Dryland Soil Research, Vol. 1, No. 2, pp. 93-101, 2025
Type of article: Original, Available online at www.dlsr.iut.ac.ir,
https://doi.org/10.47176/dlsr.01.02.1040

Carbon quantum dots loaded-micro carriers production approaches, a promising adsorbent for contaminated soils remediation (A review)

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(Received 2025/05/05, Accepted 2025/20/07)

ABSTRACT

Heavy metal contamination in soils presents a critical environmental challenge, threatening ecosystems, agricultural productivity, and human health. Conventional remediation techniques, such as biochar application, are limited by hydrophobicity, particle aggregation, and inefficient soil interaction. This study introduces a novel, sustainable adsorbent for heavy metal immobilization: carbon quantum dots (CQDs) loaded onto cyanobacteria-derived microcarriers. CQDs, with their high surface area, hydrophilicity, and abundant functional groups, offer superior adsorption potential. However, their direct use is hindered by mobility and separation challenges. To address this, cyanobacteria—rich in extracellular polymeric substances (EPS)—are utilized as dual precursors for CQD synthesis and microcarrier fabrication via the oilothermal pyrolysis method. This innovative technique employs an oil medium to prevent EPS dissolution during pyrolysis, enabling simultaneous carbonization of cyanobacterial cells and EPS into stable, spherical CQD-microcarrier composites. The resulting adsorbent combines the high adsorption capacity of CQDs with the structural advantages of microcarriers, ensuring uniform soil distribution, resistance to microbial degradation, and ease of separation. Experimental results demonstrate exceptional efficacy in immobilizing cadmium, with adsorption capacities exceeding traditional biochar by 40–60%, attributed to the composite's hydrophilic functional groups (e.g., -OH, -COOH) and enhanced soil contact. The oilothermal method eliminates the need for costly precursors or hazardous equipment, offering a scalable, cost-effective, and eco-friendly solution. By integrating cyanobacteria cultivation, waste valorization, and one-step synthesis, this approach advances in-situ soil remediation, overcoming the limitations of existing technologies. The study underscores the potential of bio-based nanomaterials in sustainable environmental management, providing a blueprint for efficient, low-cost heavy metal mitigation while aligning with circular economy principles.

Keywords: Adsorbent, Cyanobacteria, Nano, Heavy Metals, Cadmium.

1. Introduction

Soils, the foundation of life on Earth, face a growing threat: pollution with heavy metals (Rodríguez-Eugenio et al., 2019). These persistent elements, including lead, arsenic, cadmium, and mercury, are accumulating in soils worldwide, driven by numerous human activities (Rai et al., 2024). This silent crisis poses a significant risk to the environment, human health, and food security (Food and Agriculture Organization of the United Nations, 2021). Human activities, particularly industrial ones, are the primary culprits (Dehkordi et al., 2024). The rapid expansion of industries such as mining, metal processing, and chemical manufacturing is a major source of heavy metal contamination in the environment (Adnan et al., 2024). Greenhouse gas emissions, waste disposal methods, and accidental leaks often find their way into the soil, exceeding natural levels and disrupting the delicate balance of ecosystems (Mokhtari et al., 2020; Siddiqua et al., 2022; Nuruzzaman et al., 2025). Agricultural activities, including the use of chemical fertilizers, pesticides, and sewage sludge, can also increase metal concentrations in soils (A Shahbazi et al., 2018). Furthermore, fossil fuels and the weathering of mineral-rich rocks contribute to the deposition of these elements, affecting even remote areas (Angon et al., 2024). Unlike organic pollutants, heavy metals do not readily degrade. They accumulate in the soil over time, becoming increasingly concentrated and posing long-term threats (Edo et al., 2024). Their mobility and uptake by plants further complicate the issue, potentially entering the food chain and ultimately ending up on people's tables (Zhao et al., 2022). The consequences of heavy metal contamination in the environment are widespread and often devastating (Kotnala et al., 2025). Soil loses its fertility, leading to reduced crop yields and decreased food production (Alengebawy et al., 2021). Aquatic ecosystems are also affected by contaminated runoff, jeopardizing the health and diversity of freshwater and marine life (Mustafa et al., 2024). Chronic human exposure to heavy metals can lead to a range of health problems, including cancer, neurological disorders, and developmental delays in children (Balali-Mood et al., 2021). Therefore, the remediation of heavy metal-contaminated soils is a necessity for maintaining food security and health.

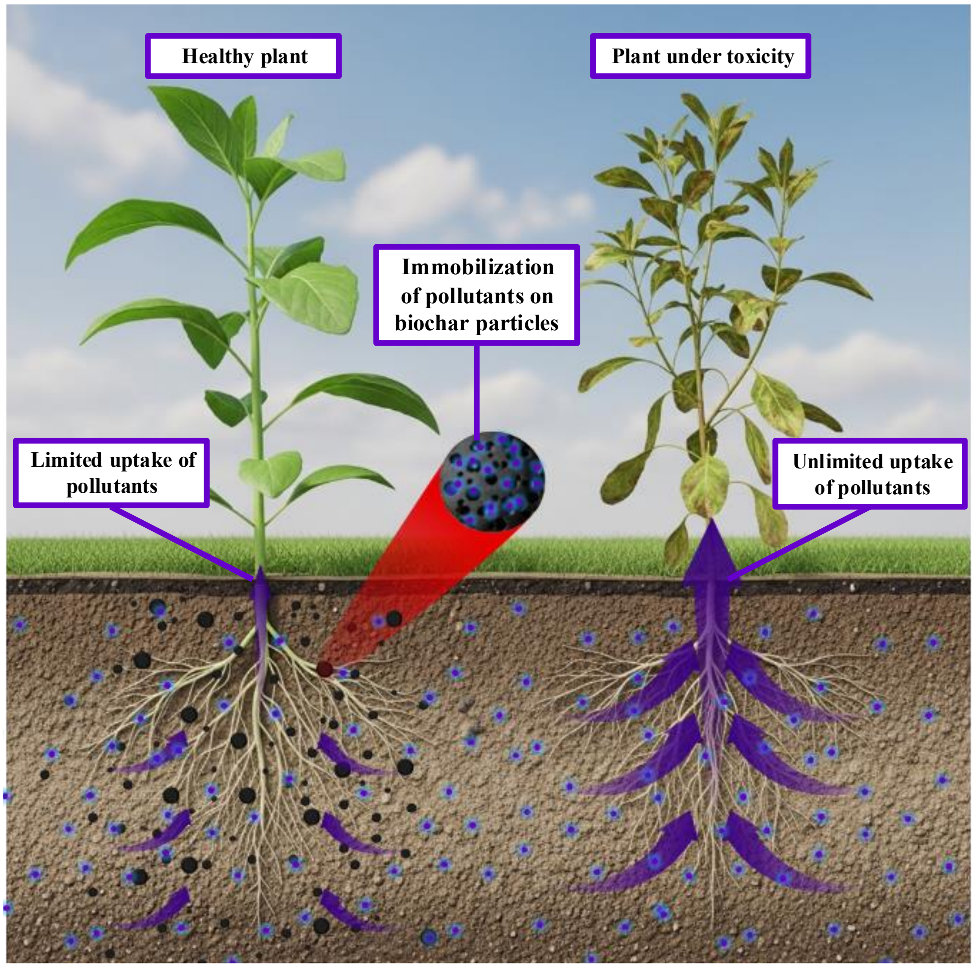

Figure 1. An example of In-situ soil amendment using biochar.

2. Remediation of heavy metal contaminated soils

Generally, methods for remediating heavy metal-contaminated soils are divided into two main categories: 1- In-situ remediation and 2- Ex-situ remediation (Raklami et al., 2022). In the first method, contaminated soil is remediated in its original location without excavation or removal. In-situ remediation methods include physical, chemical, and biological approaches (Figure 1). Physical methods include soil flushing or thermal desorption. Chemical methods involve adding amendments to immobilize heavy metals. Biological methods utilize plants or microorganisms to extract, stabilize, or degrade heavy metals (Deng et al., 2023; Selina et al., 2022; Kapahi and Sachdeva, 2019; Guba et al., 1999).

The second method involves excavating contaminated soil and treating it elsewhere (Figure 2). Common methods include physical separation techniques such as soil washing or screening. Chemical methods often involve immobilization or stabilization to reduce metal mobility. Biological methods such as composting or landfarming can also be used in ex-situ scenarios (Kumar et al., 2023; Chaukeura et al., 2022; United States Environmental Protection Agency, 2017).

2.1. The selection of an appropriate method for the remediation of heavy metal-contaminated soils

Each of these two categories is further divided into physical, chemical, biological, thermal, and electrical modifications, offering a wide range of options to address soil contamination challenges (Liao et al., 2022). However, in general, in-situ remediation methods are more common than ex-situ methods due to lower costs, less disruption to the soil and surrounding environment, faster remediation times, reduced risk of exposure to contamination during remediation, and the ability to be implemented on a large scale (Yuan et al., 2024; Ray, 2022; Ben, 2016). Among the various in-situ remediation methods, chemical stabilization is more efficient, cheaper, and easier (Utilities One, 2023). The adsorption technique is one of the most efficient chemical stabilization techniques widely used for the remediation of

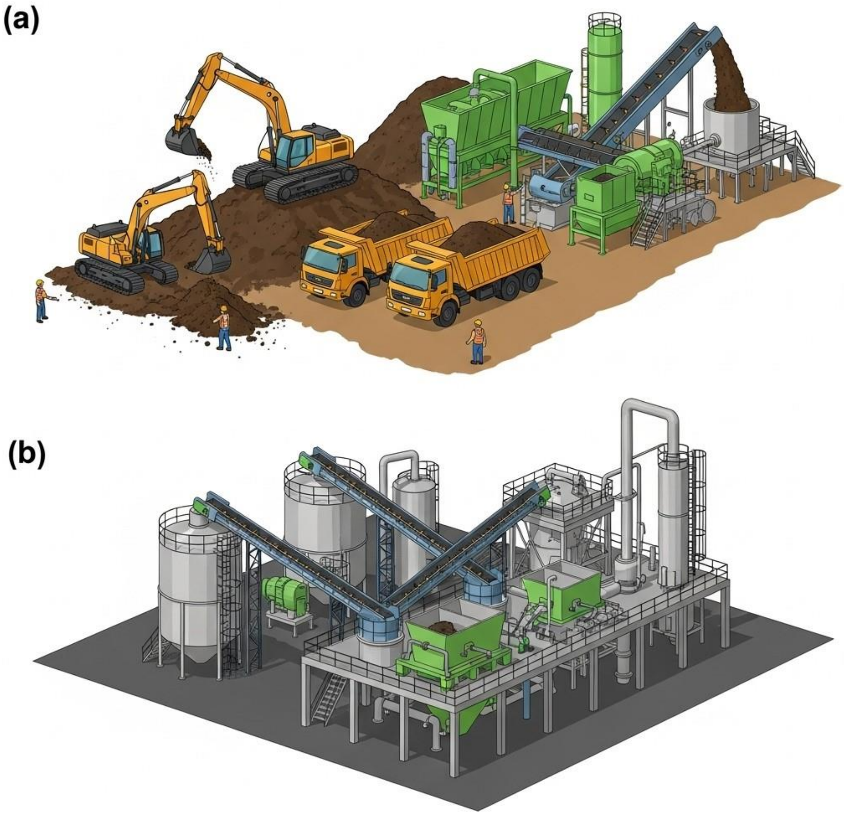

Figure 2. Ex-situ soil remediation: a) Excavation, removal and transport of contaminated soil, b) Treatment and remediation of contaminated soil at another location.

contaminated soils (Hong et al., 2019). The advantages of heavy metal stabilization in soil through the adsorption process include high efficiency, environmental compatibility, low cost, simplicity, and no production of by-products (Mishra et al., 2023, Utilities One, 2023). Remediating heavy metal-contaminated environments through the adsorption process requires the application of adsorbent materials to adsorb and immobilize heavy metals in the environment.

2.2. Properties of a suitable adsorbent

Adsorbability is a very important factor in the adsorption process. Therefore, the most suitable material should be used as an adsorbent. An ideal adsorbent should have properties such as high specific surface area, abundant adsorption sites, a multi-reactive surface, high adsorption rate, and low cost (Ghaedi et al., 2021; Mohammadi et al., 2020). Today, the use of carbon-based materials as adsorbents for heavy metals is one of the most economical and efficient approaches (Mahesh et al., 2022; Ghaedi et al., 2021).

2.2.1. Carbon-based materials as adsorbents

Carbon-based materials is a good choice for heavy metal adsorption due to their unique physical and chemical properties, environmental compatibility, effective and efficient adsorption (Ghaedi et al., 2021; Akhtar et al., 2021; Sabzemeydani et al., 2021). Biochar is one type of carbon-based material produced by the thermochemical decomposition of biomass in an oxygen-free or low-oxygen atmosphere. The unique properties of biochar, including its porous structure, high specific surface area, abundant functional groups, predominantly alkaline nature, high cation exchange capacity, and the ability to be produced from organic wastes such as agricultural residues, have made this carbon-based material an efficient and relatively economical adsorbent for the remediation of heavy metal-contaminated soils through adsorption and immobilization (Gholami and Rahimi, 2022). In the in-situ remediation method using adsorption, the adsorbent material is usually mixed with the soil only once upon addition and then remains almost stationary in the soil. Therefore, it is very important that the added adsorbent covers as much of the soil matrix as possible and that a significant portion of its specific surface area is in contact with it. The specific surface area and cation exchange capacity of biochar as a porous material are mainly related to its internal surfaces, and what is in contact with the soil matrix is mainly its external surfaces. Biochar, due to the formation of volatile organic

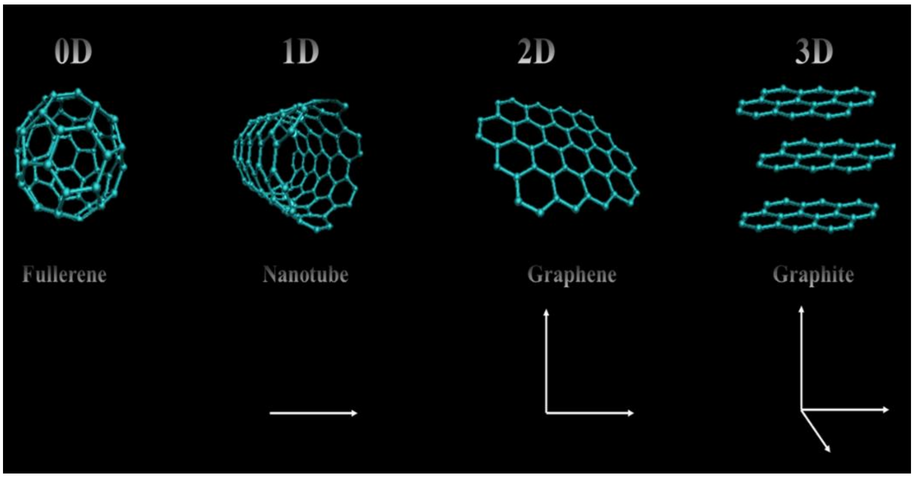

Figure 3. Dimensionality in nanomaterials, consider the structures of fullerene (0D), carbon nanotubes (1D), graphene (2D), and graphite (3D).

compounds and their accumulation on its surfaces during biomass pyrolysis, has a relatively hydrophobic nature (Adhikari et al., 2023). This relatively hydrophobic nature prevents the soil solution from effectively reaching its internal surfaces in a stationary state. It might seem that by reducing the size of biochar particles, the specific surface area of biochar could be brought into more effective contact with the soil matrix, but it has been reported that the hydrophobicity of biochar particles increases even further with decreasing particle size (Odeh and Menšík, 2022). Therefore, the need for finding a suitable alternative that lacks the aforementioned disadvantages of biochar is increasingly felt. Carbon nanomaterials are one type of carbon-based material whose use has expanded today due to their unique properties such as easy physical and chemical modification, high surface areas, tunable properties for specific applications, and high capacity for microbial purification and removal of biological and chemical contaminants (Liu et al., 2018; Khalid et al., 2017).

2.2.1.1. Carbon nanomaterials

In general, carbon nanomaterials are divided into four nanostructural groups: 1- Three-dimensional nanostructures, 2- Two-dimensional nanostructures, 3- One-dimensional nanostructures, and 4- Zero-dimensional nanostructures (Li et al., 2018) (Figure 3).

3. Carbon quantum dots (CQDs)

Carbon quantum dots (CQDs) belong to the group of zero-dimensional carbon nanostructures (Figure 4). They have the smallest size among other carbon nanostructure groups, with a size of less than 10 nanometers (Tuerhong et al., 2017). Carbon dots have fluorescent properties and can emit visible wavelengths in the presence of ultraviolet radiation (Jelinek, 2016). These nanostructures, due to their much smaller size, have a larger specific surface area compared to other carbon nanostructures. For example, graphene-based CQDs can have a specific surface area of over 3000 square meters per gram (Hsiao and Lin, 2020). An important point about CQDs is that in addition to having a high specific surface area, they are also highly hydrophilic (Khaivari Farid and Rahimi, 2022; Gan et al., 2020). This property is attributed to several factors, including the presence of oxygen-containing functional groups. CQDs often have abundant functional groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O) on their surface (Hong et al., 2022) (Figure 4).

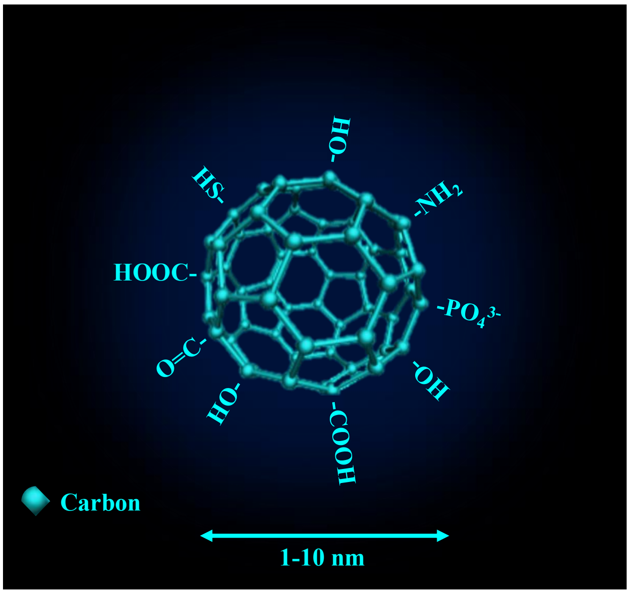

Figure 4. A typical schematic of a carbon quantum dot and possible functional groups on its surface (depending on the precursor or functionalization process).

These groups, due to hydrogen bonding, have a high affinity for water molecules and increase the hydrophilic nature of the dots (Long et al., 2022).

CQDs typically range in size from 1 to 10 nm, resulting in a significantly higher surface area to volume ratio compared to bulk materials. This large surface area, coupled with abundant hydrophilic functional groups, enhances interaction with water molecules (Shijin et al., 2023). The CQDs important properties are including:

- **Electronic properties:** The conjugated π-electron system in CQDs can create electrostatic interactions with water molecules, contributing to their hydrophilicity (Yang et al., 2023; Witz et al., 2016).
- The high hydrophilicity of CQDs offers several advantages for their various applications:
- **Enhanced biocompatibility:** In biological applications, the water solubility of CQDs facilitates their interaction with cells and tissues, making them useful for drug delivery, bioimaging, and biosensing.
- **Improved dispersion and stability:** In aqueous environments, CQDs disperse well and prevent aggregation and sedimentation.
- **Easy surface modification:** Due to the abundant functional groups, CQDs can be easily modified with additional molecules to tailor their properties for specific applications (Kumar et al., 2022).

However, the direct use of CQDs as adsorbents for heavy metals from aqueous or soil environments is not very efficient because, due to the very small size and high hydrophilicity of these particles, their separation from the water environment is difficult. Also, due to their mobility in the soil solution, they can move in the soil along with the heavy metals they have adsorbed, which contradicts the approach of heavy metal immobilization. Therefore, before using CQDs as heavy metal adsorbents, they should be immobilized on micro-scale microcarriers, and then the resulting composite should be used as an adsorbent in aqueous or soil environments (Khaivari Farid and Rahimi, 2022).

In a recent study that used a CQDs-based composite for the adsorption and pre-concentration of cadmium from an aqueous environment, citric acid was used as a precursor for the synthesis of CQDs by the hydrothermal method, and cytopore microgranules were used as microcarriers for CQDs (Li et al., 2018). Citric acid may be a relatively inexpensive precursor for the synthesis of CQDs, but cytopores, with a price of over $1000 per 20 grams of precursor, are not a cost-effective option for CQDs microcarriers for use as heavy metal adsorbents in soil. On the other hand, due to the cellulosic and biodegradable nature of cytopores, if the resulting composite is to be used as a heavy metal adsorbent in the soil environment, their gradual decomposition will lead to the release of CQDs along with the adsorbed heavy metals. Therefore, it is better for CQDs microcarriers to be cost-effective and resistant to degradation. Carbon-based materials can be a suitable option for use as CQDs microcarriers because, in addition to being obtainable from a wide range of organic materials and wastes, due to their hard carbon-rich nature, they are very resistant to microbial degradation and are also biocompatible. Carbon-based materials that are to be used as CQDs microcarriers should preferably have a spherical structure and uniform size. The spherical structure will have low friction with soil particles and will help in their faster mixing with the soil. The uniform size of the spherical microcarriers will also help in their uniform distribution in the soil matrix. The best suggestion for the precursor of spherical carbon-based microcarriers is single-celled microorganisms with spherical and separate cells. These single-celled microorganisms should be photoautotrophic. Photoautotrophs have simple biological needs, and therefore, their cultivation and reproduction will be less costly. Photoautotrophic single-celled microorganisms include single-celled algae, green sulfur bacteria, and cyanobacteria. Cyanobacteria are the most self-sufficient organisms on Earth, and due to their simple growth requirements, they can be used to produce valuable commercial products (Singh et al., 2019). Therefore, the cultivation and reproduction of cyanobacteria are less expensive than other photoautotrophic single-celled microorganisms. In addition to being a suitable precursor for the production of CQDs microcarriers, cyanobacteria also have another advantage that makes them a good precursor for the synthesis of CQDs. Cyanobacteria produce extracellular polymeric substances (EPS), which mainly include exopolysaccharides, proteins, lipids, and even DNA in the form of heteropolymers such as glycoproteins and lipopolysaccharides (Singh et al., 2019; Decho and Gutierrez, 2017). The EPS layer of cyanobacteria covers their cell surface (Singh et al., 2019). Neutral sugars such as glucose, xylose, mannose, and arabinose are abundant in EPS (Singh et al., 2019; Parikh and Madamwar, 2006; Philippis et al., 1998; Gloguen and Palenik, 1995). CQDs can be obtained by the polymerization of saccharides, citric acid, and amino acids (Tuerhong et al., 2017). Therefore, cyanobacteria EPS can be a suitable precursor for the production of CQDs. Since the EPS layer is attached to the cyanobacteria cells, pyrolysis of these cells can simultaneously produce microcarrier particles and CQDs and immobilize them on each other. In this way, all three stages of CQDs composite fabrication are carried out in one step, saving time and cost. In general, CQDs synthesis methods are divided into two categories: bottom-up methods and top-down methods. Bottom-up methods are much more common due to their simplicity and uniformity in the synthesized

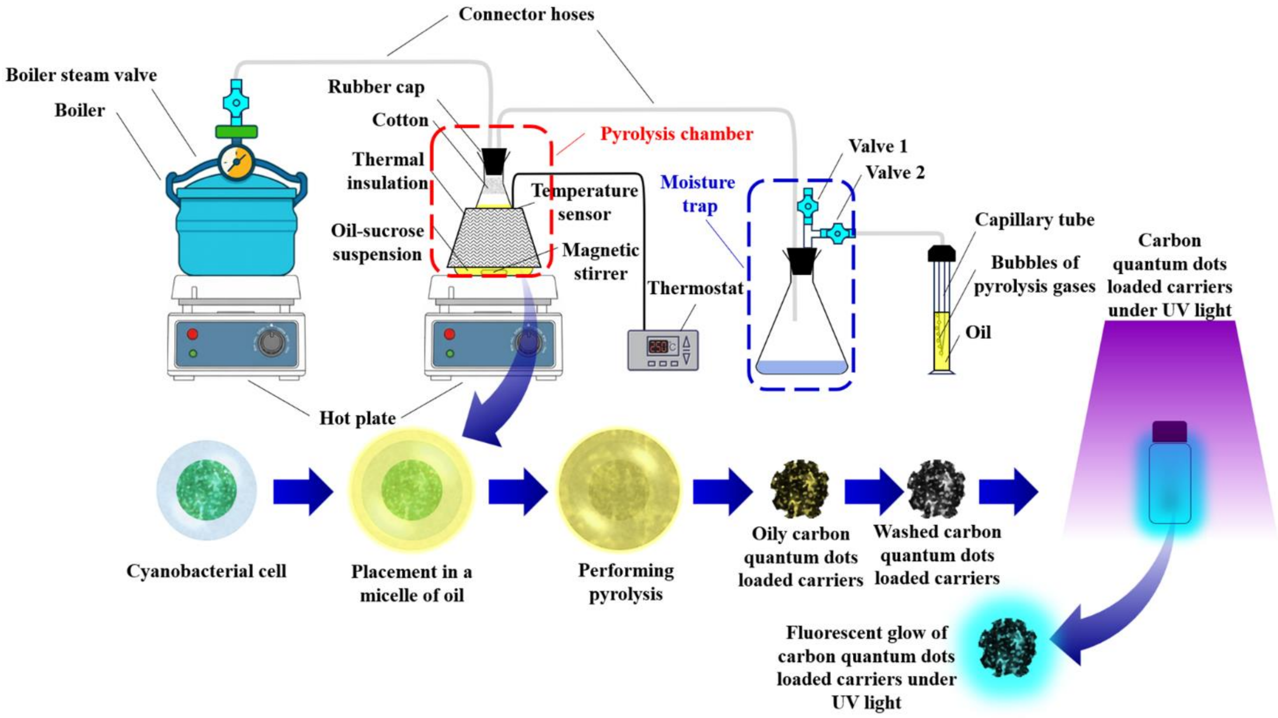

Figure 5. Graphical abstract of the mechanism of converting cyanobacterial cells into CQDs composites.

CQDs. The hydrothermal method is one of the most common bottom-up methods for CQDs synthesis. This method requires expensive and relatively dangerous equipment called a hydrothermal reactor. In this method, the CQDs precursor is dissolved in water and placed inside the hydrothermal reactor, and then it is converted to CQDs under high pressure and temperature. The hydrothermal method is not a suitable method for converting cyanobacteria cells into CQDs composites. The EPS layerof cyanobacteria is hydrophilic, and since the hydrothermal method is carried out in a superheated water medium, the EPS layer dissolves and disperses away from the cell. This causes the EPS and the cell to carbonize separately, and as a result, CQDs are not immobilized on the carbonized cell. On the other hand, the carbonized cells stick together and form a carbonized mass that lacks a granular and separate structure (Khaivari Farid and Rahimi, 2022). Khaivari Farid and Rahimi (2022) designed a specific pyrolysis method called the oilothermal method for converting cyanobacteria cells into CQDs composites (Figure 5). This method, which is carried out in an oil medium, allows each cyanobacteria cell to be placed inside an oil micelle and pyrolyzed separately from other cells. The hydrophobic and non-polar nature of the oil prevents the dissolution and dispersion of the EPS layer away from the cell, so both carbonize together. In this way, CQDs are obtained from the carbonization of EPS, and the microcarrier is obtained from the carbonization of the cyanobacteria cell, and then the resulting CQDs are immobilized on the microcarrier. Khaivari Farid and Rahimi (2022) successfully used the CQDs composite made from cyanobacteria by the oilothermal method for the solid-phase extraction of cadmium.

Also, Mohammadi Aryan et al. (2023) successfully converted a precursor consisting of *Scenedesmus* algae cells treated with cyanobacteria EPS into a CQDs composite using the oilothermal method (Figure 6). They successfully used this composite for the solid-phase extraction of cadmium from an aqueous environment.

4. Conclusion

The remediation of heavy metal-contaminated soils is a necessity for maintaining food security and health, and this necessity requires an appropriate technique. The adsorption technique is one of the most efficient chemical stabilization techniques. Carbon-based materials with high specific surface area are considered suitable adsorbents for the removal of heavy metals. Among carbon-based materials, cyanobacteria, due to the presence of EPS, can be a suitable precursor for the production of CQDs. Because the EPS layer is attached to the cyanobacteria cells, pyrolysis of these cells can simultaneously produce microcarrier particles and CQDs and immobilize them on each other. Given the impossibility of using the hydrothermal method for converting cyanobacteria cells into CQDs composites, the oilothermal pyrolysis method is a very suitable alternative for converting cyanobacteria cells into CQDs composites.

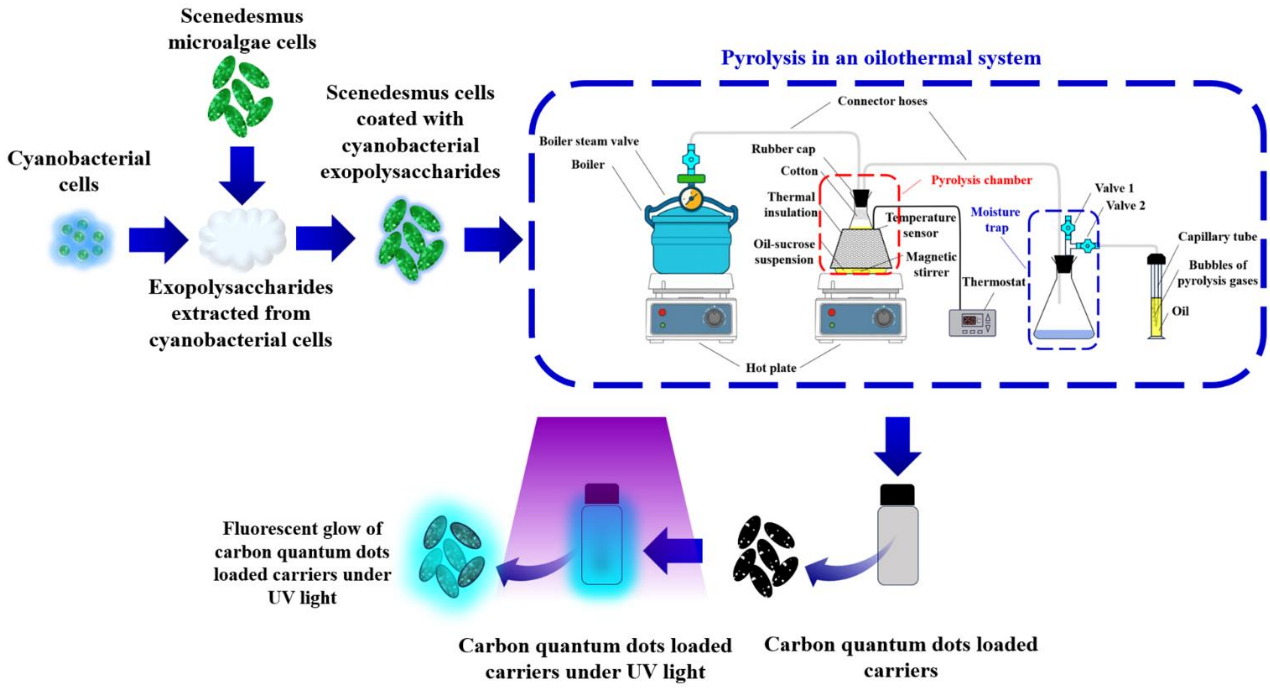

Figure 6. Graphical abstract of the conversion of Scenedesmus algae cells treated with cyanobacteria EPS into CQDs composites using the oilothermal method for use in the solid-phase extraction of cadmium.

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