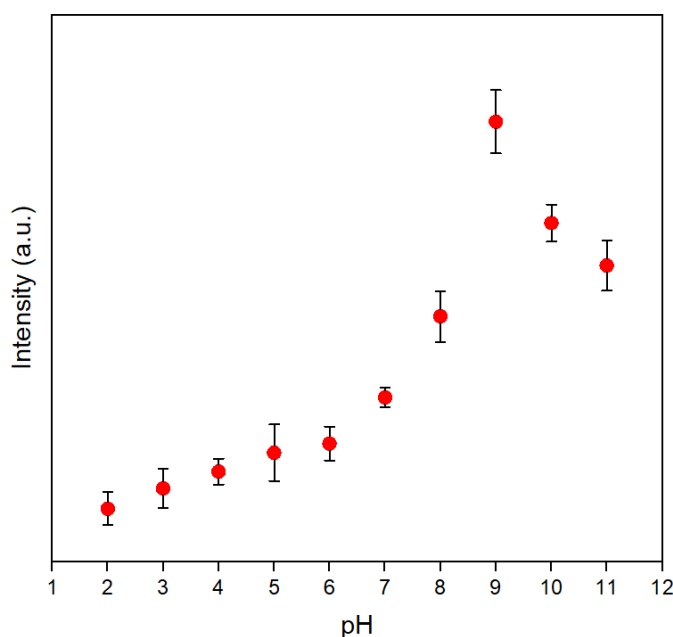
Figure 19c presents the excitation and emission spectra of the Ce-CDs. The maximum excitation occurs at 360 nm, leading to a blue emission centered at 435 nm, consistent with the intense blue fluorescence observed visually. When comparing Ce-doped and undoped CDs, both materials display optimal excitation at 360 nm. However, the emission maximum shifts slightly from 445 nm (undoped CDs) to 435 nm (Ce-CDs). This subtle variation in the Stokes shift suggests that cerium doping induces small changes in the surface states or emissive centers, likely associated with the introduction of electronic levels linked to  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ions. Although minor, this behavior is consistent with literature reports, where rare earth dopants modulate electronic trap states and optical emission even at low concentrations (Li *et al.*, 2022; Thakur *et al.*, 2022; Zhang *et al.*, 2019).

Importantly, this modification of surface states is reflected in a pronounced enhancement of photoluminescent efficiency. While the undoped CDs synthesized under optimized conditions (220 °C, 3% w/v, 4 h) exhibited a quantum yield of approximately 14%, the Ce-doped CDs reached a significantly higher quantum yield of 23.77%. This substantial increase indicates that cerium incorporation effectively suppresses non-radiative recombination pathways. The enhancement in quantum yield observed for Ce-CDs is therefore primarily associated with surface-state modulation rather than the formation of a distinct crystalline phase. The mixed  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox behavior enables effective coordination with oxygen-containing functional groups on the carbon dot surface, such as carboxyl and hydroxyl moieties, leading to improved surface passivation.

This passivation reduces the density of non-radiative recombination centers and suppresses deep surface trap states, which are typically responsible for vibrational relaxation and thermal dissipation, also observed in studies of Zhang *et al.* (2021). In addition, the incorporation of cerium introduces shallow electronic states that facilitate radiative electron–hole recombination, acting as intermediate emissive centers and enhancing fluorescence efficiency (Thakur *et al.*, 2022). As a result, a larger fraction of the absorbed excitation energy is released as photoluminescence rather than being dissipated as heat, which explains the significant increase in quantum yield observed for Ce-CDs compared to undoped CDs synthesized under the same conditions. Such an increase in radiative recombination efficiency is particularly advantageous for sensing applications, as it directly enhances signal intensity and improves analytical sensitivity, according to Li *et al.* (2019).

The fluorescence intensity of Ce-CDs displayed a clear dependence on the pH medium, as illustrated in Figure 20. A progressive enhancement in emission was observed from acidic to alkaline conditions, reaching a maximum at pH 9, followed by a slight decline at pH 10 and 11. This pH-responsive photoluminescence behavior is closely associated with the protonation and deprotonation dynamics of surface functional groups, which modulate the electronic environment of the CDs (Yuan *et al.*, 2018).

Figure 20 – Fluorescence intensity of Ce-CDs as a function of pH



Source: elaborated by the author (2025).

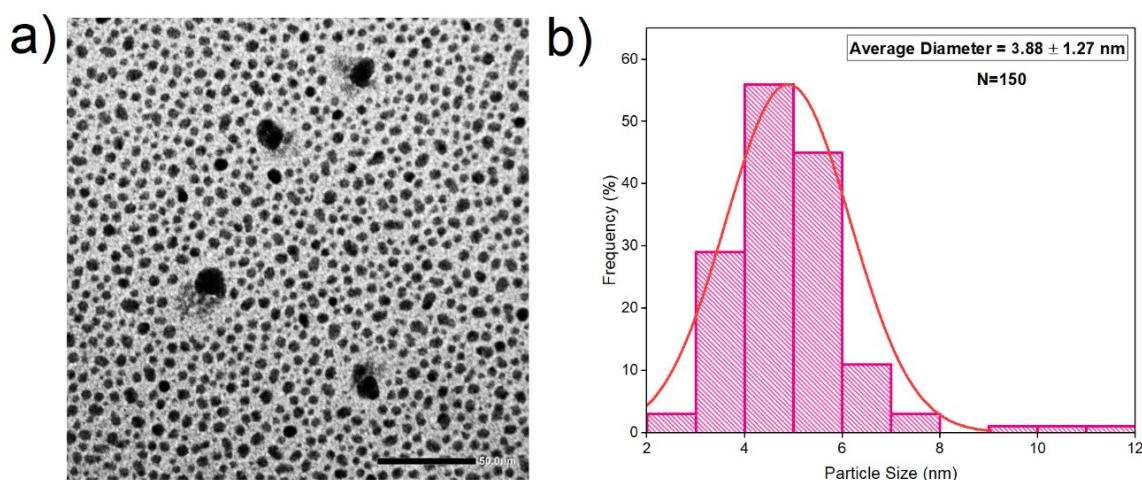
The observed decrease in fluorescence intensity under acidic conditions (pH 2–6) arises from the protonation of surface oxygenated groups ( $-\text{COOH}$ ,  $-\text{OH}$ ), which reduces surface passivation and facilitates non-radiative decay. In contrast, at alkaline pH values, deprotonation enhances the negative surface charge density, stabilizing the emissive surface states and promoting radiative recombination. This behavior indicates that the fluorescence enhancement at pH 9 corresponds to an optimal equilibrium between surface charge and exciton confinement, consistent with previously reported protonation–deprotonation mechanisms governing pH-dependent photoluminescence of carbon dots (Ehtesabi *et al.*, 2020).

At higher pH values (10–11), the observed decline in fluorescence may be a result of over-deprotonation or ionic screening effects, which can perturb the colloidal stability or lead to partial aggregation of nanoparticles, thus impacting their optical response. These results align with the findings of Szapoczka *et al.* (2023), who investigated the pH sensitivity of carbon dots and reported similar emission modulation trends driven by surface state chemistry and charge distribution.

Their study demonstrated that both fluorescence intensity and lifetime are significantly influenced by pH variations, with the response strongly dependent on the type of surface functional groups and the specific synthetic method used. Based on these results, pH 9 was selected as the optimal condition for all subsequent sensing and analytical experiments, ensuring maximum fluorescence intensity and signal stability. Figure 21 presents the TEM image and the corresponding particle size distribution histogram of the Ce-CDs.

As shown in Figure 21a, the Ce-CDs exhibit a nearly spherical morphology with good particle dispersion. The size distribution histogram in Figure 21b, obtained from the analysis of 150 individual particles, indicates an average diameter of  $3.88 \text{ nm} \pm 1.27 \text{ nm}$ , with most particles falling within the 2.5 nm – 5.5 nm range. The observed particle size is consistent with values reported for Ce-doped carbon dots synthesized via hydrothermal methods.

Figure 21 – Morphological analysis of Ce-CDs: a) TEM image and b) Histogram of particle size distribution



Source: elaborated by the author (2025).

For instance, Zhang *et al.* (2021) reported sizes ranging from 2 nm to 4 nm, while Gong *et al.* (2021) obtained Ce-doped CDs with an average diameter of approximately 5 nm. Similarly, Liu *et al.* (2022) synthesized Ce-CDs with an average size of 3.6 nm for tetracycline detection, and Li *et al.* (2022) reported Ce-CDs with diameters around 3.8 nm for Fe (III) detection. The values obtained are consistent with the main characteristic of R-CDs, i.e., a size of less than 10 nm (Li *et al.*, 2019). The increase in the average diameter of Ce-doped carbon dots compared to non-doped CDs (2.17 nm) can be attributed to the incorporation of  $\text{Ce}^{3+}$  ions during the hydrothermal synthesis process. These ions can alter the nucleation and growth dynamics of the carbonaceous structures by forming coordination interactions with oxygen-containing functional groups on the CD surface, such as carboxyl and hydroxyl groups.

Such interactions may favor the formation of larger carbon nuclei, slow down surface contraction during carbonization, and promote partial aggregation, ultimately resulting in an increased average particle size. This behavior is consistent with literature reports on rare-earth-doped carbon dots, which commonly present particle sizes in the range of approximately 2–5 nm, depending on dopant type and synthesis conditions (Zhang; Fan, 2019; Yang *et al.*, 2021; Zhang *et al.*, 2019). The presence of rare-earth ions is often associated with enhanced structural complexity and modified

growth pathways, leading to slightly larger nanoparticles compared to undoped CDs (Liu *et al.*, 2022).

XPS was employed to investigate the surface chemical composition and bonding states of Ce-CDs. As observed in the survey spectrum (Fig. 22a), six distinct peaks were identified at binding energies of approximately 106 eV (Si 2p), 158 eV (Si 2s), 285 eV (C 1s), 533 eV (O 1s), 888 eV (Ce 3d<sub>5/2</sub>) and 978 eV (Ce 3d<sub>3/2</sub>). These peaks confirm the presence of silicon, carbon, oxygen, and cerium, indicating successful synthesis of Ce-CDs from rice husk precursors with effective Ce incorporation.

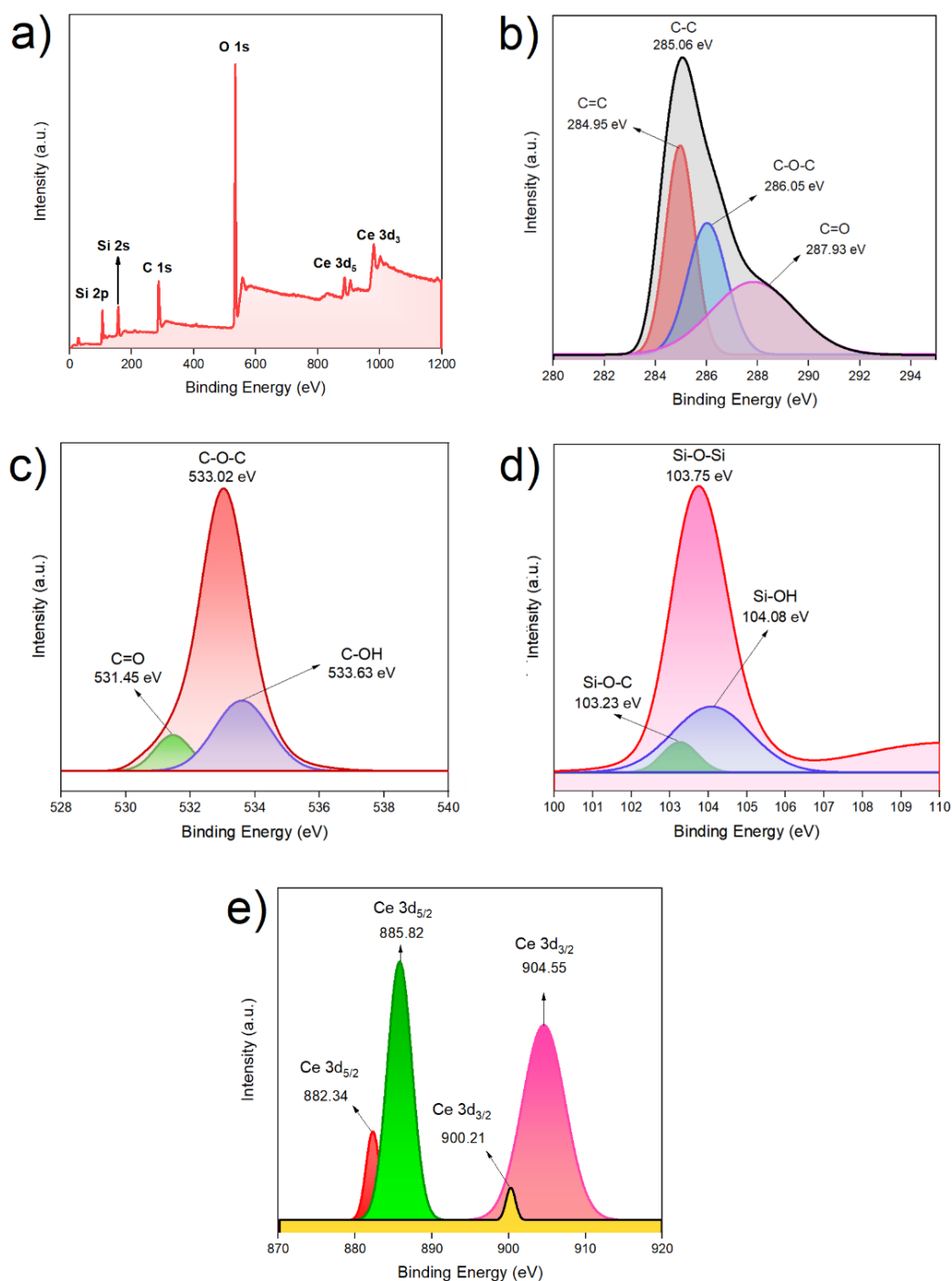
The high-resolution C 1s spectrum (Fig. 22b) was deconvoluted into four main components centered at 284.95 eV (C = C), 285.06 eV (C – C), 286.05 eV (C – O – C), and 287.93 eV (C = O). These species are commonly observed in carbon-based nanomaterials and indicate the presence of graphitic carbon and oxygenated functionalities on the surface of the CDs, which contribute to their hydrophilicity and photoluminescent behavior, according to Du *et al.* (2020). In the O 1s spectrum (Fig. 22c), the deconvoluted peaks at 530.27 eV, 531.45 eV, 533.03 eV, and 533.6 eV can be attributed to different oxygen-containing bonds such as O = C – O (carboxyl), C – O – C (ether), O – H (hydroxyl), and adsorbed H<sub>2</sub>O, respectively. These functional groups not only confirm the hydrophilic nature of the Ce-CDs but also support their role in metal coordination and potential photoluminescent behavior.

The Si 2p spectrum (Fig. 22d) revealed peaks at 102.93 eV (Si – O – C), 103.75 eV (Si – O – Si), and 104.06 eV (Si – OH), which are indicative of biogenic silica residues from rice husk. These findings are corroborated by the FTIR spectrum (Fig. 18a), where characteristic Si – O – Si and Si –OH bands were also observed. The presence of silica-related species confirms the structural influence of the precursor biomass and the formation of a hybrid carbon–silica matrix (Shobana *et al.*, 2023).

The high-resolution Ce 3d spectrum (Fig. 22e) shows characteristic peaks at 882.34 eV, 885.82 eV (Ce 3d<sub>5/2</sub>), 900.21 eV, and 904.55 eV (Ce 3d<sub>3/2</sub>). These peaks correspond to the mixed oxidation states of cerium, Ce<sup>3+</sup> and Ce<sup>4+</sup>, which is consistent with CeO<sub>2</sub>-like surface chemistry. According to studies by Cai *et al.* (2021) and Zhang

*et al.* (2019), the coexistence of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  oxidation states creates redox-active sites that are closely associated with improved catalytic activity and enhanced sensing performance in Ce-doped carbon dots.

Figure 22 – The XPS spectrum of Ce-CDS: a) XPS survey spectrum; b) high-resolution C 1s; c) high-resolution O 1s peaks; d) high-resolution Si 2p and e) high-resolution of Ce 3d



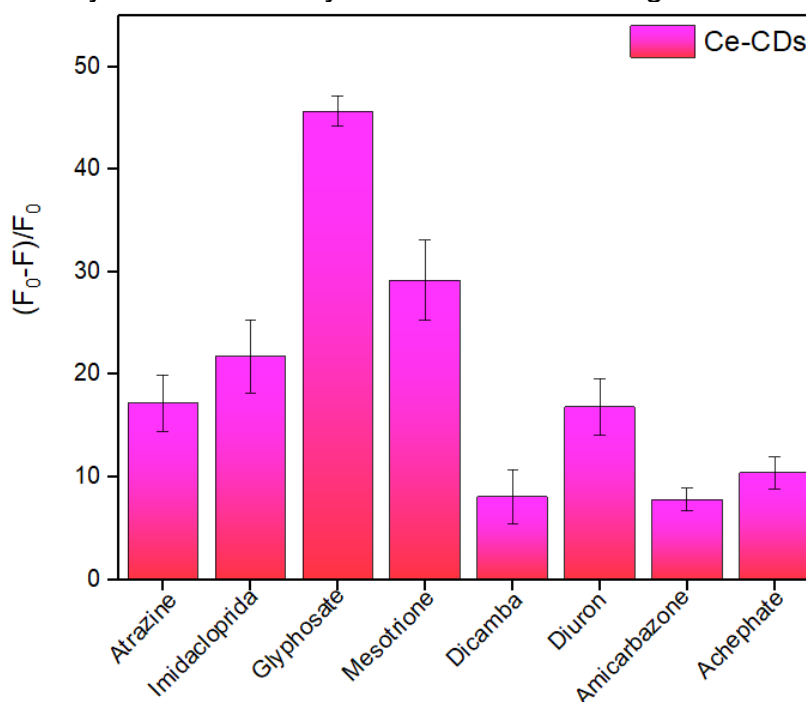
Source: elaborated by the author (2025).

Taken together, XPS results confirm the successful incorporation of cerium into the carbon dot structure, the presence of a functionalized carbon framework, and the retention of siliceous moieties from the rice husk precursor. FTIR analysis supports a surface-localized incorporation, revealing modifications in oxygen-containing functional groups associated with coordination interactions between  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ions and carboxyl, hydroxyl, or siloxane-related moieties. This core–shell-like configuration, with cerium species anchored at the shell, alters surface electronic states, explaining the enhanced photoluminescence and confirming cerium as an efficient dopant.

### 6.5.2 Application of Ce-CDs on Agrochemical Detection

The fluorometric response of Ce-CDs was evaluated against various potential interfering agrochemicals, including atrazine, imidacloprid, glyphosate, mesotrione, dicamba, diuron, amicarbazone, and acephate, each added at a final concentration of 500  $\mu\text{mol/L}$ . As shown in Figure 23, the Ce-CDs exhibited a markedly higher fluorescence quenching effect in the presence of glyphosate compared to the other analytes tested. This selective response indicates a strong interaction between glyphosate and the surface functionalities of the Ce-CDs.

Figure 23 – Study of the selectivity of Ce-CDs concerning different agrochemicals

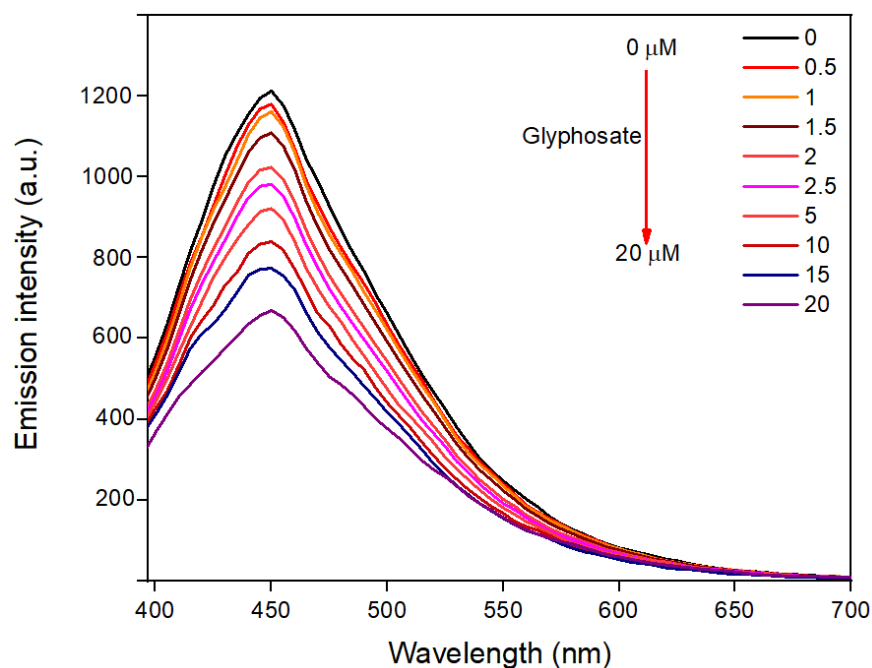


Source: elaborated by the author (2025).

The considerable decrease in fluorescence intensity observed upon glyphosate addition is likely due to the presence of phosphonate groups in their molecular structure, which are known to exhibit strong affinity toward positively charged surfaces. This behavior can be attributed to electrostatic and coordination interactions between the phosphonate moieties and cerium ions ( $\text{Ce}^{+3}/\text{Ce}^{+4}$ ) present on the nanoparticle surface. Similar interactions have been described in the literature for other phosphate-containing analytes interacting with metal-doped carbon dots, as reported by Dewangan *et al.* (2022) and Sasikumar *et al.* (2024).

To assess the sensitivity and dynamic response range of the sensor system, a series of fluorescence emission spectra were recorded upon incremental additions of glyphosate ( $0.5\ \mu\text{mol/L}$  –  $20\ \mu\text{mol/L}$ ) to aqueous Ce-CDs suspensions (Figure 24). The results revealed a gradual and concentration-dependent decrease in fluorescence intensity without any significant shift in the emission maximum, indicating a static quenching mechanism. At the maximum concentration tested ( $20\ \mu\text{mol/L}$ ), a pronounced fluorescence quenching was observed, confirming the strong interaction and efficient detection capacity of the Ce-CDs for glyphosate.

Figure 24 – Emission spectra of Ce-CDs with increasing concentrations of glyphosate  $0.5\ \mu\text{mol/L}$  –  $20\ \mu\text{mol/L}$



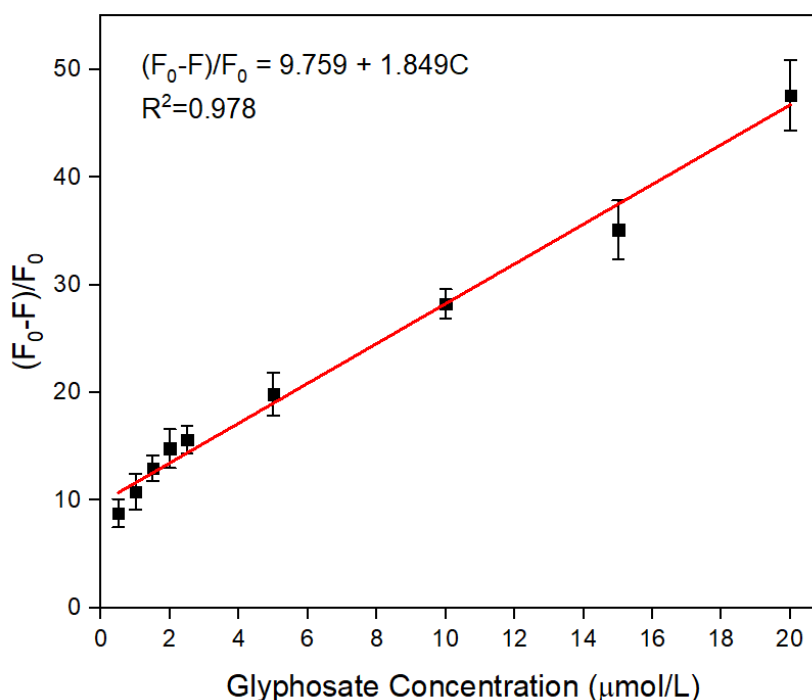
Source: elaborated by the author (2025).

A calibration curve was constructed using the relative fluorescence quenching  $[(F_0 - F)/F_0]$  as a function of glyphosate concentration, resulting in a linear relationship in the range of 0.5  $\mu\text{mol/L}$  – 20  $\mu\text{mol/L}$ , with a correlation coefficient of  $R^2 = 0.978$  (Figure 25). The linear fitting is given by Equation (11):

$$\frac{F_0 - F}{F_0} = 9.759C + 1.849 \quad (11)$$

where  $C$  is the glyphosate concentration in  $\mu\text{mol/L}$ . Based on the calibration data and using the standard  $3\sigma/\text{slope}$  criterion, the limit of detection (LOD) was calculated to be 1.78  $\mu\text{mol/L}$ , equivalent to approximately 0.30  $\mu\text{g/L}$ .

Figure 25 – Linear band of increasing intensity and concentration of glyphosate (0.5  $\mu\text{mol/L}$  – 20  $\mu\text{mol/L}$ )



Source: elaborated by the author (2025).

This LOD is lower than the maximum contaminant level (MCL) for glyphosate in drinking water established by Brazilian regulations, which is 500  $\mu\text{g/L}$  (corresponding to approximately 2.96  $\mu\text{mol/L}$ ) (Brasil, 2021). This result demonstrates the adequate analytical sensitivity of the developed nanomaterial for environmental monitoring

applications. The combination of selective surface interactions and efficient fluorescence quenching supports the suitability of Ce-CDs as a promising sensing platform for glyphosate detection in aqueous systems.

The selectivity of the proposed sensor was evaluated using a set of agrochemicals selected based on their environmental relevance and chemical diversity, including herbicides and insecticides with distinct functional groups and physicochemical properties. Although official validation guidelines, such as those proposed by AOAC, recommend the evaluation of a broader number of potential interferents, the compounds investigated here represent realistic coexisting contaminants in agricultural and aquatic environments. This strategy prioritizes environmental representativeness over the arbitrary inclusion of additional compounds. Considering the widespread agricultural use of glyphosate, its mobility in water bodies, and the growing public health concerns associated with chronic exposure, the ability of Ce-CDs to detect glyphosate at concentrations well below regulatory limits reinforces their potential applicability for environmental monitoring and water quality assessment.

## 6.6 GADOLINIUM-DOPED CARBON DOTS (GD-CDS)

The Gd-CDs synthesized in this study exhibited QY of 13.10%, 15.93%, and 14.56% for dopant masses of 3.00 g, 1.50 g, and 0.75 g, respectively. The best fluorescence efficiency was achieved with an intermediate dopant mass (1.50 g), indicating that both insufficient and excessive gadolinium content may negatively affect emission performance. The result suggests a possible balance between doping level, surface passivation, and defect formation that favors radiative recombination. When compared with previous studies, the QY of 15.93% obtained here is higher than the 11.7% reported by Li *et al.* (2020) for Gd-CDs synthesized via microwave-assisted methods using ethylenediamine, but lower than the 48.32% reported by Huang *et al.* (2020) and the 54% reported by Molaei (2022), both using citric acid-based precursors.

It is important to note that the CDs developed in this study were derived from rice husk, a lignocellulosic biomass with inherent structural complexity and high silica content, which may limit surface passivation efficiency. Nonetheless, the QY values

obtained are significant given the low-cost, renewable origin of the precursor, and they confirm the viability of rice husk for producing luminescent Gd-doped CDs suitable for optical sensing applications. Considering its superior quantum yield, the Gd-CD synthesized with 1.50 g of dopant was selected for further physicochemical characterization and sensing studies. Detailed analyses confirmed the successful incorporation of gadolinium and the preservation of desirable nanoscale features. This nanomaterial was subsequently applied as a fluorescent probe for mesotrione detection, demonstrating promising performance in both ultrapure and natural water samples.

### 6.6.1 Characterization of Gd-CDs

Figure 26a displays the FTIR spectrum of Gd-CDs, revealing the presence of several functional groups involved in surface chemistry and potential interactions with the Gd dopant. A broad absorption band centered at  $3409\text{ cm}^{-1}$  corresponds to the stretching vibrations of hydroxyl (O – H) groups, which are commonly present on the surface of CDs due to incomplete carbonization and hydration of oxygenated species. This band may also include contributions from N – H stretching, although no strong nitrogen signature was observed in the XPS analysis, suggesting predominance of oxygen-rich functionalities. Similar broad O – H absorptions have been reported in the FTIR spectra of Gd-CDs by Chen *et al.* (2016) and Wei *et al.* (2023), typically around  $3400^{-1} - 3440\text{ cm}^{-1}$ .

The band observed at  $1605\text{ cm}^{-1}$  is attributed to the bending vibrations of H – O – H from adsorbed water and/or the stretching of C = O groups in carboxylates or amide-like structures. This assignment aligns with findings from Fang *et al.* (2020) and Gong *et al.* (2014), who attributed similar bands ( $1580\text{ cm}^{-1} - 1650\text{ cm}^{-1}$ ) to carbonyl or C = C bonds in aromatic domains. A distinct peak at  $1384\text{ cm}^{-1}$  is associated with bending of CH<sub>3</sub>/CH<sub>2</sub> groups. Comparable bands in the  $1380\text{ cm}^{-1} - 1420\text{ cm}^{-1}$  range were reported in Gd-CDs synthesized by Huang *et al.* (2020) and Sur *et al.* (2020), indicating surface passivation and the presence of heteroatoms in the carbon framework.

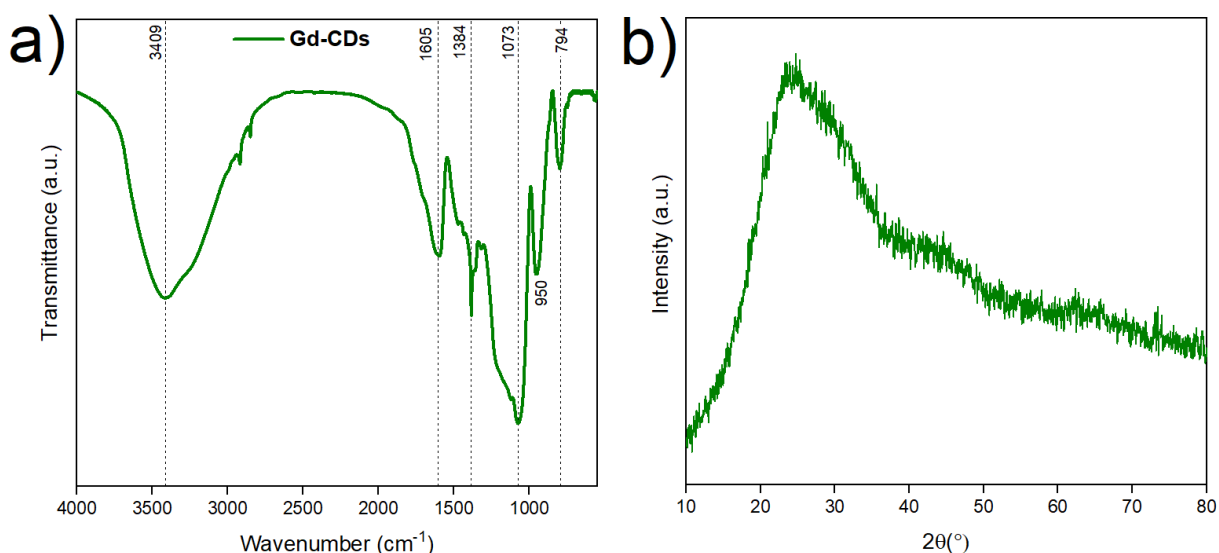
The strong band at  $1073\text{ cm}^{-1}$  is ascribed to C – O – C asymmetric stretching or stretching vibrations of C – O in alcohols and ethers. This absorption is characteristic of CDs and is often intensified by the presence of  $\text{Gd}^{3+}$ , which can coordinate with oxygen-containing groups on the surface, enhancing the interaction with polar functional moieties. Similar observations were made by Zhang *et al.* (2023) and Devi *et al.* (2022) in Gd-CDs exhibiting comparable surface oxygen functionalities. Notably, the weaker band observed at  $950\text{ cm}^{-1}$  could be related to out-of-plane bending of O – H or may also indicate the formation of Gd – O – C or Gd – O interactions. Although such metal–oxygen vibrations are typically weak in FTIR and often overlapped by stronger organic bands, similar features were observed in the work by Chen *et al.* (2016), who attributed absorptions below  $1000\text{ cm}^{-1}$  to Gd – O vibrational modes integrated into the carbon matrix.

Finally, the signal at  $794\text{ cm}^{-1}$  may be linked to C – H out-of-plane bending from aromatic structures or deformation modes related to metal–oxygen–carbon linkages, as also suggested by Fang *et al.* (2020). These results confirm the presence of various oxygenated surface groups (hydroxyls, carbonyls, and carboxylates) on the Gd-CDs, providing anchoring sites for  $\text{Gd}^{3+}$  ions. The observed bands are in strong agreement with those reported in literature for Gd-doped carbon dots and support successful doping through coordination with oxygen-containing functionalities on the CDs surface.

Figure 26b shows the XRD pattern of the synthesized Gd-CDs, revealing a broad diffraction peak centered at approximately  $26^\circ$  ( $2\theta$ ). This diffuse and asymmetric feature is characteristic of amorphous or low-crystallinity carbonaceous materials, typically attributed to the (0 0 2) plane of graphitic carbon structures. The absence of sharp peaks indicates that the Gd-CDs possess a disordered arrangement of  $sp^2$  domains, with limited long-range order. Similar broad features have been widely reported for Gd-CDs synthesized via hydrothermal or solvothermal routes. For example, Gong *et al.* (2016) and Fang *et al.* (2020) both observed broad peaks near  $25^\circ - 26^\circ$ , corresponding to disordered graphitic carbon, and confirmed the amorphous nature of the CDs based on the absence of crystalline  $\text{Gd}_2\text{O}_3$  or other sharp diffraction signals.

Likewise, Chen *et al.* (2016) attributed similar patterns to the presence of small  $sp^2$  domains interspersed within an amorphous carbon matrix, with minimal contribution from crystalline phases of the dopant. The incorporation of  $Gd^{+3}$  into the carbon matrix does not significantly alter the overall amorphous structure of the CDs, as evidenced by the absence of any additional crystalline peaks associated with gadolinium oxide or metallic gadolinium phases. This suggests a high dispersion or atomic-level integration of Gd species within the carbon framework, in agreement with observations by Zhang *et al.* (2024), who reported similar XRD profiles for Gd-CDs with efficient Gd doping but no phase segregation.

Figure 26 – Characterization of Gd-CDs: a) IR spectra; and b) XRD patterns

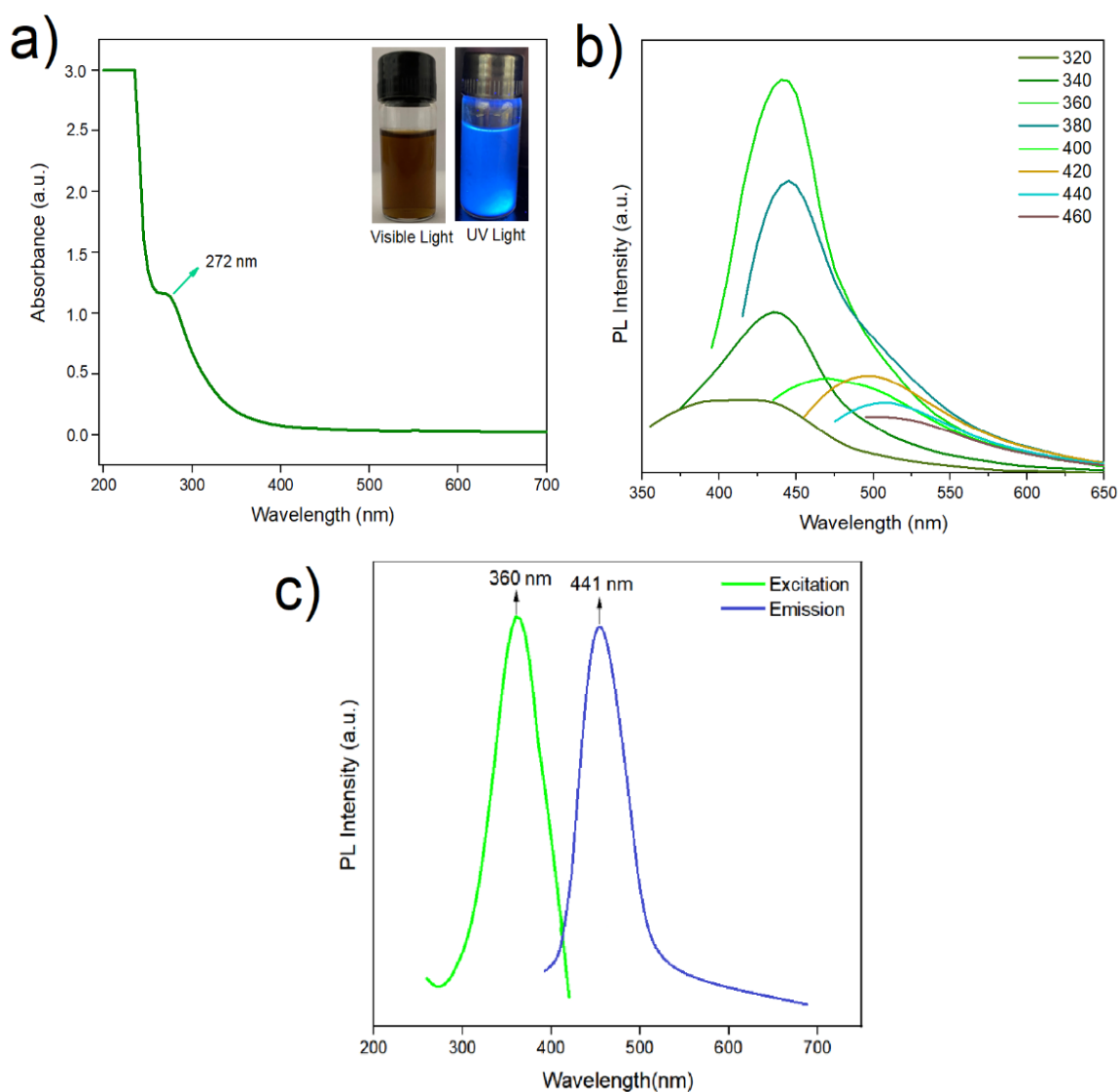


Source: elaborated by the author (2025).

Figure 27a shows the UV-Vis absorption spectrum of the Gd-CDs, displaying a pronounced absorption band centered at 272 nm. This band is attributed to the  $\pi-\pi^*$  transitions of aromatic C = C bonds, commonly present in the  $sp^2$ -hybridized carbon domains of carbon dots. Such transitions are a signature of graphitic-like core structures and are consistent with the optical behavior of carbon dots synthesized via hydrothermal methods. Chen *et al.* (2016) observed two prominent absorption bands at 240 nm and 350 nm in Gd-CDs, which were attributed to the  $\pi-\pi^*$  transitions of aromatic C = C and  $n-\pi^*$  transitions of C = O, respectively. Similarly, Wei *et al.* (2023) reported a peak at 270 nm associated with  $n-\pi^*$  transitions, while Jiang *et al.* (2021) detected shoulders at 283 nm and 340 nm, corresponding to  $\pi-\pi^*$  and  $n-\pi^*$  transitions.

These spectral features support the role of  $\text{Gd}^{3+}$  doping in modulating the electronic transitions of the carbon core. The Gd-CDs exhibited a brown coloration under ambient light and displayed intense blue fluorescence under 365 nm UV excitation, indicative of well-passivated carbon dots with emissive surface states. This behavior supports efficient photoluminescence, which is enhanced by the presence of  $\text{Gd}^{3+}$  ions acting as auxiliary energy donors or trap states, a phenomenon also discussed by Fang *et al.* (2020) and Molaei *et al.* (2022) in their optical studies on lanthanide-doped CDs.

Figure 27 – Optical analysis of Gd-CDs: a) UV–visible absorption spectrum; b) fluorescence spectra at different excitation wavelengths from 320 nm to 460 nm; and c) emission and excitation spectrum of synthesized Ce-CDs



Source: elaborated by the author (2025).

Figure 27b displays the photoluminescence emission spectra of Gd-CDs under excitation wavelengths ranging from 320 nm to 460 nm. The data clearly demonstrates the excitation-dependent emission behavior, a well-known characteristic of carbon dots, and particularly pronounced in heteroatom-doped systems such as Gd-CDs. The emission peaks are located predominantly in the blue to green region (approximately 430 nm – 480 nm), with the maximum photoluminescence intensity observed at an excitation wavelength of 360 nm. As the excitation wavelength increases, a red shift in the emission maximum is observed, along with a gradual decrease in intensity. This behavior is indicative of the presence of multiple emissive surface states, size heterogeneity, and trap sites within the CDs, which contribute to radiative recombination pathways at varying energy levels. These features are commonly reported for doped carbon dots and are consistent with studies by Fang *et al.* (2020) and Wei *et al.* (2023), who observed similar excitation-dependent emission profiles in Gd-CDs synthesized via hydrothermal methods.

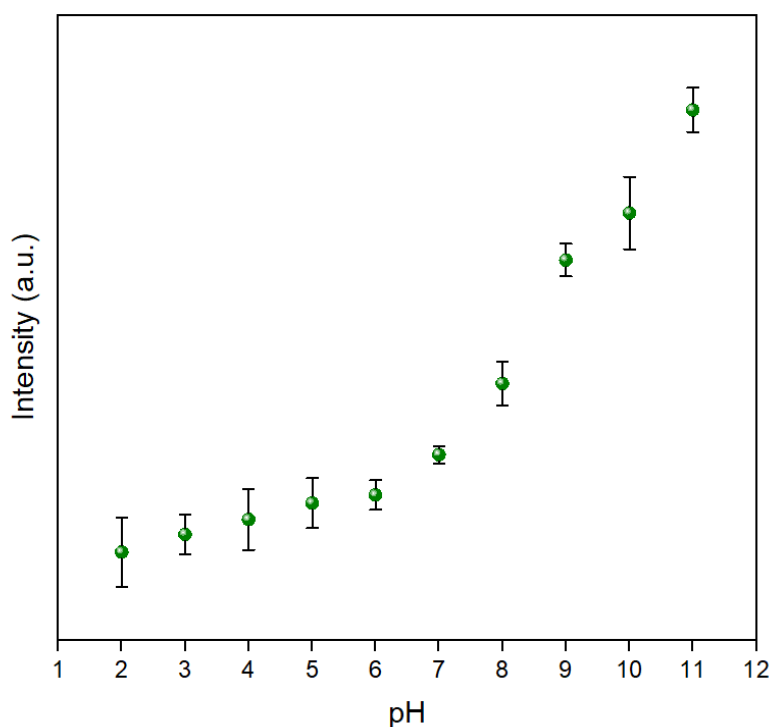
Excitation-dependent photoluminescence in CDs is commonly attributed to variations in surface functional groups, oxidation degree, and defect-related emissive states introduced by surface chemistry or heteroatom doping (Dong *et al.*, 2014). In this study, the incorporation of Gd<sup>3+</sup> into the carbon dot structure resulted in a measurable enhancement of photoluminescent efficiency. While undoped CDs synthesized under optimized conditions exhibited a quantum yield of approximately 14%, the Gd-CDs reached a higher quantum yield of 15.93%, indicating an improvement in optical performance upon rare-earth doping.

This enhancement can be attributed to the role of Gd<sup>3+</sup> ions in modifying surface electronic states rather than inducing significant structural or spectral changes. Gadolinium ions are known to interact with oxygen-containing functional groups, such as carboxyl and hydroxyl moieties, creating additional shallow surface states or defect-related energy traps. These states can partially suppress non-radiative recombination pathways and facilitate radiative electron–hole recombination. Similar behavior has been reported by Chen *et al.* (2016) and Jiang *et al.* (2021), who observed enhanced photoluminescence intensity and modulation of excitation–emission behavior in Gd-doped carbon dots due to surface-state interactions. Figure 27c displays the excitation and emission spectra of Gd-CDs. The maximum excitation occurred at 360 nm, while

the strongest photoluminescence emission was observed at 441 nm, corresponding to an intense blue fluorescence. This emission profile is consistent with the behavior of Gd-CDs reported in the literature, such as by Jiang *et al.* (2021) and Wei *et al.* (2023), who observed similar excitation-emission pairs in the range of 350 nm – 370 nm (excitation) and 430 nm – 450 nm (emission).

The fluorescence intensity of Gd-CDs showed a steady increase with increasing pH, reaching its maximum at pH 11 (Figure 28). This trend is attributed to the progressive deprotonation of surface functional groups, such as carboxyl and hydroxyl moieties, which improves surface passivation and promotes radiative recombination. The absence of a fluorescence drop at high pH, unlike what was observed for Ce-doped CDs, suggests that Gd-CDs possess greater colloidal and optical stability under alkaline conditions (Liu *et al.*, 2014). Based on these results, pH 11 was selected as the optimal condition for all subsequent sensing experiments involving Gd-CDs, ensuring maximum fluorescence intensity and signal stability.

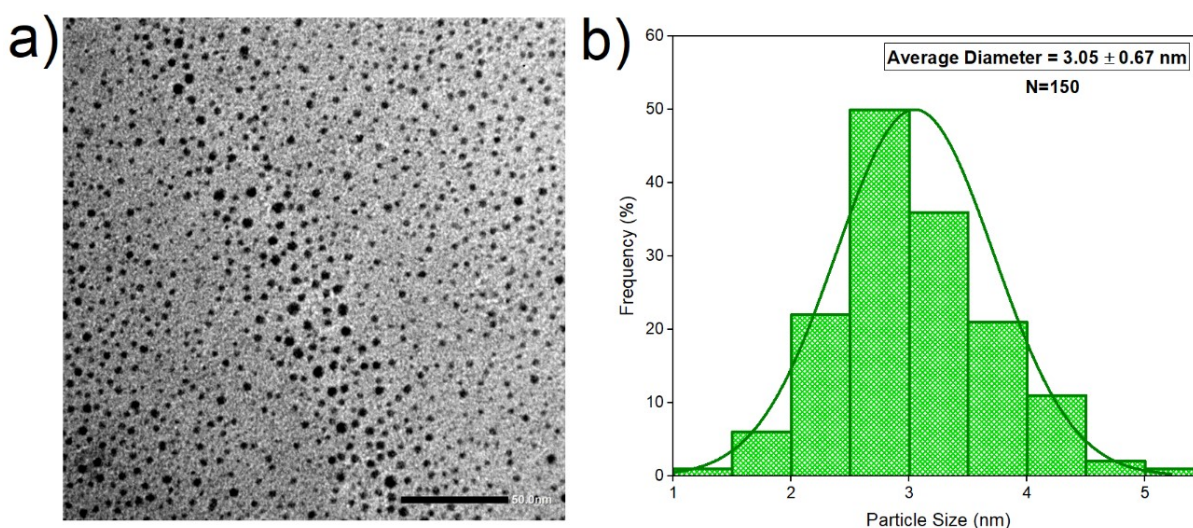
Figure 28 – Fluorescence intensity of Gd-CDs as a function of pH



Source: elaborated by the author (2025).

Figure 29a displays the morphological characterization of Gd-CDs, as observed by TEM and the corresponding particle size distribution histogram (Figure 29b). The Gd-CDs appeared as well-dispersed, quasi-spherical nanoparticles with uniform contrast. The histogram derived from the measurement of 150 particles revealed an average diameter of  $3.05 \text{ nm} \pm 0.67 \text{ nm}$ , with most particles distributed between 2.4 nm and 3.7 nm. The particle size obtained in this study aligns well with values reported for Gd-doped carbon dots synthesized under comparable hydrothermal conditions. For example, Jiang *et al.* (2021) reported Gd@CDs with an average diameter of 2.58 nm, while Chen *et al.* (2016) obtained Gd-doped CDs with a size distribution ranging from 2.3 nm to 4.5 nm and a mean diameter of 2.9 nm using a similar hydrothermal approach.

Figure 29 – Morphological analysis of Gd-CDs: a) TEM image; and b) histogram of particle size distribution

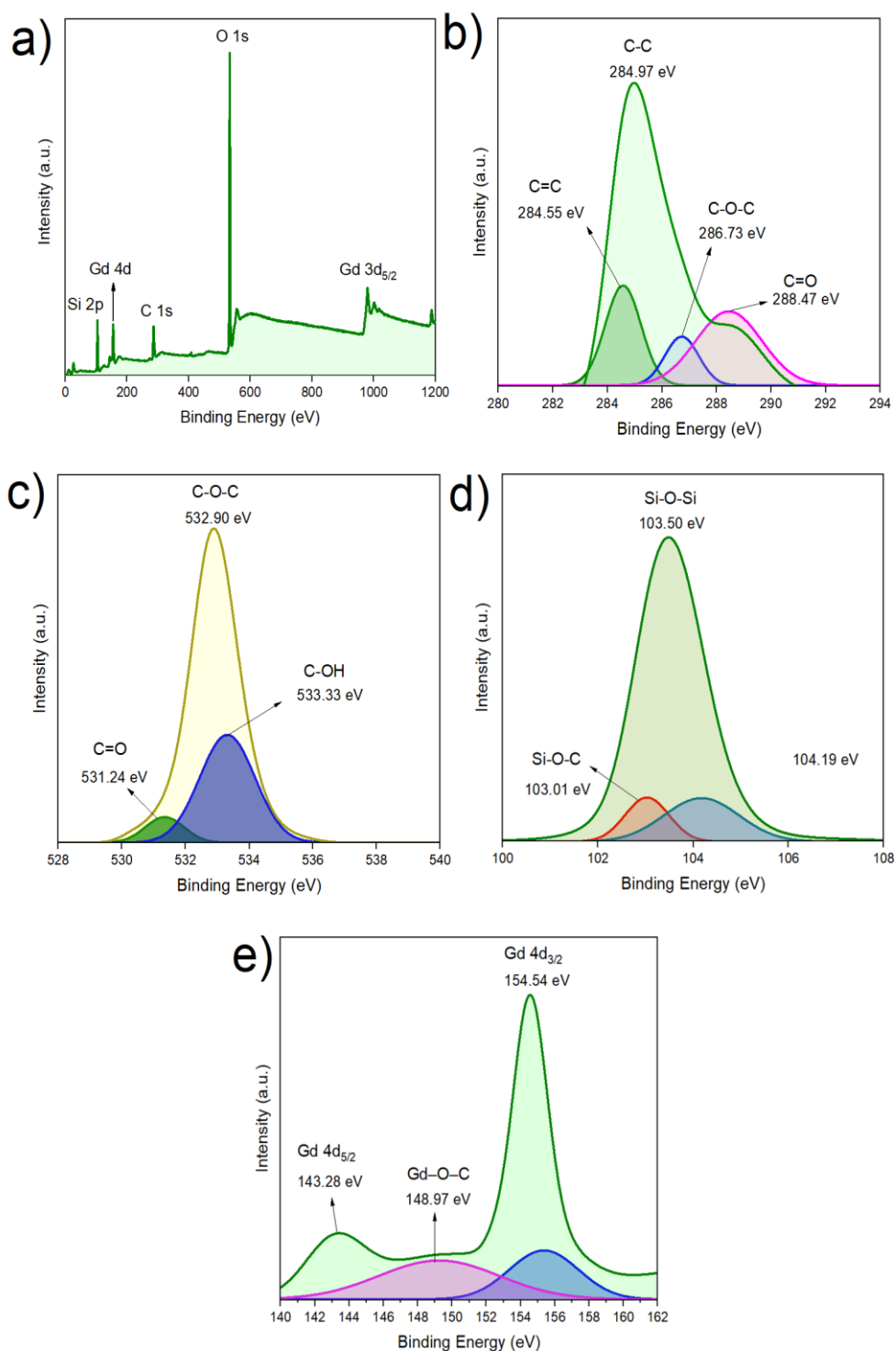


Source: elaborated by the author (2025).

The incorporation of  $\text{Gd}^{3+}$  ions, due to their large ionic radius and trivalent state, likely contributes to the slightly larger average size of Gd-CDs compared to undoped CDs (2.17 nm) through interactions with oxygen-containing surface groups. TEM images show good dispersibility, uniform morphology, and a narrow size distribution. These features enhance the surface-to-volume ratio and favor efficient analyte interactions, which are essential for fluorescence-based environmental sensing.

The surface elemental composition and chemical states of Gd-CDs were investigated by XPS, as shown in Figure 30.

Figure 30 – The XPS spectrum of Gd-CDS: a) XPS survey spectrum; b) high-resolution C 1s; c) high-resolution O 1s peaks; d) high-resolution Si 2p; and e) high-resolution of Gd 4d



Source: elaborated by the author (2025).

The wide scan spectrum (Figure 30a) revealed the presence of the main elements constituting the Gd-CDs: carbon (C 1s at ~285 eV), oxygen (O 1s at ~532 eV), gadolinium (Gd 4d between ~143 eV and 155 eV, and Gd 3d<sub>5/2</sub> at ~1185 eV – 1195 eV), and silicon (Si 2p at ~102 eV). The presence of Gd 4d and Gd 3d signals confirms the successful incorporation of gadolinium into the carbonaceous matrix, consistent with the values reported for Gd<sup>3+</sup> species in Gd-doped carbon nanomaterials by Zhang *et al.* (2024) and Zhu *et al.* (2019).

High-resolution deconvolution of the C 1s spectrum (Figure 30b) exhibited four distinct components, corresponding to various carbon bonding environments. The peaks at 284.55 eV and 284.97 eV are attributed to *sp*<sup>2</sup> and *sp*<sup>3</sup> hybridized carbon (C = C and C – C), respectively, typical of graphitic domains. The component at 286.73 eV corresponds to ether or epoxide groups (C – O – C), while the signal at 288.47 eV is associated with carbonyl functionalities (C = O). These oxygen-rich surface groups are commonly observed in biomass-derived carbon dots and are essential for the anchoring of metal ions such as Gd<sup>3+</sup>. Similar surface chemistry has been reported for Gd-functionalized carbon materials in studies by Sur *et al.* (2020) and Wei *et al.* (2023), reinforcing the proposed bonding interactions in the present work.

The O 1s spectrum (Figure 30c) showed a well-defined profile with contributions from C = O (531.24 eV), C – O – C (532.90 eV), and C – OH (533.33 eV) groups. The dominance of oxidized oxygen species is in line with the C 1s results and reflects a high density of functional groups that can chelate Gd<sup>3+</sup> ions through oxygen coordination. This agrees with findings reported by Jiaou *et al.* (2022), who observed similar oxygenated functionalities acting as anchoring sites for rare-earth dopants in carbon-based nanostructures.

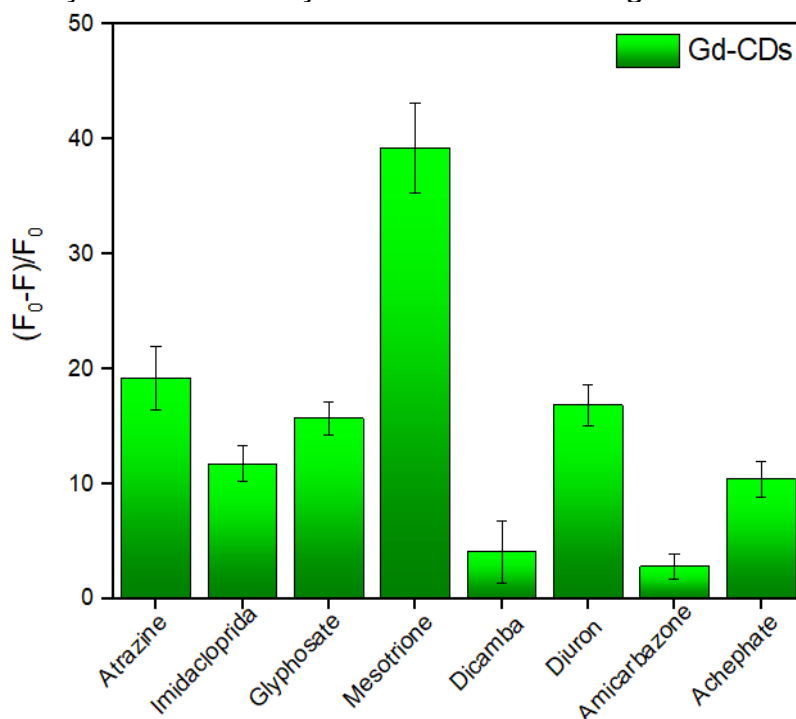
The Si 2p region (Figure 30d) displayed peaks at 103.01 and 103.50 eV, corresponding to Si – O – C and Si – O – Si bonds, respectively. A weaker signal at 104.19 eV may be attributed to partially oxidized silicon species. These peaks are attributed to the intrinsic presence of silica (SiO<sub>2</sub>) in the rice husk precursor, which is well-known for its high silicon content. Zainal Abidin *et al.* (2020) also reported similar Si-related features in carbon nanomaterials synthesized from silica-rich biomass.

Most importantly, the high-resolution spectrum of Gd 4d (Figure 30e) revealed clear spin–orbit splitting consistent with  $\text{Gd}^{3+}$ . The peak at 143.28 eV corresponds to Gd 4d<sub>5/2</sub> and is characteristic of gadolinium in its trivalent oxidation state ( $\text{Gd}_2\text{O}_3$ ), as documented by Zheng *et al.* (2019). The major peak at 154.54 eV represents the Gd 4d<sub>3/2</sub> component, while the intermediate feature at 148.97 eV is attributed to Gd – O – C interactions, indicating coordination of Gd with oxygenated groups present on the carbon dots surface, in agreement with Zhang *et al.* (2023) and Sur *et al.* (2020).

### 6.6.2 Application Gd-CDs

Figure 31 illustrates the fluorometric response of Gd-CDs when exposed to a series of agrochemicals, each at a fixed concentration of 500  $\mu\text{mol/L}$ . Notably, the Gd-CDs exhibited a pronounced fluorescence quenching in the presence of mesotrione, suggesting a strong and specific interaction between the nanomaterial surface and this herbicide. This high quenching efficiency, significantly higher than that observed for other compounds such as atrazine, glyphosate, or dicamba, indicates a favorable binding affinity or electronic interaction, possibly facilitated by mesotrione's electron-withdrawing groups or aromatic moieties.

Figure 31 – Study of the selectivity of Gd-CDs concerning different agrochemicals

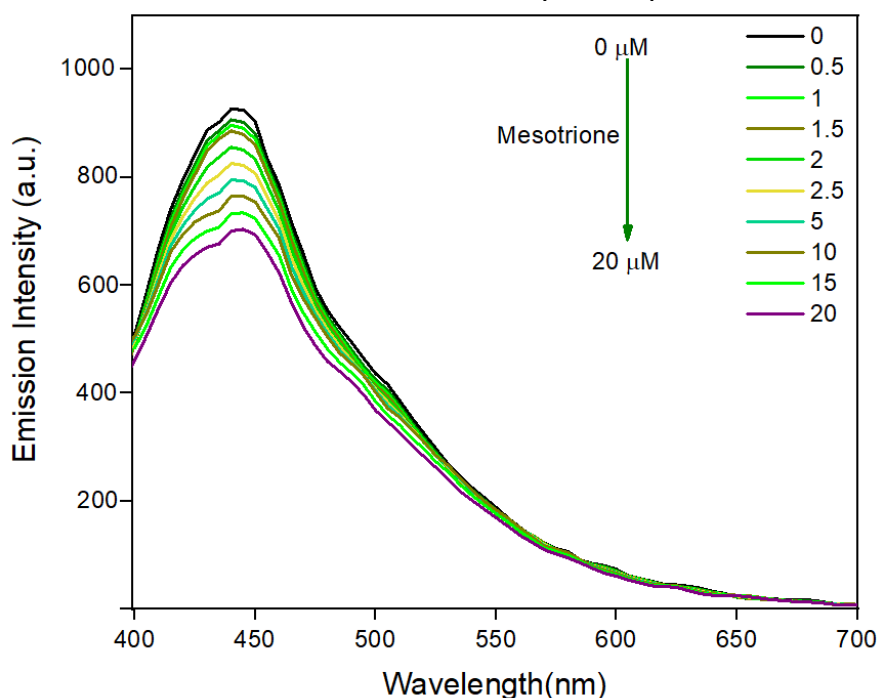


Source: elaborated by the author (2025).

Similar fluorescence-based sensing behavior has been described for CDs designed to detect glyphosate, as demonstrated by Sasikumar *et al.* (2024), where fluorescence quenching occurred via static mechanisms involving ground-state complex formation between the probe and the analyte. Additionally, Devi *et al.* (2022) highlighted the role of heteroatom doping and surface functionalities in tuning the selectivity and sensitivity of CDs toward specific pesticides.

The sensitivity and applicability of the Gd-CDs as fluorescent sensors for mesotrione detection were further evaluated by titrating increasing concentrations of the analyte (0  $\mu\text{mol/L}$  to 20  $\mu\text{mol/L}$ ) into an aqueous Gd-CDs solution, while monitoring the photoluminescence response (Figure 32). A progressive and concentration-dependent decrease in fluorescence intensity was observed, indicating efficient quenching of the emission signal by mesotrione.

Figure 32 – Fluorescence emission spectra of Gd-CDs recorded with increasing mesotrione concentrations up to 20  $\mu\text{mol/L}$

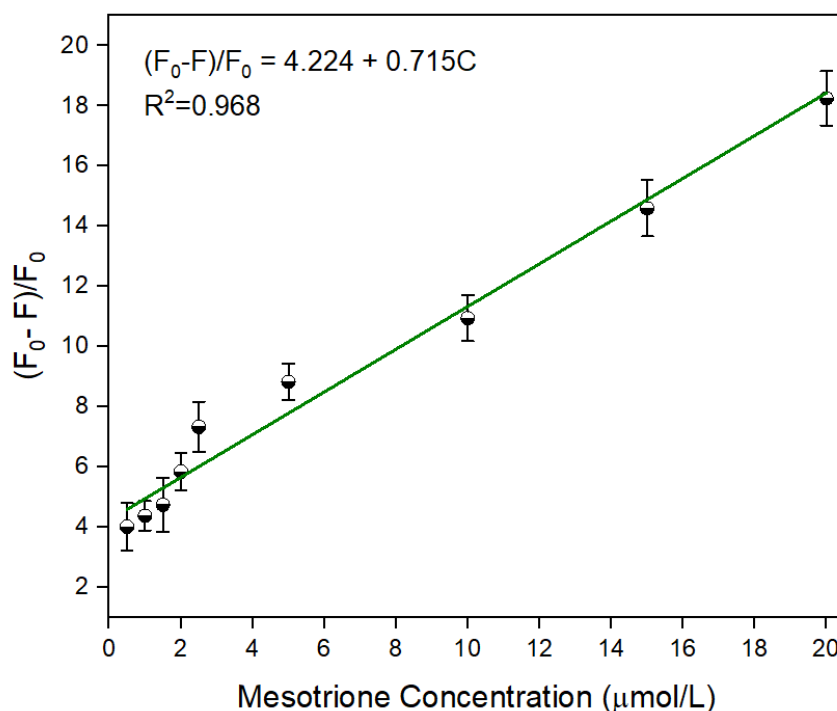


Source: elaborated by the author (2025).

Importantly, no shift in the emission maximum was detected, suggesting that the interaction mechanism predominantly involves static or dynamic quenching pathways rather than changes in the electronic structure of the emissive sites. At the highest

tested concentration (20  $\mu\text{mol/L}$ ), the Gd-CDs exhibited a pronounced reduction in emission intensity. However, when compared to the response obtained with Ce-CDs, the overall quenching efficiency was slightly lower, indicating a possible difference in the interaction affinity between mesotrione and the doped surfaces. Based on the fluorescence data, a calibration curve was established for mesotrione detection using Gd-CDs, revealing a linear correlation between the relative fluorescence quenching and mesotrione concentrations in the range of 0.5  $\mu\text{mol/L}$  to 20  $\mu\text{mol/L}$ , with a correlation coefficient ( $R^2$ ) of 0.968 (Figure 33).

Figure 33 – Linear band of increasing intensity and concentration of mesotrione (0.5  $\mu\text{mol/L}$  to 20  $\mu\text{mol/L}$ )



Source: elaborated by the author (2025).

The linear fitting equation is given by Equation (12):

$$\frac{F_0 - F}{F_0} = 0.715 \cdot C + 4.224 \quad (12)$$

where  $C$  is the mesotrione concentration. The calculated limit of detection (LOD), based on the  $3\sigma/k$  criterion, was 4.3  $\mu\text{mol/L}$  (approximately 1.21  $\mu\text{g/L}$ ). Although no

specific regulatory limit for mesotrione in drinking water is established in Brazil, its frequent detection in surface and groundwater, combined with its high mobility and moderate persistence, has raised increasing environmental concern (Carles; Joly; Joly, 2017).

The LOD obtained in this study falls within the concentration range commonly reported in environmental monitoring studies, demonstrating the suitability of the proposed sensor for the detection of mesotrione at environmentally relevant levels. Mesotrione is a selective herbicide widely used in maize cultivation, and its residues have raised concern due to potential ecotoxicological impacts and endocrine-disrupting effects on aquatic organisms (Carles; Joly; Joly, 2017).

The high quenching efficiency observed in this study suggests a strong interaction between mesotrione molecules and the surface functional groups of the Gd-CDs, likely involving hydrogen bonding and  $\pi$ - $\pi$  stacking interactions, which promote non-radiative recombination pathways. This behavior is consistent with previous studies employing carbon dot-based sensors for herbicide detection, which reported similar quenching mechanisms and highlighted their environmental relevance (Sasikumar *et al.*, 2024; Yuan *et al.*, 2017). These findings demonstrate the effectiveness of Gd-CDs as a fluorescent probe for mesotrione, enabling sensitive and reliable detection at environmentally relevant concentration levels.

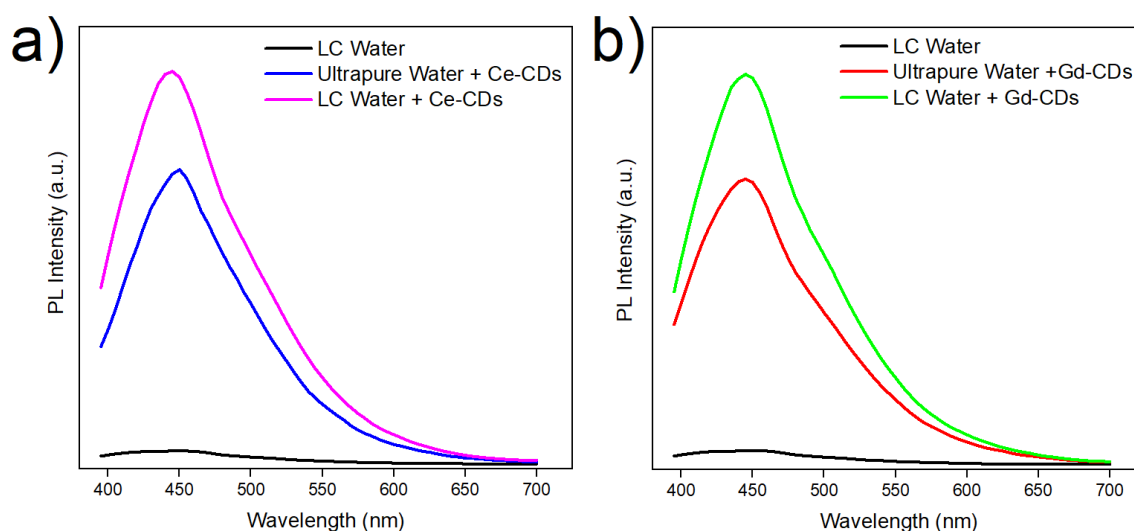
## 6.7 DETECTION OF DOPED CDS IN REAL SAMPLES

Figure 34 presents the emission spectra of Ce-CDs and Gd-CDs, dispersed in two distinct matrices: ultrapure water and real samples from Lagoa da Conceição (LC) located in Florianópolis, SC, Brazil. This comparison aims to assess the influence of the aqueous matrix on the fluorescence response of the nanosensors, which is a critical element for validating their applicability in natural environments.

It was observed that for both materials, fluorescence intensity was higher when dispersed in lagoon water. In the case of Ce-CDs (Figure 34a), the maximum emission intensity obtained in lagoon water exceeded that observed in ultrapure water. This

difference can be attributed to the presence of natural components such as metal ions, dissolved organic matter, and potential fluorophoric molecules in the water, and others. These factors may stabilize the excited states of the CDs, enhance radiative processes and influence emission behavior. A similar trend was observed for Gd-CDs (Figure 34b), with even more pronounced emission enhancement in lagoon water. This effect suggests a stronger interaction between the Gd-CDs and chemical species present in the natural matrix, potentially altering the surface organization of the CDs or enhancing the dopant effect.

Figure 34 – Emission spectra of rare-earth-doped carbon dots (Ce-CDs and Gd-CDs) in different aqueous media: a) emission spectra of Ce-CDs in ultrapure water and lagoon water, compared with the spectrum of lagoon water without CDs; and b) emission spectra of Gd-CD



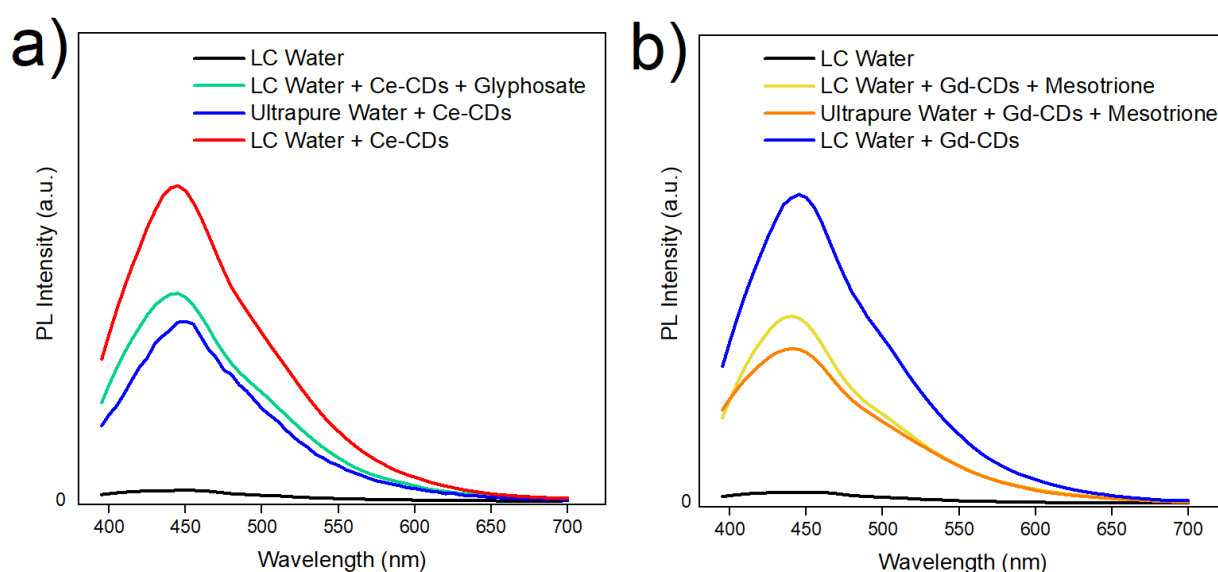
Source: elaborated by the author (2025).

Figure 35 presents the emission spectra of Ce-CDs and Gd-CDs in the presence of the pesticides glyphosate and mesotrione, respectively. Both ultrapure water and real lagoon water samples were used, with and without the addition of contaminants, enabling the evaluation of sensor selectivity. In Figure 35a, Ce-CDs dispersed in lagoon water without glyphosate exhibited high fluorescence emission, with a peak around 440 nm. Upon addition of glyphosate, a clear decrease in fluorescence was observed, consistent with a detection mechanism based on emission quenching, according to Sasikumar *et al.* (2024). The emission profile of the sample containing glyphosate in lagoon water closely resembled that in ultrapure water,

suggesting that the real matrix may contain quenching species with optical behavior similar to glyphosate, or background components capable of inducing comparable fluorescence suppression effects.

A similar behavior was observed in Figure 35b for Gd-CDs in the presence of mesotrione. The intense fluorescence in lagoon water decreased following pesticide addition, and the resulting emission curve overlapped with that obtained in ultrapure water. This indicates effective detection in both matrices and suggests that components present in the environmental matrix may induce fluorescence quenching behavior similar to that observed for mesotrione (Carles; Joly; Joly, 2017). These results confirm that the doped CDs selectively respond to the pesticides studied, exhibiting strong fluorescence in the absence of analytes and significant quenching when they are present (Alvandi *et al.*, 2021). The similarity between the emission spectra in both matrices reinforces the feasibility of using these nanomaterials as sensors for environmental monitoring (Jessy Mercy *et al.*, 2023).

Figure 35 – a) Photoluminescence spectra of Ce-CDs dispersed in lagoon water without contaminant (red), lagoon water containing glyphosate (green), ultrapure water with Ce-CDs (blue), and lagoon water alone (black); and  
b) Photoluminescence spectra of Gd-CDs dispersed in lagoon water without contaminant (blue), lagoon water containing mesotrione (yellow), ultrapure water with Gd-CDs and mesotrione (orange), and lagoon water alone (black).



Source: elaborated by the author (2025).

Although the doped carbon dots exhibited spectral responses that closely resembled those observed for spiked and unspiked lagoon water samples, the observed spectral overlap suggests the possible presence of compounds with similar quenching behavior to glyphosate and mesotrione in the environmental matrix. However, to conclusively confirm the presence of these contaminants, it is necessary to apply confirmatory analytical techniques with higher specificity and sensitivity, such as liquid chromatography coupled with mass spectrometry (LC-MS/MS), gas chromatography (GC-MS), or validated spectrophotometric methods. Implementing these techniques in future studies will allow validation of the nanosensor results and accurate quantification of pesticide levels in environmental matrices.

### 6.7.1 Sensor Performance

As described in the methodology (Section 5.6), recovery experiments were conducted using Ce-doped and Gd-doped carbon dots to detect glyphosate and mesotrione, respectively, in real water samples collected from five different sites within Lagoa da Conceição (Florianópolis, SC, Brazil). The results obtained are summarized in Tables 9 and 10. The results presented in Table 9 demonstrate that Ce-doped CDs exhibited high efficiency in glyphosate detection, with recovery rates ranging from 72.7% to 93.4% and relative deviations between 1.05% and 3.77%. The slight reduction in efficiency at higher concentrations may indicate saturation effects or nonspecific interactions. Nevertheless, the sensors showed good precision, reproducibility, and field applicability.

Table 9 – Performance of cerium-doped CDs in real samples for glyphosate detection (to be continued)

| Pesticide  | Sample                                     | Added Pesticide Concentration ( $\mu\text{mol/L}$ ) | Calculated Pesticide Concentration ( $\mu\text{mol/L}$ ) | Recovery (%) | SD (%) |
|------------|--------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|--------------|--------|
| Glyphosate | Water from Lagoa da Conceição: Bar do Boni | 1                                                   | 0.87                                                     | 87.0         | 1.99   |
|            |                                            | 2                                                   | 1.79                                                     | 89.5         | 2.38   |
|            |                                            | 5                                                   | 4.67                                                     | 93.4         | 1.18   |
|            |                                            | 10                                                  | 8.97                                                     | 89.7         | 1.59   |
|            |                                            | 15                                                  | 13.17                                                    | 87.8         | 2.23   |
|            |                                            | 20                                                  | 15.76                                                    | 78.8         | 2.09   |

Table 9 – Performance of cerium-doped CDs in real samples for glyphosate detection  
(conclusion)

| Pesticide  | Sample                                        | Added Pesticide Concentration (μmol/L) | Calculated Pesticide Concentration (μmol/L) | Recovery (%) | SD (%) |
|------------|-----------------------------------------------|----------------------------------------|---------------------------------------------|--------------|--------|
| Glyphosate | Water from Lagoa da Conceição: Barra da Lagoa | 1                                      | 0.77                                        | 77.0         | 3.44   |
|            |                                               | 2                                      | 1.66                                        | 83.0         | 2.67   |
|            |                                               | 5                                      | 4.37                                        | 87.4         | 1.79   |
|            |                                               | 10                                     | 9.11                                        | 91.1         | 1.05   |
|            |                                               | 15                                     | 12.97                                       | 86.47        | 3.02   |
|            |                                               | 20                                     | 14.55                                       | 72.7         | 2.99   |
| Glyphosate | Water from Lagoa da Conceição: Centrinho      | 1                                      | 0.81                                        | 81.0         | 3.12   |
|            |                                               | 2                                      | 1.73                                        | 86.5         | 2.54   |
|            |                                               | 5                                      | 4.52                                        | 90.4         | 1.36   |
|            |                                               | 10                                     | 9.11                                        | 91.1         | 1.48   |
|            |                                               | 15                                     | 13.02                                       | 86.8         | 2.29   |
|            |                                               | 20                                     | 15.89                                       | 79.5         | 2.76   |
| Glyphosate | Water from Lagoa da Conceição: Costa da Lagoa | 1                                      | 0.74                                        | 74.0         | 3.77   |
|            |                                               | 2                                      | 1.61                                        | 80.5         | 2.89   |
|            |                                               | 5                                      | 4.25                                        | 85.0         | 1.91   |
|            |                                               | 10                                     | 8.79                                        | 87.9         | 1.72   |
|            |                                               | 15                                     | 12.45                                       | 83.0         | 2.53   |
|            |                                               | 20                                     | 14.54                                       | 72.7         | 3.05   |
| Glyphosate | Water from Lagoa da Conceição: Rio Vermelho   | 1                                      | 0.79                                        | 79.0         | 3.21   |
|            |                                               | 2                                      | 1.70                                        | 85.0         | 2.61   |
|            |                                               | 5                                      | 4.48                                        | 89.6         | 1.42   |
|            |                                               | 10                                     | 9.06                                        | 90.6         | 1.52   |
|            |                                               | 15                                     | 13.11                                       | 87.4         | 2.34   |
|            |                                               | 20                                     | 15.67                                       | 78.4         | 2.92   |

Source: elaborated by the author (2025).

Table 10 – Performance of gadolinium-doped CDs in real samples for mesotrione detection

(to be continued)

| Pesticide  | Sample                                     | Added Pesticide Concentration (μmol/L) | Calculated Pesticide Concentration (μmol/L) | Recovery (%) | SD (%) |
|------------|--------------------------------------------|----------------------------------------|---------------------------------------------|--------------|--------|
| Mesotrione | Water from Lagoa da Conceição: Bar do Boni | 1                                      | 0.78                                        | 78.0         | 2,15   |
|            |                                            | 2                                      | 1.69                                        | 84.5         | 2,48   |
|            |                                            | 5                                      | 4.42                                        | 88.4         | 1,72   |
|            |                                            | 10                                     | 8.74                                        | 87.4         | 1,95   |
|            |                                            | 15                                     | 12.45                                       | 83.0         | 2,36   |
|            |                                            | 20                                     | 14.26                                       | 71.3         | 3,12   |

Table 10 – Performance of gadolinium-doped CDs in real samples for mesotrione detection

(conclusion)

| Pesticide  | Sample                                        | Added Pesticide Concentration ( $\mu\text{mol/L}$ ) | Calculated Pesticide Concentration ( $\mu\text{mol/L}$ ) | Recovery (%) | SD (%) |
|------------|-----------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|--------------|--------|
| Mesotrione | Water from Lagoa da Conceição: Barra da Lagoa | 1                                                   | 0.72                                                     | 72.0         | 3.61   |
|            |                                               | 2                                                   | 1.61                                                     | 80.5         | 2.88   |
|            |                                               | 5                                                   | 4.28                                                     | 85.6         | 2.11   |
|            |                                               | 10                                                  | 8.55                                                     | 85.5         | 2.34   |
|            |                                               | 15                                                  | 11.93                                                    | 79.5         | 2.75   |
|            |                                               | 20                                                  | 13.97                                                    | 69.8         | 3.35   |
| Mesotrione | Water from Lagoa da Conceição: Centrinho      | 1                                                   | 0.75                                                     | 75.0         | 3.22   |
|            |                                               | 2                                                   | 1.65                                                     | 82.5         | 2.71   |
|            |                                               | 5                                                   | 4.37                                                     | 87.4         | 1.89   |
|            |                                               | 10                                                  | 8.67                                                     | 86.7         | 2.15   |
|            |                                               | 15                                                  | 12.31                                                    | 82.1         | 2.48   |
|            |                                               | 20                                                  | 14.18                                                    | 70.9         | 3.28   |
| Mesotrione | Water from Lagoa da Conceição: Costa da Lagoa | 1                                                   | 0.69                                                     | 69.0         | 3.88   |
|            |                                               | 2                                                   | 1.55                                                     | 77.5         | 3.02   |
|            |                                               | 5                                                   | 4.12                                                     | 82.4         | 4.23   |
|            |                                               | 10                                                  | 8.34                                                     | 83.4         | 2.56   |
|            |                                               | 15                                                  | 11.67                                                    | 77.8         | 2.93   |
|            |                                               | 20                                                  | 13.35                                                    | 66.7         | 3.72   |
| Mesotrione | Water from Lagoa da Conceição: Rio Vermelho   | 1                                                   | 0.74                                                     | 74.0         | 3.35   |
|            |                                               | 2                                                   | 1.63                                                     | 81.5         | 2.79   |
|            |                                               | 5                                                   | 4.35                                                     | 87.0         | 1.98   |
|            |                                               | 10                                                  | 8.71                                                     | 87.1         | 2.19   |
|            |                                               | 15                                                  | 12.25                                                    | 81.7         | 2.61   |
|            |                                               | 20                                                  | 14.26                                                    | 71.3         | 3.41   |

Source: elaborated by the author (2025).

For Gd-CDs, recovery rates ranged from 66.7% to 89.3%, with deviations between 1.72% and 4.23%. Although the results are satisfactory, the performance was slightly lower compared to that of Ce-CDs. This may suggest a lower affinity of Gd for mesotrione or a higher susceptibility to matrix interferences. Nonetheless, Gd-CDs maintained functionality in real samples, proving useful as preliminary sensors for environmental screening.

Overall, the doped CDs proved to be promising platforms for preliminary screening applications. Ce-CDs exhibited good selectivity toward glyphosate, whereas

Gd-CDs showed good sensitivity to mesotrione, even under complex matrix conditions. However, the lack of definitive analyte identification in real matrices and the difficulty in assessing interference from structurally similar compounds represent important limitations of this study. Future investigations should therefore include tests with complex pesticide mixtures, multivariate spectral analysis, and cross-validation using robust instrumental techniques. In conclusion, this study demonstrates the successful development of rare-earth-doped carbon dots synthesized through a green and sustainable route using rice husk biomass. The combined optimization of synthesis parameters, kinetic analysis of biomass degradation, and comprehensive physicochemical characterization provided valuable insights into the formation mechanism of the carbon dots. The incorporation of cerium and gadolinium enhanced the photoluminescent performance and sensing capabilities of the materials, and the satisfactory analytical performance in real water matrices highlights their potential as sustainable and cost-effective fluorescent sensors for in situ environmental monitoring.

## 7 CONCLUSIONS

In summary, this study developed a comprehensive and innovative strategy to elucidate the formation mechanism of rice husk-derived carbon dots (R-CDs), aiming to valorize an abundant agro-industrial waste into sustainable nanomaterials for sensing applications. The integrated analysis of biomass composition before and after hydrothermal synthesis, alongside the characterization of the resulting R-CDs, provided fundamental mechanistic insights. Specifically, it was demonstrated that synthesis parameters, particularly solid loading and temperature, influenced the degree of biomass carbonization and the conversion efficiency into carbonaceous nanostructures.

Elevated synthesis temperatures led to a substantial reduction of cellulose in the solid phase, complete degradation of hemicellulose, and a relative enrichment of residual lignin and ash. This transformation favored the solubilization of glucan and xylan into the liquid fraction, which underwent depolymerization into oligosaccharides and monosaccharides such as glucose, xylose, and arabinose. These intermediates further reacted to form furfural and hydroxymethylfurfural, ultimately driving the nucleation and growth of carbonaceous cores that evolved into fluorescent R-CDs. The combination of the experimental design approach and kinetic studies enabled the identification of optimized synthesis conditions (220 °C, 3% w/v, 4 h), under which a balance between efficient biomass conversion and high quantum yield was achieved.

Beyond synthetic optimization, this work successfully introduced rare-earth doping as a strategy to enhance the structural and functional properties of the R-CDs. Doping with cerium and gadolinium resulted in substantial improvements, as confirmed by FTIR and XPS analyses, which evidenced abundant oxygenated surface groups and the formation of Ce – O – C and Gd – O – C bonds. XRD patterns corroborated the amorphous nature of the doped CDs, free from crystalline contaminants, while TEM analysis revealed spherical, monodisperse nanoparticles with sizes in the range of 3 nm – 4 nm. Optical characterization showed intense blue emission and excitation-dependent behavior.

Functionally, the doped CDs displayed high sensitivity and selectivity in the detection of agrochemicals: Ce-CDs reached a detection limit of 1.78  $\mu\text{mol/L}$  for glyphosate, and Gd-CDs detected mesotrione at 4.3  $\mu\text{mol/L}$ . These results were consistent even in real water samples collected from Lagoa da Conceição, with analytical recoveries between 66.7% and 93.4%, confirming the robustness of the system under environmentally relevant conditions. Taken together, these findings demonstrate that the combination of biomass valorization, optimized hydrothermal synthesis, and strategic rare-earth doping can yield high-performance, sustainable nanomaterials for environmental monitoring. This work provides a solid foundation for future development of green, fluorescent sensors and broadens the horizon for applications of carbon-based nanotechnology in analytical and environmental sciences.

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