

Broadening the scope of on-site detection and bioanalytical perspective of toxic elements using fluorescent sensing constructs

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ABSTRACT

The pursuit of industrial and biotechnological revolutions has led to a growing problem of environmental pollution around the world. The fast-growing contamination of numerous environmental matrices is one of the major problems facing humanity due to the controlled and/or uncontrolled discharge of toxic elements from several industrial sectors. Due to several adverse consequences of persistent toxic elements, there is imperative to propose and deploy strategic measures and robust bioanalytical tools with greater efficiency and accuracy to detect a broader range of harmful pollutants. The expansion of pollution detecting tools can further aid real-time and on-site monitoring of the production and release of environmental contaminants in different industrial sectors. Considering the above critiques, the remarkable efforts of various regulatory/legalities authorities are urgently needed to tackle the growing environmental pollution dilemma efficiently. With key scientific and nanotechnological advancements, a unique modality has arisen in fluorescent sensing constructs to effectively sense and monitor this problem. The authentic scientific databases, including Scopus and PubMed, were used to perform the literature survey. For a said purpose, in this paper, a standardized methodology based on inclusion-exclusion criteria was followed to review the literature within the last ten years range to justify the scientific theme of the work and make sure to cover the recent and relevant literature contents.

Introduction

The ever-increasing discharge of environmental pollutants, for example, toxic elements, pharmaceutical residues, antibiotics, synthetic toxic dyes, and leaching pesticides into water matrices, pose severe health and environmental issues. In addition, an array of harmful heavy metal ions has increased much consideration due to severe problems related to health and the environment unreceptive to human and biotic life in the entire living ecosystem. Likewise, the unwanted occurrence of bioactive residues either from pharmaceutical compounds, antibiotics, dyes, or pesticides has been spotted in aquatic environments, including groundwater and surface water matrices [1–7]. Thus, aiming to sustain the environmental matrices, several adequate measures must be taken to control the water pollution [8,9].

Besides other analytical tools, fluorescent sensing constructs have been emerged and proved to be advantageous for monitoring toxic pollutants, even in small sample volumes along with low concentra-

tions of biological components [10,11], which most of the other traditional methods fails to detect. This is primarily due to the deficiency of high-end sensitivity and sample selectivity of in-practice traditional detection processes, thus are considered significant bottlenecks. In addition, chromatography-based procedures limit their on-site deployment and require long time-consuming processes and specialized sample processing. Moreover, several other standard methods that have been extensively used to detect and/or monitor toxic elements include inductively coupled plasma mass spectrometry, cold vapor atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, and electrochemical sensors [12]. However, the above-mentioned standard methods are considered highly selective and sensitive against several analytes. However, several countable limitations restrict their practical use, for instance, low cost-effective (highly expensive), complex in processing and time-intensive, and multi-step sample preparation [13], thus are not suitable for real-time and/or on-site evaluations.

Furthermore, the real-time on-site monitoring could also diminish the disproportionate consumption of harsh chemicals and reagents by

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fulfilling the green analytical chemistry (GAC) principles. Following GAC principles, the development and deployment of on-site detection methodologies are equally important and necessary to improve the quality of chemical analyses. Thus, notable efforts are being made to lessen the negative impression of chemical analyzes on the environment and allow the execution of justifiable progress in analytical measures [14]. In this regard, low-cost and highly efficient fluorescent sensing constructs (sensors) equipped with GAC principles can monitor toxic pollutants in real-time with little or no chemical involvement and minimum time consumption, thus ideal for aquatic and biotic environmental monitoring. Considering the advantages, unremitting efforts have been considered to engineer robust sensors for on-site and/or real-time toxic pollutants detection without lengthy sample preparation procedures [15,16]. Among various sensor types, fluorescent and visual-based sensors are the most appropriate for low-limit detection and high-end sensitivity and sample selectivity. Intercellular detection is another important advantage of fluorescent sensors compared to traditional methods [17].

On-site detection and bio-analytics – a drive towards optimum performance

The term ‘on-site’ covers several necessary considerations while discussing the importance of on-site applications to meet the sustainability concept of the modern world. It can be defined as a synergistic system in which excretions full of waste entities and wastewater loaded with polluting agents, such as toxic elements, bio-actives from pharmaceuticals, antibiotics-based bioactive residues, and pesticide compounds are collected and treated at a particular place or site, where they are generated. By considering the various types of rising environmental pollution issues and their adverse health impacts, first the on-site detection, and then second a facile treatment of polluting agents that persist

in groundwater and surface water are important to green our environment for a better tomorrow. Several polluting agents, including toxic elements, bio-actives from pharmaceuticals, antibiotics-based bioactive residues, and pesticide compounds, are closely linked to anthropogenic activities. Most environmentally-related pollutants, e.g., pharmaceutically active compounds (PhACs) are mainly transported through water matrices [1,18]. Fig. 1 shows possible sources of PhACs contamination and various biocatalytic treatment units [1].

On-site wastewater treatment is usually secondhand in zones with relatively low uptown density, and central wastewater treatment is expensive. The on-site detection/monitoring and treatment process must start at the point resource of contaminants before their discharge into the aquatic environment [16]. Considering the free flow transportation of PhACs, as shown in Fig. 1, on-site detection/monitoring and treatment is crucial to preventing these hazardous pollutants from spreading over all aquatic environments. Such on-site practices will help (1) to effectively mitigate or at least minimize the pollutant concentrations to acceptable levels before released into water matrices, (2) to prevent water cycle contamination, (3) to provide a safe living ecosystem for all living beings, (4) to share real-time monitory information to regulatory/legalities authorities, and (5) finally, to take appropriate action about the release of an unacceptable level of contaminants into water bodies to avoid unexpected contamination, which unless otherwise will impact adversely.

Detection and monitoring – conventional vs. fluorescent sensing constructs

Many pollutants of emerging concern have been detected and monitored from numerous water matrices by deploying conventional treatment systems [19,20]. Inappropriately, several in-practice remediations

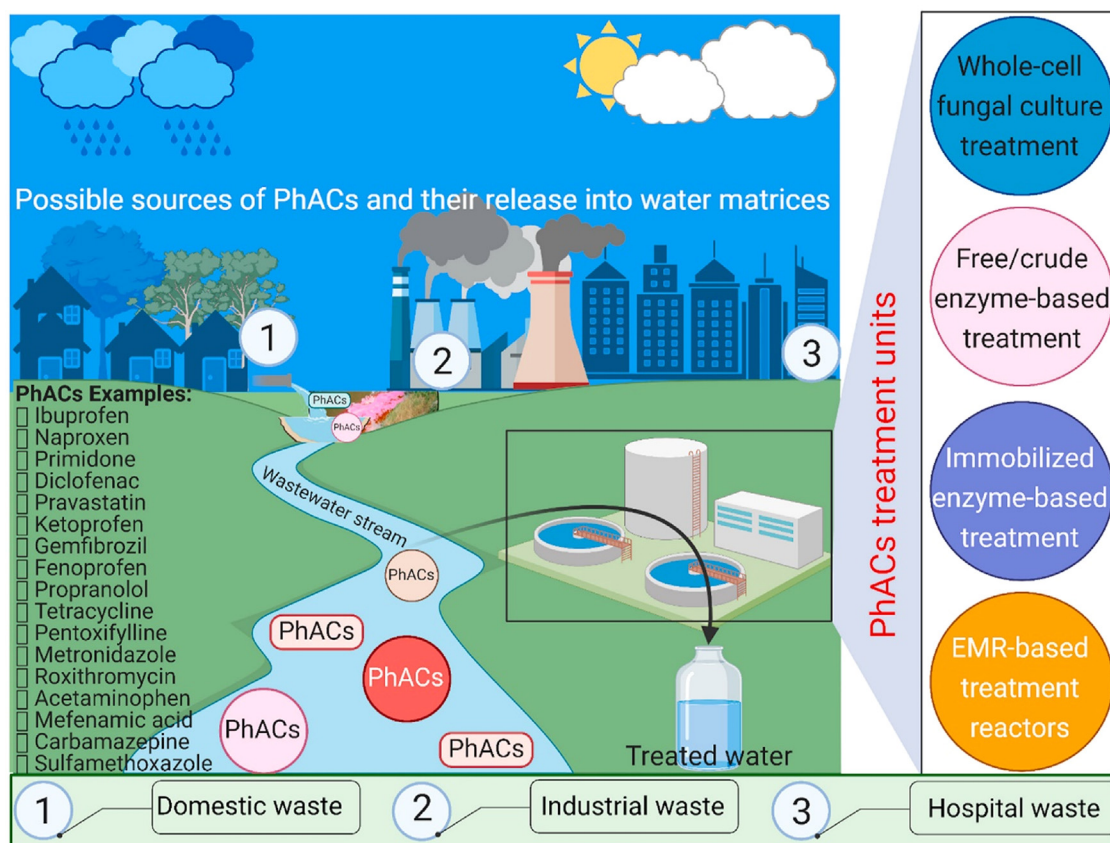


Fig. 1. Possible sources of PhACs contamination and various biocatalytic treatment units. Reprinted from Ref. [1] with permission from Elsevier. License Number: 5303770471091.

and monitoring systems are inadequate to detect and/or mitigate environmental pollutants from environmental matrices [21–24]. Consequently, the expansion of new frontiers and robust materials with efficient detection and catalytic attributes are equally required, which subsequently led to the use of carbon-based nanomaterials in the form of fluorescent sensing constructs, e.g., carbon dots (CDs) [22]. Indeed, the most widely used carbon nanomaterials for water remediation are carbon nanotubes and graphene-based nanomaterials. However, as a new alternative to already explored materials, CDs have gained much attention in recent years. CDs, termed carbon quantum dots (CQDs), or carbon nanoparticles (CNPs), have been represented as a new class of carbon-based nano-constructs that offer numerous characteristic attributes, such as stable fluorescence properties, solid optical features, significant biocompatibility, low-cost preparation from waste materials (e.g., via pyrolysis of waste tiers), great aqueous solubility, notable recyclability among others [25–28]. CDs are largely quasi-spherical NPs encompassing amorphous to nanocrystalline appearance. From the chemistry and functional group perspective, CDs always comprise sp^2/sp^3 carbon, oxygen/nitrogen-based groups, and post-modified chemical groups [29]. The above-mentioned functional groups in CDs are tunable to enhance further and impart fluorescent properties. For instance, the condensation reaction, chemical manipulations, or, most commonly doping with other elements, such as nitrogen, boron, and phosphorus, can induce the photoemission of CDs. The above-mentioned multi-functional characteristic of these newly emerged materials, i.e., CDs/CQDs/CNPs, make them ideal candidates for more comprehensive spectrum applications, e.g., sensing, monitoring, bioimaging, bioanalytical, biocatalysis, and other photo-related applications. In recent past, various review articles have been reported in the literature that have been comprehensively report the synthesis aspects of CDs, tunable functionalization, and various applications [26,27]. However, a focused review on the detection and monitoring or decontamination of environmental matrices using CDs remains unavailable in the literature.

CDs-assisted sensing of toxic elements

The occurrence of various toxic elements is a foremost environmental issue faced by the world's population. Rapid industrialization primes the ongoing manufacturing expansion, which also causes a perpetual surge of metal concentration in different environmental matrices. This is mainly due to the inappropriate disposal and dumping of industrial waste products directly/indirectly into water bodies and land areas [30]. Metals in bulk can be toxic to all living forms, including microorganisms, plants, animals, and humans. Additionally, they can enter the environment through water and soil, where they can bioaccumulate for a long time and through agricultural routes can reach humans. Accumulation of toxic metals into the human body creates severe health consequences such as growth and developmental abnormalities, neuromuscular defects, and failure of metabolic activities [31]. Major consequences and adverse health effects of some model toxic elements are shown in Fig. 2.

Considering the above critiques, it is necessary to standardize measures for on-site detection of toxic elements. CDs have emerged as new robust materials with multi-functional sensing and catalytic potentialities. CDs have revealed prodigious capabilities to sense metal ions because of their tunable fluorescence (FL) attributes, water solubility, biocompatibility, and ease in surface modification, among others [26]. Nevertheless, primeval CDs characteristically report low values of FL quantum yield and high chances of contamination, which hinder their practical applications [32,33]. Therefore, the synthesis of CDs with high FL quantum yield through scalable processes has been recently the focus of research [32]. To enhance the FL properties of CDs and their performance for metal sensing applications, researchers have explored different strategies, including element doping and surface passivation (Fig. 3). For most CDs-based FL sensors, metal ions are detected by a turn-off FL response, either via static or dynamic quenching. Ferric ions (Fe^{3+}) could sensitively and selectively quench the FL of CDs, with a detection

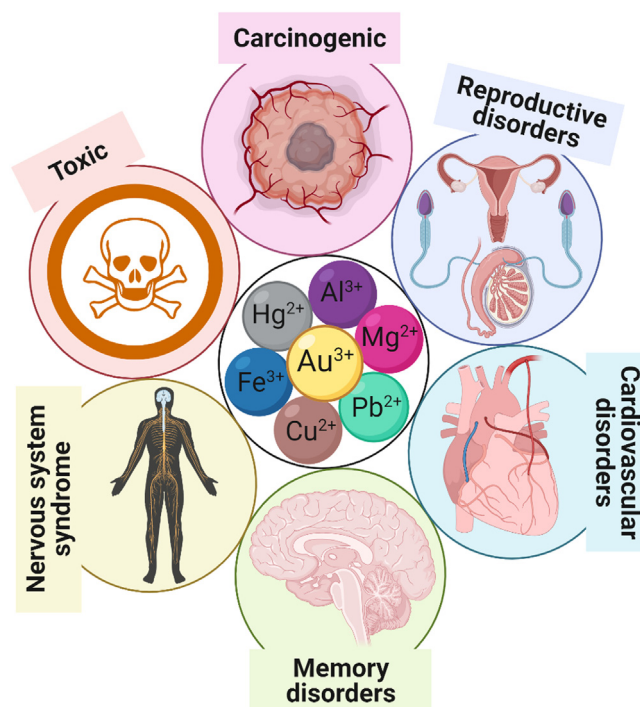


Fig. 2. Major consequences and adverse health effects of some model toxic elements. Created with BioRender.com and extracted under premium membership.

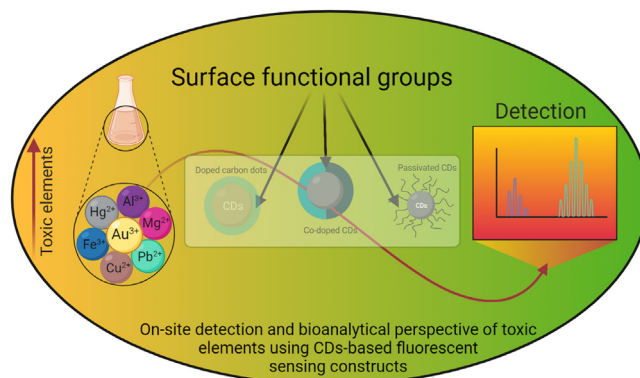


Fig. 3. Strategies to enhance the on-site detection and bioanalytical perspective of toxic elements using CDs-based fluorescent sensing constructs. Created with BioRender.com and extracted under premium membership.

limit of $18 \mu M$. The strong interplay between Fe^{3+} ions and some surface functional groups of CDs, such as hydroxyl groups, majorly supports the quenching phenomena. Furthermore, the FL quenching may be donated to nonradiative electron transfer the intricate transfer of electrons in the excited state to the d orbital of Fe^{3+} . Additionally, the on/off FL in Fe^{2+}/Fe^{3+} medium could be attained via an oxidation mechanism. The recognition of Fe^{3+} ions through a visible FL-based process would significantly benefit. The meaningfully abridged lifetime after adding Fe^{3+} ions indicated dynamic quenching during the sensing process. Radhakrishnan et al. [34] fabricated fluorescent CDs, as a multi-functional sensor that can selectivity detect different metal ions, including mercury ions (Hg^{2+}), copper ions (Cu^{2+}), lead ions (Pb^{2+}), and ferric ions (Fe^{3+}). As developed CDs were first surface-functionalized using different organic precursors (L-cysteine (N, S), ethylenediamine (N) and glycine (N, O)). The surface tuned CDs were designated IDs as N,S/Iy-CDs, N/Iy-CDs and N,O/Iy-CDs (passivated CDs). Among all developed CDs, Iy-CDs displayed selectivity for Hg^{2+} with a detection limit of 3.3 nM. While, N,S/Iy-CDs, N/Iy-CDs, and N,O/Iy-CDs showed high selec-

Table 1
Sensing mechanisms followed by CDs on the detection of different metal ions. Reprinted from Ref. [36] with permission from Elsevier. License Number: 5303770832971.

| CDs/GQDs | Mechanism | Metal ion | Linear range (μM) | LOD (μM) | Refs. |
|----------|----------------|------------------|--------------------------------|-----------------------|--------------------|
| CDs | Turn-off (SFQ) | Hg ²⁺ | 0 – 0.025 | 0.0033 | [34] |
| | | Cu ²⁺ | 0 – 30 | 0.045 | |
| | | Pb ²⁺ | 0 – 0.2 | 0.27 | |
| | | Fe ³⁺ | 0 – 0.60 | 6.2 | |
| CDs | Turn-off (SFQ) | Fe ³⁺ | 0.025 – 100 | 0.0055 | [38] |
| | | Hg ²⁺ | 0.01 – 100 | 0.075 | |
| CDs | Turn-off (SFQ) | Hg ²⁺ | 0.1 – 60 | 0.0187 | [39] |
| CDs | Turn-off (SFQ) | H ⁺ | 4.45 – 7 | NR | [40] |
| CDs | Turn-off (SFQ) | Fe ³⁺ | 0 – 2 | 70 | [41] |
| CDs | Turn-off (SFQ) | Fe ³⁺ | 0 – 3000 | 0.14 | [42] |
| CDs | Dynamic FQ | Pb ²⁺ | 0.01 – 0.03 | 0.014 | [43] |
| CDs | Turn-off (SFQ) | Hg ²⁺ | 0.35 – 0.442 | 0.3 | [35] |
| CDs | Turn-off (DFQ) | Fe ³⁺ | 0.06 – 10 | 0.039 | [44]. |
| | | Cr(VI) | 0.5 – 50 | 0.386 | |
| CDs | Turn-off (SFQ) | Cu ²⁺ | 0.01 – 0.1 | 0.0119 | [45] |
| CDs | Turn-off (SFQ) | Fe ³⁺ | 3 – 60 | 0.31 | [46] |
| | | Cu ²⁺ | 0 – 15 | 0.056 | |
| CDs | Turn-off (DFQ) | Fe ³⁺ | 0.05 – 5e ⁺⁶ | 50000 | [47] |
| CDs | Turn-off (SFQ) | Cu ²⁺ | NR | NR | [48] |
| | | Ag(I) | | | |
| CDs | Turn-off | Fe ³⁺ | 1.0-60 | 0.28 | [49] |
| CDs | Turn-off | Cr(VI) | 5-200 | 4.16 | [50] |
| GQDs | Turn-off (SFQ) | Pb ²⁺ | 33-8000 | 50 | [51] |
| GQDs | Turn-off | Hg ²⁺ | 10-100 | 0.09 | [52] |
| GQDs | Turn-on | Hg ²⁺ | 0.005-0.625 | 0.05 | [53] |
| GQDs | Turn-off | Hg ²⁺ | 2.5-800 | 2.5 | (Liu et al., 2019) |

Abbreviations: CDs (carbon dots); GQDs (graphene quantum dots); SFQ (static fluorescence quenching); DFQ (dynamic fluorescence quenching); LOD (limit of detection); NR (not reported); QY (Quantum yield).

tivity for Cu²⁺, Pb²⁺ and Fe³⁺ with lower detection limits, i.e., 0.045, 0.27 and 6.2 μM , respectively [34]. Cai et al. [35] detected mercury ions using CDs as Turn Off-On fluorescent sensors, with the detection limit of mercury (II) as low as 0.41 μM . Table 1 summarizes the most recent studies on carbon dots indicating the sensing mechanism for detecting different metal ions [36]. Fig. 4 shows schematic illustration of “turn off-on” fluorescence response of CDs to detect Fe³⁺ and Cd²⁺ as representative metal ions [37]).

CDs-assisted sensing of PhACs

PhACs are complex organic compounds that have been primarily developed and used as medicinal drugs to treat medical conditions, both simple and complex. Undoubtedly, PhACs have had an optimistic impact on longevity and human health. However, their excessive and misuse practices also lead to environmental pollution consequences due to their direct/indirect release into water bodies via industrial wastewater

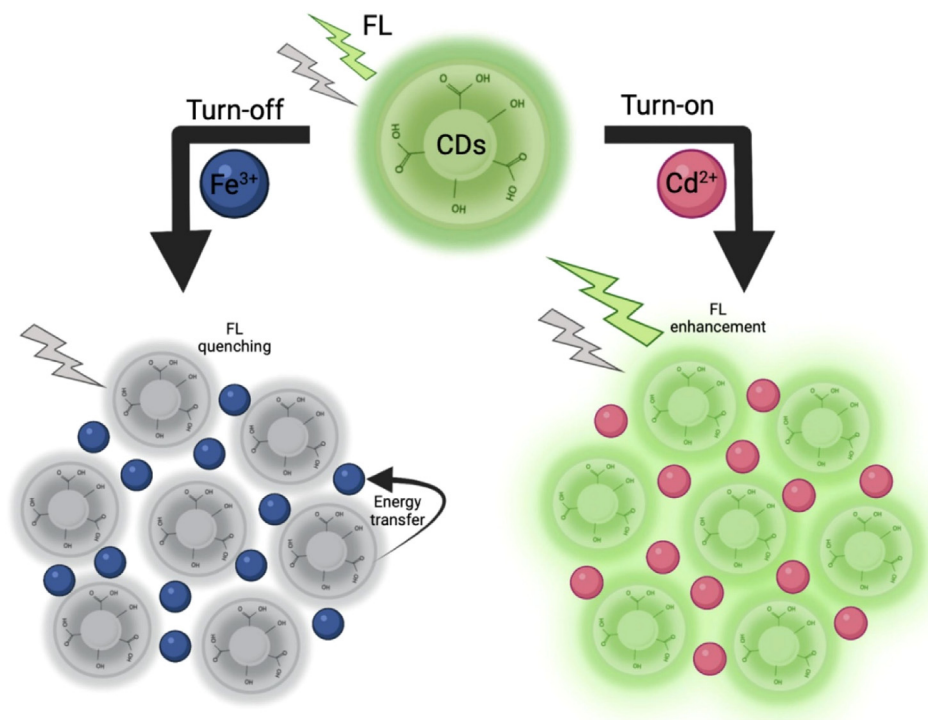


Fig. 4. Schematic representation of (a) “turn-on” and (b) “turn-off” fluorescence response for the detection of Fe³⁺ and Cd²⁺ as representative metal ions. Abbreviations: CDs – carbon dots, FL – fluorescence. Created with BioRender.com and extracted under premium membership. Reprinted from Ref. [37] with permission. License Number: 5303770667621.

Table 2
CDS-assisted sensing of PhACs.

| CDS type | Sample | Mechanism | Detected drug | LOD (μM) | Refs. |
|----------------------|---------------------------------|-------------------------------------------------------|-------------------|-----------------------|-------|
| Nitrogen-doped CDS | Human serum and urine samples | Light-induced electron transfer and dynamic quenching | Baicalin | .0438 | [57] |
| Nitrogen-doped CDS | Solution | Fluorescence quenching | Tetracycline | 0.39 | [56] |
| Nitrogen-doped CDS | Solution in ultra-pure water | Fluorescence quenching | Tetracycline | 0.6 | [58] |
| Nitrogen-doped CDS | Real samples | Fluorescence quenching | Metronidazole | 0.22 | [59] |
| Nitrogen-doped CDS | Water | Fluorescence quenching | Tetracycline | 0.2367 | [60] |
| Nitrogen-doped CQDs | Tap water | Fluorescence quenching | Chlortetracycline | 0.2791 | |
| | | | Tetracycline | 4.9363 | |
| | | | | 15.642 | |
| | | | | 25.8553 | |
| | Tap water | Fluorescence quenching | Tetracycline | 4.8497 | |
| | | | | 14.497 | |
| | | | | 24.2384 | |
| Blue emitting CDS | Water based solution | Fluorescence quenching | Metronidazole | 2.67 μM | [61] |
| | | | Doxycycline | 13.48 μM | |
| | | | Tetracycline | 0.53 μM | |
| | | | Chlortetracycline | 6.28 μM | |
| | | | Oxytetracycline | 8.47 μM | |
| | | | Chloramphenicol | 1.17 μM | |
| | | | Sulfadiazine | 11.24 μM | |
| Photoluminescent CDS | Water based solution | Turn-on system | D-Penicillamine | 0.085 μM | [62] |
| CQDs | Solution (0–400 μM) | Fluorescence enhancement | Amoxicillin | 0.475 | [63] |
| Aptamer-based CDS | Amino-modified kanamycin | Fluorescence quenching | Kanamycin | 1.1 | [64] |

streams, household sanitary sewages, and biomedical waste streams. So far, several methods have been developed and deployed to detect, treat and mitigate PhACs from different environmental matrices, and each of them has its own merits and demerits [8,4]. The sustainable detection of PhACs in water matrices demands environmentally friendlier materials and methods to be easily detected on-site before being discharged intentionally or unintentionally. In this context, there have been several research efforts and reports on the facile synthesis of CDS as robust sensing constructs ([25,27] and also deployed to detect PhACs and other related environmental pollutants [54,55]. Akhgari et al. [54] fabricated CDS via one-pot synthesis and directly used them as fluorophores to detect cefixime (CEF), a third-generation cephalosporin antibiotic, based on the inner filter effect (IFE). CEF is being primarily used to treat urinary tract infections, which ultimately leads its way to the domestic sanitary sewages, thus requiring attention for monitoring low levels of CEF. Recently, Yuan et al. [56] developed a nitrogen-doped CD and tested it to detect tetracycline, the most common antibiotic used in human and animal husbandry practices, with 0.39 μM (LOD). Upon oral administration, tetracycline is challenging to be absorbed fully by the intestines and stomach. Thus, leftovers are discharged into the sewage in the form of the parent compound, which causes irreversible damage to the natural environment. Table 2 summarizes the most recent studies on CDS indicating the sensing mechanism and detection of different PhACs.

Current challenges

The great potential of CDS in environmental monitoring is mainly attributed to their fascinating characteristics like their unique physicochemical properties, affordability, high biocompatibility, and eco-friendliness. However, to achieve practical applicability in real wastewater samples, some challenges of current concern should be addressed. For instance, the wide variety of raw materials or precursors and the many possible synthetic approaches lead to uncertainty or difficulties in understanding CDS' properties. In addition, the effects of CDS released into the environment on biological populations and ecosystems have been uncommonly researched. Therefore, CDS' biological toxicity and ecological effects should be considered for further research.

The literature reports various synthesis techniques for producing CDS with variable properties. Researchers have been exploring innovative, green, and straightforward synthetic strategies to fulfill the requirements of affordable and eco-friendly CDS for multiple applications. In this regard, further efforts should be conducted to use natu-

ral biomass/waste materials as the carbon source and understand their consequent tuned properties. Moreover, improvements in the synthesis treatments should focus on reducing requirements like high temperatures, energy consumption, and solvents while considering ease of operation, scalability, reaction time, and environmental impact.

Significant advancements have been made in developing CDS-based sensory platforms; however, there are still some challenges to overcome. Wastewater is typically a complex mixture of pollutants; thus, CDS-based sensors with an independent detection of multiple metal ions and anti-interference capacities are highly desired. Also, future studies should consider the effect of parameters such as co-existing molecules and different pH values. Indeed, the performance of CDS' in real and complex water systems should be examined in detail. Similarly, further efforts should be conducted to shed light on understanding the mechanisms involved in the selectivity of the metal ions. Strategies to improve recoveries and reusability of CDS fluorescent probes should also be explored. In this regard, CDS' immobilization into solid substrates could represent an alternative to developing commercial tests.

Conclusions and recommendations

In conclusion, the current advances in CDS as fluorescent sensing constructs with multi-functional characteristic attributes make them ideal candidates for sensing applications. The effects caused by the selection of precursors and synthesis methods on CDS' sensing potential, the mechanisms involved in CDS' ability to detect environmental pollutants, including toxic elements and related PhACs, and the strategies to enhance their optical features and overall sensing performance are all equally important to be considered in future studies. In this context, CDS surface functionalization via doping and surface passivation epitomize excellent replacements to improve the performance of CDS, reaching superior FL quantum yields and high sensitivity. However, considering the great demand for affordable, accurate, and sustainable fluorescent probes for environmental monitoring, the current challenges of CDS require attention. For instance, some key directions are recommended as follows: (1) the optimization of the response in real and complex water samples, (2) an in-depth understanding of the mechanisms involved in the selectivity of metal ions, (3) an in-depth understanding of the mechanisms involved in the selectivity and sensitivity of PhACs and related environmental pollutants, (4) the development of strategies to improve recoveries and reusability of CDS-based fluorescent probes; and 5) the evaluation of the ecological effects caused by the application of CDS.

Likewise, some of the key characteristics that distinguish PhACs pollutants from conventional pollutants must be considered while directing future research with on-site detection measures. For instance, (1) PhACs extant widespread variations based on molecular weight, structural, functional, and shape that can limit the deployment of a single type CDs sensing constructs; (2) some of the PhACs are polar and accompanied by ionizable groups, thus are highly dependent on the pH of the medium, which could influence the detection interaction of CDs, and (3) PhACs undergo metabolic reactions which modify their chemical structure and even released in super low concentrations making them challenging to detect.

Declaration of Competing Interest

The authors declare that there is no conflict of interest to express.

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