FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 8 No. 1, February, 2024, pp 93 - 102
DOI: https://doi.org/10.33003/fjs-2024-0801-2208

CARBON QUANTUM DOTS FOR WASTEWATER TREATMENT: PRESENT PROGRESS AND FUTURE PROSPECTS

***[1]Agbogo, U. V., [2]Rifore, B. S., [2]Arum, C. T., [2]Iorver, P. D., [2]Mathew, J., [2]Tanko, S. A.**

[1]Nigerian Army University, Department of Chemistry, Biu
[2]Nigerian Defense Academy, Department of Chemistry, Kaduna

*Corresponding authors' email: rifore.belief@gmail.com

ABSTRACT

Wastewater has continued to pose environmental pollution as various industrial and domestic processes effluents are released daily. As man's activities increase daily, the possibility of facing water scarcity is imminent, coupled with the climate impacts of wastewater on aquatic lives, soil microorganisms, and agricultural produce. Therefore, several innovative developments have considered using carbon-based nanomaterials like carbon quantum dots (CQDs) to treat and recycle wastewater before they are discharged. These CQDs, just like activated carbon, possess adsorptive abilities that can remove heavy metals, solid pollutants, and foul odors from wastewater. However, they are more unique and effective than the traditional adsorbents because they display quantum effects, fluorescence, high stability, tough compatibility, water solubility, little toxicity, easy to produce, and affordable. This review discusses the nature of CQDs, their chemistries, adsorption abilities, limitations, and recommendations for future application and innovation for economical uses.

Keywords: Carbon Quantum Dots, Adsorption, Fluorescence, Wastewater, Nanomaterials

INTRODUCTION

Carbon quantum dots (CDQs) are nanomaterials with a high tendency to spearhead massive development in nanotechnology. They have led to groundbreaking innovations and developments in solving environmental problems caused by the discharge of wastewater into the soil and water bodies. Moungi G. Bawendi, Louis E. Brus and Aleksey Yekimov were bestowed the Nobel Prize in Chemistry 2023 for the innovation and synthesis of quantum dots. CQDs are recent thrilling carbon-based nanoparticles that are beginning to have varied applications in fields like biomedicine, engineering, agriculture and health. They possess exceptional features like large surface area and fluorescence that allows them to be impeccable materials for the adsorption and treatment of wastewater in industries (Papaioannou et al., 2018).

According to Joshi et al. (2018), CQDs are fluorescent nanomaterials because they possess potent quantum confinement influence and extremely adjustable photo optoelectronic and luminescent characteristics. To display the quantum confinement effects, the oxygenated functional groups on the surfaces of CQDs have changed the particle sizes and surface configurations of CQDs. In addition, CQD reservoir characteristics and electron transfers may be used to isolate photo-generated electrons (Liang et al., 2018). Since they have high steadiness, tough biocompatibility, little toxicity, high water solubility, cheap manufacturing cost, and unique photo-stability (Das et al., 2018), they offer remarkable potential in wastewater treatment (Lim et al., 2018). Based on their optical stability qualities and quantum confinement effect, CQDs exhibit robustness, chemical inertness, moderate photoluminescent signal, and strong fluorescence (Shi et al., 2019; Saud et al., 2015).

According to Fig. 1, CQDs would become bright blue fluorescent when subjected to UV light irradiation. Certain CQDs electrons can be stimulated into greater energy states when their surfaces are exposed to UV light. Rajabi et al. (2013) state that a photon is released as a luminous blue when electrons come back to their ground state. The tiny particle sizes of CQDs could be to blame for this phenomenon. However, the reflective qualities of the carbon originators utilized as the starting material also impact the fluorescent qualities of CQDs. According to Gyulai et al. (2019), many carbon precursors may be used to create photo-luminescent CQDs. A variety of raw materials with a high concentration of carbon precursors, including citric acid, sugars, and carbohydrates, have been utilized in the past to create CQDs because of their intricate organic structures (Papaioannou et al., 2018; Dong et al., 2012). Because of their band gaps, which perfectly match the irradiation light spectrum and render them active when exposed to UV light, CQDs may thus be used as effective photo-catalysts.

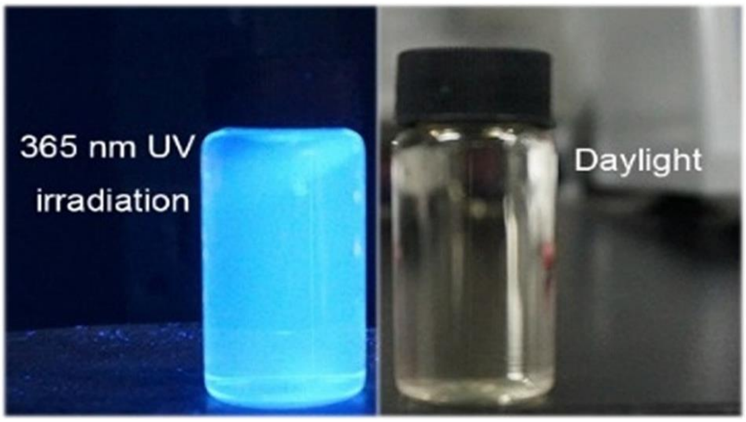

Figure 1: CQDs solution exposed to UV-light irradiation and daylight (Reproduced with permission from (Shi et al., 2019) copyright 2019, Elsevier).

This review aims to report the recent findings accompanying the use of CQDs for treating wastewater, and their adsorption mechanism. Future insights have been made based on the identification of research gaps from the literature and other possible exciting opportunities in the utilization of CQDs for wastewate treatment.

Configuration of CQDs

Tang et al. (2012) found that CQDs had core-shell structures that may be both amorphous (a mixture of sp^2 and sp^3 carbon) or graphitic crystalline (made chiefly of sp^2 carbon) depending on the amount of sp^2 carbon present in the core. Multiple studies by (Hola et al., 2014; Sciortino et al., 2016; Dager et al., 2019) have documented graphitic crystalline (sp2) cores. The cores are very tiny, ranging from 2 to 3 nanometers, and their lattice spacing is around 0.2 nanometers, as reported by Zhang et al. (2015)..

The cores are classified based on the production process, the precursors utilized, and other synthetic factors such as temperature, time, pH, etc. (Martindale et al., 2017). Typically, a graphitization (sp2) structure formation occurs at reaction temperatures over 300 ◦C. However, unstructured cores are formed at lesser temperatures unless sp2/sp3-hybridized carbon is existent in the initial substance (Tingting et al., 2018).

To ascertain the fundamental arrangement of CQDs, diverse analytical methods, including Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) or High Resolution (HR) TEM, and Raman spectroscopy are used. To define the dimensions and structure of the CQDs, SEM or TEM analysis is conducted (Haitao et al., 2012). The SAED patterns indicate whether the CQDs are amorphous or crystalline (Zheng et al., 2015). The XRD pattern is used to ascertain the crystal arrangement of CQDs. The presence of a broad peak at 2θ 23◦ suggests that the CQD is amorphous, whereas the appearance of two broad peaks at 2θ 25◦ and 44◦ implies a low-graphitic carbon structure similar to the diffraction patterns of (002) and (100) planes (Hou et al., 2015). The identification of the overall arrangement and various functional groups on the surface of CQDs is accomplished through the utilization of XPS, FT-IR spectroscopy, Elemental analysis (EA), and nuclear magnetic resonance (NMR) techniques (Semeniuk et al., 2019; Bomben et al., 2019). The surface area of the carbon nanoparticles is determined using nitrogen sorption analysis (Semeniuk et al., 2019). To determine the optical features and qualitative data related to the existence of C=C and C=O in CQDs, researchers conducted UV-Vis absorption spectroscopy (Zhou et al., 2017). To ascertain the polarity of the surface charge on CQDs and the magnitude of the electrostatic interface amid them, the zeta potential is measured (Kolanowska et al., 2022; Qiang et al., 2022).

Figure 2 depicts the standard arrangement of CQDs, illustrating several functional groups (such as CHO, CO, OH, COOH, NH_2, etc.) on the surface of CQDs. The identification of these functional groups was verified using analytical methods such as FTIR and XPS (Gayen et al., 2019).

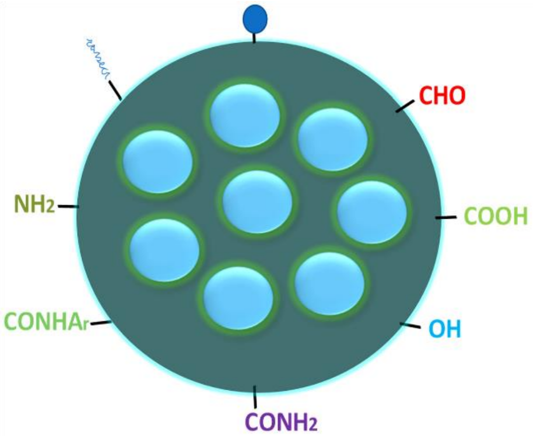

Figure 2: Characteristic configuration of CQDs with diverse functional groups on the surface (Yadav et al., 2023)

Synthesis of CQD

Since their discovery, various efficient methods for producing CQDs have developed. These methods are easy and affordable, allow size control, and enable large-scale manufacturing. The production of CQDs involves using two main approaches: top-down and bottom-up (Figure 3). CQDs may be generated using either the bottom-up or the top-down technique. The bottom-up approach is superior due to its ecological sustainability and economic feasibility, while it exhibits limited precision in regulating the size of CQDs. Conversely, the top-down approaches are costly. Biological and chemical precursors are utilized in the production of CQDs and they have impressive optical characteristics and demonstrate exceptional water solubility, little toxicity, compatibility with biological systems, and environmentally pleasant qualities (Yadav et al., 2023).

While the synthesis of CQDs is relatively easy, specific difficulties associated with their production include the tendency of nanomaterials to aggregate, the need to adjust surface qualities, and the control of size and homogeneity (Kaur et al., 2022). In order to boost the performance of CQDs, post-treatment may be carried out using one of the two techniques to modify the functional groups existing on the surface. The quantum yields (QYs) of CQDs may be increased by surface passivation, which removes the emissive traps on the surface. For example, Wang and Wu (2014) reported that cadmium quantum dots (CQDs) that have been doped with heteroatoms, namely nitrogen (N) and phosphorus (P), or metals like gold (Au) or magnesium (Mg). They exhibit enhanced electrical conductivity and solubility. The production of CQDs has used both the top-down and bottom-up methodologies. However, the bottom-up, environmentally friendly and cost-effective strategy is the most often utilized method (Sofia et al., 2016).

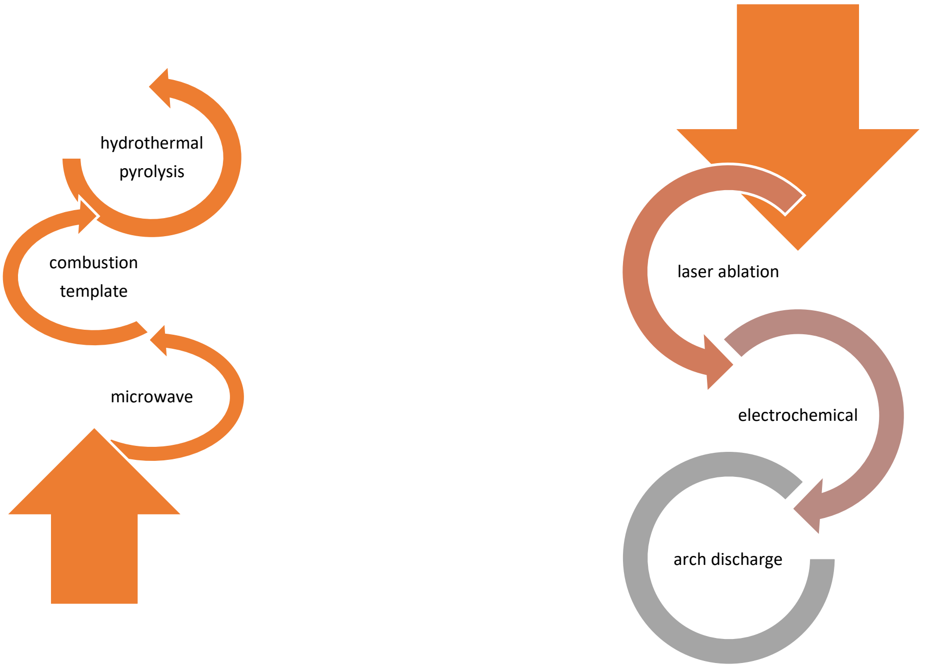

Figure 3: Typical methods for the synthesis of CQDs

Top-Down Approach

The more considerable carbon materials, such as fullerene, carbon nanotubes, graphene, carbon soot, graphite, activated carbon, etc., are fragmented into reduced components using various techniques, including laser ablation, electrochemical methods, and arch discharge in a top-down method (Chae et al., 2017; Liu et al., 2020; Li et al., 2018; Zhao et al., 2019). Carbon structures exhibiting sp2 hybridization and lacking adequate energy or band gaps are often used as initial materials for top-down processes. While the top-down approach is beneficial and appropriate for microsystem industries, it has certain limits. For instance, obtaining pure nanomaterials directly from the significant carbon precursor is impossible. The purification process is expensive and needs to allow accurate control over CQDs' morphology and size distribution (Yuan et al., 2022).

Bottom-Up Approach

The bottom-up strategy involves the combination of tinnier carbon materials, such as polymers, amino acids, carbohydrates, proteins, and waste materials, to generate CQDs using various procedures such as hydrothermal/solvothermal, combustion, microwave irradiation, and pyrolysis. The structure and dimension of CQDs in this approach are influenced by many parameters, including the solvent, precursor molecule structures, and reaction environments (such as pressure, temperature, and reaction time). The reaction environments are essential as they impact both the reactants and CQDs' very spontaneous nucleation and evolution technique. This technique enhances the material chemistry due to its simplicity of operation, reduced cost, and greater feasibility for large-scale manufacturing (Wang et al., 2015).

The precursor used for synthesizing CQDs can be chemical and biological (figure 4). The chemical precursors consist of sucrose, glucose, citric acid, ascorbic acid, lactic acid, glycerol, ethylene glycol, and others (Inderbir et al., 2018; Qu et al., 2018; Kaixin et al., 2022; Henriquez et al., 2022; Nammahachak et al., 2022; Jamila et al., 2021; Qiu et al., 2021). The natural sources of materials include seeds from *Artocarpous lakoocha*, rice husks, leaves from *Azadirachta indica*, peel from pomelo, latex from *Ficus benghalensis*, and *aloe vera*. These sources have been studied by many researchers (Inderbir et al., 2018; Qu et al., 2018; Kaixin et al., 2022; Henriquez et al., 2022; Nammahachak et al., 2022; Jamila et al., 2021).

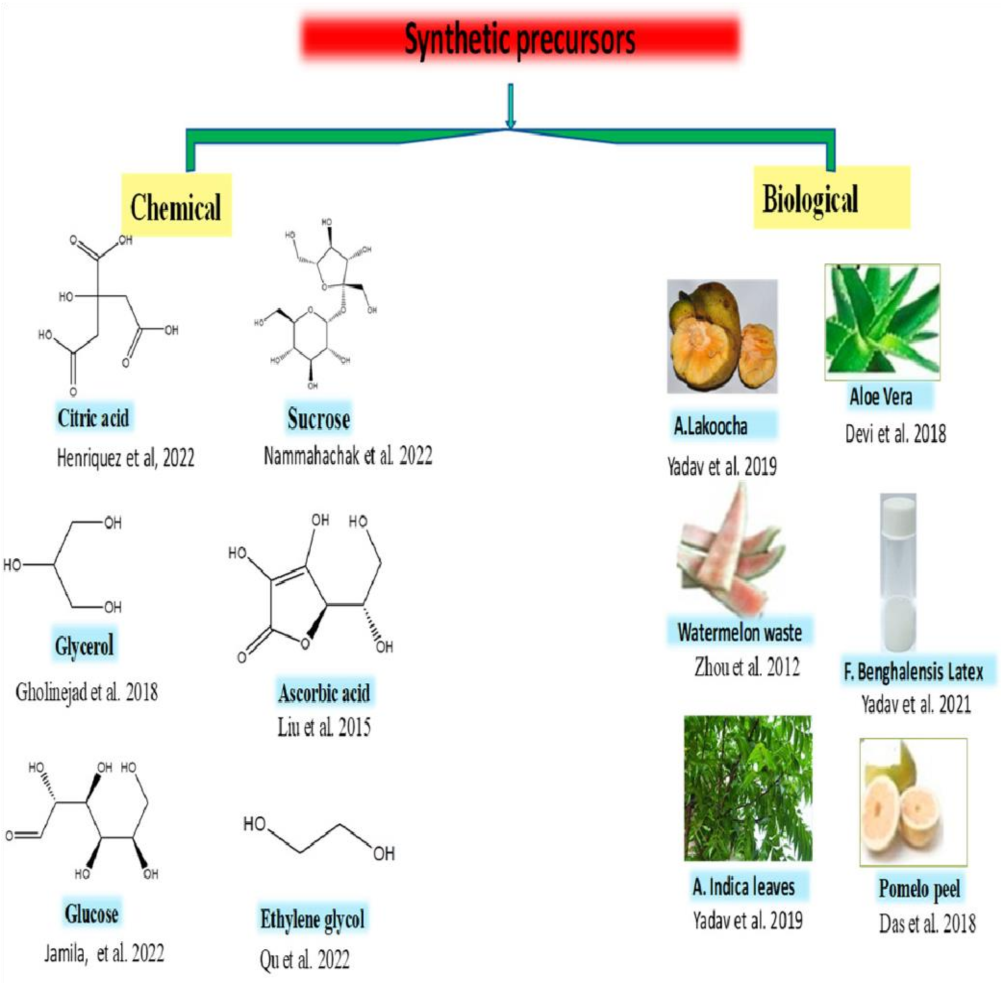

Figure 4 : Chemical and biological precursors employed for the production of CQDs (Wang et al., 2015; Inderbir et al., 2018; Qu et al., 2018; Kaixin et al., 2022; Henriquez et al., 2022; Nammahachak et al., 2022; Jamila et al., 2021; Qiu et al., 2021; El-Broslv et al., 2022; Yao et al., 2022)

Application of CQDs in Wastewater Treatment

Numerous studies have studied the treatment of wastewater using CQDs. Tohamy et al. (2023) used a microwave heating method and startup materials comprising of urea with bagasse (SCB), carboxymethyl cellulose (CMC), or cellulose (C), to create CQDs in a cost-effective, environmentally friendly, and one-step process. The produced CQDs were categorized by a range of spectroscopic methods; they included their small size, strong ultraviolet absorption, and excitation wavelength-dependent fluorescence. For the adsorption of Pb (II) from an aqueous solution, the produced CQDs were employed. The percentages of removal efficiency (R %) for QCMC, QC, and QSCB were 99.16, 96.36, and 98.48%, in that order. The results confirmed that the CQDs made from cellulose, SCB, and CMC were effective and would make great materials for use in the environmental domains of chemical sensing, adsorption, and wastewater pollution detection. All CQD isotherms were found to fit the Langmuir model better than the Freundlich and Temkin models based on the kinetics and isotherms tested. R2 indicates that the first-order fit fits with QC and QSCB, but the pseudo-second-order fits the adsorption of QCMC.

Carbon dots CDs were created by Jlassi et al. (2020) by hydrothermal action in the company of ammonia from petroleum coke waste. This led to the development of exceptional monodispersed sub-5 nm CDs that are water soluble, photoluminescent, biocompatible, and have a high yield. The CDs have 0.2% S and a high 10% N doping. The prepared CDs are a unique and effective pH sensor since they exhibit previously unheard-of photoluminescent qualities throughout a wide pH range. To remove Cd^{2+} metal from wastewater, chitosan (CH)–CDs mix hydrogel nanocomposite film was additionally developed as a platform membrane. Based on their flexibility and ability to withstand stress, the as-prepared CH–CDs membranes have comparatively decent mechanical qualities that make handling easier. In five minutes, the equilibrium state was attained. Interestingly, the photoluminescent CDs' Cd^{2+} removal efficiency was significantly increased by 4× faster under the UV light illuminations. It was discovered that pseudo-second-order kinetic and Langmuir isotherm models were followed by adsorption. It was discovered that at pH 8, the maximal adsorption capacity at 25 °C was 112.4 mg g^{-1}. This exploration opens up new uses for CDs in the water treatment industry.

In research by Sabet and Mahdav (2018) nitrogen-doped CQDs (N-CQD) from grass were developed using the hydrothermal method and used to eliminate organic and inorganic water pollutants. N-CQD was discovered to be very vigorous in both surface adsorption and photocatalytic reaction and can be utilized to eliminate both organic and heavy metal pollutants from wastewater. The results obtained for surface adsorption indicated that N-CQD has an extraordinary surface activity that can adsorb 37% Cd^{2+} and

75% Pb^{2+} on its particle surfaces. Also, the Photocatalytic activity of N-CQD was examined by degradation of six different dyes and the results revealed N-CQD is vigorous both under visible and ultraviolet radiation showing great photocatalytic action of the product.

Preethi et al. (2022) synthesized fluorescent CQD using muskmelon peel as a starting material for the catalytic breakdown of rhodamine B upon exposure to sunlight and ultrasonication. The outcomes proved that the breakdown effectiveness of CQD on Rhodamine B is 99.11% under sunlight with a degradation rate constant of $0.06943\ min^{-1}$ and 83.04% under ultrasonication.

Nizam et al. (2023) assessed CQDs made from rubber seed shells in another investigation. FTIR, XRD, photoluminescence spectroscopy, zeta potential analysis, field emission scanning electron microscopy (FESEM) outfitted with energy-dispersive X-ray spectroscopy (EDX), and RS were utilized to characterize the QDs. Multi-layered planes with extremely porous and irregular surfaces that included numerous oxygen-functional groups (OH, COOH, and CO) were revealed by the morphological examination. The plotting results revealed a broad, homogeneous distribution of oxygen and carbon on the surface of QDs, with carbon making up a higher percentage of weight (72.4%) than oxygen (23.6%). The production of superior CQD exhibiting blue-greenish fluorescence emissions was validated by spectroscopic and photoluminescence investigations. These findings have demonstrated biomass-based QDs that, because of their special qualities, offer promise for use in wastewater treatment. As a result, it is possible to see the produced biomass-based QDs as a viable and affordable adsorbent for the treatment of wastewater.

To achieve sensitive and focused sulfide and ferric ion detection, Zheng et al. (2021) produced nitrogen/sulfur codoped CQD (N, S-CQDs). At a revealing limit of about 0.35 μg/L, the blue fluorescent N, S-CQDs were created through the hydrothermal process using ammonium citrate and L-cysteine as raw materials. They have a 16.1% fluorescence quantum yield and an excitation wavelength dependence for the careful discovery of sulfides. Selective ferric ion detection with a detection limit of 14.0 nM (~0.8 μg/L) was achieved using CQDs that had no excitation requirement and much better fluorescence quantum yields (69%) when citric acid was employed in place of ammonium citrate. The fluorescence change in color of dual-emission sensing can be employed for semiquantitative and visual identification of phosphate, and the approach has been efficiently used for finding total phosphorus in human urine and surface water.

Mashkani et al. (2017) researched preconcentration and removal of lead ions in vegetable and water samples using N-doped CQD modified with Fe_3O_4 as a green and surface adsorbent. The prepared product was used for detecting Pb^{2+} in different environmental water samples. The dependability and accuracy of the technique was examined using different quantities of the metal ions to spike the samples at optimal settings. The retrieval of spiked samples was adequately sensible.

A comparative analysis of composite photocatalysts based on CQDs for water purification was conducted by Hassan et al. in 2022. Recent discoveries involving CQDs and TiO_2 have shown to be very advantageous since they offer methyl orange (MO) dye photocatalytic degradation in an environmentally benign manner. TiO_2 and CQDS were made using the hydrothermal technique. Using TEM, the size range and shape involved in the adsorption process of CQDs and CQDS/TiO_2 were extensively determined. With a size of 5 nm, the artificial CQDs and CQDs/TiO_2 morphology was tiny and semi-spherical. The photocatalytic activity result showed that, when pure CQDs or CQDs/TiO_2 composites were present, photocatalytic degradation of MO occurred, with a reduction in concentration with time. The higher photocatalytic activity was shown by CQDs/TiO2, indicating that both materials contributed significantly to the high photocatalytic activity under visible light irradiation.

Another study by Nizam et al. (2023) examined the photocatalytic degradation capacity of CQDs obtained from rubber seed shells as an adsorbent for batch adsorption of dyes, specifically methylene blue (MB) and congo red (CR). Batch adsorption tests were used to evaluate the qualities, performance, behavior, and photoluminescence characteristics of CQDs. The experiments were conducted under specific operating factors, such as pH, temperature, and dose. The morphological study demonstrated the high porosity, homogeneity, close alignment, and multilayer structure of CQDs. The importance of the oxygenated functional groups was demonstrated by the existence of hydroxyl, carboxyl, and carbonyl functional groups. The photoluminescent property of CQDs was confirmed by spectral analysis, as they demonstrated greenish-blue fluorescence under UV radiation and a high excitation intensity. For both CR and MB dyes, the clearance percentage of the dyes adsorbed was 77% and 75%, respectively. The adsorption results were well-fitted by pseudo-second-order models and the Langmuir isotherm. The adsorption process was exothermic, spontaneous, and had good stability and reusability, according to a thermodynamics study. Under solar radiation, CQDs' degradation effectiveness on both dyes exceeded 90% and followed the first-order kinetic model. These findings showed that CQDs are a superb photocatalyst and adsorbents for the breakdown of organic dyes.

Koulivanda et al. (2019) conducted research on the development of carbon dot-modified polyethersulfone membranes for improvement of permeation, nanofiltration, and antifouling performance. The results obtained indicated introducing the Carbon dots into polyethersulfone membranes is an exceptional membrane modifier for wastewater treatment applications.

Wang et al. (2018) carried out research to back up CQDs on NH2-MIL-125 for a superior photocatalytic breakdown of organic contaminants under broad spectrum irradiation. The NH2-MIL-125 supported CQDs (CQDs/NH2-MIL-125) exhibited meaningfully improved photocatalytic action equated to NH2-MIL-125 for Rhodamine B (RhB) breakdown, irrespective of the wide-ranging light source from the visible light, full-spectrum or even near-infrared light

Adsorption Treatment of Waste Water Using CQDs

According to Ramar et al. (2018), the mechanisms of CQDs in the adsorption process involve various processes and interactions, which are:

i. Surface Adsorption: CQDs typically possess a high definite surface area and plentiful surface functional groups. These surface molecules, such as COOH, OH, and NH_2, can interact with pollutants through chemical adsorption or electrostatic interactions. The adsorbate molecules are attracted to the CQD surface, leading to their attachment and removal from the wastewater.

ii. π -π stacking: Due to their graphitic carbon structure, CQDs can undergo π-π stacking interactions with aromatic pollutants. This interaction is a non-covalent bonding mechanism that involves the interaction between electron-rich areas of the CQDs and electron-deficient areas of the pollutants. This can enhance the adsorption capacity of CQDs for aromatic compounds, such as dyes or aromatic hydrocarbons.

iii. Hydrophobic Interaction: CQDs possess hydrophobic regions on their surface, which can interact with nonpolar or hydrophobic pollutants present in the wastewater. Hydrophobic interaction involves the partitioning of hydrophobic molecules between the aqueous phase and the hydrophobic surface of CQDs, resulting in their effective removal from the wastewater.

iv. Chelation or Coordination: Some pollutants, particularly heavy metal ions, can form coordination or chelation complexes with functional groups attached to the CQD surface. The functional groups, such as carboxyl or amino groups, can act as ligands to form stable complexes with the metal ions. This chelation mechanism increases the adsorption capacity of CQDs for metal ions.

v. Photocatalytic Degradation: In addition to adsorption, CQDs may also possess photocatalytic properties. Under appropriate conditions, CQDs can generate reactive oxygen species (ROS) or undergo redox reactions when exposed to light. These ROS can degrade organic pollutants through oxidation, contributing to the overall removal of contaminants from wastewater.

CQDs can be utilized for adsorption treatment to remove both organic and inorganic contaminants. In one study, CQDs were changed to become nitrogen-doped CQDs (N-CQDs), and wastewater-derived Cd^{2+} and Pb^{2+} ions were used to measure the N-CQDs' surface activity (Sabet et al., 2019). N-CQDs are efficient at eliminating Cd^{2+} and Pb^{2+} ions from water via surface adsorption due to their widespread variable surface chemistry, surface area, and non-corrosive nature. According to Agarwal et al. (2019), the faces or sides of CQDs can enhance the interface (physical and chemical contacts) among the particles. Additionally, it could improve the adsorption capacity and modify the quantum dots' energy band gap (Agarwal et al., 2019). It was discovered that the N-CQDs can promote the adsorption of heavy metal ions from water due to their large precise surface area. The remarkable proficiency in the adsorption of heavy metals from water can be accredited to the huge surface area of NCQDs when their particle sizes are approximately 10 nm. Furthermore, N-CQD surfaces containing N and O functional groups may serve as active sites for metal ion adsorption (Dou et al., 2019).

As stated earlier, CQDs can be regarded as real adsorbents in the elimination of detrimental complexes from wastewater because of the abundance of functional groups and different polar moieties on their surfaces. A variety of functional groups, together with amine and carboxyl groups, can function as sites of action to bind metal ions via π-π stacking contacts and electrostatic pull (Zhang et al., 2017).

A study has created an adsorbent nanocomposite (PECQDs/$MnFe_2O_4$) by merging the polyethyleneimine-modified CQDs with magnetic materials ($MnFe_2O_4$) (Huang et al., 2019). This nanocomposite demonstrated a potent magnetic field and an exceptional adsorption capability, making it a valuable tool for the effective removal of uranium. Uranium and the +ve charged surface of the adsorbent exhibit substantial electrostatic repulsion, as evidenced by the high amount of adsorption (91%) observed in the manufactured PECQDs/$MnFe_2O_4$. Furthermore, the enhancement of uranium adsorption was facilitated by the contacts between uranium ions and various functional groups, including OH, NH_2, and COOH. Furthermore, CQD surfaces with oxygenated functional groups may be more hydrophilic, which would increase adsorption action. However, the use of $MnFe_2O_4$ as adsorbent, without CQDs, can only achieve uranium adsorption of 25%.

The pH of the solution has a substantial influence on the adsorption capability. The adsorption competence declines with declining solution pH (Zhang et al., 2015). Metal and hydrogen ions compete with one another for adsorption sites in an acidic solution. Because metal ions repel one another, the great concentration of hydrogen ions in the acidic solution may prevent metal ions from sticking to the adsorbent (Lei Y et al., 2019). On the other hand, the deprotonation by hydroxyl ions causes the adsorbent surface to become negatively charged at higher solution pHs. The process of deprotonation intensifies the forces of attraction between the metal ions and the adsorbent (Chaudhry et al., 2016). Therefore, the combination of sorbent and adsorbent can be facilitated by electrostatic interactions, which helps to promote effective adsorption.

The two primary variables in the adsorption route are characteristically the polarity and surface area of the adsorbent materials. Because of their huge surface area—which may reach up to 1690 m^2/g, CQDs have been engaged broadly in adsorption studies (Ren et al., 2019). The Brunauer-Emmett-Teller (BET) surface area and pore volume measurements can be utilized to investigate the surface area and textural physiognomies of CQDs. For example, researchers have eliminated benzopyrene (BaP) from wastewater samples using three different types of iron oxide adsorbents: Fe_3O_4, C11-Fe_3O_4, and CQDs/C11-Fe_3O_4 (Yang et al., 2019). The BET measurement yielded surface areas of 88.2, 163.5, and 289.8 m2 g^{-1} for Fe_3O_4, C11-Fe_3O_4, and CQDs/C11-Fe_3O_4, respectively. The presence of CQDs was linked to a higher BET surface area. As a result, CQDs/C11-Fe_3O_4 can offer high surface adsorption sites, or 93.9% of the adsorption capability, for the BaP.

A different study by Mou et al. (2019) compared the BET surface area measurements of bismuth oxychloride (BiOCl) and BiOCl/NCQDs. The BET surface area of BiOCl was determined to be 33.1 m2 g^{-1}, whereas BiOCl/NCQDs had a surface area of 60.0 m^2 g^{-1}. BiOCl and BiOCl/NCQDs had pore volumes of 0.168 and 0.239 cm^3 g^{-1}, in that order. Since NCQDs were present in the composite adsorbents, the BET surface area increased and the adsorption capacity towards metal ions increased.

Nitrogen-doped CQDs (NCQDs) were synthesized in a study using dicyandiamide and citric acid as basic ingredients. An adsorbent for the elimination of lead was created by conjugating NCQDs with iron oxide (Fe_3O_4). The great adsorption capability is the result of using nitrogen atoms as dopant agents. The interaction between the lead ions' vacant d orbitals and the lone pair electrons of nitrogen atoms in the NCQD structures explains this adsorption (Mou et al., 2019). It is anticipated that the amino groups in the NCQDs will function as adsorption sites to increase the adsorbents' capacity for adsorption (Copur et al., 2018).

Rhahmanian et al. (2017) examined the adsorption kinetics of cadmium utilizing CQDs composited with zinc-aluminum layered double hydroxide (CQDs/ZnAl-LDH). A huge amount of active adsorption sites were delivered by the multiplicity of functional groups on the CQDs/ZnAl-LDH composite, increasing the adsorption capability towards cadmium. At 20 minutes, the maximum cadmium content on the CQDs/ZnAl-LDH composite was 12.60 mg/g. Utilizing the pseudo-second-order model, the CQDs/ZnAl-LDH composite displayed a good correlation coefficient value (0.9998). The outcome validated that the adsorption method was primarily heterogeneous by fitting well with the Freundlich and intra-particle diffusion models.

Present Progress and Future Prospects

The application of CQDs for the management of wastewater has shown massive progress as far as our review of literature is concerned. Their unique features make them efficient adsorbents for eradicating heavy metals, dyes, and foul odor from water. However, such notable improvements have been made in the laboratory, with a strong need for these innovations to be produced for large-scale wastewater treatment. As far as several industries are concerned, the use of traditional materials like activated carbon, silica gel, and alumina is the most economical method for treating wastewater. Thus, CQDs are yet to be fully used for large water treatment purposes because they are expensive to produce on a large scale. This limitation opens up further opportunities for scientists to develop easier and novel methods for large-scale production of this material.

Furthermore, CQDs are quite difficult to purify. Purification of CQDs is necessary, especially for biomass precursors that may contain contaminants and other impurities. Setting up a dialysis process to purify these materials will be expensive for large-scale purification of the CQDs, and as such, the development of novel approaches to purify them should be the next area of concentration. Another limitation is that most research that looked into the synthesis of CQDs did not necessarily focus on the quantum yield as it is mostly low for the synthesis process. The majority of the synthesis methods can barely produce quantum yields up to 80% which remains a hindrance to the large-scale use of these materials for water treatment. Lastly, understanding the structural-property of CQDs can be ambiguous as their features can vary and several impacts on their adsorption properties.

REFERENCES

Agarwal S, Sadeghi N, Tyagi I, Gupta VK, Fakhri A. (2016). Adsorption of toxic carbamate pesticide oxamyl from liquid phase by newly synthesized and characterized graphene quantum dots nanomaterials. *J Colloid Interface Sci.* Sep 15;478:430-8. https://doi:10.1016/j.jcis.2016.06.029

Bomben, K.D.; Moulder, J.F.; Stickle, W.F.; Sobol, P.E. (1995). Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS, Physical Electronics, Eden Prairie; Perkin-Elmer Corporation: Waltham, MA, USA.

Chae, A.Y.; Choi, S.J.; Paoprasert, N.P.; Park, S.Y.; In, I. (2017). Microwave-assisted synthesis of fuorescent carbon quantum dots from an A2/B3 monomer set. *RSC Adv. 7*, 12663–12669.

Chaudhry SA, Khan TA, Ali I (2016). Adsorptive removal of Pb (II) and Zn (II) from water onto manganese oxide-coated sand : Isotherm , thermodynamic and kinetic studies. *Egyptian Journal of Basic and Applied Sciences*, Volume 3, Issue 3, Pg 287-300 https://doi:10.1016/j.ejbas.2016.06.002

Copur F, Bekar N, Zor E, Alpaydin S, Bingol H (2019). Nanopaper-based photoluminescent enantioselective sensing of L-Lysine by L-Cysteine modified carbon quantum dots. Sensors Actuators B C. *Sci Rep.* 25;12(1):17861. https://doi:10.1038/s41598-022-22837-2.

Dager, A.; Uchida, T.; Maekawa, T.; Tachibana, M. (2019). Synthesis and characterization of Mono-disperse Carbon Quantum Dots from Fennel Seeds: Photoluminescence analysis using Machine Learning. *Sci. Rep.*, *9*, 14004.

Das R, Bandyopadhyay R, Pramanik P. (2018). Carbon quantum dots from natural resource: A review. *Mater Today Chem* *8*:96–109. https://doi.org/10.1016/j.mtchem.2018.03.003.

Dong Y, Shao J, Chen C, Li H, Wang R, Chi Y, et al. (2012). Blue luminescent graphene quantum dots and graphene oxide prepared by tuning the carbonization degree of citric acid. *Carbon N Y 50*:4738–43. https://doi./10.1016/j.carbon.2012.06.002

Dou J, Gan D, Huang Q, Liu M, Chen J, Deng F, Zhu X, Wen Y, Zhang X, Wei Y (2019). Functionalization of carbon nanotubes with chitosan based on MALI multicomponent reaction for Cu2+ removal. *Int J Biol Macromol.* 2019 Sep 1;136:476-485. https://doi:10.1016/j.ijbiomac.2019.06.112.

El-Brolsy, H.M.E.M.; Hanafy, N.A.N.; El-Kemary, M.A.(2022). Fighting Non-Small Lung Cancer Cells Using Optimal Functionalization of Targeted Carbon Quantum Dots Derived from Natural Sources Might Provide Potential Therapeutic and Cancer Bio Image Strategies. *Int. J. Mol. Sci.* 2022*, 23*, 13283.

Gayen, B.; Palchoudhury, S.; Chowdhury, J. (2019). Carbon Dots: A Mystic Star in the World of Nanoscience. *J. Nanomater*, 1–19.

Gyulai G, Ouanzi F, Bertóti I, Mohai M, Kolonits T, Horváti K, et al. (2019). Chemical structure and in vitro cellular uptake of luminescent carbon quantum dots prepared by solvothermal and microwave assisted techniques. *J Colloid Interface Sci 549*: 150–61. https://doi.org/10.1016/j.jcis.2019.04.058

Haitao, L.; Kang, Z.; Liu, Y.; Lee, S.-T. (2012). Carbon nanodots: Synthesis, properties and applications. *J. Mater. Chem.*, *46*, 24230–24253.

Hanafiah, M. M. et al. (2018). Removal of chromium from aqueous solutions using a palm kernel shell adsorbent. *Desalin. 118*: 172-180

Hasan, F.F.C, Mohd Zahidi, N.A.W., Bahar, V.S., Remli, U.R.R.P., Abd Aziz, A., (2022). Carbon Quantum Dots (CQDs) Based Composites Photocatalyst for Wastewater Purification. *In Materials Science Forum*, Vol. 1056, pp. 111–117. Trans Tech Publications, Ltd. https://doi./10.4028/pftn9wh

Henriquez, G.; Ahlawat, J.; Fairman, R.; Narayan, M. (2022) Citric Acid-Derived Carbon Quantum Dots Attenuate Paraquat-Induced Neuronal Compromise In Vitro and In Vivo. *ACS Chem. Neurosci. 13*, 2399–2409.

Hola, K.; Bourlinos, A.B.; Kozak, O.; Berka, K.; Siskova, K.M.; Havrdova, M.; Tucek, J.; Safarova, K.; Otyepka, M.; Giannelis, E.P.; et al.(2014). Photoluminescence effects of graphitic core size and surface functional groups in carbon dots: COO− induced red-shift emission. *Carbon 70*, 279–286.

Hou, H.; Banks, C.E.; Jing, M.; Zhang, Y.; Ji, X. (2015) Carbon Quantum Dots and Their Derivative 3D Porous Carbon Frameworks for Sodium-Ion Batteries with Ultralong Cycle Life. *Adv. Mater. 27*, 7861–7866.

Huang S, Jiang S, Pang H, Wen T, Asiri AM, Alamry KA, Alsaedi A, Wang X, Wang S (2019). Dual functional nanocomposites of magnetic MnFe2O4 and fluorescent carbon dots for efficient U(VI) removal. https://doi:10.1016/j.cej.2019.03.015.

Inderbir S.; Arora R.; Dhiman H.; Pahwa R. (2018) Carbon quantum dots: Synthesis, characterization and biomedical applications. *Turk. J. Pharm. Sci. 2*, 219–230.

Jamila, G.S.; Sajjad, S.; Leghari, S.A.K.; Kallio, T.; Flox, C. (2021) Glucose derived carbon quantum dots on tungstate-titanate nanocomposite for hydrogen energy evolution and solar light catalysis. *J. Nanostruct. Chem. 12*, 611–623.

Jlassi, K., Eid, K., Sliem, M.H. *et al.* (2020). Rational synthesis, characterization, and application of environmentally friendly (polymer–carbon dot) hybrid composite film for fast and efficient UV-assisted Cd^{2+} removal from water. *Environ Sci Eur* 32, 12. https://doi./10.1186/s12302-020-0292-z

Joshi PN, Mathias A, Mishra A, Mathias A. (2018). Synthesis of ecofriendly fluorescent carbon dots and their biomedical and environmental applications. *Mater Technol 33*:672–80. https://doi./10.1080/10667857.2018.1492683.

Kaixin, C.; Zhu, Q.; Qi, L.; Guo, M.; Gao, W.; Gao, Q. (2022). Synthesis and Properties of Nitro-gen-Doped Carbon Quantum Dots Using Lactic Acid as Carbon Source. *Materials 15*, 466.

Kaur, A.; Pandey, K.; Kaur, R.; Vashishat, N.; Kaur, M. (2022). Nanocomposites of Carbon Quantum Dots and Graphene Quantum Dots: Environmental Applications as Sensors. *Chemosensors 10*, 367.

Kolanowska, A.; Dzido, G.; Krzywiecki, M.; Tomczyk, M.M.; Łukowiec, D.; Ruczka, S.; Boncel, S. (2022). Carbon Quantum Dots from Amino Acids Revisited: Survey of Renewable Precursors toward High Quan-tum-Yield Blue and Green Fluorescence. *ACS Omega 45*, 41165–41176.

Koulivanda H., Shahbazia A., Vatanpourb V.,& Rahmandoust M. (2019). Development of carbon dot-modified polyethersulfone membranes for enhancement of nanofiltration, permeation and antifouling performance. *Separation and Purification Technology* 1115895

Lei Y, Cui Y, Huang Q, Dou J, Gan D, Deng F, Liu M, Li X, Zhang X, Wei Y (2019). Facile preparation of sulfonic groups functionalized Mxenes for efficient removal of methylene blue. *Ceramics International*. Volume 45, Issue 14. Pg. 17653-17661, https://doi:10.1016/j.ceramint.2019.05.331.

Li, H.; Xu, Y.; Zhao, L.; Ding, J.; Chen, M.; Chen, G.; Li, Y.; Ding, L(2018). Synthesis of tiny carbon dots with high quantum yield using multi-walled carbon nanotubes as support for selective "turn-off-on" detection of rutin and Al3+. *Carbon 143*, 391–401. [CrossRef]

Liang Z, Yang J, Zhou C, Mo Q, Zhang Y. (2018). Carbon quantum dots modified BiOBr microspheres with enhanced visible light photocatalytic performance. *Inorg Chem Commun; 90*:97–100. https://doi./10.1016/j.inoche.2018.02.013.

Lim H, Liu Y, Kim HY, Son DI. Facile synthesis and characterization of carbon quantum dots and photovoltaic applications. Thin Solid Films 2018;660:672–7. https:// doi.org/10.1016/j.tsf.2018.04.019Qiu, Y.; Li, D.; Li, Y.; Ma, X.; Li, J. (2021) Green carbon quantum dots from sustainable lignocellulosic biomass and its application in the detection of Fe3+. *Cellulose 29*, 367–378.

Liu, Y.; Huang, H.; Cao, W.; Mao, B.; Liu, Y.; Kang, Z. (2020). Advances in carbon dots: From the perspective of traditional quantum dots. *Mater. Chem. Front. 4*, 1586–1613.

Martindale, B.C.M.; Hutton, G.A.M.; Caputo, C.A.; Prantl, S.; Godin, R.; Durrant, J.R.; Reisner, E. (2017) Enhancing Light Absorption and Charge Transfer Efficiency in Carbon Dots through Graphitization and Core Nitrogen Doping. *Angew. Chem. 129*, 6559–6563.

Mashkani, M., Mehdinia, A., Jabbari, A., Bide, Y., Reza Nabid, M., Preconcentration and extraction of lead ions in vegetable and water samples by N-doped carbon quantum dot conjugated with Fe_3O_4 as a green and facial adsorbent. *Food Chem.*239:1019-1026. https://doi:10.1016/j.foodchem.2017.07.042

Mou Z, Zhang H, Liu Z, Sun J, Zhu M (2019). Ultrathin BiOCl/nitrogen-doped grapheme quantum dots composites with strong adsorption and effective photocatalytic activity for the degradation of antibiotic ciprofloxacin. *Applied Surface Science*, Volume 496, 143655. https://doi:10.1016/j.apsusc.2019.143655.

Nammahachak, N.; Aup-Ngoen, K.K.; Asanithi, P.; Horpratum, M.; Chuangchote, S.; Ratanaphan, S.; Surareungchai, W. (2022) Hydrothermal synthesis of carbon quantum dots with size tunability *via* heterogeneous nucleation. *RSC Adv. 12*, 31729–31733.

Nizam N U M et al. (2020). Effective adsorptive removal of dyes and heavy metal using graphene oxide based pre-treated with NaOH/H2SO4 rubber seed shells synthetic graphite precursor: Equilibrium isotherm, kinetics and thermodynamic studies Sep. *Purif. Technol. 289* 120730

Nizam, N.U.M., Hanafiah, M.M., Mahmoudi, E. *et al.* (2023). Synthesis of highly fluorescent carbon quantum dots from rubber seed shells for the adsorption and photocatalytic degradation of dyes. *Sci Rep* 13, 12777. https://doi./10.1038/s41598-023-40069-w

Palani G et al. (2021). Current trends in the application of nanomaterials for the removal of pollutants from industrial wastewater treatment—A Review. *Molecules 26* 2799

Papaioannou N, Marinovic A, Yoshizawa N, Goode AE, Fay M, Khlobystov A, et al. (2018). Structure and solvents effects on the optical properties of sugar-derived carbon nanodots. *Sci Rep 8*:1–10. https://doi./10.1038/s41598-018-25012-8.

Preethi M., Viswanathan C., &Ponpandian N. (2022) A metal-free, dual catalyst for the removal of Rhodamine B using novel carbon quantum dots from muskmelon peel under sunlight and ultrasonication: A green way to clean the environment. *Journal of Photochemistry and Photobiology*. 426 113765 http://doi/10.1016/j.jphotochem.2021.113765

Qiang, S.; Zhang, L.; Li, Z.; Liang, J.; Li, P.; Song, J.; Guo, K.; Wang, Z.; Fan, Q. (2022). New Insights into the Cellular Toxicity of Carbon Quantum Dots to *Escherichia coli*. *Antioxidants 11*, 2475.

Qu, Y.; Li, X.; Zhang, H.; Huang, R.; Qi, W.; Su, R.; He, Z.(2022) Controllable synthesis of a sponge-like Z-scheme N, S-CQDs/Bi2MoO6@ TiO2 film with enhanced photocatalytic and antimicrobial activity under visi-ble/NIR light irradiation. *J. Hazard. Mater. 429*, 128310.

Rahmanian O, Dinari M, Abdolmaleki MK (2018). Carbon quantum dots/layered double hydroxide hybrid for fast and efficient decontamination of Cd (II): The adsorption kinetics and isotherms Appl. *Surf. Sci. 428* 272-279. https://doi:10.1016/j.apsusc.2017.09.152.

Rajabi HR, Khani O, Shamsipur M, Vatanpour V. (2013). High-performance pure and Fe3+- ion doped ZnS quantum dots as green nanophotocatalysts for the removal of malachite green under UV-light irradiation. *J Hazard Mater 250–251*:370–8. https://doi./10.1016/j.jhazmat.2013.02.007.

Ramar V, Moothattu S, Balasubramanian K (2018). The mechanisms of carbon quantum dots (CQDs) in the adsorption process. *Solar Energy* 169:120-127. https://doi:10.1016/j.solener.2018.04.0.

Rani U A et al. (2020). A review of carbon quantum dots and their applications in wastewater treatment Adv. *Colloid Interface Sci. 278* 102124

Ren X, Zhang F, Guo B, Gao N, Zhang X (2019) . Synthesis of N-Doped Micropore Carbon Quantum Dots with High Quantum Yield and Dual-Wavelength Photoluminescence Emission from Biomass for Cellular Imaging. https://doi:10.3390/nano9040495.

Sabet, M. and Mahdavi, K. (2018). Green synthesis of high photoluminescence nitrogen-doped carbon quantum dots from grass via a simple hydrothermal method for removing organic and inorganic water pollutions. *Applied Surface Science*, 463, 283-291. https://doi.10.1016/j.apsusc.2018.08.22

Saud PS, Pant B, Alam A-M, Ghouri ZK, Park M, Kim H-Y. (2015). Carbon quantum dots anchored TiO2 nanofibers: Effective photocatalyst for waste water treatment. *Ceram Int 41*:11953–9. https://doi/10.1016/j.ceramint.2015.06.007.

Sciortino, A.; Marino, E.; van Dam, B.; Schall, P.; Cannas, M.; Messina, F.(2016) Solvatochromism un-ravels the emission mechanism of carbon nanodots. *J. Phys. Chem. Lett. 17*, 3419–3423.

Semeniuk, M.; Yi, Z.; Poursorkhabi, V.; Tjong, J.; Jaffer, S.; Lu, Z.-H.; Sain, M. (2019). Future per-spectives and review on organic carbon dots in electronic applications. *ACS Nano* 13(6):6224-6255. https://doi:10.1021/acsnano.9b00688.

Shi Y, Liu X, Wang M, Huang J, Jiang X, Pang J, et al. (2019). Synthesis of N-doped carbon quantum dots from bio-waste lignin for selective irons detection and cellular imaging. *Int J Biol Macromol 128*:537–45. https://doi./10.1016/j.ijbiomac.2019.01.146.

Sofia, P.; Palomares, E.; Martinez-Ferrero, E. (2016). Graphene and carbon quantum dot-based materials in pho-tovoltaic devices: From synthesis to applications. *Nanomaterials* 2016, *6*, 157.

Tang, L.; Ji, R.; Cao, X.; Lin, J.; Jiang, H.; Li, X.; Teng, K.S.; Luk, C.M.; Zeng, S.; Hao, J.; et al. (2012). Deep Ultraviolet Photoluminescence of Water-Soluble Self-Passivated Graphene Quantum Dots. *ACS Nano 6*, 5102–5110.

Tingting, Y.; Wang, H.; Guo, C.; Zhai, Y.; Yang, J.; Yuan, J. (2018) A rapid microwave synthesis of green-emissive carbon dots with solid-state fluorescence and pH-sensitive properties. *R. Soc. Open Sci. 7*, 180245.

Tohamy, H.S., El-Sakhawy, M. and Kamel, S. Eco-friendly Synthesis of Carbon Quantum Dots as an Effective Adsorbent. *J Fluoresc* 33, 423–435 (2023). https://doi./10.1007/s10895-022-03085-z

Wang Q., Wang G.,Liang X.,Dong X., & Zhang X. (2018) Supporting carbon quantum dots on NH2-MIL-125 for enhanced photocatalytic degradation of organic pollutants under a broad spectrum irradiation, *Applied Surface Science*, Volumes 467–468, Pages 320-327. https://doi.org/10.1016/j.apsusc.2018.10.165

Wang, Y.; Hu, A. (2014). Carbon quantum dots: Synthesis, properties and applications. *J. Mater. Chem. C*, *34*, 6921–6939.

Yadav, P. K., Subhash C., Vivek K., Deepak K., and Syed H. (2023). "Carbon Quantum Dots: Synthesis, Structure, Properties, and Catalytic Applications for Organic Synthesis" *Catalysts* 13, no. 2: 422. https://doi.org/10.3390/catal13020422

Yang D, Tammina SK, Li X, Yang Y (2019). Enhanced removal and detection of benzo[a]pyrene in environmental water samples using carbon dots-modified magnetic nanocomposites. *Ecotoxicol Environ Saf.*; 170:383-390. https://doi:10.1016/j.ecoenv.2018.11.138.

Yao, L.; Zhao, M.-M.; Luo, Q.-W.; Zhang, Y.-C.; Liu, T.-T.; Yang, Z.; Liao, M.; Tu, P.; Zeng, K.-W. (2022). Carbon Quantum Dots-Based Nanozyme from Coffee Induces Cancer Cell Ferroptosis to Activate Antitumor Immunity. *ACS Nano 16*, 9228–9239.

Yuan, F.; Su, W.; Gao, F. (2022). Monolayer 2D polymeric fullerene: A new member of the carbon material family. *Chem 8*, 2079–2081.

Zhang X, Huang Q, Liu M, Tian J, Zeng G, Li Z, Wang K, Zhang Q, Wan Q, Deng F, Wei Y (2015). Preparation of amine functionalized carbon nanotubes via a bioinspired strategy and their application in Cu^{2+} removal. https://doi:10.1016/j.apsusc.2015.03.081.

Zhang, W.; Yu, S.F.; Fei, L.; Jin, L.; Pan, S.; Lin, P. (2017). Large-area color controllable remote carbon white-light light-emitting diodes. *Carbon 85*, 344–350.

Zhao, M.; Zhang, J.; Xiao, H.; Hu, T.; Jia, J.; Wu, H. (2019). Facile *in situ* synthesis of a carbon quantum dot/graphene heterostructure as an efficient metal-free electrocatalyst for overall water splitting. *Chem. Commun. 55*, 1635–1638.

Zheng, G., Li, S., Zhang, T., Zhu,F., Sun,J., Li, S., and You, L. (2021). Water Pollution Control and Treatment Based on Quantum Dot Chemical and Biological High-Sensitivity Sensing. *Hindawi Journal of Sensors*. Volume, Article ID 8704363. https://doi./10.1155/2021/8704363

Zheng, Y.; Yang, D.; Wu, X.; Yan, H.; Zhao, Y.; Feng, B.; Duan, K.; Weng, J.; Wang, J. (2015). A facile approach for the synthesis of highly luminescent carbon dots using vitamin-based small organic molecules with benzene ring structure as precursors. *RSC Adv.*, *5*, 90245–90254.

Zhou S, Liu N, Zhao J. (2017). Phosphorus quantum dots as visible-light photocatalyst for water splitting. *Comput Mater Sci 130*:56–63. https://doi./10.1016/j.commatsci.2017.01.009