Photocatalytic Degradation and Antioxidant Properties of Carbon Quantum Dots Derived from Leaves of *Antigonon leptopus*

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Abstract:
The carbon quantum dots (CQDs) from *Antigonon leptopus* leaves in the present study was done using conventional microwave irradiation. The optical properties of the CQDs were characterized by UV-Vis spectroscopy, revealing distinct excitations at 266 nm and 320 nm. Fourier transform infrared spectroscopy (FTIR) analysis found surface functionalization on carbon core such as hydroxyl and carbonyl, contributing to the CQDs electron transfer capabilities. X-ray diffraction (XRD) analysis confirmed the common amorphous property, and photoluminescence spectroscopy showed multiple emission peaks, indicating complex optical behaviour. High-resolution transmission electron microscopy (HRTEM) revealed spherical CQDs with an average particle size of 3.3 nm. The *in vitro* antioxidant activity was evaluated using the DPPH assay, and calculated IC_{50} value is 20.23 µg mL^{-1}. The photocatalytic degradation of methylene blue (MB) and eosin yellow (EY) dyes was assessed under visible light, with the CQDs achieving up to 74.87% degradation for MB and 79.8% for EY at optimal concentrations. Rate constants indicated efficient photocatalysis, with MB degrading faster than EY. The present study revealed potential of *Antigonon leptopus*-derived CQDs as effective photocatalysts for dye degradation and antioxidant applications.

Keywords: Methylene Blue, Eosin Yellow, Carbon Quantum Dots, DPPH, *Antigonon leptopus*

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1. INTRODUCTION:

Textile dyes are complex environmental contaminants that are often released into water bodies without adequate treatment, leading to ecosystem contamination. These dyes can disrupt aquatic ecosystems, affect water quality, and ultimately affect the life [1]. Methylene blue (MB) and eosin yellow (EY) are two dyes with significant industrial applications, each serving distinct roles across various sectors. The former (MB) is prevalently used in industries such as textiles, rubber, plastics, leather, pharmaceuticals, cosmetics, and food, primarily as a colouring and staining agent. The latter (EY), on the other hand, is predominantly used in biological staining and as a spectroscopic probe in chemical and pharmaceutical analysis [2]. The effluents containing these dyes released into the aquatic environment cause great risk to the aquatic and its associated life forms. In industrial wastewaters, photocatalysis of these dyes presents a promising and efficient method for degradation in the presence of irradiated light, generating reactive species [3].

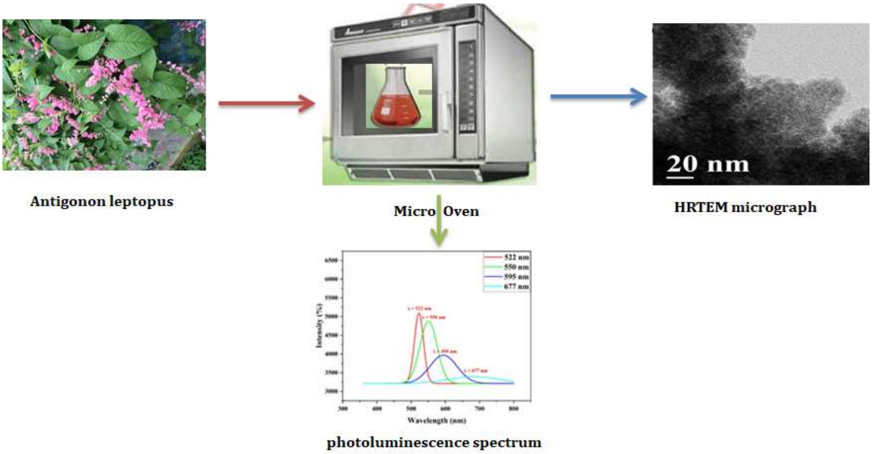
Several studies were carried out previously to evaluate the photocatalytic degradation of textile dyes in *in vitro*, *ex-situ*, and *in-situ* conditions. Materials such as metal nanoparticles, metal organic frameworks (MOFs), nanohybrid materials, semiconductor metal oxides, etc. have successfully degraded the dyes [4]. The disadvantages associated with these materials are high band gap energy, limited light absorption, recombination of electron-hole pairs, formation of harmful intermediates and by-products, and large-scale operational challenges [5]. In order to overcome the challenges, researchers are developing new compatible and eco-friendly materials that are effective in catalyzing the degradation reaction and able to produce non-harmful by-products [6].

One of the efficient and novel photocatalytic materials are versatile, zero-dimensional, carbon quantum dots (CQDs), belongs to carbon nanomaterials family. CQDs are known for their wide photoluminescence emissions, biocompatibility, hydrophilic nature, and low toxicity, making CQDs suitable for a broad range of applications in fields such as biomedicine, sensing, catalysis, and energy conversion

[7]. CQDs, due to their unique optical and electronic properties, have been extensively studied for their ability to degrade various dyes under UV and Visible light irradiations [8]. CQDs are synthesized using various precursors such as graphene, citric acid, glucose, ascorbic acid, ethylenediamine, ammonium citrate, and biomass. Biomass-derived CQDs are advantageous over CQDs derived from other chemical precursors because of renewable precursors, eco-friendliness, and no further requirement of surface functionalization [9]. Common synthesis methods of CQDs are pyrolysis, carbonization, hydrothermal, and microwave-assisted. Due to its rapidity and efficiency, as well as its lower energy and time consumption compared to other methods, the microwave-assisted method finds widespread use in the synthesis of CQDs [10].

After thorough literature survey, it was found that many of the CQDs derived from green precursors successfully degraded the MB and EY, and still more novel studies are necessary to understand the effect of surface functionalization on degradation properties of CQDs. Thus, the present study chooses *Antigonon leptopus* (AL), a naturally abundant creeper weed, for the synthesis of CQDs. *Antigonon leptopus*, commonly known as coral vine, is a versatile plant able to grow in tropical and subtropical regions. It is recognized for its ornamental value, ecological benefits, and potential as an invasive species. It is widely recognized for serving as a crucial source of food for insects and for acting as a biological pest on fireworms. Previous studies found that AL plant consists of various phytochemicals such as polyphenols, carbohydrates, and saponins with a wide range of pharmacological properties. These molecules serve as precursors for the synthesis of CQDs without further requirements for surface functionalization with heteroatoms [11, 12].

The objectives of the present study are (1) to synthesize the *Antigonon leptopus leaf CQDs* using the microwave-assisted method, (2) to evaluate the optical and morphological properties of AL-CQDs, and (3) to understand the antioxidant and photocatalytic degradation of MB and EY properties.



Schematic Representation of AI-CQDs

2. METHODOLOGY:

The present study involves microwave assisted synthesis of AL-CQDs and evaluation of optical and morphological properties using various analytical techniques. The AL-CQDs are further subjected to evaluate their *in vitro* antioxidant properties and photo-catalytic degradation of MB and EY.

2 grams pulverized powder of *Antigonon leptopus* (AL) leaves was dispersed in distilled water and subjected to irradiation at 640 W for 10 mins using conventional microwave oven with interval of 30 seconds. The reaction mixture was purified to obtain AL-CDs using various filtration steps such as Whatman No 1 filter paper, Ultra centrifugation and 0.22 μ PVDF membrane syringe filters [13]. The formation and properties AL-CQDs was confirmed using various analytical techniques such as UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Fluorescence spectroscopy (FLS), and High resolution transmission electron microscopy (HRTEM).

Further, *in vitro* antioxidant and photocatalytic degradation of MB and EY of AL-CQDs were evaluated. The *in vitro* antioxidant property of AL-CQDs was evaluated using scavenging assay of 2'2-diphenyl-1-picrylhydrazyl (DPPH). In this assay different concentrations of (10-40 µg mL^{-1}) AL-CQDs dissolved in methanol was added to the 3 mM of methanol dissolved DPPH and the samples were incubated for 30 min at 25°C under in dark conditions. The absorbance was measured at 540 nm and the inhibitory concentration 50 (IC_{50}) was calculated according to the equation 1 compared with standard ascorbic acid [14].

The photocatalytic degradation of MB and EY dyes was carried out under visible light irradiation (100 W tungsten bulb) with total reaction time of 90 min. Two different concentrations (10 and 20 µM) of MB and EY were prepared in distilled water and each dye was exposed to four concentrations of AL-CQDs (25-100 µg mL^{-1}) under constant stirring. For every 10 minutes of interval, 2 mL of sample was collected from each reaction mixture under stirring, centrifuged at 5000 rpm for 5 min and optical density of supernatant was measured at 664 nm (MB) and 517 nm (EY) [15]. The degradation (%) was calculated using equation 2 and C/C_0 curve was plotted to determine the pseudo first order kinetics and rate constants.

$$IC_{50} = Y = \frac{Max - M}{1 + \left(\frac{X}{IC_{50}}\right)^{Hill\,coefficien}} \qquad \text{Eqs...1}$$

$$\text{Degradation (\%)} = \frac{Absorbance\ of\ the\ control - Absorbanc\ \ of\ the\ sample}{Absorbance\ of\ the\ control} \times 100 \quad \text{Eqs..2.}$$

3. RESULT AND DISCUSSION:

Optical Properties:

The optical properties of the AL-CQDs such as absorbance spectrum, surface functionalization, phase analysis and photoluminescence properties were assessed.

Absorbance spectrum:

The formation of AL-CQDs after purification was assessed using UV-Vis spectroscopy analysis as a preliminary examination from 200-800 nm wavelength region and found two distinct excitations at 266 nm and 320 nm, along with a tail extending towards the visible region (Fig 1(a)). These two excitations are corresponding to π-π* and n-π* electronic transition present on aromatic sp^2 carbon of AL-CQDs and these transitions are likely due to the functional groups consists of oxygen such as C=O, COOH etc., on the CQD surface while the broad absorption tail in the wavelength region from 400-800 nm (visible region) suggests potential for visible-light-driven applications [16].

Functional groups:

The AL-CQDs were subjected to FTIR analysis to identify the functional groups from 500 to 4000 cm1 (Fig. 1(b)). This revealed major transmission peaks at 3311 and 1629 cm1, along with minor peaks at 2105, 1208, and 1368 cm^{-1}. The broad peak at 3311 cm^{-1} is characteristic vibrations of O-H stretching and represents the surface hydroxyl groups of CQDs, which contributes to their hydrophilic property. The peak at 1629 cm^{-1} is the carbonyl group (C=O), which has electron transfer capability. The minor peaks at 2105, 1208, and 1368 cm^{-1} are indicative of C≡C, C–O, and C–N stretching vibrations, respectively, which may originate from various functional groups introduced during synthesis from leaf biomolecules. The diverse surface functionalization, hydrophilicity, and electron transfer capabilities of AL-CQDs play a significant role in oxidant-antioxidant properties [17].

Phase analysis:

CQDs typically exhibit amorphous properties and are analyzed using XRD at a 2θ angle (10 to 100°). AL-CQDs exhibited diffraction peaks at 2θ values of 28.05° (111), 31.20° (200), 39.85° (211), 49.41° (221), 58.01° (222), and 72.83° (411) (Fig 1(c)). The broad nature of the diffraction peaks suggests that the carbon dots are predominantly amorphous. The absence of sharp crystalline peaks further supports the lack of well-defined crystalline order, characteristic of amorphous carbon materials [17].

Photoluminescence Properties:

Figure 1(d) represents the photoluminescence spectrum of AL-CQDs analysed using fluorescence spectrophotometer from 300-800 nm wavelength region. An excitation was originated from 360 nm with multiple emission peaks at 522 nm, 550 nm, 595 nm, and 677 nm, indicating the complex optical behaviour of the CQDs. The wide spectrum emissions are due mainly due to surface functional groups and quantum confinement effects [18].

Morphology and Size Distribution:

The HRTEM analysis of the AL-CQDs revealed the distribution of particle size diameter ranging from 1 to 6 nm, and calculated average of particle size diameter is 3.3 nm (Fig 2(b)). The Fig. 2(a), of HRTEM micrograph of AL-CQDs showing particles are moderately agglomerated and exhibit spherical nature, and the presence of C, N, O, and H is confirmed using the EDX spectrum (Fig. 2(c)).

This nanoscale size confirms the quantum dot nature of the particles, enabling unique optical and electronic properties due to quantum confinement effects, where the electron-hole pairs are spatially confined. Such confinement enhances the photoluminescence behaviour of CQDs, suitable for applications in biomedical field particularly in imaging and sensing. The narrow size distribution further contributes to the consistency in optical properties, as smaller particle sizes lead to higher energy emissions. This uniformity in particle size underscores the efficiency of the microwave-assisted synthesis method, yielding CQDs with desirable and consistent nano structural properties.

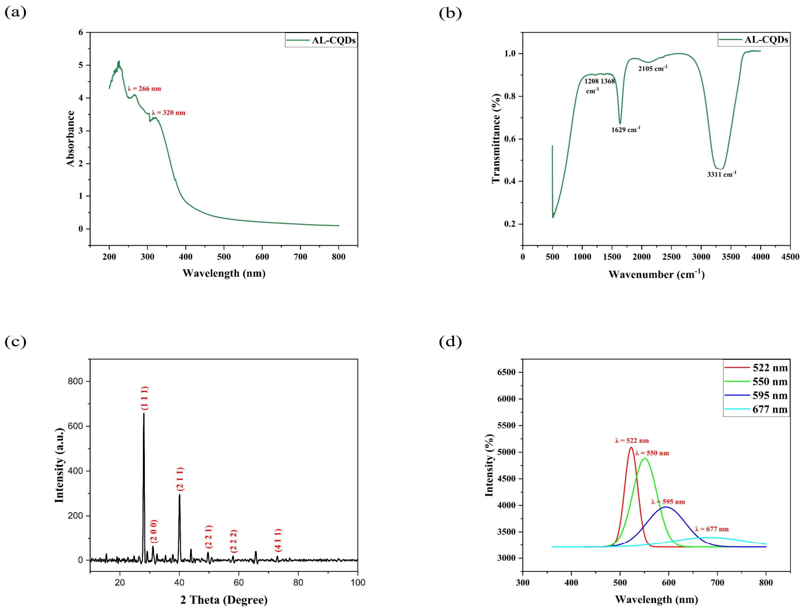


Figure 1: Optical Properties of AL-CQDs (a) Absorbance spectrum (b) surface functional groups (c) phase analysis and (d) photoluminescence spectrum.

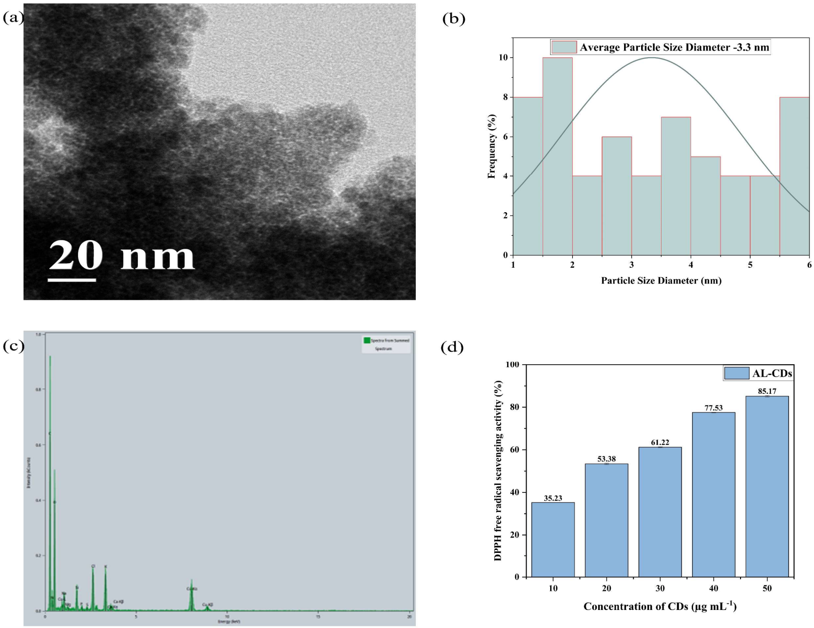


Figure 2: Morphological and Antioxidant Properties (a) HRTEM micrograph (b) Particle size diameter histogram (c) EDX spectrum and (d) DPPH free radical scavenging activity.

Antioxidant Properties:

The DPPH assay was used to evaluate the free radical scavenging property of AL-CQDs using various concentrations (10-50 µg mL^{-1}) of AL-CQDs. DPPH is a nitrogen free radical, and AL-CQDs effectively neutralized the 3 mM of DPPH and calculate IC_{50} value of 20.23 µg mL^{-1}. The concentration-dependent DPPH activity ranged from 35.23% to 85.17% (Fig. 2(d)).

Photocatalytic Degradation of MB and EY:

The photocatalytic degradation of methylene blue (MB) and eosin yellow (EY) dyes using AL-CQDs was assessed at two dye concentrations (10 µM and 20 µM) with varying CQD concentrations (25-100 µg/mL) of AL-CQDs over a maximum time of 80 minutes represented in Fig 3. The degradation (%) of both MB and EY efficiency by

AL-CQDS exhibited an inverse relationship with the dye concentration. For MB, a higher degradation percentage was observed with a 10 μM solution compared to 20 μM, achieving up to 74.87% degradation at 100 μg/mL CQD concentration for 10 μM MB, whereas only 66.65% was reached for 20 μM under similar conditions. Similarly, EY at 10 μM achieved a higher degradation percentage (79.8%) than EY at 20 μM (17.8%) at the highest CQD concentration. This trend indicates that lower dye concentrations facilitate better photon absorption by CQDs, allowing efficient generation of reactive species for dye breakdown. Increasing the concentration of CQDs from 25 μg mL^{-1} to 100 μg mL^{-1} results in enhanced degradation of both dyes, representing the effect of increased concentration of AL-CQDs. The degradation of both dyes remains unaffected by time, reaching its maximum only after 80 minutes.

The efficiency of AL-CQDs degradation was also observed by calculating rate constants, which reflect the reaction kinetics and photocatalytic efficiency. For MB at 10 μM, rate constants ranged from 0.0055 to 0.0058 min^{-1}; similarly, for MB at 20 μM, the rate constants ranged from 0.0054 to 0.0059 min^{-1}, indicating efficient but relatively slower degradation at higher dye concentrations. In the case of EY, rate constants for 10 μM ranged from 0.00212 to 0.00278 min^{-1}, whereas for 20 μM, they were significantly lower, between 0.0006 and 0.0009 min^{-1}. Higher rate constants suggest a more efficient photocatalytic process, with MB showing faster degradation than EY, likely due to different molecular structures affecting reactivity. These rate constants show the role of CQDs as effective catalysts for enhancing the degradation kinetics of organic pollutants.

CQDs facilitate photocatalytic degradation primarily through the generation of ROS, such as hydroxyl radicals (•OH) and superoxide anions (O_2^{-}•), when irradiated under visible light. The dye molecules when exposed to ROS breakdown into small molecules which are safe for both life and environment. The presence of surface functional groups, such as O-H and C=O groups, enhances the CQDs' capability to capture light and generate ROS, which are crucial for the oxidation process [18].

Previous studies reported CDs derived from various biological precursors effectively shown degradation of MB and EY. EY treated with CDs synthesised using *Aloe barbadensis miller* (aloe vera) achieved 98.55 % of degradation at 100 min with rate constant of 0.02079 min^{-1} [15]. CDs synthesized using Bougainvillea functionalized on r-Mg-N (r-Mg-N-CDs) degraded 99.0 % of MB at 120 mins [19]. Green N-doped CQDs successfully degraded (100%) MB and EY under visible light irradiation at 90 minutes [20].

4. Conclusion:

Dye toxicity presents significant environmental challenges, particularly in aquatic ecosystems, making their efficient degradation crucial for mitigating water pollution. In this regard, plant-derived carbon quantum dots (CQDs) offer a promising approach due to their less toxic and effective photocatalytic properties. The present study reported the successful synthesis of CQDs from *Antigonon leptopus* leaves using a microwave-assisted method, demonstrating their strong photoluminescence, surface functionalization, and amorphous structure. The CQDs exhibited impressive *in vitro* DPPH activity and calculated IC_{50} value of 20.23 μg mL^{-1} and also showed effective photocatalytic degradation of methylene blue (MB) and eosin yellow (EY) dyes under irradiation of visible light, achieving up to 74.87% and 79.8% degradation, respectively. The degradation efficiency was influenced by dye concentration and CQD dosage, with the rate constants confirming their role as efficient catalysts. These results revealed the potential of plant-derived CQDs in environmental remediation and antioxidant applications. Future studies could explore the scalability and broader environmental applications of these materials.

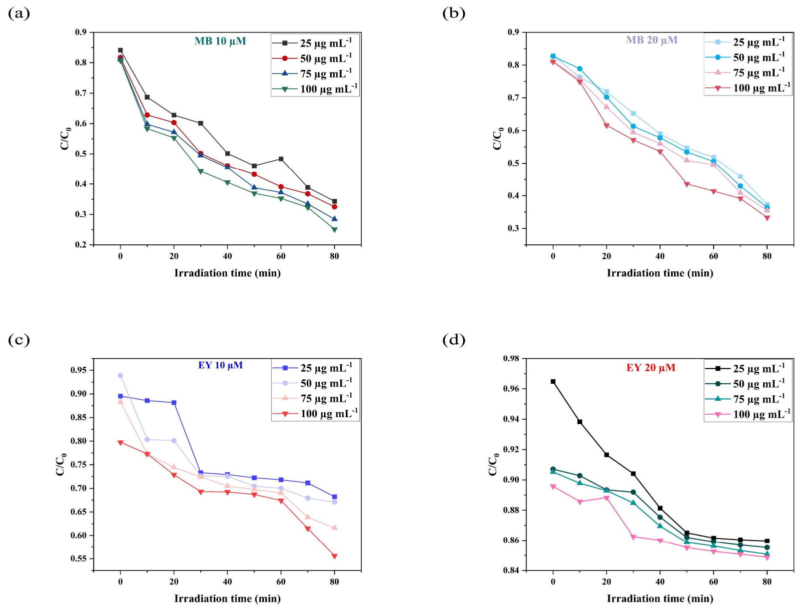


Figure 3: Pseudo-first order kinetics of AL-CQDs (a) 10 µM of MB (b) 20 µM of MB (c) 10 µM EY and (d) 20 µM EY.

Declaration. The authors declare no competing interest.

5. References:

1. Dutta S, Adhikary S, Bhattacharya S, Roy D, Chatterjee S, Chakraborty A, Banerjee D, Ganguly A, Nanda S, Rajak P (2024) Contamination of textile dyes in aquatic environment: Adverse impacts on aquatic ecosystem and human health, and its management using bioremediation. J Environ Manage 353:120103. https://doi.org/https://doi.org/10.1016/j.jenvman.2024.120103
2. Azhar FH, Harun Z, Hussin R, Ibrahim SA, Raja Ahmad RA, Shohur MF (2023) Methylene Blue Dye Wastewater Treatment Based On Tertiary Stage of Industrial Wastewater Treatment Process: A Review. Emerg Adv Integr Technol 3:37–51. https://doi.org/10.30880/emait.2022.03.02.004
3. Ali F, De Juan-Corpuz LM, Corpuz RD (2024) Unlocking the potential of carbon quantum dots: Versatile photocatalysts for methylene blue degradation—A comprehensive review of synthesis, catalytic mechanisms, and environmental applications. J Chinese Chem Soc 71:1154–1171. https://doi.org/https://doi.org/10.1002/jccs.202400112
4. Mutalib AAA, Jaafar NF (2023) Photocatalytic Degradation of Textile Dyes Using Nanohybrid Materials BT - Nanohybrid Materials for Treatment of Textiles Dyes. In: Ahmad A, Jawaid M, Mohamad Ibrahim MN, Yaqoob AA, Alshammari MB (eds). Springer Nature Singapore, Singapore, pp 203–222
5. Kumari H, Sonia, Suman, Ranga R, Chahal S, Devi S, Sharma S, Kumar S, Kumar P, Kumar S, Kumar A, Parmar R (2023) A Review on Photocatalysis Used For Wastewater Treatment: Dye Degradation. Springer International Publishing
6. Khan S, Noor T, Iqbal N, Yaqoob L (2024) Photocatalytic Dye Degradation from Textile Wastewater: A Review. ACS Omega 9:21751–21767. https://doi.org/10.1021/acsomega.4c00887
7. Etefa HF, Tessema AA, Dejene FB (2024) Carbon Dots for Future Prospects: Synthesis, Characterizations and Recent Applications: A Review (2019–2023). C 10:60. https://doi.org/10.3390/c10030060
8. Dhiman R, Kumar J, Singh M (2024) Fluorescent carbon dots for sensing applications: a review. Anal Sci 40:1387–1396. https://doi.org/10.1007/s44211-024-00609-4
9. John BK, Mathew J, K S, K RE, Mathew B (2024) Biomass derived carbon quantum dots as a versatile platform for fluorescent sensing, catalytic reduction, fluorescent ink and anticancer agents. Mater Today Sustain 26:100715. https://doi.org/https://doi.org/10.1016/j.mtsust.2024.100715
10. Christoph E, Yu L, Newby SD, Rivera Orsini MA, Scroggins J, Keffer DJ, Harper DP,

Dhar M (2024) Novel Kraft Softwood Lignin-Derived Carbon Quantum Dots: Synthesis, Characterization, and In Vitro Cytocompatibility. Nanomaterials 14:1–15. https://doi.org/10.3390/nano14121029

11. Ho PXJ, Mohd Zin Z, Portman KL, Mamat H, Rusli ND, Scott DJ, Zainol MK (2024) Effect of Antigonon leptopus extract in corn starch-glycerol based film as colourimetric indicator film for monitoring fish freshness. Food Res 8:476–486. https://doi.org/10.26656/fr.2017.8(3).592

12. Anuradha S, Mahesh Kumar D, Swaroopa Rani V (2022) In Vitro Studies on α-Amylase And α-Glucosidase Inhibitory Activity Of Antigonon leptopus (Hook Et. Arn) Leaf Extract and its Fractions. Int J Zool Investig 08:67–74. https://doi.org/10.33745/ijzi.2022.v08i0s.008

13. George HS, Selvaraj H, Ilangovan A, Chandrasekaran K, Kannan VR, Parthipan P, Almutairi BO, Balu R (2023) Green synthesis of biomass derived carbon dots via microwave-assisted method for selective detection of Fe3+ ions in an aqueous medium. Inorg Chem Commun 157:111348. https://doi.org/https://doi.org/10.1016/j.inoche.2023.111348

14. Wen F, Li P, Zhang Y, Zhong H, Yan H, Su W (2023) Preparation, characterization of green tea carbon quantum dots/curcumin antioxidant and antibacterial nanocomposites. J Mol Struct 1273:134247. https://doi.org/10.1016/j.molstruc.2022.134247

15. Malavika JP, Shobana C, Ragupathi M, Kumar P, Lee YS, Govarthanan M, Selvan RK (2021) A sustainable green synthesis of functionalized biocompatible carbon quantum dots from Aloe barbadensis Miller and its multifunctional applications. Environ Res 200:111414. https://doi.org/https://doi.org/10.1016/j.envres.2021.111414

16. Choi Y, Zheng XT, Tan YN (2020) Bioinspired carbon dots (biodots): Emerging fluorophores with tailored multiple functionalities for biomedical, agricultural and environmental applications. Mol Syst Des Eng 5:67–90. https://doi.org/10.1039/c9me00086k

17. Shaikh AF, Tamboli MS, Patil RH, Bhan A, Ambekar JD, Kale BB (2018) Bioinspired Carbon Quantum Dots: An Antibiofilm Agents. J Nanosci Nanotechnol 19:2339–2345. https://doi.org/10.1166/jnn.2019.16537

18. Elugoke SE, Uwaya GE, Quadri TW, Ebenso EE (2024) Carbon Quantum Dots: Basics, Properties, and Fundamentals. ACS Symp Ser 1465:3–42. https://doi.org/10.1021/bk-2024-1465.ch001

19. Liu J, Li R, Yang B (2020) Carbon Dots: A New Type of Carbon-Based Nanomaterial with Wide Applications. ACS Cent Sci 6:2179–2195. https://doi.org/10.1021/acscentsci.0c01306

20. Sabet M, Mahdavi K (2019) Green synthesis of high photoluminescence nitrogen-doped carbon quantum dots from grass via a simple hydrothermal method for removing organic and inorganic water pollutions. Appl Surf Sci 463:283–291. https://doi.org/https://doi.org/10.1016/j.apsusc.2018.08.223