Fluorescent Properties of Carbon Quantum Dots (CQDs) Synthesized from Lemon Juice Using Hydrothermal Techniques for Adsorption Application

Gadisa Deme Megersa

A Thesis Submitted to the Department of Applied Physics
School of Applied Natural Science

Presented in Partial Fulfillment of the Requirement for the Degree of
Master's in Applied Physics
(Laser Spectroscopy)

Office of Graduate Studies
Adama Science and Technology University

June, 2022

Adama, Ethiopia

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DECLARATION

I hereby declare that this Master thesis entitled **‘‘Fluorescent Properties of Carbon Quantum Dots (CQDs) Synthesized from Lemon Juice Using Hydrothermal Techniques for Adsorption Application’’** is my original work and has not been submitted for the award of any academic degree, diploma, or certificate in any other university for a similar purpose. All sources of materials that are used in this research work are duly recognized and acknowledged through proper citation.

Name of the Student	Signature	Date

RECOMMENDATION

We, the advisor of this thesis, hereby certify that we have read the revised version of the thesis entitled **''Fluorescent Properties of Carbon Quantum Dots (CQDs) Synthesized from Lemon Juice Using Hydrothermal Techniques for Adsorption Application''** prepared under our guidance by **Gadisa Deme Megersa** submitted in partial fulfillment of the requirements for the degree of Master's of Science in Applied Physics. Therefore, we recommend the submission of the revised version of the thesis to the department following the applicable procedures.

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Name of Advisor	Signature	Date
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Name of Co-advisor	Signature	Date

APPROVAL SHEET

We, the advisors of the thesis entitled **‘‘Fluorescent Properties of Carbon Quantum Dots (CQDs) Synthesized from Lemon Juice Using Hydrothermal Techniques for Adsorption Application’’** and developed by **Gadisa Deme Megersa**, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Major Advisor	Signature	Date
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by **Gadisa Deme Megersa** have read and evaluated the thesis entitled **‘‘Fluorescent Properties of Carbon Quantum Dots (CQDs) Synthesized from Lemon Juice Using Hydrothermal Techniques for Adsorption Application’’** and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the Degree of Master’s of Science in Applied Physics.

Chairperson	Signature	Date
Internal Examiner	Signature	Date
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Finally, approval and acceptance of the thesis are contingent upon the submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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School Dean	Signature	Date
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LIST OF ACRONYMS

CNTs……………………………..Carbon Nanotubes

CQDs……………………………..Carbon Quantum Dots

DI…………………………………Deionized Water

E_g…………………………...........Bandgap energy

FT-IR……………………………..Fourier Transform Infra-Red

GQDs……………………………..Graphene Quantum Dots

MB………………………………..Methylene Blue

PAGE……………………………..Polyacrylamide Gel Electrophoresis

PL…………………………………Photoluminescence

RT………………………………...Room Temperature

SQDs……………………………...Semiconductor Quantum Dots

SWCNTs…………………………Single-Walled Carbon Nanotubes

TiO_2..Titanium Dioxide

UV………………………………..Ultraviolet

UV-Vis…………………………...Ultraviolet-Visible

XRD……………………………...X-Ray Diffractometer

ZnS………………………………Zinc Sulfide

λ_{em}…………………………..…….Emission Wavelength

λ_{ex}…………………………..….......Excitation Wavelength

Φ………………………………....Quantum Yield

ABSTRACT

In this research, the optical properties of CQDs synthesis from lemon juice via hydrothermal techniques under different temperatures and their applications for the adsorption of MB dyes in an aqueous solution were investigated. The synthesized CQDs were characterized by XRD, UV-Vis, UV lamp, PL, FT-IR spectroscopic, and zeta potential techniques. An XRD analysis indicated maximum peaks at a 2θ value of 20.1°, 18.07°, and 14.57° were observed at the temperature of 160, 180, and 200 °C respectively, and had an amorphous structure. Similarly, UV-Vis spectrophotometric confirmed the presence of two absorption peaks at 217.5 and 282 nm at 160 °C. While CQDs synthesized at 180, and 200 °C display shoulders peaks at 222 and 219.5 nm respectively. The synthesized CQDs were illuminated by UV light with different excitation wavelengths, (254 nm, 365 nm, and visible regions) and green, blue, and dark brownish colors respectively. Photoluminescence (PL) spectral analysis of synthesized CQDs confirmed excitation-dependent emission peaks at different excitation-wavelength from 360 to 520 nm with the 20 nm interval. The obtained quantum yield (Φ) of CQDs ranges from 14 to 41 % for synthesized at 160, 180, and 200 °C the difference is attributed to functional groups of CQDs. Also, the FT-IR spectrum of CQDs confirmed the presence of different functional groups such as N-H/OH(3270.23 cm^{-1}), COOH(2360.48 cm^{-1}), C=O(1635 cm^{-1}), and C-O(1228 cm^{-1}) for CQDs synthesized at 160°C, N-H/OH (3315.08 cm^{-1}), C=O (1637.29 cm^{-1}), and C-O (1222.66 cm^{-1}) for CQDs synthesized at 180°C, and N-H/OH (3282.3 cm^{-1}), and C=O (1637.3 cm) for CQDs synthesized at 200°C. Zeta potential result shows that CQDs are ~1.55 mV. After confirmation and characterization, the synthesized CQDs were further evaluated for their effectiveness in the adsorption of MB dyes. The result shows that synthesized CQDs are excellent adsorbents for effective adsorption of MB with a removal efficiency of 60 - 82 % in an aqueous solution and an extremely fast adsorption rate of 5.525×10^{-2} min^{-1} for MB dye in a short contact time. CQDs synthesized via hydrothermal techniques may be useful for resolving the critical problems in the drinking water the world facing due to MB dye contaminations.

Keywords: *Adsorption application, carbon quantum dots, hydrothermal technique, lemon juice, photoluminescence.*

1. INTRODUCTION

1.1 Background of the Study

Nowadays, it is very common to use various materials in our daily lives for many purposes. It is no longer a wonder what human being lifelike if these materials not be developed (Porto *et al*., 2020). Very recently, the combinations of nanotechnology with several disciplines of science such as biology, chemistry, and physics have driven the search for new advanced nanoscale materials (1-100 nm) as a particular interest for modern science (Lu, 2012). Carbon quantum dots (CQDs) are one especially active field in nanotechnology research. In particular, CQDs (Bottini *et al*., 2006), have garnered masses interest from researcher groups over the last eighteen years due to their unique properties which consist of advanced structural, physicochemical properties, easy functionalization, high abundance, large surface area, large pore volume, low toxicity, tunable fluorescence, high photostability, highly water solubility, excellent biocompatibility, and eco-friendly properties over various materials (Koutsogiannis *et al*., 2020). In addition, their emission color can be adjusted by varying the excitation wavelength (λ_{ex}), facile surface modification, simple and inexpensive synthesis. Due to these attractive properties, CQDs are widely used in a variety of scientific fields such as photocatalytic reactions, adsorption, biomedicine, bioimaging, sensing, drug delivery, and drug synthesis applications (Pan *et al*., 2020). Moreover, CQDs are potential competitors to traditional metal-based semiconductor quantum dots such as TiO_2, and CdZnO owing to their extremely interesting properties. CQDs also show size-dependent optical properties such as photoluminescence, chemiluminescence, electrochemical luminescence, and photo-induced electron transfer (Khatokar *et al*., 2020).

Carbon quantum dots were first discovered in 2004 by Xu and coworkers with preparative gel electrophoresis during the separation and purification of single-walled carbon nanotubes (SWCNTs) using arc-discharge routes (Akbar *et al*., 2021). Subsequently, in 2006 Sun *et al*. synthesized CQDs from graphite powder and cement by surface passivation and laser ablation methods and named these fluorescent nanomaterials carbon quantum dots (CQDs) (Kumar *et al*., 2022). These CQDs can be described as discrete, quasi-spherical particles with sizes with in a ranges of 1 to 10 nm. Because quantum dots (QDs) are considered a kind of quasi-spherical nanomaterials with a size less than 10 nm and are composed of the periodic group II-VI elements (Liu *et al*., 2020). Fundamental to the rising interest in these carbon-based nanomaterials is due to their unique properties such as chemical inertness, simple synthesis accession, accessibility, rich in multiple functional groups, and high carbon precursor abundance. Starting were discovered, especially begin from 2005 the number of researcher publications related to CQDs rapidly increased (Atabaev, 2018). The most traditional fluorescent materials are organic dyes and CdSe/ZnS quantum dots (QDs) are the most extensively utilized fluorescent materials. However, their photobleaching, quenching of fluorescent molecule dyes, high toxicity, and high cost are drawbacks to their applications in various fields (Zuo *et al*., 2015).

Carbon quantum dots (CQDs) are similar to quantum dots (QDs) and structurally similar to graphite oxide particles (Qu *et al*., 2012). CQDs belong to a class of zero-dimensional nanomaterials with excellent photoluminescence (PL) properties and carbon-based nanosized. Also, CQDs have similar properties to heavy metal-based quantum dots, but with excellent water solubility, cheap starting materials, heavy metal-free, and efficient synthesis process (Zuo *et al*., 2016).

There are numerous synthesis methods for carbon quantum dots (CQDs), mainly classified into two approaches that are top-down and bottom-up approaches to synthesis have been described for the CQDs synthesis. The top-down approach, refers to the breakdown of large carbon structures into nanoscale particles, while the bottom-up approach, refers to the synthesis of the CQDs from small organic molecules (El-Shabasy *et al*., 2021).

Carbon quantum dots (CQDs) can be synthesized from any carbon-containing starting material, however their fluorescence will vary depending on the source of starting materials. CQDs were synthesized from lemon juice, candle soot, apple juice, orange peel, and various amino acids. Thus CQDs attracted the attention of researchers because of their simple and inexpensive preparation (Sugiarti and Darmawan, 2015). Functional groups such as carbonyl (-C=O), carboxylic (-COOH), hydroxyl (-OH), amine (-NH), and other functional groups on the surface of starting material of organic compounds are highly significant in the synthesis of CQDs, according to a report by (Hsu and Chang, 2012). In this research study, it was decided to use lemon juice as a precursor because it is a simple organic acid, highly abundant, eco-friendly, and much like orange juice. CQDs synthesis and noted that there is still no standard for CQDs as they are synthesized from many sources of carbon-containing material using different methods (Kang *et al*., 2020).

Many researcher communities have focused on the preparation of these fluorescent carbon quantum dots. Highly fluorescent CQDs can be synthesized cost-effectively via one-step approaches on high quality, large scale and replace the conventional quantum dots (QDs) in many applications to overcome the use of heavy metals such as cadmium and selenium, which can lead to health effects due to their high toxicity and environmental problems. The hydrothermal bottom-up methods have become the most widely utilized techniques of CQDs synthesis and in comparison with other methods are simple operation, cost-effective, and eco-friendly (Shaikh *et al*., 2018). Furthermore, the immense potential of CQDs for a variety of applications requires the development of large-scale synthesis. Because of its simplicity, low cost, and high efficiency, hydrothermal synthesis has become the most used approach in this regard.

Generally, the synthesis of CQDs involves the carbonization of carbon sources. There are a variety of carbon sources, and among different resources, natural sources become widely accepted as green precursors, which have numerous advantages in many applications because they are facile, repeatable, low toxicity, environment friendly, and cost-effective for the synthesis of carbon quantum dots (CQDs). For this reason, significant effort has been devoted to the synthesis of carbon quantum dots (CQDs) from numerous natural resources. For example, CQDs synthesized from apple juice emit a wavelength of 428 nm with a quantum yield (Φ) of 6.4% under the excitation of ultraviolet light of 340 nm (Xu *et al*., 2014). In addition, the quantum yield (Φ) of carbon quantum dots prepared from strawberries is 6.3%. The maximum wavelength was 427 nm when they were excited by a wavelength of 340 nm (Huang *et al*., 2013). On the other hand, in addition to synthesis methods and precursors, there is various feedstock on CQDs that affect its properties, especially optical properties. These parameters include aging, hydrothermal temperature, reaction time, purification techniques, and solvents.

Besides the synthesis of CQDs, analytical separation techniques were required (González-González *et al*., 2022). There are various analytical separation techniques for the purification of synthesized carbon quantum dots (CQDs), including electrophoresis, chromatography, density gradient centrifugation, solvent extraction, and dialysis are the most commonly used methods (de Andrés and Ríos, 2021). In this research work, were investigating various characterization and analytical separation methods for carbon quantum dots synthesized from lemon juice using hydrothermal synthesis techniques, were investigated.

Recently, many research groups have been interested in developing new synthetic techniques and have insights into new applications for these newly discovered CQDs, so need to fully understand the basic properties of carbon quantum dots (CQDs). For the last eighteen years, intensive research efforts were devoted by the scientific community and now have a much better understanding of the structural, photophysical, and chemical properties of CQDs. However, the complete characterization of carbon quantum dots mixture remains challenging. This is owing to the reality that CQDs products exist as a complex mixture comprising components with different sizes and distinctive surface functionalities and complex mixtures of carbon quantum dots (CQDs) samples only represent the average properties of all individual carbon quantum dots (Hu *et al*., 2017). With this in mind, efficient analytical separation techniques for separating high-quality CQDs fractions and characterization techniques to understand their basic characteristics, were been developed.

Furthermore, their unique properties such as optical properties, surface area, in particular, fluorescence emissions, and as well as wide excitation and emission spectra have increased interest in various applications purposes in particular adsorption applications. For this reason, more benign fluorescent CQDs have gained significant research attention in the last eighteen years (Liu *et al*., 2016). There have been great achievements in various scientific fields regarding the application of CQDs. To remove organic dyes from wastewater or drink water a range of treatment methods have been used, including photocatalytic, biodegradation, and adsorption (Shindhal *et al*., 2021). An adsorption is an effective approach for removing a variety of contaminants from wastewater due to its high efficiency, ease of operation, cheapness, and short treatment time compared to other methods such as photocatalytic applications (Dutta *et al*., 2021). Water is one of the most important resources, and water pollution has become a series of issues of health with the rapid growth of the human population and industries (Ruan *et al*., 2019). Today, various dyes are released from industries and domestic waste into running water without being purified. There are more than $7x10^5$ tons of organic dyes over $1x10^4$ types used as dyes in the various industries particularly food, textile, and other industries (Shanker *et al*., 2017). Over 10-15 % of dyes discharge into running water bodies during manufacturing and application processes (Ahmed *et al*., 2016).

Methylene blue is a pollutant dye commonly used in a variety of industries including food industries, textiles, and drug industries in medical fields (Teymoorian *et al*., 2021). As a result, wastewater containing a high amount of dyes, in particular methylene blue (MB), must be treated (Ramli *et al*., 2014). The materials and methods required for long-term wastewater treatment are still being studied extensively by the previously scientific community, in particular, adsorption methods of removing organic dyes are a great focus. As a result, the importance of developing materials and substances that can effectively and efficiently remove pollutants from aqueous water is overemphasized (Katheresan *et al*., 2018). CQDs is used as adsorbent of methylene blue (MB) dye from wastewater bodies owing to their large surface area properties (Long *et al*., 2021).

During the last few decades, advances have been made in carbon quantum dots (CQDs) synthesis, characterization, and application development and improvement. Nowadays, the carbonization of naturally available biological resources has attracted considerable interest in the development of labor, materials, and energy efficiency for low heating temperatures synthesis. Beginning from the time of their discovery study concerns about carbon quantum dots have been increasing rapidly. But carbon sources and their importance have been widely ignored. Furthermore, despite the synthesis of highly PL carbon quantum dots (CQDs) nanomaterials from lemon juice it is challenging to obtain long-term stable and luminescence carbon quantum dots (CQDs) nanomaterials. For this reason, in this study, were investigated the aging of CQDs samples to study the photostability of fluorescence emission of CQDs. Especially, the properties of easy methodology, organic solvent-free reaction, economic efficiency, and easy operation, hydrothermal methods synthesis is one of the most promising ways toward the preparation of high fluorescence quantum yield (Φ) carbon quantum dots (CQDs) from lemon juice.

In general, this study evaluated the synthesized novel carbon quantum dots (CQDs) nanomaterials as highly fluorescence nanomaterials for the adsorption application of removing methylene blue (MB) dye to partially fill the above mentioned research gaps and also as motivation of work.

1.2 Objectives of the Study

1.2.1 General Objective

The general objective of this research is to study the fluorescent properties of carbon quantum dots (CQDs) synthesized from lemon juice using hydrothermal techniques for adsorption applications.

1.2.2 Specific Objective

The specific objectives of the study are to:

- Synthesize highly fluorescent CQDs from lemon juice via hydrothermal method.
- Characterize structure and optical properties such as quantum yield (Φ) CQDs.
- Apply the synthesized CQDs for adsorption to remove methylene blue (MB) dye and

- Study the effect of contact time (min) on the removal (R %) of methylene blue (MB) dye by CQDs.

1.3 Thesis Organization

This thesis has been organized into five chapters. Each chapter focused on a particular aspect. The first chapter deals with the general introductory part which contains, an overview of the study of carbon quantum dots (CQDs). The general and specific objectives of the thesis are also presented. Chapter two presented a review of literature on the properties of carbon quantum dots (CQDs) for different applications and were also discussed in detail. In chapter three, the research materials and methods were presented. In this chapter, the chemicals, solvents, apparatus, and instruments used to carry out this work were described. Chapter four presents the results and discussion. Finally, in chapter five, conclusions and recommendations for future works were provided.

2. REVIEW OF THE LITERATURE

In this chapter, the concepts of the difference between bulk materials and nanomaterials, bulk carbons, carbon-based nanomaterials, comparison of quantum dots (QDs) and carbon quantum dots (CQDs), nanoscience and nanotechnology, carbon precursors in the synthesis of CQDs, synthesis of carbon quantum dots from lemon juice, properties of carbon quantum dots (CQDs) nanomaterials, structural and optical properties of carbon quantum dots (CQDs) nanomaterials, methods of synthesizing carbon quantum dots (CQDs) nanomaterials, purification techniques of carbon quantum dots (CQDs) nanomaterials**,** characterization methods of carbon quantum dots (CQDs) nanomaterials and applications of carbon quantum dots (CQDs) nanomaterials were reviewed in the literature broadly. In additionally, the basic properties related to carbon quantum dots (CQDs) nanomaterials, and specifically, their applications in adsorption activity were discussed.

2.1 Difference Between Bulk Materials and Nanomaterials

Bulk materials are over 100 nm in all dimensions, but nanomaterials sizes range from 1 to 100 nm in at least one dimension. For nanomaterials, it is not their chemical composition that only determines their properties, but their morphological and surface properties. These properties do not change much compared to the corresponding bulk material, but they do change between different nanoscales of the same material. Changes in these physicochemical properties can lead to changes in chemical properties, reactivity, and applied activity. On the other hand, working within the nanoscale of increasing surface area increases activity (Schwirn *et al*., 2014).

2.2 Bulk Carbon

Carbon is the most abundant substance and is known as the black substance (Jumardin *et al*., 2021). For the last few years, carbon materials accept as low water-soluble and non-photoluminescence (PL) materials (Wang and Hu, 2014). Today, the concepts of nanoscience and nanotechnology support the formation of nanoscale carbon or carbon-based nanomaterials, offering great potential for researchers (Liu *et al*., 2020). The synthesized nanoscale carbon structure and optical properties differ from those of traditional bulk carbon materials. Carbon quantum dots are a kind of carbon-based nanostructured material that can contain a significant amount of oxygen and hydrogen. Furthermore, research on CQDs has increased interest in their optical properties, especially fluorescence emission and applications (Zuo *et al*., 2016). A new class of carbon-based nanomaterials is an alternative to traditional fluorescent materials due to its excellent luminescent properties, lack of blinking, high biocompatibility, non-toxicity, and high solubility in water.

2.3 Carbon Based Nanomaterials

There are numerous carbon-based nanomaterials including fullerenes, fluorescent carbon quantum dots (CQDs) nanomaterials, graphene sheets, carbon nanotubes, and nanodiamonds. Due to their immense potential for a wide variety of technical applications, these carbon-based materials have attracted the attention of the researchers (Lim *et al*., 2014).

2.4 Comparison of Quantum Dots (QDs) and Carbon Quantum Dots (CQDs)

Quantum dots (QDs) were first discovered in glass crystals by the Russian physicist Ekimov in 1984. Initially, the research was limited to CdSe/CdS and CdSe/ZnS quantum dots (QDs), but other core-shell quantum dots were later developed and studied. Cadmium (Cd) was the main component of traditional quantum dots (QDs), but cadmium causes cytotoxicity, which limits its use. The hazard caused by the leakage of more cadmium ions is the reason for the discovery of the more biocompatible quantum dots. Due to the high demand for highly compatible quantum dots (QDs), the focus has shifted to the development of cadmium-free quantum dots, which are less toxic and have many uses (Singh *et al*., 2018). Quantum dots (QDs) are nanoparticles that exhibit a 3D quantum confinement effect and offer many unique optical and transport properties. Quantum dots (QDs) also known as semiconductor nanoparticles, exhibit a variety of unique properties, including size-dependent emission wavelength, narrow emission peak, and wide excitation wavelength. Semiconductor nanocrystals are well-researched forms of nanoscale semiconductors and currently have a solid theoretical basis that makes it possible to understand most of their optical properties. As a result, various quantum dots (QDs) such as carbon quantum dots (CQDs) nanomaterials, graphene quantum dots (GQDs), and silicon quantum dots were formed.

Carbon quantum dots were discovered by Xu *et al* in 2004. Many researcher groups have better understood the origin of their photophysical behavior, developed better synthetic routes, and new applications for these emerging nanomaterials. Nanomaterials have been researched and synthesized in the hope of developing applications. CQDs have a wide range of excitation (λ_{ex}) and emission (λ_{em}) wavelengths. All the zero-dimensional carbon-based nanomaterials with high photoluminescence synthetic routes were first reported by Sun *et al* in 2006. Based on the concept of carbon-quantum dots (CQDs) nanoparticles in 2006, it is called carbon quantum dots (CQDs) nanomaterials (Wang *et al.*, 2017). In general, all nanoscale materials are mainly composed of carbon skeletons and can be called carbon quantum dots (CQDs) nanomaterials. In addition, they have 1D at least less than 10 nm and fluorescence properties.

Some other traditional fluorescent materials have a wide range of applications such as bioimaging, biosensors, optoelectronic devices, photocatalysts, metal ion detection, etc. Due to their unique fluorescent properties and functions. These fluorescent materials include semiconductor quantum dots (SQDs), fluorescent metal clusters, organic dyes, and polymer dots. However, these conventional fluorescent materials have drawbacks due to their toxicity, poor water dispersibility (solubility), environmental pollution, and complex synthetic techniques. CQDs are carbon-based materials that replace traditional quantum dots (QDs) in a variety of application areas. Carbon quantum dots overcome the limitation of traditional fluorescent materials because are low toxicity, high water solubility, suitable biocompatibility, chemical inactive, easy functionalization, environmentally friendly, and highly PL (Zaib *et al*., 2021). These advanced properties of CQDs have enhanced potential applications especially biomedical and as well as adsorption applications.

Therefore, carbon quantum dots nanomaterials are preferred over metal-based quantum dots. For this reason, this research work focuses on carbon quantum dots nanomaterials because of their very interesting properties and high applicability, as shown in Figure 2.1. The carbon quantum dots combine the unique optical properties of quantum dots (QDs) with the excellent electrical properties of sp^2 carbon materials, which makes them unique from conventional semiconductor quantum dots or other carbon nanomaterials such as a graphene and carbon nanotubes (CNTs) (Wang *et al*., 2017). On the other hand, carbon quantum dots (CQDs) nanomaterials exhibit similar properties to inorganic quantum dots (QDs), but carbon quantum dots have considerable potential for biomedical applications owing to their excellent biocompatibility and low cytotoxicity. In general, the CQDs have the following advantage over traditional metal-based quantum dots (QDs);

- High abundance
- Inexpensive
- Photostability

- High resistance to photobleaching
- High photoluminescence
- Low toxicity
- Good biocompatibility and simple synthesized. These all make carbon quantum dots (CQDs) a rising star as a nanocarbon family.

2.5 Nanoscience and Nanotechnology

Nano is about with sizes between 1 and 100 nm. In the case of materials, sizes become nanoscale their mechanical, electric, optical, and magnetic properties can change. The quantum effect becomes dominant due to the small size of the object. Nanoscience is approximately the area that occurs in a system with nanometer dimensions, whose properties differ significantly from bulk materials. In addition, the concept of nanoscience and nanotechnology is historically credited to Richard Feynman (Bayda *et al*., 2020).

The idea of nanotechnology was recognized as a hands-on lecture by Feynman, who won the popular Noble Price in physics at the American Physical Society's annual meeting on December 29th, 1959 (Khan *et al*., 2019). Nanotechnology is the manipulation of materials with dimensions less than 100 nm. This is based on the fact that the physical and chemical properties of a substance change significantly at the nanoscale compared to the macroscale (Rizvi *et al*., 2010). In general, nanoscience and nanotechnology are widely recognized as having great potential to benefit a variety of research and application areas and are receiving increasing attention from researchers.

2.6 Carbon Precursors in Synthesis of Carbon Quantum Dots (CQDs)

Various natural and synthetic (man-made) carbonaceous substances are used as sources of carbon for the synthesis of carbon quantum dots nanomaterials. Since the high fluorescence properties of carbon quantum dots (CQDs) were dependent on the carbon source it is necessary to consider precursors during the CQDs synthesis process. Organic products are plentifully available precursors of carbon for the fabrication of organic products-based carbon quantum dots nanomaterials (Kwee *et al*., 2021). Also, organic product-based synthesis methods are known as green methods due to their being green and eco-friendly incomparable with other synthetic carbon quantum dots. Man-made precursors of carbon quantum dots (CQDs) may contain toxic materials, oxidation chemical agents, expensive, and time-consuming, while organic products are alternative to man-made carbon sources owing to their easily available, abundant, low toxicity, eco-friendly, and inexpensive.

2.7 Synthesis of Carbon Quantum Dots (CQDs) from Lemon Juice

Green method-based synthesis of CQDs involves the use of simple, ready, and available bacteria, plants, or microorganisms. The raw materials used in the green strategy are natural and non-toxic products. The advantages of using plants as a raw material are versatility, reliability, ease of use, reproducibility, economic efficiency, biodegradability, high biocompatibility, and environmental friendliness (Huston *et al*., 2021). Therefore, this work uses the green method to synthesize carbon quantum dots from lemon juice. Next, the adsorption and removal of methylene blue (MB) dye from drink water or wastewater using these carbon quantum dots nanomaterials were investigated.

Lemon is mainly composed of carbohydrates (10 %) and water (88-89 %). Lemon is low in fat and protein. Lemon juice usually contains fiber and sugar such as sucrose, fructose, and glucose. CQDs can be made from any carbohydrate that contains C, H, and O in a 1:2: 1 ratio, where C and O promote in a form that facilitates dehydration under hydrothermal circumstances, according to suggestions of researchers (Siddique *et al*., 2018). These constitutes has to attribute to PL emission of synthesized CQDs. The main constituents of the synthesized carbon quantum dots are carbon, hydrogen, and oxygen. Even also constituents of lemon can vary from place to place owing to air-conditioning and soil kinds. This can affect result obtained at different time by various researchers using lemon juice because elements contained in lemon has a huge contribution to results.

2.8 Properties of Carbon Quantum Dots (CQDs)

Numerous researchers have reported the very interesting properties of CQDs as seen in Figure 2.1. This exceeds the properties of existing materials. These fascinating properties allow CQDs to be used in a variety of application areas, especially in the adsorption of environmentally harmful organic dyes from wastewater. According to various studies, size and surface state play an important role in determining the properties of CQDs. Moreover, much research has demonstrated that both synthetic and post-treatment methods play important roles in adjusting the properties of CQDs nanomaterials (Kurian and Paul, 2021).

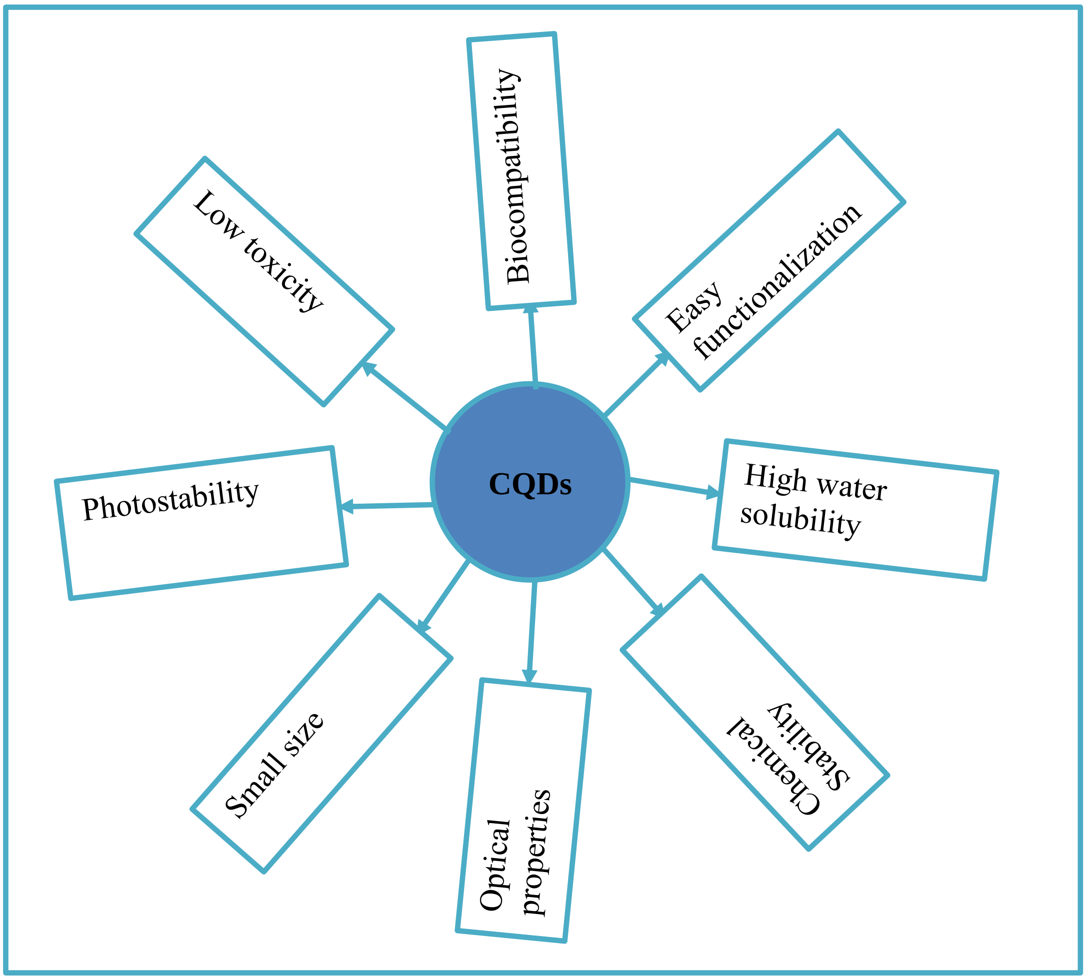


Figure 2. 1: CQDs with unique fascinating properties have extensive applications in biomedical, bioimaging, biological sensing, adsorption, chemically sensing, photocatalytic, and antibacterial.

Carbon quantum dots, in addition to their excellent optical properties, have the desirable advantages of low toxicity, eco-friendliness, low cost, high abundance, easy synthesis, and large-scale production.

2.9 Structural and Optical Properties of Carbon Quantum Dots (CQDs)

2.9.1 Chemical structure of carbon quantum dots (CQDs)

CQDs are recently discovered carbon-based material with 0D, quasi-spherical, size between 1-10 nm and mainly composed of amorphous to nanocrystalline carbon core as seen in Figure 2.2 (Lim *et al.*, 2014). Moreover, CQDs are also known as carbogenic core nanomaterials along with surface functional groups as well as they contain functional groups rich with hydrogen and oxygen atoms. CQDs nanomaterials exist in different compositions and properties among various kinds of available carbon-based fluorescent materials (Li *et* *al*., 2012). These manipulations in structure, size, composition, as well as elements incorporated into the carbon network and surface state show tunable physicochemical, optical and electronic properties. On the other hand, carbon quantum dots nanomaterials are modern carbon-based nanomaterials that have been developed as a star in advanced science fields and have special significance due to their unique properties (Das *et al*., 2021).

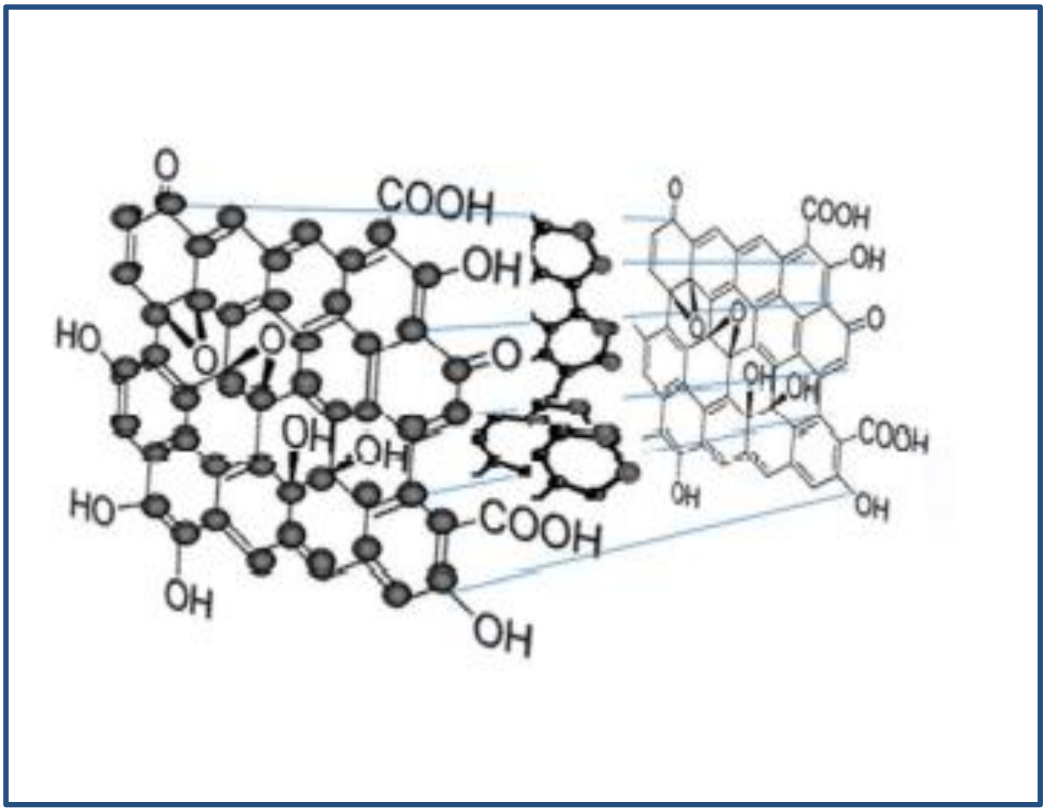


Figure 2. 2: Chemical structure of CQDs (Lim et al., 2014).

2.9.2 Optical properties of carbon quantum dots (CQDs)

Fluorescence is the process by which a material emits light of a longer wavelength (lower energy) after absorbing light of a shorter wavelength (higher energy). When the light source is pulled out (removed), fluorescence stops after a few hundreds of nanoseconds. Fluorescence quantum yield (Φ) is the ratio of emitted photons to absorbed photons. Fluorescence lifetime, on the other hand, is the average time that the fluorophore remains excited before the photons are emitted. As a result, the productions of low cost, low toxicity, and environmentally friend highly fluorescent CQDs with a high quantum yield (Φ) and a long fluorescence lifetime are highly desirable for a variety of applications. Carbon quantum dots often exhibit high photoluminescence (PL), which is dependent on the excitation wavelength. Another factor that contributes to the high fluorescence of carbon quantum dots (CQDs) nanomaterials is their surface functional groups, which include carboxylic acid, carbonyls, hydroxyls, and amide groups, which also give them excellent water solubility (Baker and Baker, 2010).

The CQDs nanomaterials have suitable functional groups and can be easily functionalized with other organic, polymer, and inorganic compounds. Furthermore, these functional groups also contribute to their multicolor emission, which is concentrated in the blue and green regions of the visible light spectrum (Miao *et al*., 2018). Temperature and reaction time are other factors that affect the size and optical properties of carbon quantum dots (CQDs). This work, illustrates carbon quantum dots synthesis techniques, precursors, solvents, temperature, time, optical properties, and factors that influence applications. However, the hydrothermal time of reaction is expected to affect only the PL intensity of carbon quantum dots and its peak position remains without shifts.

In general, there are some significant properties of CQDs nanomaterials including tunable fluorescence, sustainability, nontoxicity, small size distribution, excellent photostability, and electrochemiluminescence, and these properties are characterized and analyzed using various instruments. The optical properties of carbon quantum dots nanomaterials have been studied using UV-Visible and PL emission spectrophotometers. In addition, X-ray diffractometers are used to identify the functional groups and confirm the formation of CQDs nanomaterials. Photographs of produced CQDs nanomaterials were observed using UV analyzer instruments. The photostability of produced carbon quantum dots nanomaterials is characterized using zeta potential instruments.

i) Quantum Confinement Effect on Photoluminescence (PL) Emission

The quantum effect is a phenomenon in which a quasi-continuous electron level near the Fermi level transitions to a discrete energy level as the particle size decrease to the nanoscale. Therefore, nanomaterials, especially material particle sizes less than 10 nm, exhibit different optical properties from their block counterparts (Tuerhong *et al*., 2017).

CQDs nanomaterials possess tunable fluorescence emissions, which is a unique property. One of the most interesting properties of carbon quantum dots nanomaterials is the tunable photoluminescence property due to the quantum confinement effect, size, excitation wavelength, solvents, etc. This quantum confinement effect also affects the quantum efficiency resulting from the emission traps on the surface of the carbon quantum dots. It is possible to synthesize carbon quantum dots nanomaterials in the range from UV to red. In addition, the optical properties of CQDs depend on the size, functional groups, and synthetic method of the synthesized CQDs nanomaterials. Also, the PL emission of CQDs consists of two separate emissions, originating from the mechanisms of quantum confinement and oxidate-related surface effects or functional group, which can be competed by changing the excitation wavelength (Ghamsari *et al*., 2016).

2.10 Methods of Synthesizing Carbon Quantum Dots (CQDs)

The approaches for the synthesizing of carbon quantum dots nanomaterials can be broadly divided into two main methods, the bottom-up approach and the top-down approach as shown in Figure 2.3. These can be achieved through chemical, electrochemical, and physical processes. To synthesize CQDs nanomaterials, significant advances have been made in the synthesis, properties, and applications of CQDs (Huang *et al*., 2013). Since changing reaction parameters during synthesis can change the properties of the resulting carbon quantum dots (CQDs) nanomaterials, in particular, different starting materials and synthetic approaches are employed to generate different CQDs nanomaterials. Arc-discharge techniques are the first methods used for the fabrication of carbon quantum dots (CQDs) nanomaterials (He *et al*., 2021).

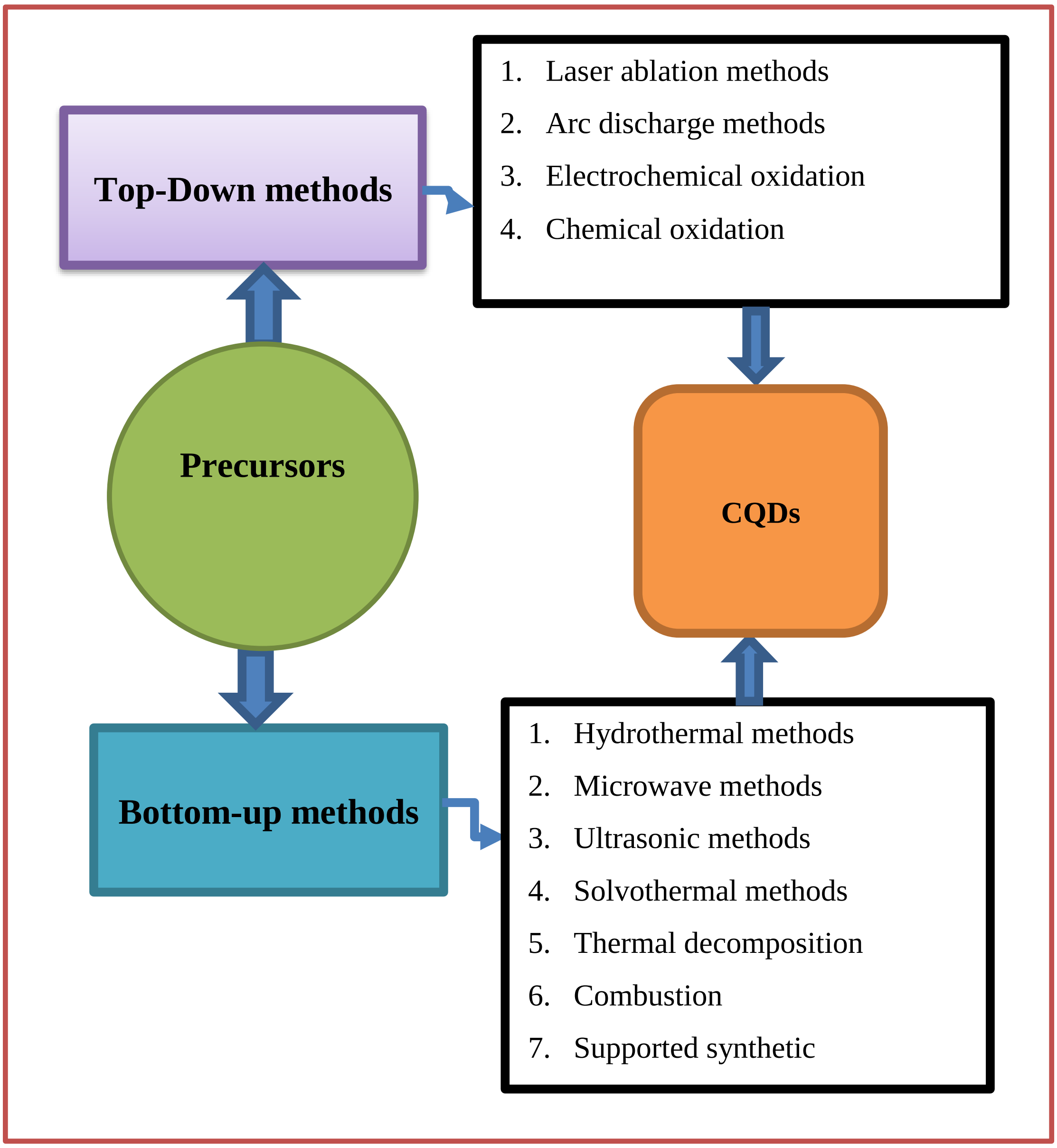


Figure 2. 3: Schematic illustrations of CQDs preparation via top-down and bottom-up approaches.

2.10.1 Top-down Techniques

Top-down refers to the subtraction from bulk starting materials or the fabrication methods begin with bulk materials (top) that are subsequently reduced into nanoparticles (down) by way of physical, chemical, or mechanical processes. For example, larger carbon structures like carbon nanotubes (CNTs), and graphite are reduced into smaller carbon structures under these techniques. The top-down methods include arc-discharge, electrochemical oxidation, chemical oxidations, ultrasonic synthesis, and laser ablations techniques. All these synthetic strategies allow, up to some degree, planning to prepare moderately high-quality carbon quantum dots with relatively high PL Φ. However, a few of these engineered or synthetic strategies suffer from restrictions such as complex equipment setup, high energy waste, time-consuming, costly beginning materials, required high-cost instruments, energy-consuming, complex preparations techniques, tedious post-treatment manner, and further robust acid extensively utilized in a few methods (Mehta *et al*., 2014).

2.10.2 Bottom-up Techniques

A bottom-up process that starts with an atom and molecule (bottom) or adds an atom or molecular starting material. These atoms or molecules react under chemical or physical conditions to form nanomaterials (up). Very recently, various non-conventional green strategies are developed to accomplish this purpose effectively. For the synthesis of luminescence carbon quantum dots (CQDs) nanomaterials, bottom-up approaches such as carbonization of glucose, sucrose, fructose, glycol, lemon juice, orange peel, apple juice, citric acid, and other carbon-containing materials have attracted the attention of the scientific community for the synthesis of fluorescent carbon quantum dots (Wang *et al*., 2021).

However, most of these synthesis processes need many steps, strong acids, and post-treatment with surface passivation agents to increase water solubility and luminescence. To fabricate self-passivated photoluminescent CQDs nanomaterials, a one-step, simple technique with cost-effective chemistry is urgently required. Bottom-up methods include combustion, thermal decomposition, hydrothermal, supported synthesis, microwave, ultrasonic, and solution chemistry methods during which carbon quantum dots (CQDs) are synthesized from different carbon-rich precursors. In general, this approach is to convert small molecule precursors into the desired size.

In general, the production of carbon quantum dots in the bottom-up approach typically involves three steps:

- high-temperature decomposition (pyrolysis) of carbonaceous precursors,
- carbonization, and nucleation
- Followed by surface passivation with stabilizers.

i) Hydrothermal methods

Carbonization is involved in the synthesis of CQDs nanomaterials from carbon-rich precursors. Hydrothermal techniques are the process of synthesizing carbon quantum dots nanomaterials in water or an aqueous solvent under high temperature and high pressure. In this carbonization process, there is a temperature and pressure (with autoclave pressure ~103.421 kPa) combination effect. This is a facile and attractive method for the fabrication of carbon quantum dots (CQDs) due to its low cost, cheap apparatus, easy operation instruments, one-step synthesis accession, energy-saving, high quantum efficiency, and being environmentally friendly. In typical research work, the carbon source or precursor mixed with deionized (DI) water is transferred to a Teflon-lined stainless steel autoclave available for hydrothermal process and heated at 100 - 280 ^{0}C for 12 hrs (Hoan *et al*., 2019a).

Next, a variety of purification techniques are used to remove large particles or impurities to obtain nanoscale CQDs nanomaterials. Furthermore, these methods are the most useful methods for preparing carbon quantum dots (CQDs) from a variety of natural and synthetic precursors. Various precursors such as sugars, lemon juice, orange juice, orange peel, apple juice, and ascorbic acid can be used in the fabrication of carbon quantum dots. For example, the use sugar cane juice as precursors for the preparation of carbon quantum dots via single-step hydrothermal techniques. Usually, the particle sizes of the solid product are referred to as range between 10 nm - 10 µm. Since hydrothermal is a bottom-up approach, the particle with a size of less than 10 nm remains in the liquid phase known as process liquid.

The synthesis of carbon quantum dots from lemon juice involves the carbonization of its constituents at high temperatures and pressure. In the lemon juice precursors, hydrothermal treatments will proceed with dehydration, polymerization, and carbonization of its constituents due to a combination of high temperatures and pressure under the hydrothermal process. This high temperature and high-pressure process in the hydrothermal autoclave prior cause the dehydration and pyrolysis of the lemon juice and next carbonization of the lemon juice in carbon quantum dots nanomaterials without any by-products. In this thesis study, high emission carbon quantum dots (CQDs) nanomaterials with high quantum yield (Φ) will be obtained without surface passivation. Moreover, inspiring the great advantages of hydrothermal techniques to synthesize CQDs with lemon juices as precursors and deionized (DI) water as solvents at 160, 180, and 200 ˚C for 6 hrs. In this work, deionized water (DI) is used as a solvent because it is more reactive and behaves as a polar owing to its high dipole moment and dielectric constant. Also, carbon quantum dots (CQDs) nanomaterials are synthesized from lemon juice at three different temperatures using hydrothermal techniques to control the photoluminescence of carbon quantum dots (CQDs) nanomaterials.

In general, the synthesis of carbon quantum dots (CQDs) under this method passes through four successive stages (Wu *et al*., 2017).

- Dehydration
- Polymerization
- Carbonization and
- Passivation-in case of our experiment CQDs is self-passivation because of precursors (lemon juice) containing various functional groups that contribute to passivation.

In the synthesis of CQDs, there is the possibility of carbonaceous aggregation that tends to form during the carbonization process. This challenge is overcome by bottom-up synthesis, in particular pyrolysis, microwave-assisted methods, and hydrothermal methods.

ii) Microwave-assisted Methods

Microwave-assisted synthesis is a simple, fast, environmentally friendly, inexpensive synthesis method that also produces carbon quantum dots with relatively high quantum yields (Φ) (Khayal *et al*., 2021). Compared to other fabrication methods, this technique does not require strict reaction conditions and is easy to carry out (Guo *et al*., 2018).

In general, there are many ways to synthesize carbon quantum dots (CQDs) nanomaterials as seen in Table 2.1, but this work focuses primarily on hydrothermal methods. Since this method is exceptionally as it is very facile to operate, fast, inexpensive, relatively less energy-consuming, and eco-friendly. Furthermore, the toxicity issues can also be overcome with the use of green precursors such as lemon juices easily since it’s abundant. Although there are a variety of fabrication ways for producing carbon quantum dots from diverse precursors, hydrothermal carbonization has been regarded as a cost-effective and environmentally friendly method for producing large quantities of highly luminescence carbon quantum dots (CQDs) nanomaterials. Due to its difficulty to control reaction rates during synthesis resulting in poor homogeneity (heterogeneity) in their structure, chemical composition, and surface chemistry.

Table 2. 1: The comparison of top-down and bottom-up fabrication techniques of CQDs (Choi *et al*., 2018).

Categories	**Methods**	**Advantages**	**Disadvantages**
Top-down methods	Arc-discharge Laser ablation Electrochemical Ultrasonication	Stable optical property	Complicated method Low Φ Costly starting materials
Bottom-up methods	Hydrothermal Solvothermal Microwave Template	Simple method High quantum yield Inexpensive starting materials	Single emission wavelength

2.11 Purification Techniques of Carbon Quantum Dots (CQDs)

CQDs products exist as a complex mixture containing components of various sizes, distinctive surface features, and polydisperse carbon quantum dots samples are the sum of all individual or average properties types of CQDs nanomaterials. For this reason, it is important to purify the sample and isolate the carbon quantum dots from the rest of the solution, after the formation of CQDs nanomaterials. The resulting carbon quantum dots are further separated by size and composition, allowing the selection of carbon quantum dots with a specific wavelength of emission (Domingo-Tafalla *et al*., 2022). Various techniques have been used to separate carbon quantum dots (CQDs) nanomaterials from a solution including gel electrophoresis, column chromatography, centrifugation (for example, density gradient centrifugation, and differential centrifugation), solvent extraction, dialysis, and filtration (González-González *et al*., 2022). Different methods can produce different results. Nowadays, almost every procedure involves filtration and centrifugation of raw samples. This is because these routes efficiently perform the initial separation of nanoparticles from the larger species in the remaining solution. Usually, centrifugation and filtration are utilized in the laboratory because available and inexpensive. Finally, after purifying the desired nano-sized carbon quantum dots nanomaterials and separating them from the rest of the solution, the precipitate is likely to contain larger particles, impurities, and aggregates, while the result is in the supernatant form (Jorns and Pappas, 2021).

In 2004, CQDs were first separated from SWCNTs by polyacrylamide gel electrophoresis (PAGE), and there are increasing reports on analytical separation strategies for carbon quantum dots. Success in this area includes not only electrophoresis, but also chromatography, density gradient centrifuges, differential centrifugation, solvent extraction methods, and dialysis (Gao et al., 2019). In general, several analytical techniques have been developed to separate and purify carbon quantum dots (CQDs) nanomaterials from a variety of rest solutions to better understand the essential properties of carbon quantum dots (CQDs) nanomaterials. These post-treatment techniques help to maintain the unique properties of carbon quantum dots (CQDs) nanomaterials.

2.12 Characterization Methods of Carbon Quantum Dots (CQDs)

Over the last few years, the researchers understoond much better than ever structural, photophysical, photostability, and chemical properties of CQDs nanomaterials . The chemical composition, fluorescence, photostability, and structure are key important factors that decide the special and outstanding properties of carbon quantum dots CQDs. For this reason, many efforts devoted recently to investigating reliable characterization instruments for carbon quantum dots (CQDs) nanomaterials. However, a complete characterization and analysis of the carbon quantum dots nanomaterials mixture remains and faces significant challenges.

Several non-destructive imaging and microscopic techniques have been developed for the morphology, size, chemical composition, fluorescence, photostability, and structural characterization of nanomaterials. The microscopy methods developed for the characterizations of carbon quantum dots nanomaterials are diffraction methods such as X-ray diffraction (XRD). Furthermore, different spectroscopy techniques have been depicted for carbon quantum dots (CQDs) nanomaterial characterization, ultraviolet-visible (UV-Vis), UV analyzer, photoluminescence (PL), Fourier Transform Infra-Red (FT-IR) spectroscopy, and zeta potential.

2.12.1 X-ray Diffractometer (XRD)

X-ray diffraction (XRD) is a fast analytical method used for the phase identification, crystal structure, and characterization of crystalline materials based on their diffraction pattern.

When the X-rays interact with a crystalline carbon quantum dots (CQDs) nanomaterials sample, constructive interference is produced, and these diffracted X-rays are then detected, processed, and counted, revealing the average structure of CQDs nanomaterials (Zheng *et al., 2020)*. Furthermore, XRD also provides information about the purity of a synthesized carbon quantum dots (CQDs) sample. Although the XRD may be a profitable characterization device for obtaining the basic features of carbon quantum dots (CQDs) nanomaterials with a crystalline structure, it does not apply to characterizing amorphous CQDs nanomaterials. In general, XRD is used to determine the microstructure of carbon quantum dots nanomaterials and XRD was used to confirm the existence of CQDs synthesized from lemon juice nanomaterials. It is expected from the result of XRD that the peak intensity of microstructure of synthesized carbon quantum dots (CQDs) nanomaterials decreased as synthesis temperature increases.

The crystal structure was studied by X-ray diffraction (XRD) based on Wulf-Bragg's law shown in Eq. (2.1). According to Bragg's law (Smrithi *et al*., 2022).

$$n\lambda = 2d\sin\theta \qquad (2.\ 1)$$

Where n is the order of diffraction (usually n = 1) , λ is the X-ray wavelength and d is the spacing between planes of given Miller indices h, k, and l, and θ is angle of diffraction. The average crystallite size of the synthesized carbon quantum dots (CQDs) nanomaterials was calculated from the XRD spectrum using Debye-Scherrer's Eq.(2.2) (Yu et al., 2020).

$$D = \frac{K\lambda}{\beta_{hkl}(\cos\theta)} \qquad (2.2)$$

Where D (nm) is the average crystallite size of the particle, λ (1.5406 A°) is the wavelength of the incident X-ray, β is the angular peak width that is half the maximum value in radians, and θ is the Bragg diffraction angle. The average crystallite sizes (D) are usually calculated from the most intense peak in the XRD pattern. However, the calculation of the crystalline size from one peak is not suitable. Therefore we will have to calculate the average crystalline size, which is the calculation of the crystallite sizes from all peaks, and then we will have to average those crystallite sizes. For spherical crystallites, K is 0.94.

2.12.2 Ultraviolet-Visible (UV-Vis) Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is a well-established, reliable, widely accessible, and robust spectroscopic technique that has been used to measure the optical properties of

CQDs nanomaterials. Almost all types of carbon quantum dots (CQDs) nanomaterials are active in the UV-vis region of the electromagnetic spectrum. Carbon quantum dots show a wide absorption range in UV and extended into the near-visible region. The information from the absorbance values of the synthesized CQDs nanomaterials is used to calculate their bandgap energies. The bandgap energy, which is the energy required for an electron to transition from lower energy (E_1) state to higher energy (E_2) state, corresponds to the energy of electromagnetic radiation (photon energy) that causes the transitions. Bandgap energy is expected to increase as we move from bulk to nanomaterials. On the other hand, this shows the relationship between the quantum confinement effect, size, and bandgap energy.
The bandgap energy can be determined by substituting the value of the maximum absorption peak at a given wavelength into Eq. (2.3) (Zhou *et al.*, 2019).

$$E_g = E_2 - E_1 = h\nu = h\frac{c}{\lambda} = \frac{1.240}{\lambda_{\max}}[keV] \quad (2.3)$$

Where Eg is the bandgap energy (eV), E_1 and E_2 are lower and higher energy states respectively, h is Planck's constant (6.626 x 10^{-34} J.s), and c is the velocity of light (3 x 10^8 m/s) and λ is the wavelength (nm) of absorption onset.
The optical bandgap energy (E_g) is determined from a Tauc-plot of Eq. (2.4)(Jumardin *et al.*, 2021).

$$\alpha h\nu = A(h\nu - E_g)^{n} \quad (2.4)$$

Where α is the absorbance coefficient, h is the Planck's constant, *v* is the frequency of light radiation and E_g is the bandgap energy where 'n' takes the values of ½ allowed direct transition.

2.12.3 Illumination UV Lamp Analyzer

The synthesized carbon quantum dots (CQDs) were investigated with help of a UV analyzer. The synthesized dark brownish color CQDs solution was placed in a UV analyzer (254 nm and 365 nm) for the analysis, as a result UV light passed on a sample holder containing a dark brownish solution of CQDs.

2.12.4 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) spectroscopy is one of the most common and readily available spectroscopic methods for measuring the optical properties of CQDs nanomaterials. The fluorescence emission of carbon quantum dots is expected to be affected by the excitation wavelength (λ_{ex}). Furthermore, utilizing UV-Vis and PL spectroscopy in combination, the quantum yield (Φ) of carbon quantum dots nanomaterials may be measured. The quantum yield of CQDs sample is determined using a comparison technique using methylene blue (MB) with known Φ as the reference. Both methylene blue (MB) solutions and CQDs nanomaterials have their photoluminescence (PL) spectra essentially recorded. As a result, the quantum yield of the CQDs nanomaterials can be calculated using a simple ratio of the integrated PL intensities of the two solutions. Because of size-dependent optical properties, the optical absorbance and PL of CQDs nanomaterials are related to confinement quantum effects (Yan *et al.*, 2019). The optical properties of carbon quantum dots (CQDs) nanomaterials vary due to the different sizes of carbon quantum dots nanomaterials and the various emissive traps on the surface. The emission spectra of carbon quantum dots are expected to range from the blue region to the near-IR region.

However, due to the lack of experimental and theoretical information, the photoluminescence mechanisms of carbon quantum dots are still unknown, which has hindered the development of carbon quantum dots (CQDs) nanomaterials with desirable optical properties. The surface state of CQDs nanomaterials, which is based on synergistic hybrids between carbon backbones and linked functional groups, is now thought to be the most important factor (Speranza, 2021). The photoluminescent emission properties of CQDs are influenced by a variety of factors. There are three types of model parameters that influence the origins of PL, one of which is the surface state. The temperature of the hydrothermal treatment should be able to tune the emission wavelength of these carbon quantum dots. As a result of their multicolor emission capabilities and nontoxic qualities, these carbon quantum dots (CQDs) can be used in a variety of applications. The emission wavelength of PL is supposed to be longer than the excitation wavelength, as predicted by the Stoke shifts (energy of the emitted photon is smaller than the absorbed photon).

In both their fundamental and application point of views, the most interesting aspect of carbon quantum dots nanomaterials is their photoluminescence (PL). The influence of hydrothermal temperature and time on the luminescence CQDs under comparatively various excitation wavelengths was investigated in this study. Furthermore, the aging of CQDs solution and the effect of excitation on the fluorescence of carbon quantum dots was also investigated. This might help provide additional research information on CQDs applications, particularly in producing powerful and photostable emissions in various fields. Thus the goal of the CQDs preparation and analysis is to get high PL quantum yield (Φ).

The key factor that determines the luminescence properties of nanomaterials is quantum yield (Φ). The value of quantum yield (Φ) is usually between 0 and 1. Comparing the PL intensity of the sample with the standard compound is the easiest approach for determining the quantum yield (Φ). The most popular method for calculating the quantum yield (Φ) of PL is to use reference standards. However, there is another method for determining the absolute value, but specialized and expensive apparatus is required. While using a reference only requires the use of traditional UV-vis and fluorescence spectrophotometers. Quantum yield (Φ) is the ratio of emitted photons to absorbed photons according to Eq. (2.5) (Mintz *et al*., 2019).

$$\Phi = \frac{Photons\,emitted}{Photons\,absorbed} \tag{2.5}$$

However, the most common method employed to obtain Φ of carbon quantum dots (CQDs) nanomaterials, is according to Eq. (2.6) (Alkian *et al*., 2022).

$$\Phi_{CQDs} = \Phi_{ref} \frac{I_{CQDs}}{I_{ref}} \frac{A_{ref}}{A_{CQDs}} \frac{(n_{CQDs})^2}{(n_{ref})^2} \tag{2.6}$$

Equations (2.6) show how to compute a substance's relative quantum yield (Φ) concerning a reference material with a high quantum yield (Φ). Typically methylene blue (MB) (Φ = 0.52) is used as the reference material. The term ‘‘CQDs’’ refers to the sample being analyzed and the ‘‘ref’’ stands for reference material. While ‘‘I’’ refer to the integrated emission intensity curve of the sample and reference. Where ‘‘A’’ refers to the UV-Vis absorption intensity of the sample and reference, and ‘‘n’’ refers to the refractive index of the solvents used for the sample (Water = 1.333) and reference (Ethanol = 1.3614) measurements. Using this method researcher easily calculated the quantum yield (Φ) of CQDs. Methods of synthesis and precursors are key factors that influence quantum yield (Φ).

The sizes, crystalline degree, and functional groups of CQDs nanomaterials all influence their photoluminescence capabilities. Carbon quantum dots nanomaterials have been reported to have low photoluminescence (PL) quantum yield (Φ) in recent years, but this can be improved using various techniques such as the surface modification or functionalization, as well as a simple synthesis to obtain high PL quantum yield (Φ) of carbon quantum dots (CQDs) and a crystalline carbon core synthesis (Lin *et al*., 2019). Furthermore, due to the chemical structure of the carbon core and the surface state of carbon quantum dots fabricated from various carbon precursors, the carbon source of CQDs has a significant impact on the photoluminescence (PL) properties.

2.12.5 Fourier Transformed Infra-Red (FT-IR) Spectroscopy

FT-IR spectroscopy is used to identify the changes in functional groups on the surface of carbon quantum dots. Furthermore, FT-IR also investigated chemical bonding constituents in CQDs nanomaterials synthesized from natural product precursors. In the case of FT-IR investigation of carbon quantum dots (CQDs) samples, apart from the evaluation of hydroxyl (-OH), carbonyl (C=O), and carboxylic acid functional groups on the carbon quantum dots (CQDs) nanomaterials surface, it is also able to analyze the doping of heteroatoms into the carbon quantum dots framework. The advantages of this technique for the characterization of surface functionalization of CQDs are being cost-effective, facile, fast, and easy for sample preparation (Hoan *et al*., 2019a).

2.12.6 Zeta Potential

Zeta potential instruments are used to study the surface charge and photostability of fluorescent carbon quantum dots (CQDs) nanomaterials (Zhou *et al*., 2019). The zeta potential investigation was carried out using the zetasizer Nano series (Malvern) (Zetasizer Ver.8.02, MAL 1149420). The zeta potential of the CQDs, known as the electrokinetic potential of the synthesized fluorescent carbon quantum dots, this technique also provides insights into the properties of the CQDs, including double-layer attributes with multiple hydrophilic functional groups (hydroxyl, carboxyl, and carbonyl). The zeta potential measurement may be presented as a useful and efficient method for evaluating the ability of the CQDs to adsorb pollutants in the aqueous environment.

2.13 Applications of Carbon Quantum Dots (CQDs)

Carbon quantum dots exhibit the most interesting properties such as high water solubility, excellent biocompatibility, good elasticity in modifications, and unique luminescence properties. Due to these unique properties, CQDs nanomaterials have great potential applications in a variety of area, particularly for adsorption of pollutant organic dyes applications. Also, their unique high resistance to photobleaching, good biocompatibility, durable photostability, and chemical inertness make them widely applied in bioimaging, biosensing, chemical sensing, and as well as adsorption applications.

2.13.1 Carbon quantum dots (CQDs) nanomaterials for adsorption applications

Recently, the pace of growth of the modern industry has had a great impact on living organisms and environmental contamination. Different organic compounds add color to different substrates, including water. Methylene blue (MB) dye is a type that pollutes water bodies and drinking water. This affects human health and causes problems such as anemia and blood pressure. In addition, methylene blue (MB) dyes absorb light that promotes the growth of life, thus inhibiting the growth of organisms in an aqueous solution. For this reason, extensive research has been conducted on the removal of dyes. There are many fluorescent materials, such as semiconductor quantum dots and carbon quantum dots (CQDs) that are attracting the attention of researchers who adsorb dyes to remove contaminants from aqueous solutions. However, CQDs nanomaterials do not contain heavy metals such as Cd, Te, Se, and Pb, so it is an alternative to semiconductor quantum dots (Teymoorian *et al*., 2021). Also, commonly used high carbon bulk materials such as biochar, chitosan, and activated carbon have the same drawbacks in removal efficiency due to their small surface area (Pudza *et al*., 2020).

Today, environmental friendliness, cost-effective, and highly efficient removal of organic dyes are needed. To realize this possibility, we studied the removal of methylene blue (MB) dye using carbon quantum dots nanomaterials. This study focuses on the adsorption activity using CQDs from lemon juice by hydrothermal techniques. Because carbon quantum dots is a high surface area, excellent optical properties, ease of synthesis accession, easy functionalization, inexpensive, and low toxicity. In this study, a procedure was followed to mix a certain amount of CQDs with an appropriate concentration of methylene blue (MB) dye solution. Dye molecules are absorbed on the surface of the adsorbent by hydrogen bonds, van der Waals interactions, or hydrophobic forces (Shanker *et al*., 2017). Carbon quantum dots nanomaterials are used as catalysts in many reactions, especially in adsorption applications. Several factors affect the adsorption efficiency of carbon quantum dots (CQDs) that adsorb nanomaterials, such as adsorbent dose, surface area, pore-volume, contact time, and initial concentration of methylene blue (MB) dyes.

CQDs exhibit properties such as a mass of hydrophilic functional groups, simple synthesis with high abundant and cheap raw materials, unique chemical nature, and a large number of surface adsorption sites because of their large surface area and small size this may be the reason why CQDs adsorb contaminants MB dyes from wastewater. Adsorption of methylene blue (MB)(cationic ions) on CQDs included multiple adsorption mechanisms such as electrostatic interactions, hydrogen bonds, and surface complexation between adsorbent and adsorbant (Chen *et al*., 2021). Electrostatic interactions may consider the significant adsorption mechanisms between CQDs-adsorbent and MB dye due to a mass of negatively charged oxygen and nitrogen-containing functional groups on the surface of CQDs. These negatively charged nitrogen and oxygen-containing functional groups on the surfaces of CQDs can provide active sites for MB dye adsorption (Long *et al*., 2021). To evaluate the kinetics of the adsorption process the experimental data were fitted to pseudo-first-order kinetic models and pseudo-second-order kinetic models.

In our case, studies of maximum equilibrium adsorption capacity q_e (mg/g) and removal efficiency (R%) of methylene blue (MB) dye using carbon quantum dots (CQDs) nanomaterials have been conducted with fixed concentration adsorbents (20 mg/100 mL and MB dyes 0.01g/L of 10 ppm stock solution with varying contact time (min). The effect of contact time (min) on the adsorption performance of carbon quantum dots (CQDs) nanomaterials was investigated.

The percentage of removal (R %) and the equilibrium adsorption capacity q_e (mg/g) of the MB dyes were calculated. The removal efficiency (R %) and equilibrium removal capacity q_e (mg/g) of the MB dye were computed by Eq. (2.7) and (2.8) (Teymoorian *et al*., 2021).

$$R\% = \left((1) - \left(\frac{C_e}{C_0} \right) \right) \times 100 \tag{2.7}$$

and

$$q_e = (C_0 - C_e) \times \frac{v}{m} \tag{2.8}$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of absorbate (mg/L) in the solution, respectively; V (L) is the volume of dye solution, and m (g) is the weight of the adsorbent (CQDs). In this study, the solution volume is fixed at 0.1 L.

Next, calculate the rate of reaction of adsorption removal reaction of MB dye using CQDs adsorbent. Usually, an adsorption removal reaction is considered a pseudo 1st order kinetic reaction. As the removal model reaction proceeds as shown in Figure 2.4.

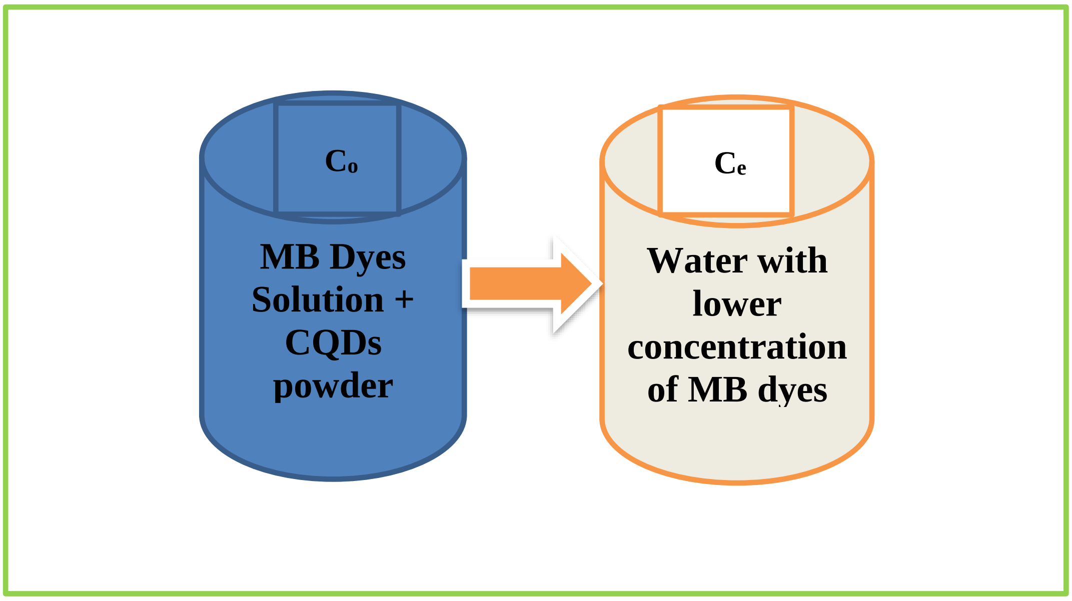


Figure 2. 4: Mechanisms of removal methylene blue (MB) from aqueous solution by using CQDs.

Adsorption of solutes from the aqueous phase system onto the adsorbent is a time-dependent process. To design an effective adsorption system, investigations should be carried out to determine the rate of adsorption. For determination of the rate of an adsorption process such as physical or chemical reaction, diffusion mechanism, and mass transfer, several kinetic models are implemented to examine the experimental data. The kinetics of adsorption illustrates the rate of adsorbate uptake by the adsorbent at a predetermined interval and equilibrium contact time. The kinetic parameters are essential for the calculations of adsorption rate, providing significant information for designing and modeling the process. Nevertheless, the characteristics of the adsorption process will entirely depend on the physical and chemical properties of the adsorbate, and adsorbent, and also on the operating variables.

According to the dynamic Langmuir-Hinshelwood model, the adsorption rate of organic dye like methylene blue (MB) can be computed according to the pseudo-first-order-kinetic as shown in Eq. (2.9) if the solution is very dilute (Peng *et al*., 2020).

$$ln[\frac{C_0}{C_e}]=k_t \tag{2.9}$$

For calculation purposes, here, C_0 and C_e are taken as the absorbance of the dyes at time zero and the absorbance of the dyes after adsorption time t, respectively; k stands for the dye adsorption rate.

3. MATERIALS AND METHODS

In this chapter, the materials used and methods of the experiment were discussed in detail. The various chemicals, apparatus, instruments, and solvents that are necessary to carry out this experiment was also briefly elaborated. And also, the methods for the synthesis of carbon quantum dots (CQDs) for absorbent activities were presented broadly.

3.1 Chemicals and Solvents

All the chemicals and solvents required for synthesizing CQDs nanomaterials were purchased and analytical reagent grade was used without any further purification. The chemicals used in this study were Nitric Acid (HNO_3) (69%) (Loba Chemie Pvt. Ltd., India), ethanol (assay; ≥ 99.8%), lemon juice, and methylene blue (MB) dyes. Deionized water (DI) has been used as a solvent throughout this experiment.

The materials required for adsorption applications are powder of carbon quantum dots (CQDs), and methylene blue (MB) dyes ($C_{16}H_{18}CIN_3S$, MW: 319.85 g mol^{-1}, λ_{max} = 665 nm).

3.2 Apparatus and Instruments

3.2.1 Apparatus

The laboratory apparatus used in synthesizing carbon quantum dots via the hydrothermal methods are were the following: Magnetic stirrer with a hot plate (ML 2 lt), different sizes of beakers, autoclave (size 25 mL), magnetic bar, thermometer, pH meter (Phs-3c), Filter papers (Wat-Mann-1) (size 110 mm), conical flask (250 mL), Syringe filters (0.45 µm), Digital electrical analytical balance (Model-FA2104, China), Vacuum oven (Model-JEIO TECH CO., LTD. KOREA), Drying oven (Model-DGH-9055, Jangasu Gangdu Mechanic Electronic Equipment Co Ltd., China), Gloves, Aluminum foils, Refrigerators, Centrifuges tubes (sizes 10 mL), Glass plate for thin-film, Pipettes, Cylinders, Sample holders, and Centrifuges machine.

3.2.2 Instruments

The laboratory instruments used for the characterization of the synthesized carbon quantum dots were: UV analyzer (UV4AC6/2, CBI02018040184, Beijing CBIO Bioscience and

Technologies CO., Ltd. China), X-Ray Diffractometer (XRD) (XRD-7000 X-RAY DIFFRACTOMETER MAXIma, SHIMADZU Corporation. Japan), UV-Visible absorption (UV-Vis) Spectroscopy (MODEL-JASCO V-770, Japan), Fourier Transformed Infra-Red Spectroscopy (FT-IR) (Perkin Elmer, Spectrum 65 FT-IR), Photoluminescence (PL) (Model, MY18490002, Cary Eclipse Fluorescence Spectrophotometer, Agilent Technologies, Malaysia) and Zeta potential (Zetasizer Ver.8.02, MAL 1149420).

3.3 Procedure for Synthesis of Fluorescent Carbon Quantum Dots (CQDs)

Carbon quantum dots were synthesized utilizing simple hydrothermal techniques at different temperatures of 160, 180, and 200 °C for 6 hr from lemon juice with deionized (DI) water as solvent. The lemon plant (also used in the food industry) was purchased from a local market, in Adama town, Ethiopia, and washed properly with clean water to remove dust and unwanted particles on the lemon surface. In this research work, 13 mL of lemon juice (pulp-free extracted lemon juice) was mixed with 7 mL of deionized (DI) water. The mixture of lemon juice extracted and deionized (DI) water was stirred for 10 min using a magnetic stirrer at room temperature (RT) before transfer into the autoclave. Then transfer into the 25 mL capacity autoclave and sealed seriously into a Teflon-lined stainless steel autoclave for hydrothermal process and heated at 160, 180, and 200 °C for 6 hr each step (Hoan *et al*., 2018).

After the reaction, the dark brownish product was obtained. By different purification techniques, large particles of impurities are removed to obtain nanoscale carbon quantum dots for later use. The best purification techniques used in this work are the combinations of centrifuges and filter paper. The brown color solution was centrifuged at 5000 rpm for 20 min to remove the impurity or large particles and filtered through 0.45 µm syringe filter paper. Furthermore, these methods have been the most common useful route to fabricate CQDs from numerous wide range of natural and synthetic precursors. Figure 3.1 shows the schematic for the fabrication of carbon quantum dots (CQDs) from lemon juice via hydrothermal methods.

Figure 3. 1: Show a schematic of the synthesis of carbon quantum dots (CQDs) from lemon juice using hydrothermal techniques.

As shown in Figure 3.1 the ivory-white solution of lemon juices mixed with deionized (DI) water was changed to a brown color solution, which indicates the formations of carbon quantum dots (CQDs).

3.4 Characterization Methods

The X-ray diffraction (XRD) patterns of carbon quantum dots (CQDs) were obtained from an X-Ray Diffractometer (XRD) (XRD-7000 X-RAY DIFFRACTOMETER MAXIma, SHIMADZU Corporation. Japan) which is equipped with Cu-Kα_1 radiation ($\lambda = 1.5406$ A$^{\circ}$) and operates at a voltage of 40 kV and an applied current of 30 mA with a scanning speed of 3.00 degrees per minute, with the collected data scanned at a range of $\sim 2\theta = 10^{\circ} \leq 2\theta^{\circ} \leq 80^{\circ}$. Furthermore, X-ray diffractometers are used to evaluate the average crystalline particle size of synthesized CQDs nanomaterials by using the relation expressed in Eq. (2.2).

The UV-Vis absorption spectra were obtained with UV-Vis spectroscopy (MODEL-JASCO V-770, Japan) in the wavelength region of 200-800 nm at room temperature. After the resulted dark brown suspension was filtered to separate the precipitate from the supernatant. The supernatant containing carbon quantum dots (CQDs) was diluted with deionized (DI) water and then optically characterized to determine their optical absorption spectra using a UV-Vis spectrophotometer. In short, for each scan, 3 mL of diluted carbon quantum dots (CQDs) nanomaterials samples were taken in a quartz cuvette and absorption was monitored for a wavelength range of 200-800 nm. In the area of the blank scan deionized (DI) water was used to observe the absorption capability of the carbon quantum dots (CQDs) nanomaterials. A computer that interfaced with the equipment collected the ASCII files of the measured spectra. Finally, using OriginPro 2021 software, the absorption spectra of produced carbon quantum dots were investigated. Equation (2.4) was used to compute the optical energy bandgap of synthesized carbon quantum dots (CQDs).

For confirmation, the synthesized carbon quantum dots (CQDs) were also investigated with help of a UV analyzer. The synthesized dark brownish color CQDs solution was placed in a UV analyzer and (254 and 365 nm) and UV analyzer light was passed on a sample holder containing the dark brownish solution of CQDs.

The fluorescence (PL) spectra of produced carbon quantum dots (CQDs) nanomaterials were recorded using a fluorescence spectrophotometer (Model, MY18490002, Cary Eclipse Fluorescence Spectrophotometer, Agilent Technologies, Malaysia) at room temperature. The emission spectra of the carbon quantum dots (CQDs) nanomaterials sample were measured by a 1cm quartz cuvette and before measurement, our sample dilutes with deionized (DI) water. The synthesized carbon quantum dots (CQDs) nanomaterials had their excitation wavelengths measured at 360, 380, 400, 420, 440, 460, 480, 500, and 520 nm, and the emission spectral shift toward higher wavelengths was recorded. During emission spectra of carbon quantum dots (CQDs) measurement the slit width of emission and excitation was set to 10 nm.

The Fourier Transform Infra-Red (FT-IR) (Perkin Elmer, Spectrum 65 FT-IR) was measurement conducted at room temperature (RT) using a KBr pellet ranging from 400 - 4000 cm^{-1} with the resolution of 4 cm^{-1}. FT-IR spectroscopy was used to identify the main functional groups and chemical groups attached to the carbon quantum dots (CQDs) nanomaterials.

Zeta potential (Zetasizer Ver.8.02, MAL 1149420) instruments were used to study the surface charge and photostability of carbon quantum dots (CQDs) nanomaterials.

The organic dye removal efficiency and equilibrium adsorbed capacity of synthesized carbon quantum dots (CQDs) nanomaterials were evaluated by the adsorption of methylene blue (MB) dye in aqueous solutions.

3.5 Experimental Procedure for the Adsorption Removal of Methylene Blue (MB) Dyes

Adsorption performance of fluorescent CQDs was employing for the adsorptive removal of highly toxic methylene blue (MB) dyes from drink water or wastewater in 24 min. The adsorption experiment of removal of methylene blue (MB) dyes was carried out by using carbon quantum dots (CQDs) nanomaterials powder as our chosen absorbent. The adsorption studies were carried out by adding 20 mg of absorbent or carbon quantum dots (CQDs) nanomaterials powder with a 0.001 g/100 mL (0.01 g/L) concentration of MB into 250 mL of conical flasks with contact time from 0 to 24 min under room temperature (25 $^{\circ}$C). After adding the dye solution with the adsorbent stirred with a magnetic stirrer at 150 rpm for 24 min and the solution was measured at 3 min intervals to observe the removal efficiency (R%) and the equilibrium adsorbed capacity q_e (mg/g) of the methylene blue (MB) dye using UV-Vis spectroscopy. The experiment studies were carried out to inspect the influences of contact time on MB adsorption as shown in Figure 3.2.

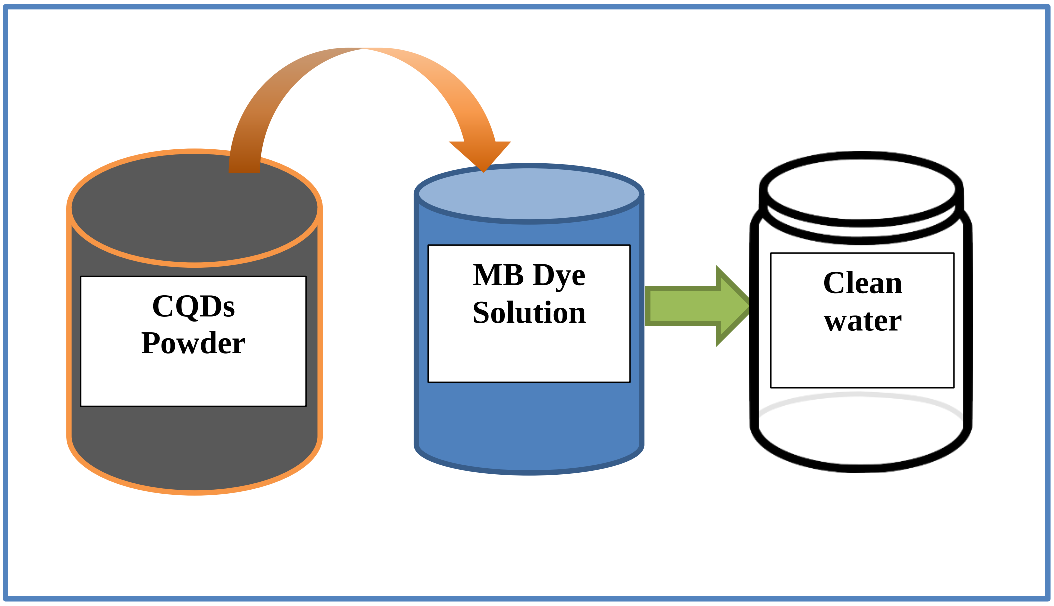


Figure 3. 2: Illustrates the mechanisms of adsorption of MB using CQDs nanomaterials.

The removal efficiency (R %) and the equilibrium adsorption capacity q_e (mg/g) of the MB dye were computed by using Eq. (2.7) and (2.8) respectively.

4. RESULTS AND DISCUSSION

The results and discussions of the experiments were reported in this chapter. First the basic crystal or amorphous structure of carbon quantum dots (CQDs) was discussed in detail using an X-ray diffractometer (XRD). In the subsequent section, the absorbance spectra of synthesized carbon quantum dots (CQDs) were introduced. Photograph of synthesized carbon quantum dots which was obtained using UV lamp analyzer instruments is presented in section three. The photoluminescence (PL) spectra with a different excitation wavelength of synthesized carbon quantum dots were also extensively elaborated on in the fourth section. The functional groups of synthesized carbon quantum dots (CQDs) nanomaterials were briefly discussed in the fifth section. In the sixth section, the zeta potential which demonstrates surface charge carriers and photostability of synthesized CQDs, is presented. Finally, the adsorption activity of CQDs which was synthesized using hydrothermal synthesis techniques is also presented.

4.1 X-ray Diffraction (XRD) Analysis

An X-ray diffractometer study has been carried out to investigate the crystal structure or amorphous of the synthesized carbon quantum dots (CQDs). As seen in Figure 4.1 (a, b, and c), the smoothed XRD patterns result of carbon quantum dots were synthesized at different temperatures of 160, 180, and 200 $^{\circ}$C under hydrothermal treatment. This result shows that the X-ray diffractometer (XRD) pattern exhibit a wide diffraction peak at ~2 θ = 20.1°, 18.07°, and 14.57° respectively for 160, 180, and 200 $^{\circ}$C.

The result of XRD peaks shows that the intensity of peaks decreases as the temperature of hydrothermal increases this is due to the carbon quantum dots nanomaterials may result in disordered carbon atoms as the temperature rises. This result is consistent with previously reported results on carbon quantum dots (CQDs) synthesized using different methods. Also, the synthesized CQDs behave as it is amorphous because of the synthesis of carbon quantum dots with disordered carbon atoms.

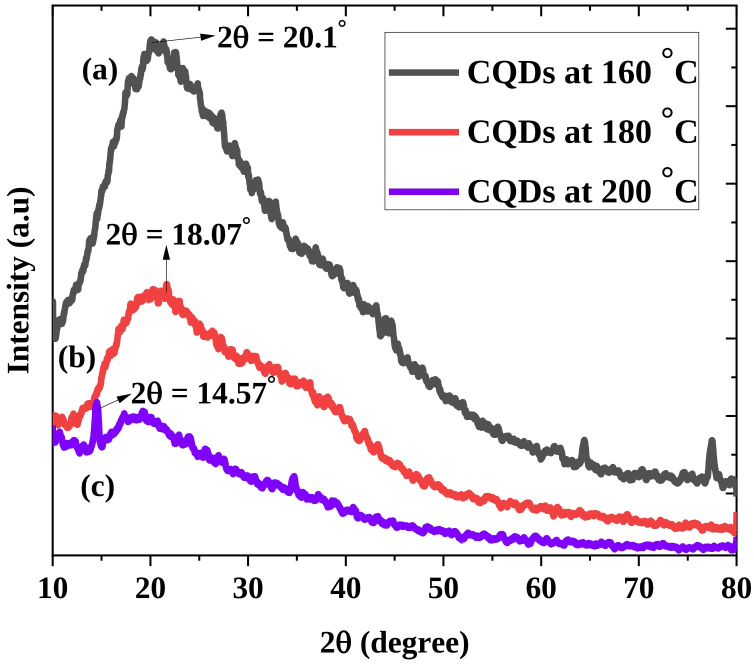


Figure 4. 1: An XRD pattern was obtained for CQDs synthesized at (a) 160 °C, (b) 180 °C, and (c) 200 °C.

4.2 Ultraviolet-Visible (UV-Vis) Absorption Spectra

Figure 4.2 shows the UV-Vis spectra of synthesized CQDs, with two absorption maxima at 217.5 nm, and 282 nm, and a tail extending into the visible range. These bands are corresponding to – C = O and C = C bond of n-π* and π-π* transitions respectively and these results confirm the early reports carbon quantum dots (CQDs) synthesized from leaves of Elettaria cardamomum for photocatalytic applications (Zaib *et al*., 2021). The non-uniform size distribution and functional groups of carbon quantum dots were responsible for the appearance of two absorption maxima. While the absorbance peaks for 180 and 200 °C are centered at 222, and 219.5 nm respectively.

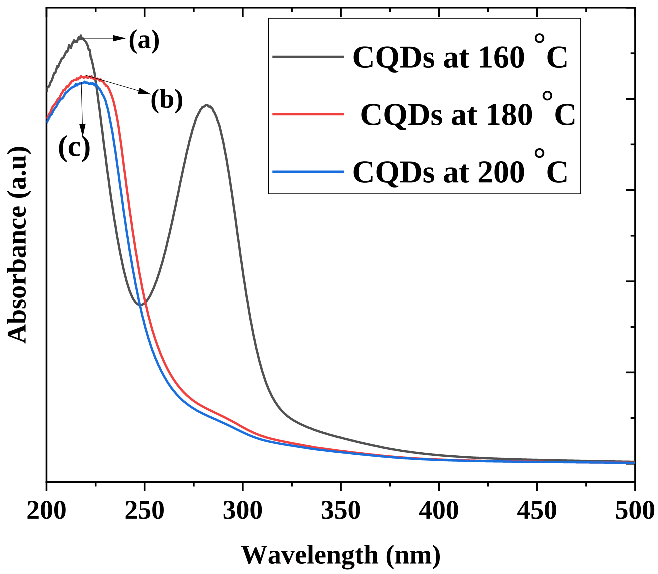
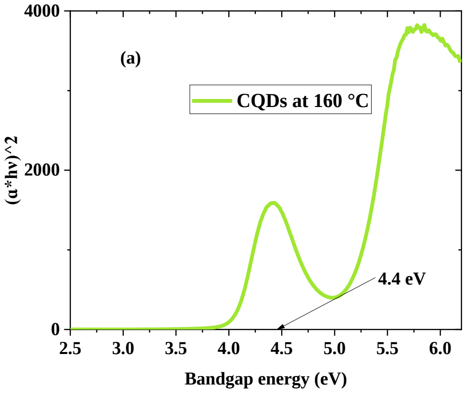
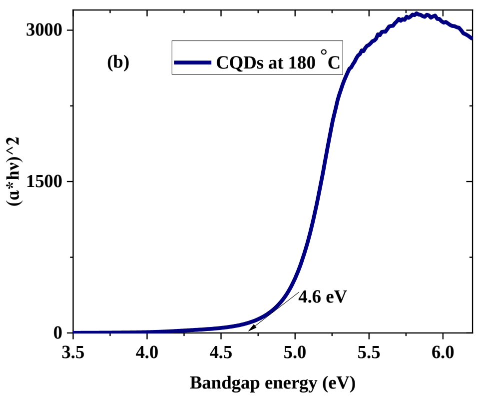


Figure 4. 2: UV absorbance of CQDs prepared at (a) 160 °C with maximum peaks of 217.5 and 282 nm, (b) 180 °C with maximum peaks of 222 nm, and (c) 200 °C with maximum peaks of 219.5 nm.

Figure 4.3 indicates the computed optical bandgap energy using Eq. (2.4). Carbon quantum dots synthesized at 160 °C have the highest absorbance peaks at 282 nm with bandgap energy of 4.4 eV and these results confirm previously synthesized carbon quantum dots via a one-step laser-passivation method (Hu *et al*., 2009). The bandgap energy values of 4.6 eV, and 4.68 eV for 180, and 200 °C respectively.





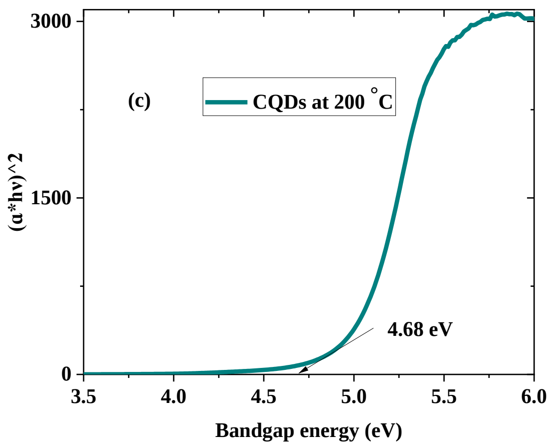


Figure 4. 3: Bandgap energy (E_g) results of synthesized CQDs at; (a) 160 °C; (b) at 180 °C; (c) 200 °C.

4.3 Illumination of UV Lamp Analyzer

A blue and green fluorescence were indicated at 254 and 365 nm respectively, which confirm the presence of carbon quantum dots (CQDs). This is due to the non-uniform particle size distribution and functional groups on CQDs surface. One of the unique properties of carbon quantum dots is tunable multicolor fluorescence and the result of the UV analyzer confirms this theory. On the other hand, in the absence of UV analyzer light (under visible light), ordinary brownish colors was observed as shown in Figure 4.4. This result shows that synthesis has dispersed particles size, however, take average particles size. In general, the UV analyzer result indicates that the synthesis of carbon quantum dots (CQDs) using hydrothermal techniques was successful.

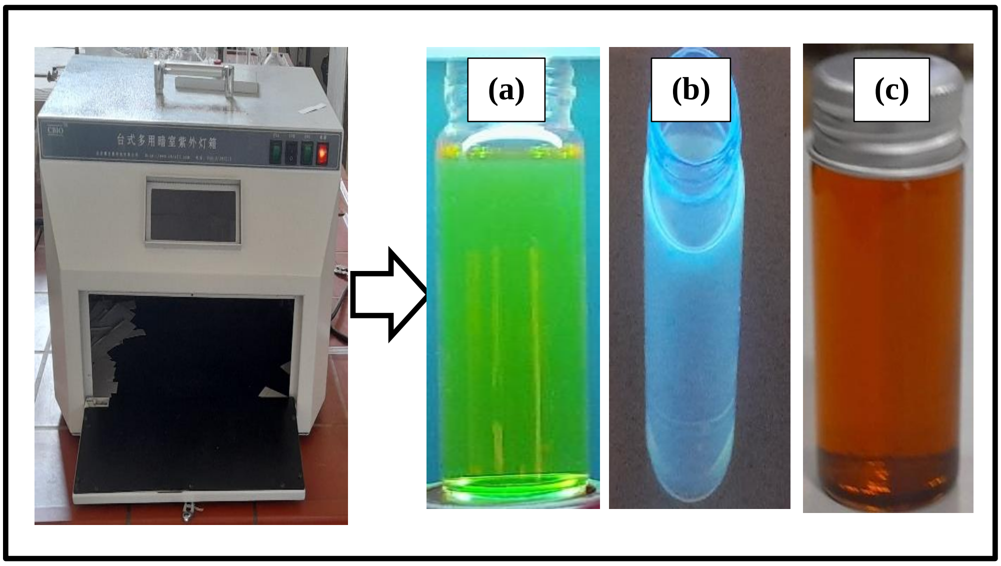


Figure 4. 4: Optical photographs of synthesized fluorescent CQDs under UV analyzer (a). UV light (365 nm) exposure appeared green in color (b). UV light (254 nm) exposure appeared blue color (c). Appeared dark brown under the visible light or absence of UV light.

Table 4. 1: The color of synthesized CQDs obtained under UV lamp analyzer instruments.

S.No	**Excitation wavelength (λ_{ex}) of exposed UV light (nm)**	**Color**
1	254	Blue
2	365	Green
3	Visible light (400-700) or in absense of UV light	Dark brown

The green and blue color luminescence under the UV analyzer light irradiation show that the synthesized solution contained quantum particles. Based on these hints we can further investigate the optical properties of CQDs. The optical properties of synthesized carbon quantum dots (CQDs) were investigated in terms of their absorption and emission properties. Also, their structure properties were observed or investigated under XRD instruments.

In addition, figure 4.5 shows the brown color of synthesized CQDs, diluted CQD with DI, and powder form of CQDs. The diluted one is used in UV analyzer investigation because irradiation light easily interacts with CQDs to obtain the desired result.

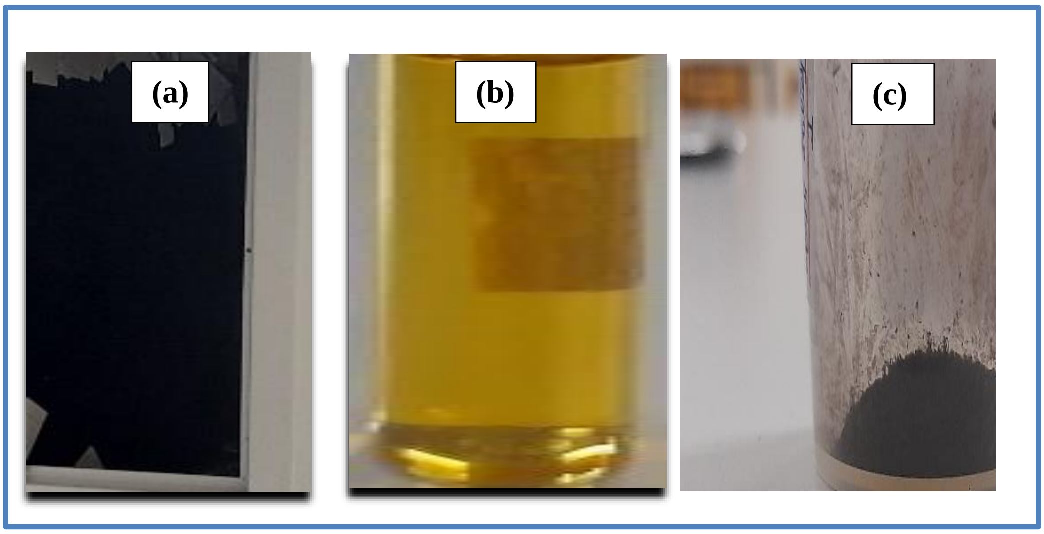


Figure 4.5: (a). Dark brownish solution of synthesized CQDs; (b). CQDs diluted with DI; (c). Powder of CQDs

4.4 Photoluminescence (PL) Analysis

In addition to the absorption properties, fluorescence emission properties of the CQDs were also investigated. Photoluminescence (PL) spectroscopy was performed at different excitation energies ranging from 360 to 520 nm. Large-scale synthesis of colorful photoluminescent carbon quantum dots (CQDs) was obtained from hydrothermal methods which may be cheap, easily operate, and eco-friendly. The formation of carbon quantum dots was confirmed with the help of the UV lamp analyzer as shown in Figure 4.4. This CQDs solution emits a visible range upon exposure to ultraviolet light excitation. Furthermore, their emission also extended up to the infra-red region, when it is excited by visible regions. As stated in the numerous literature there are three kinds of model factors that affect the origin of PL spectra amongst them one is the surface state main luminescence of carbon quantum dots.

Table 4. 2: CQDs synthesized at 160, 180, and 200 ˚C with excitation wavelength between 360 – 520 nm with the corresponding fluorescence emission.

S.No	**160 ˚C**		**180 ˚C**		**200 ˚C**	
	Wavelength (nm)		Wavelength (nm)		Wavelength (nm)	
	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}
1	360	461	360	463	360	456
2	380	466	380	471	380	470

3	400	489	400	482	400	479
4	420	501	420	498	420	496
5	440	515	440	511	440	508
6	460	528	460	518	460	516
7	480	540	480	532	480	532
8	500	548	500	546	500	542
9	520	562	520	558	520	552

The emission spectra of CQDs were obtained at various temperatures for 6 hr were illustrated. Carbon quantum dots (CQDs) synthesized at 160, 180, and 200 ˚C have maximum emissive peaks at 562, 558, and 552 nm respectively at 520 nm excitation wavelength as discussed in detail in Table 4.2. This result confirmed that carbon quantum dots (CQDs) synthesized from lemon juice with green light emission are used for labeling and detection of molybdenum ions (Hoan *et al*., 2018). The PL emission was red-shifted when the hydrothermal temperature decreased owing to many effects such as functional groups that affect the optical properties of carbon quantum dots (CQDs). This indicates the effect of increasing temperature on the particle size of the carbon quantum dots (CQDs).

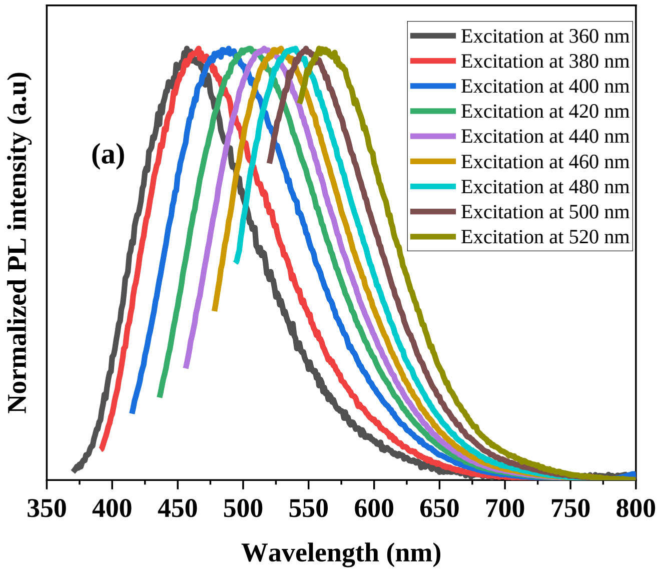


Figure 4.6: (a), Normalized PL emission spectrum of CQDs synthesized at 160 °C with excitation from 360 to 520 nm in 20 nm increment.

CQDs synthesized at 160 ˚C excited at 360, 380, 400, 420, 440, 460, 480, 500, and 520 nm with fluorescence emission peaks 461, 466, 489, 501, 515, 528, 540, 548, and 562 nm respectively. Carbon quantum dots produced at 160 ˚C have an emission spectrum of blue and green extending to the infrared region. This is because when the reaction temperature decreases, the emission spectrum of PL shifts from blue to near-infrared wavelengths. (Jorns and Pappas, 2021) reported that the lower reaction temperature was the reason for the emission spectra of carbon quantum dots were observed to shift from the blue to the red region. This result indicates, it also may be applied to the biomedical applications since their energy lower than CQDs with emission spectra in the blue region.

Similarly, carbon quantum dots (CQDs) synthesized at 180 ˚C excited at 360, 380, 400, 420, 440, 460, 480, 500, and 520 nm with fluorescence emission peaks 463, 471, 482, 498, 511, 518, 532, 546, and 558 nm respectively. This result indicates that the carbon quantum dots synthesized at different temperatures exhibit strong green light emission and can be used for wide applications including medical applications.

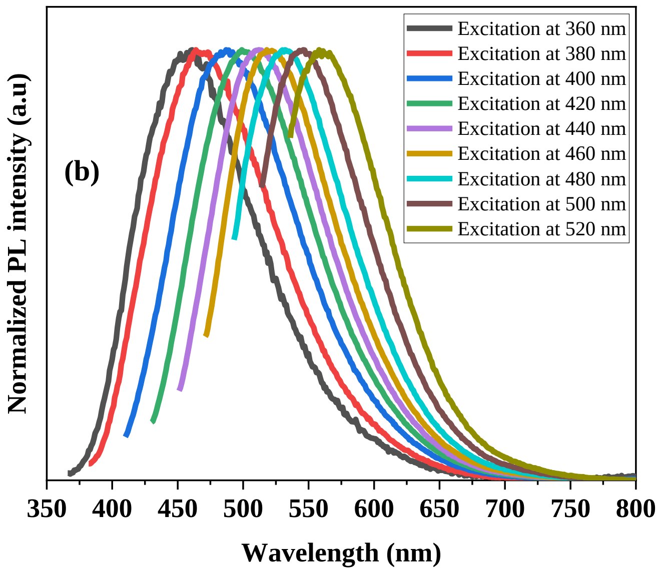


Figure 4.7: (b), Normalized PL emission spectrum of CQDs synthesized at 180 °C with excitation from 360 to 520 nm in 20 nm increment.

On the other hand, CQDs nanomaterials synthesized at 200 ˚C excited at 360, 380, 400, 420, 440, 460, 480, 500, and 520 nm with maximum fluorescence emission peaks 456, 470, 479, 496, 508, 516, 532, 542, and 552 nm respectively. Photoluminescence (PL) properties of CQDs are also signature and the most important property from their application point of view.

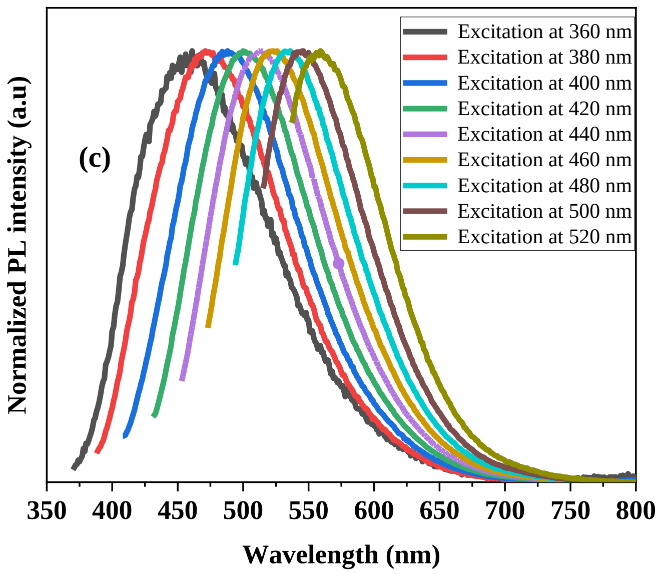


Figure 4. 8: (c) Normalized PL emission spectrum of CQDs synthesized at 200 °C with excitation from 360 to 520 nm in 20 nm increment.

Depending on the hydrothermal temperature, the emission peak is seen in the green region and all these peaks confirm that the produced carbon quantum dots (CQDs) are highly fluorescent and excitation-dependent emission spectra as seen in Figures 4.6, 4.7, and 4.8. Furthermore, the synthesized carbon quantum dot (CQDs) emission spectra range from blue to infrared wavelength spectra. This confirms the theory of PL emission and also result obtained can be utilized even for medical applications since it is in the red region have low energy. As a result of FT-IR indicate the synthesized carbon quantum dots (CQDs) containing functional groups comprise oxygen these oxygen-containing groups are the reason for PL emission shifts from blue to infrared region. The result of synthesized carbon quantum dots (CQDs) indicates that CQDs with different colors are synthesized according to our objective but most of them emit commonly in blue and green regions with tails extended up to the infrared region.

These prepared nanomaterials also confirm theoretical content about excitation-dependence emission spectra of synthesized carbon quantum dots (CQDs) and also have similar emission spectra trends that shift towards higher wavelength as excitation wavelength increases. This result confirms the recent past work on the carbon quantum dots (CQDs) by (Mehta *et al*., 2014), which produced highly fluorescent carbon quantum dots (CQDs) from sugarcane via hydrothermal treatment at 160 °C for 3 hr.

The Stock shift of observed CQDs synthesized at 160 ˚C has longer shifts than the other synthesis at temperatures of 180 and 200 ˚C. This longer shift is due to the effects of the different functional groups attached to CQDs synthesized at 160 ˚C. The least emission spectra also may trend with temperature, size, and functional groups. Although the carbon quantum dots (CQDs) were synthesized under the same hydrothermal conditions, the sizes of the synthesized carbon quantum dots were different. This may be due to the various degradation temperatures of the precursors allowing them to nucleate at different conditions, thus forming different-sized carbon quantum dots nanomaterials. Moreover, this result indicates that the CQDs can also be applied for multiple imaging since they show excitation-dependent emission properties in certain ranges. All these tunable color emissions of carbon quantum dots (CQDs) originate from the oxide-relate surface effects whereas quantum confinement is the responsible mechanism due to the presence of functional groups (Ghamsari *et al*., 2016).

As shown in Figures 4.6, 4.7, and 4.8 they all exhibit emission spectra in the wavelength range of 380 to 750 nm. These results of the PL emission spectrum of carbon quantum dots (CQDs) have been confirmed by previous studies on carbon quantum dots (CQDs) synthesis and their optical properties (Egorova *et al*., 2018).

The quantum efficiency of the CQDs was calculated using Eq. (2.6). It is calculated by comparing the integrated photoluminescence intensities of CQDs (excited at 520 nm) and the absorbance values of the carbon quantum dots (CQDs) with the references methylene blue (MB) and quantum yield (Φ) of the carbon quantum dots (CQDs) sample was determined. The calculated quantum yield (Φ) of synthesized CQDs was summarized in Table 4.3. This result is confirmed and preferred when compared to carbon quantum dots from lemon peel waste for application in sensing and photocatalysis (Tyagi *et al*., 2016).

Table 4. 3: Quantum yield (Φ) of carbon quantum dots (CQDs) at 160, 180, and 200 ˚C.

S.No	**Temperature (˚C)**	**Quantum Yield (Φ)**
1	160 ˚C	24 %
2	180 ˚C	14 %
3	200 ˚C	41 %

Since the CQDs at 160 ˚C has a longer wavelength emission than the CQDs at 200 ˚C, there is a possibility of energy loss, so the quantum yield (QY) at 160 ˚C is lower than that at 200 ˚C.

On the other hand, hydrothermal temperature also affects the PL intensity of carbon quantum dots (CQDs). Moreover, reaction time and excitation wavelength is a factor that greatly influences the PL intensity of the carbon quantum dots (CQDs). For instance, as seen in Figure 4.6, 4.7, and 4.8 as excitation wavelength increase intensity of CQDs is decreased.

As shown in Figure 4.9, when the reaction time of hydrothermal to synthesize carbon quantum dots (CQDs) increases, the PL intensity increases. The carbon quantum dots (CQDs) were synthesized using the hydrothermal method at different reaction times 2, 4, 6, and 8 hr at 160 ˚C fixed temperature. This result confirms related work by (Hoan et al., 2019b). Because in the hydrothermal process, the longer hydrothermal time could lead to more conversion of constituents into carbonization and reason for increase intensity as hydrothermal time increase. In addition, as Figure 4.9 show CQDs synthesized at 8 hrs has more intensity which means quantum yield (Φ) at this reaction time is the maximum.

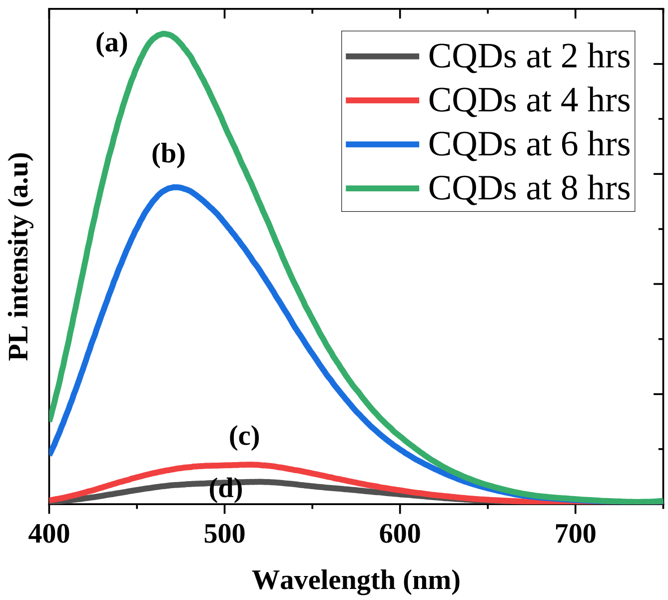


Figure 4. 9: PL emission spectra of CQDs synthesized at 160 °C with different hydrothermal times 2, 4, 6, and 8 hrs.

The other factor that can influence the PL intensity of synthesis carbon quantum dots is the aging of synthesized CQDs. Because many environmental effects such as the collisional effect may affect functional groups. The surface state of synthesized carbon quantum dots (CQDs) is significant that determining the PL emission intensity of carbon quantum dots.

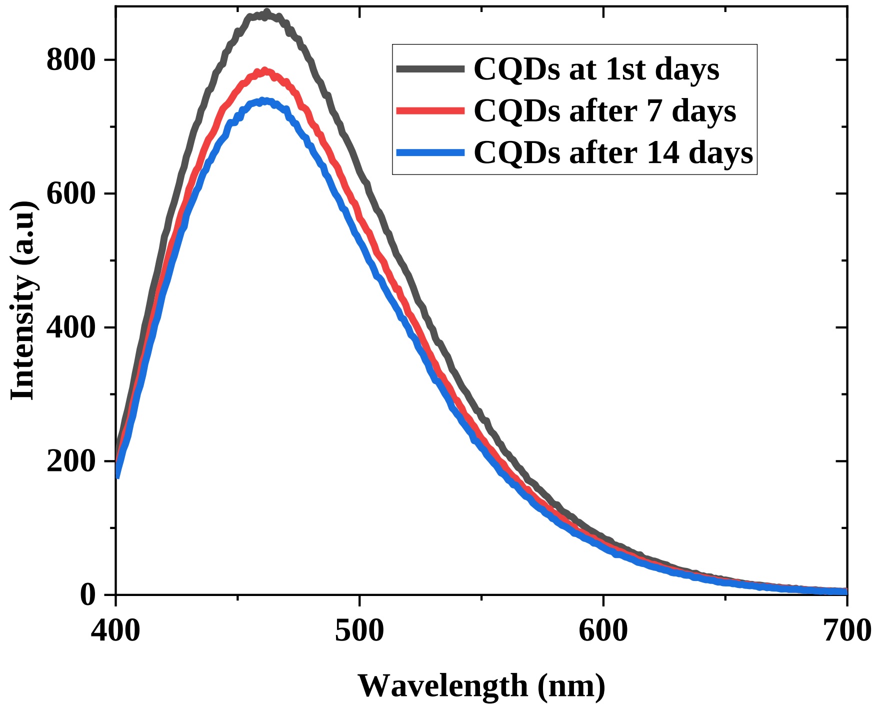


Figure 4. 10: Aging of synthesis carbon quantum dots (CQDs) nanomaterials

As seen in Figure 4.10, the PL intensity of synthesized carbon quantum dots (CQDs) decreases slowly as aging time increases on the 1^{st} day, 7^{th} day, and 14^{th} day after synthesis. As result indicates the intensity of carbon quantum dots does not change in a short time they take several days this shows carbon quantum dots (CQDs) are high photostability as confirmed with zeta potentials. On the other hand, these results exhibit that PL intensity may be affected environmental condition. In general, these results of PL intensity show that there is a different factor that influences the PL intensity of synthesized carbon quantum dots such as time of reaction, aging, and excitation wavelength of carbon quantum dots (CQDs). This is caused by different factors such as different sizes or different surface energy traps of the CQDs.

4.5 Fourier Transform Infra-Red (FT-IR) Analysis

Figures 4.11, 4.12, and 4.13 displays the FT-IR spectra result of carbon quantum dots (CQDs) synthesized by hydrothermal techniques at different temperatures. All the FT-IR spectra of synthesized carbon quantum dots (CQDs) contain functional group C=O stretching vibrations at 1635, 1637.29, and 1637.3 cm^{-1} for 160, 180, and 200 ˚C respectively and these are fundamental properties of carbon quantum dots (CQDs).

Carbon quantum dots synthesized at 160 ˚C exhibit absorption peaks at 3270.23, 2360.48, 1635, and 1228 cm^{-1} corresponding with stretching vibrational of -NH/OH, COOH, C=O, and C-O functional groups respectively as seen in Figure 4.11.

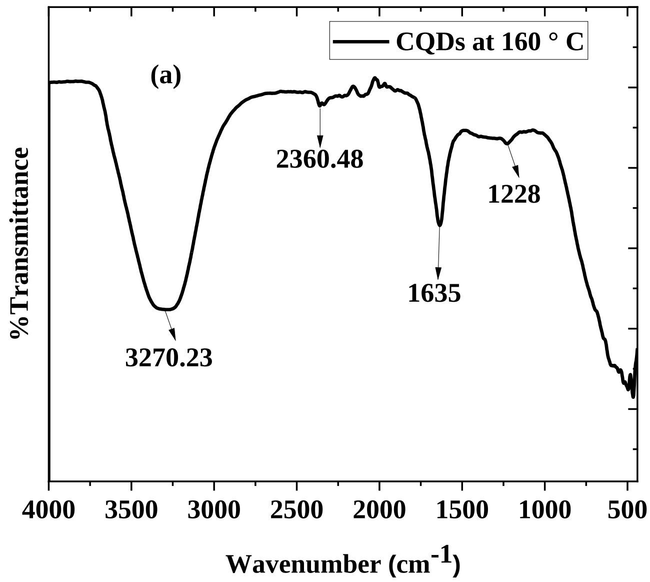


Figure 4.11: (a) FT-IR spectra of CQDs at 160 °C.

Carbon quantum dots synthesized at 180 ˚C exhibit absorption peaks at 3315.08 (-NH/OH), 1637.29 (C=O), and 1222.66 cm^{-1} (C-O) as seen in Figure 4.12.

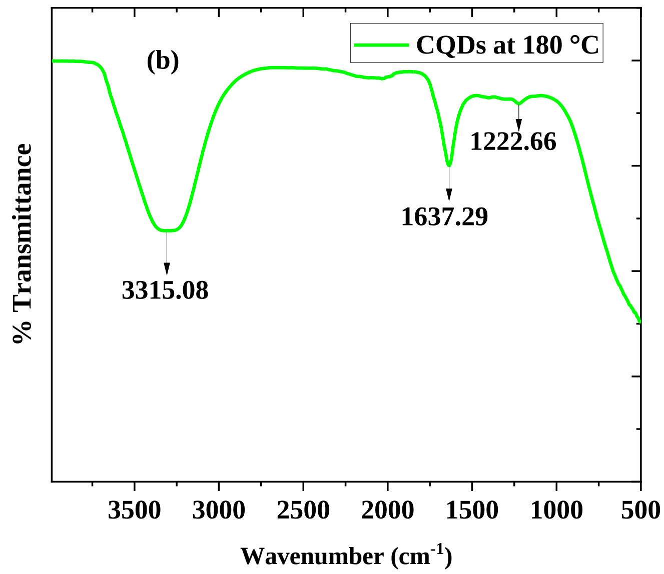


Figure 4. 12: (b) FT-IR spectra of CQDs at 180 °C.

Carbon quantum dots synthesized at 200 °C exhibit absorption peaks at 3282.30 (-NH/OH), and 1637.3 (C=O) cm^{-1} as seen in Figure 4.13.

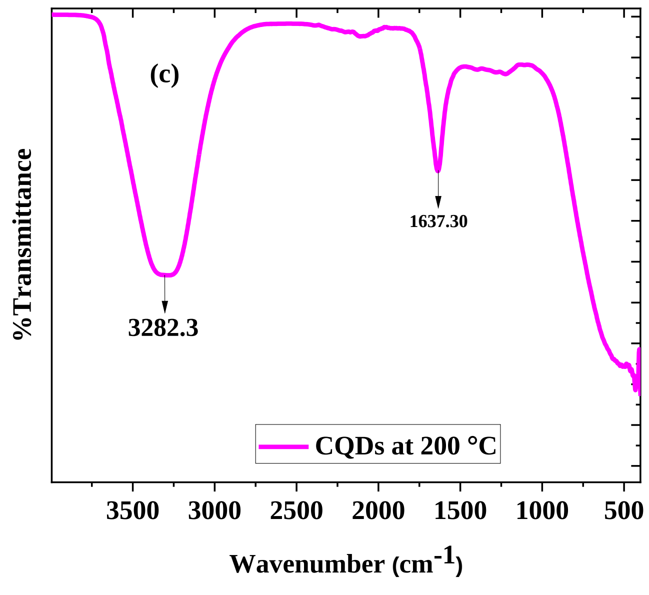


Figure 4. 13: (c) FT-IR spectra of CQDs at 200 °C.

Only a few peaks are there for carbon quantum dots (CQDs) synthesized at 180 and 200 °C these indicate many constituents of lemon juice are converted into carbon quantum dots as the temperature rises. The presence of the different functional groups in the FT-IR spectrum of the carbon quantum dots indicates that the CQDs are functionalized with carbonyl, and carboxylic acid groups as shown in Figures 4.11, 4.12, and 4.13. The water solubility of the synthesized carbon quantum dots (CQDs) was high, owing to the presence of organic functional groups like C=O of oxygen-containing functional groups on the surface of the carbon quantum dots (CQDs). The synthesized carbon quantum dots (CQDs) contained a variety of functional groups (NH, C=O, etc.) and this is the reason for different absorption behavior. All carbon quantum dots (CQDs) synthesized at 160, 180, and 200 ˚C were then characterized by FT-IR and exhibited intense adsorption bands indicative of NH, C=O, and C–O functional groups.

In general, FT-IR analysis exhibit the presence of numerous functional groups on the surface of carbon quantum dots (CQDs) which improves their PL emission, excellent water solubility, and room for further functionalization. So, carbon quantum dots (CQDs) synthesized via hydrothermal methods under different temperatures reveal functionalities on their surface, as supported by FT-IR as shown in Figures 4.11, 4.12, and 4.13. These results align with the hydrothermal process of synthesizing carbon quantum dots from tapioca (Pudza et al., 2020). The functional groups here identified are responsible for the water-soluble carbon quantum dots (CQDs), as a result, help in the effective adsorption of methylene blue (MB) dyes from an aqueous environment. These surface functional groups impart some degree of hydrophilicity to the composite and act as anchor sites for methylene blue (MB) dye molecules.

4.6 Zeta Potential

The zeta potential investigation was carried out using the zetasizer Nano series (Malvern) (Zetasizer Ver.8.02, MAL 1149420) to determine charges carriers on the surface of carbon quantum dots and the photostability of fluorescent carbon quantum dots (CQDs) nanomaterials, which is beneficial for many biomedical and adsorption applications. In this regard, CQDs are investigated by zeta potential as seen in Figure 4.14. The carbon quantum dots (CQDs) show a positive charge due to the presence of a large density of amine groups as a result of FT-IR shown in Figures 4.11, 4.12, and 4.13. The obtained zeta potential result shows that the carbon quantum dots are ~1.55 mV, which suggests relatively good dot stability.

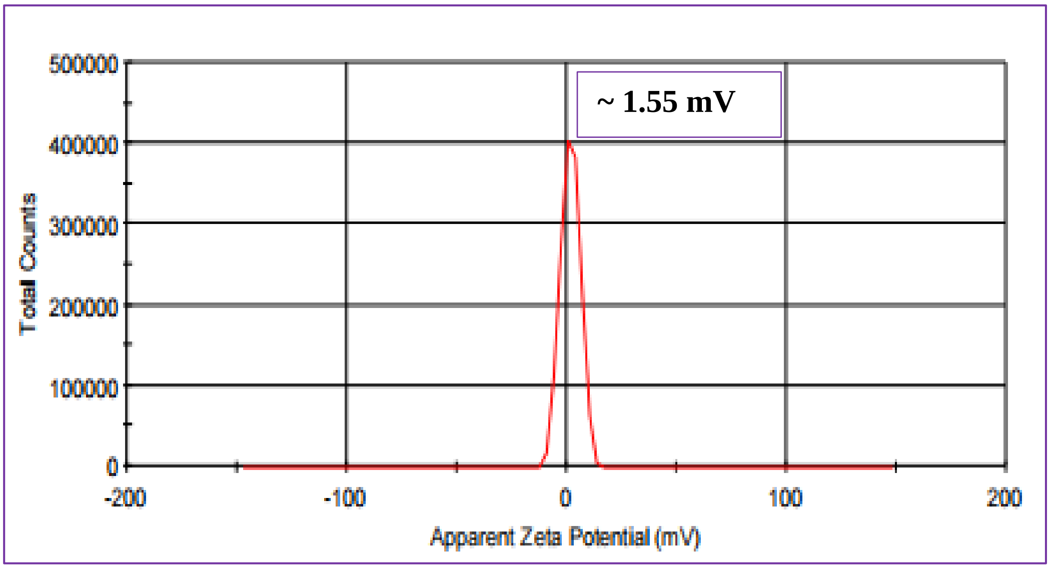


Figure 4.14: Zeta potential graph of CQDs synthesized at 160 ˚C.

4.7 Adsorption Removal of Methylene Blue (MB) Dye by Using Synthesized Carbon Quantum Dots (CQDs)

The standard curve was plotted by measuring the methylene blue (MB) dye solution with a series of concentration gradients as contact time increased as shown in Figure 4.15 and Table 4.4. After the adsorption experiment, the concentration of methylene blue (MB) left in the supernatant solution was determined by a UV-Vis spectroscopy (PG Instruments Ltd, T80+ UV/VIS Spectrometer) at 665 nm. These results can be due to the large surface area, the high water solubility of CQDs, excellent physicochemical properties, and the presence of negatively charged nitrogen elements, the carboxylic acid (COOH), and other oxygen-containing functional groups on the surface of CQDs that serves as active sites for the adsorption of MB dyes. On the other hand, electrostatic interactions, ionic exchange, and hydrogen bonding may occur between CQDs adsorbent and adsorbate (MB) dyes.

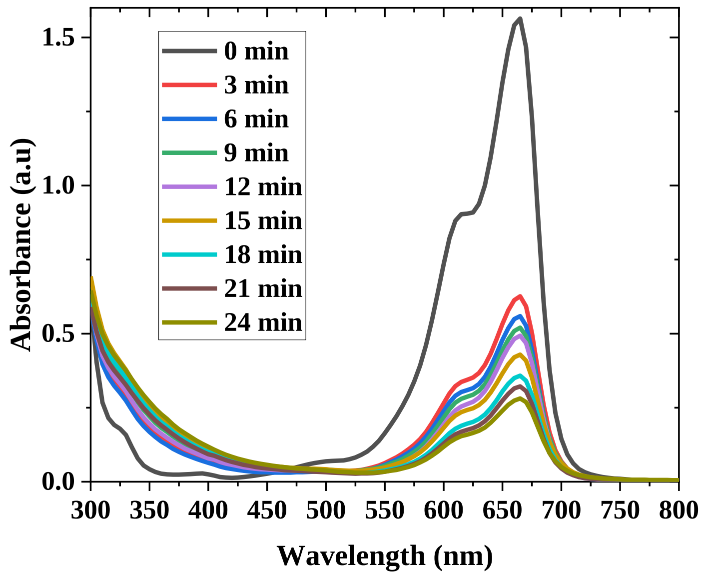


Figure 4.15: A plot of absorbance (a.u) versus wavelength (nm) adsorption of methylene blue (MB) dyes using CQDs with different time intervals.

Table 4. 4: CQDs for adsorption applications contact time (min) versus absorbance (a.u).

Time (min)	**Absorbance (a.u)**
0	1.564
3	0.626
6	0.559
9	0.520
12	0.493
15	0.429
18	0.358
21	0.322
24	0.281

Methylene blue (MB) dye removal efficiency (R %) was calculated using Eq. (2.7) as seen in Figure 4.16 and Table 4.5. Due to the large surface area and contact time of carbon quantum dots (CQDs), the surface adsorption capacity of the CQDs was studied by removing methylene blue (MB) dyes in wastewater aqueous. The results show that the product has a high surface activity capable of adsorbing these methylene blue (MB) dyes on the surface of its particles. As Figure 4.16 and Table 4.5 shows, the carbon quantum dots (CQDs) can adsorb 60, 64, 67, 68, 72, 77, 79, and 82 % at 3, 6, 9, 12, 15, 18, 21, and 24 min respectively in wastewater. The contact time (min) for optimum adsorption was 24 min with a removal efficiency (R %) of 82 % as shown in Table 4.5.

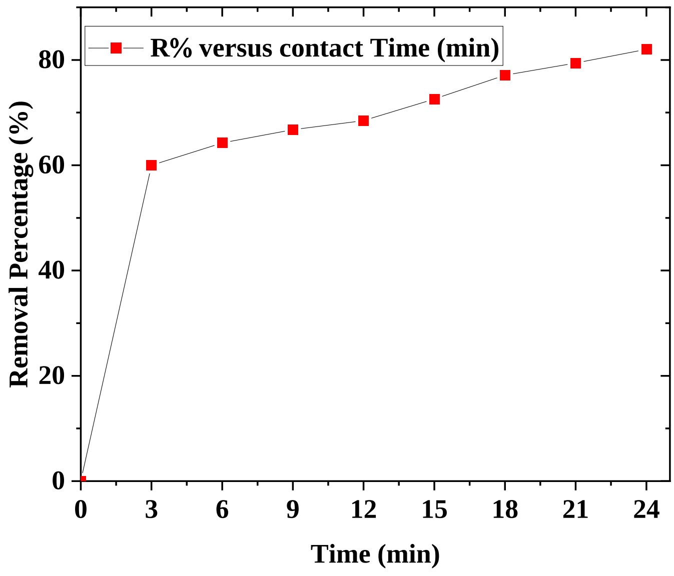


Figure 4.16: Effect of contact time (min) on the removal efficiency (R %) of methylene blue (MB) dye using CQDs.

These results exhibit a longer contact time, the lower the final concentration of the methylene blue (MB) dye, the greatest the percentage of removal as shown in Table 4.5. The rapid uptake of adsorbate (MB) and the fast establishment of equilibrium indicates the efficiency of the adsorbent for use in wastewater treatment. As seen in Figure 4.16, the efficiency of methylene blue (MB) dye removal increased dramatically during the initial adsorption stage within the contact time of 3 minutes. Because this attributes that there are more adsorption sites at the initial contact time (min).

Table 4. 5: Shows the contact time and percentage removal of methylene blue (MB) dyes.

Time (min)	**Removal percentage (R %)**
3	60
6	64
9	67
12	68
15	72
18	77

21	79
24	82

The equilibrium adsorption capacity q_e (mg/g) was calculated using Eq. (2.8) result is seen in Figure 4.17 and Table 4.6.

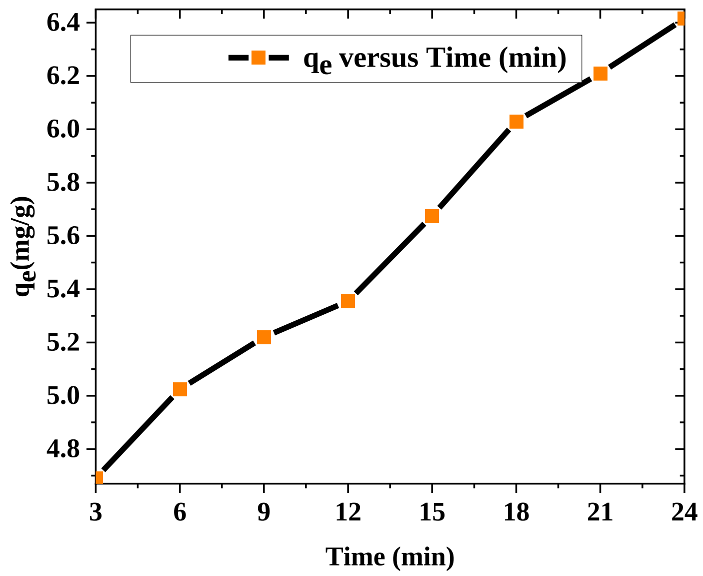


Figure 4.17: A plot shows an equilibrium adsorption capacity qe (mg/g) versus contact time (min).

Table 4. 6: Shows values of time (min) and adsorption capacity (mg/g) of CQDs.

Time (min)	**Adsorption capacity q_e (mg/g)**
3	4.69
6	5.03
9	5.22
12	5.36
15	5.68
18	6.03
21	6.21
24	6.42

Now focus on calculating the kinetic rate of adsorption of methylene blue (MB) dye using carbon quantum dots (CQDs). From the kinetic point of view, we have to calculate the rate constant of the removal reaction. Usually, an adsorption removal reaction is considered a pseudo-first-order kinetic reaction. So, we calculate the rate constant and the wavelength maximum of methylene blue (MB) dye was 665 nm. During the calculation of the rate constant, we compute also the slope.

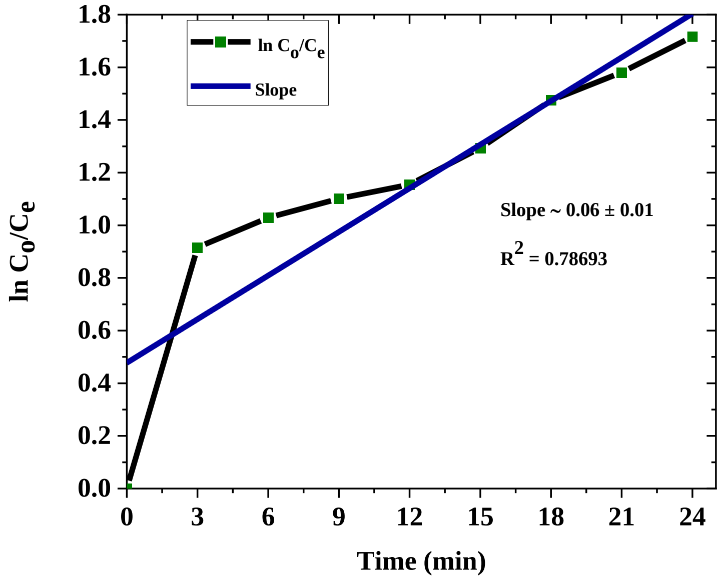


Figure 4.18: The rate of adsorption removal of methylene blue (MB) catalyzed by CQDs (20 mg/100 mL).

A result of Figure 4.18 indicates that the rate constant for adsorption of methylene blue pollutant using carbon quantum dots (CQDs) is 6 $x10^{-2}$ min^{-1} in this work.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, carbon quantum dots (CQDs) were synthesized via simple hydrothermal techniques in an autoclave from lemon juice under different temperatures and times. As the excitation wavelength increases the peak position of the emission peak shifts to the longer wavelength region for all temperatures. This emission shift towards long-wavelength can be owing to the presence of different functional groups or emission traps on the surface of carbon quantum dots (CQDs), and solvents.

The obtained quantum yield (Φ) results are within the range of values found in many previously published literature. And lemon juice is the potential competitor precursor for the synthesis of carbon quantum dots (CQDs). XRD results reveal the amorphous nature of prepared carbon quantum dots (CQDs). Carbon quantum dots (CQDs) show abundant functional groups as confirmed by FT-IR spectra techniques which improve their PL emission, excellent water solubility, and easy functionalization. Carbon quantum dots (CQDs) capacity for adsorption of methylene blue (MB) dye was confirmed with high efficiency of 82 %. The synthesized carbon quantum dots (CQDs) are excellent fluorescent materials proposed for various applications in the environmental area of drink water pollution treatment and also medical applications. In general, because of the unique optical properties of synthesized CQDs, they could be helpful in resolving critical drinking water problems world facing due to toxic dyes.

5.2 Recommendations

CQDs are extremely interesting high PL novel carbon-based materials and as well as prospective building blocks for future nanomaterials. However, there is a sense of urgency in developing better synthetic routes and conducting more extensive fundamental research on their properties as there is a lot of opportunity for improvement. Because of their ability to serve as benign substitutes for traditional heavy-metal-based quantum dots (QDs), CQDs have the potential positive impact on both health and environmental applications. Obtaining powder of CQDs is being challenged. However, to optimize the removal efficiency of methylene blue (MB) dyes the greater the mass of absorbent is needed since the greater the surface area of adsorption sites are available. So, to obtain this huge amount of powder mass of CQDs using a lemon carbon source for synthesizing is our suggestion. Because lemon precursors of carbon-based are economical and easily available.

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