

Sustainable heavy metal ion detection of waste-based carbon quantum dots

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Heavy metals contamination represents one of the noticeable challenges of the environmental pollution due to its persistence, toxicity and negative impacts on ecosystem and human health. Because of the high cost, limited sustainability of the traditional detection methods the need of green and sustainable methods has increased. In the recent years Carbon quantum dots CQDs have emerged as a valuable fluorescent nanomaterial owing to their strong photoluminescence, low toxicity, high biocompatibility, and the presence of surface functional groups that enable effective interactions with metal ions [1] In this work CQDs were green-synthesized from olive seeds kernels which consists of holocellulose, lignin, and proteins [2] using a hydrothermal method at different parameter conditions (time, temperature and citric acid) to find the best conditions that gives the higher fluorescence intensities, the CQD sample exhibiting the highest sensing performance toward Fe^{3+} ions was selected for further detection and adsorption studies.

The interaction between CQDs and Fe^{3+} ions induced pronounced photoluminescence quenching, enabling sensitive detection. The adsorption behavior of Fe^{3+} onto the selected CQDs was investigated to assess their potential not only as fluorescent sensors but also as sustainable adsorbents for heavy metal removal from aqueous solutions. Lastly olive seeds are new and friendly alternative as carbon source to synthesis CQDs and is a low-cost and sustainable solution for water quality monitoring, supporting biomass waste valorization while minimizing environmental impacts.

Keywords: carbon quantum dots (CQDs), heavy metal contamination, fluorescence intensities, photoluminescence quenching.

INTRODUCTION

Carbon quantum dots and their history

Carbon dots (CDs), also known as carbon quantum dots (CQDs), are a relatively new category of zero-dimensional fluorescent carbon-based nanomaterials, generally possessing particle sizes below 10 nm. These nanostructures were first identified in 2004 [3] marking the initial discovery of CQDs.

Properties and structure of carbon quantum dots

Carbon quantum dots (CQDs) possess unique physicochemical and optical properties, along with a nanoscale size and a high surface area, which contribute to their efficient electron transfer and strong adsorption capability. They exhibit excellent chemical stability, good water solubility and low toxicity [4]. The general structure of CQDs is shown in Fig 1. [4]

- *Green synthesis of carbon quantum dots.* Carbon quantum dots (CQDs) can be synthesized using two main approaches: top-down and bottom-up methods. The top-down approach produces CQDs by breaking down bulk carbon materials small molecular precursors using methods including irradiation, combustion, and pyrolysis [6]

Compared with top-down techniques, bottom-up methods are generally simpler, more cost- through techniques such as laser ablation, arc discharge, and electrochemical or chemical oxidation [5]. In contrast, the bottom-up approach forms CQDs from small molecular precursors using methods including hydrothermal/solvothermal synthesis, microwave irradiation, combustion, and pyrolysis [6]. Compared with top-down techniques, bottom-up methods are generally simpler, more cost-effective, scalable, and well suited for green synthesis.

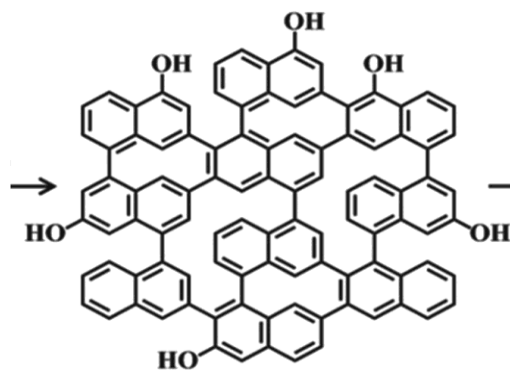


Figure 1. General chemical structure of CQD

- *Hydrothermal method.* In this method, precursor materials are dispersed in an aqueous solution, transferred into a Teflon-lined stainless-

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steel autoclave, and heated under elevated temperature and pressure for a specified reaction time. Owing to its simple operation, low cost, and environmentally friendly one-step process, the hydrothermal method has become one of the most widely used techniques for CQD synthesis. It also enables the efficient conversion of various organic precursors into CQDs with desirable optical properties hydrothermal method has become one of the most widely used techniques for CQD synthesis. It also enables the efficient conversion of various organic precursors into CQDs with desirable optical properties [7].

- *Olive pits as a biomass for green synthesis of CQD.* Olive pits are an abundant agricultural by-product rich in cellulose, hemicellulose, lignin, proteins, and other natural compounds, making them an attractive renewable precursor for the green synthesis of carbon quantum dots. Their utilization not only provides a low-cost carbon source but also contributes to biomass waste valorization and reduces the environmental impact associated with olive oil production [2].

Applications of carbon quantum dots

Because of the remarkable properties of the CQDs they have applications in a wide range of fields, including sensing, biomedicine, energy and catalysis. Sensing is one of the most extensively studied areas for heavy metal ion detection due to their strong photoluminescence and abundant surface functional groups, which facilitate interactions with metal ions and induce fluorescence quenching through electron or energy transfer mechanisms.

EXPERIMENTAL CALCULATIONS

Overview of the study

In this work CQDs were greenly synthesized from olive seeds kernels using a hydrothermal method. The schematic of green synthesis of CQDs used in this article is shown in Fig. 2. and evaluate their performance as a fluorescent nano sensor and adsorbent for Fe^{3+} ions in aqueous solutions. The synthesized CQDs were characterized using various analytical techniques to investigate their optical and physicochemical properties. Subsequently, their fluorescence sensing performance toward Fe^{3+} ions was evaluated, and adsorption experiments were conducted to assess their efficiency in removing iron ions from water. The effects of synthesis parameters, including temperature, reaction time, and citric acid addition, were investigated using an experimental design approach to optimize the properties of the obtained CQDs.

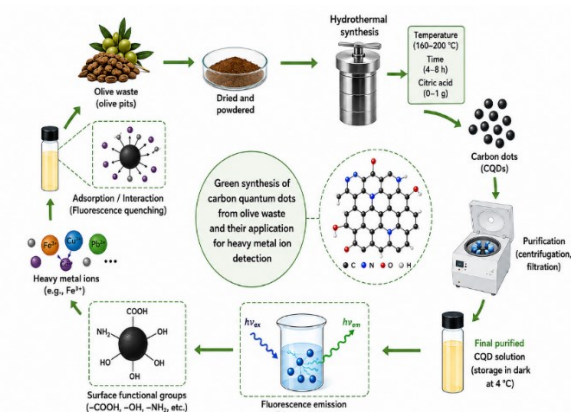


Figure 2. Schematic illustration of the green synthesis of carbon quantum dots from olive waste and their application for heavy metal ion detection.

Materials and chemicals

Olive seed kernels; citric acid; ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$); deionized water.

Preparation of olive seed kernel powder

Olive stones were collected as agricultural waste, washed thoroughly with distilled water to remove residual oil and organic impurities, approximately 60 g of olive pits were dried in a conventional laboratory oven at 60 °C for 6 h until constant weight was achieved, the olive pits were allowed to cool inside the closed oven to prevent moisture absorption, finally the dried pits were ground into a fine powder. The ground powder was sifted by mesh number 45 (345 μm) [8] to obtain homogeneous particle size and then stored in an airtight container for further use in carbon quantum dot synthesis.

Synthesis of carbon quantum dots

- *Experimental design.* A design of experiments (DOE) approach was employed using Central Composite Design (CCD) within the response surface methodology to optimize the CQD synthesis parameters, as illustrated in Table 1. Independent variables included: A: reaction temperature, B: reaction time, C: citric acid. The response variable chosen was: fluorescence intensity (1/s).

- *Hydrothermal synthesis procedure.* Carbon quantum dots (CQDs) were synthesized using the hydrothermal method. Initially, 1.5 g of olive pit powder was weighed and dispersed in 25 mL of deionized water, followed by magnetic stirring for 15 min to obtain a homogeneous suspension. The resulting mixture was then transferred into a 50 mL Teflon-lined stainless-steel autoclave as shown in

Figure 3, which was sealed and placed in a laboratory oven.

Table 1. Design of experiments by design expert software program

Experiment number	Factor A Temperature (°C)	Factor B Time (h)	Factor C Citric acid (g)
1	180	6	0.5
2	180	8	1
3	180	4	1
4	200	6	1
5	180	6	0.5
6	180	6	0.5
7	200	4	0.5
8	160	6	1
9	160	8	0.5
10	160	4	0.5
11	180	4	0
12	180	6	0.5
13	200	6	0
14	200	8	0.5
15	180	8	0
16	180	6	0.5
17	160	6	0

The hydrothermal treatment was carried out at temperatures ranging from 160 to 200 °C for 4–8 h, depending on the experimental conditions defined by the design of experiments. In selected experiments, citric acid was used as a catalyst, and amounts of 0, 0.5, or 1.0 g were added according to the experimental design. In these cases, the required amount of citric acid was first dissolved in deionized water using a magnetic stirrer for 15 min. Subsequently, the olive pit powder was added to the solution and stirred for an additional 15 min before transferring the mixture into the hydrothermal autoclave for synthesis.

- *Purification of CQDs.* After completion of the hydrothermal reaction, the autoclave was allowed to cool naturally to room temperature. The obtained product was carefully collected and initially filtered using Whatman 44 filter paper to remove large particulates. Subsequently, the filtrate was subjected to centrifugation at 15,000 rpm for 30 min to further eliminate residual solids. The supernatant was then passed through 0.22 µm membrane filters to ensure complete removal of nanoscale impurities. Finally, the purified CQD solution was stored in clean, dark glass bottles at 4°C for further characterization as shown in Fig. 4.

- After confirming that the absorbance of all samples was ≤ 0.1 to minimize inner-filter effects, as shown in Table 2, photoluminescence measurements were performed using a fluorescence spectrophotometer at an excitation wavelength of 360 nm. The resulting fluorescence intensities are presented in Table 3.



Figure 3. Hydrothermal synthesis procedure of CQD samples

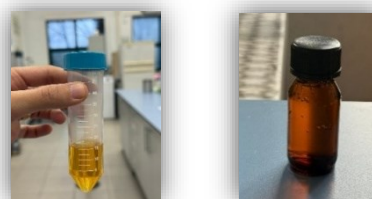


Figure 4. Final purified CQD solution

Ferric ion detection experiment

- *Selection of the optimum CQD sample.* Prior to the iron ion detection experiments, the optimum carbon quantum dot (CQD) sample was selected from the seventeen samples previously synthesized under different preparation conditions. The selection process was based on the optical properties of the prepared samples, particularly their fluorescence performance. UV–Visible absorption spectra were recorded, and the absorbance of each sample was adjusted through appropriate dilution to achieve suitable values for fluorescence measurements and to minimize inner filter effects. The absorbance was evaluated at 360 nm according to the reported literature [9]. Before proceeding with the iron ion detection and adsorption studies, all synthesized carbon quantum dot (CQD) samples were evaluated based on their photoluminescence (PL) properties. Comparison of the PL emission spectra shown in Fig. 5 revealed that sample No. 4 exhibited the highest fluorescence intensity among all prepared samples. Sample No 4 was synthesized using 1 g of citric acid as a catalyst under hydrothermal conditions at 200 °C for 6 h. The enhanced fluorescence intensity can be as a result of the combined effect of the citric acid and the synthesis temperature, which promoted carbonization,

improved surface passivation, and facilitated the formation of highly emissive surface states. Therefore, sample No (4) was selected as the optimal

sample and employed in the ferric ion Fe^{3+} sensing and adsorption studies.

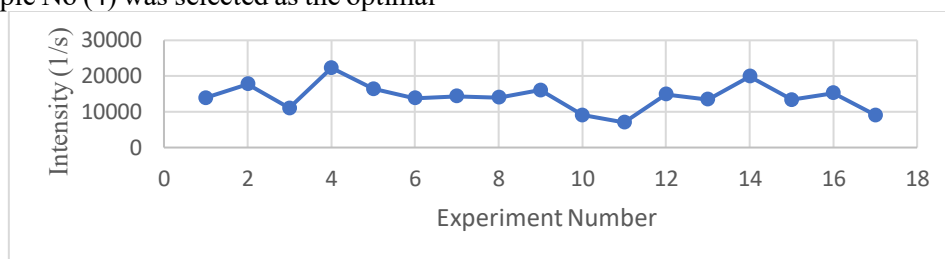


Fig. 5. Fluorescence intensity of carbon quantum dots (CQDs) prepared under different experimental conditions.

Table 2. Absorbance measurements for CQDs samples at wavelength of 360 nm before adding ferric ions

Sample	Abs. 1	Abs. 2	Abs. 3	Mean abs.
1	0.1166	0.1167	0.1170	0.11677
2	0.1104	0.1096	0.1100	0.11000
3	0.1212	0.1212	0.1215	0.12130
4	0.1051	0.1052	0.1066	0.10563
5	0.1217	0.1217	0.1207	0.12137
6	0.1116	0.1107	0.1114	0.11123
7	0.1202	0.1200	0.1193	0.11983
8	0.1167	0.1162	0.1176	0.11683
9	0.1074	0.1087	0.1088	0.10830
10	0.1157	0.1159	0.1185	0.11670
11	0.1210	0.1231	0.1221	0.12207
12	0.1124	0.1128	0.1134	0.11287
13	0.1143	0.1145	0.1148	0.11453
14	0.1072	0.1076	0.1073	0.10737
15	0.1122	0.1118	0.1112	0.11173
16	0.1120	0.1124	0.1120	0.11213
17	0.1174	0.1172	0.1173	0.11730

Table 3. Fluorescence measurements and emission wavelength for all samples

Sample No	$\lambda_{emission}$	Intensity (1/s)
1	435	13921
2	431	17723
3	431	11062
4	428	22286
5	434	16436
6	433	13850
7	426	14385
8	427	13982
9	426	16063
10	429	9102
11	425	7028
12	432	14867
13	426	13448
14	427	19909
15	428	13362
16	433	15261
17	424	9042

Preparation of Fe^{3+} solutions

- **1000 mg/L Fe^{3+} stock solution.** To prepare a 1000 mg/L Fe^{3+} stock solution ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was used.

Table 4. Molecular weight calculation of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)

Component	Molecular weight (g/mol)
Fe	55.85
3Cl	106.35
6H ₂ O	108.00
Total	270.20

Using the molecular weights provided in Table 4, the mass fraction of iron in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is: $\frac{55.85}{270.20} = 0.2067$. Thus, 1 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ contains $1 \times 0.2067 = 0.2067$ g Fe. To prepare a stock solution containing 1000 mg/L (1.0 g/L) Fe^{3+} , the required mass of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is:

$$\text{Mass of } \text{FeCl}_3 \cdot 6\text{H}_2\text{O} = \frac{1.0}{0.2067} = 4.84 \text{ g}$$

A 1000 mg/L Fe^{3+} stock solution was prepared by dissolving 4.84 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in deionized water. The salt was first dissolved in approximately 200 mL of deionized water and then transferred to a 1000 mL volumetric flask. The container was rinsed several times with deionized water, and the washings were added to the flask. The solution volume was adjusted to 1000 mL with deionized water and mixed thoroughly to ensure homogeneity.

The prepared stock solution was stored in an amber bottle at room temperature until use.

- **Preparation of calibration standards.** Calibration standards of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mg/L Fe^{3+} can be prepared using the dilution equation:

$$C_1 V_1 = C_2 V_2$$

For the preparation of the calibration standards, an intermediate solution was prepared by pipetting 10 mL of the 1000 mg/L stock solution into a 100

mL volumetric flask. The solution was subsequently diluted to volume with deionized water and mixed thoroughly before use. Using the 100 mg/L intermediate solution of Fe^{3+} , standard solutions were prepared at different concentrations as illustrated in Table 5.

Table 5. Preparation of Fe^{3+} standard solutions at different concentrations from a 100 mg/L stock solution

Desired concentration (mg/L)	Volume of 100 mg/L solution (mL)	Dilute to
0.1	0.1	100 mL
0.2	0.2	100 mL
0.3	0.3	100 ml
0.4	0.4	100 ml
0.5	0.5	100 ml
0.6	0.6	100 ml
0.7	0.7	100 ml
0.8	0.8	100 ml
0.9	0.9	100 ml

These standards can then be used to construct the calibration curve for Fe^{3+} determination and adsorption experiments involving carbon quantum dots synthesized from olive seed biomass.

• **Ferric ion detection procedure.** For the iron ion sensing study, a series of Fe^{3+} standard solutions with different concentrations was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ using deionized water. A fixed volume of the selected CQD solution was mixed with each iron standard solution and allowed to interact for a predetermined period under identical experimental conditions. The fluorescence emission spectra of the CQD solutions were recorded before and after the addition of Fe^{3+} ions, the maximum emission wavelength ($\lambda_{\text{em}}=428$ nm) of the selected sample was used as the analytical emission wavelength in the fluorescence-based detection studies to monitor the response of the CQDs toward different concentrations of Fe^{3+} ions. The sensing performance was evaluated by monitoring the fluorescence quenching effect induced by Fe^{3+} ions. The relative fluorescence response $(F_0 - F)/F_0$, where F_0 and F represent the fluorescence intensities before and after iron addition, respectively, were calculated. A calibration curve was constructed by plotting the fluorescence response against the Fe^{3+} concentration. The linear relationship obtained from the calibration plot was used to determine the CQDs performance for ferric ion detection in aqueous media.

CONCLUSION AND FUTURE WORK

In this work CQDs, which are fluorescent carbon-based nanomaterials with particle sizes below 10 nm, were green-synthesized by a hydrothermal method using olive seed kernels as a carbon source. The CQDs were used as a sensor for detection and removal of ferric ions (Fe^{3+}) from aqueous systems. At the current stage of the study the best CQD samples was selected using photoluminescence spectrometry according to the increase in fluorescence intensities. The quenching experiments for the sensing applications are still in progress.

The next step of the work will focus on adsorption experiments and evaluation of the CQDs for the removal of ferric ions from water and aqueous systems. Ultimately, this work seeks to contribute to improving water quality and reducing potential health and environmental risks associated with excessive ferric contamination in water resources.

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