

A review on functionalized fluorescent nanomaterials for detection of heavy metals in wastewater

Ritika Berry^{a*}, Jagdeep Kumar^a, Fanyana Mtunzi^b, Nishtha Paul^c

^a Department of Chemistry, University Institute of Sciences, Chandigarh University, Gharuan, Mohali, Punjab, India

^b Institute of Chemical and Biotechnology, Vaal University of Technology, Vanderbijlpark, South Africa

^c Department of Biosciences, University Institute of Biotechnology, Chandigarh University, Gharuan, Mohali, Punjab, India

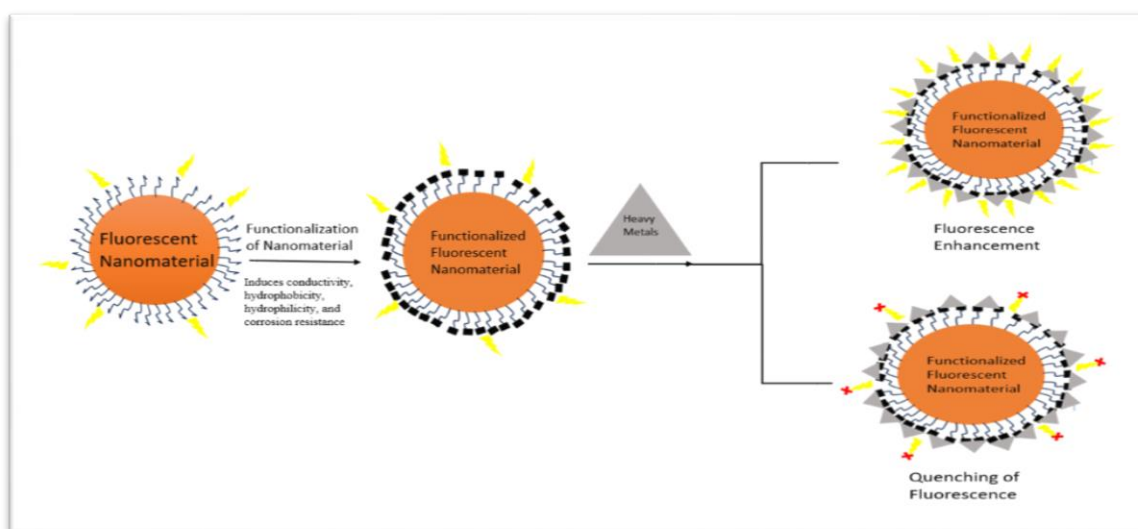
Email-berryratika05@gmail.com

Abstract:

Water contaminated by heavy metals is one of the worst health hazards for human driven mainly from natural disasters and anthropogenic activities. Heavy metals disrupt metabolic pathways and also induce phytotoxicity in plants affecting growth, development, metabolism. Traditional techniques for measuring heavy metals are effective, but they often fall short in sample preparation and analysis time. Such an approach opens cost-effective and efficient options based on advanced protocols utilizing fluorescent chemosensors, nanomaterials. The most widely used nanomaterials for this purpose are functionalized fluorescent units (carbon dots, QDs) that change the fluorescence intensity in response to trace ions by either enhancing or quenching it. Besides, metal nanoclusters, nanoparticles and metal-organic frameworks (MOFs) can also be employed for heavy-metal selective detection in an increasingly sensitive way. So far, such methods provide economically viable and effective ways to mitigate water contaminations with heavy metals which is important for safe/common exploitation of public drinking sources.

Keywords: Heavy metals, Nanomaterials, Functionalized Fluorescent nanomaterials, Carbon dots, Quantum dots, Metal nanoclusters, Metal Nanoparticles, Metal-organic frameworks (MOFs)

Graphical Abstract:



Introduction:

One of the biggest health hazards to humans in today's era is caused due to the contamination of water with heavy metals[1]. Numerous natural calamities, such as volcanic eruptions, metal corrosion, soil erosion, and rock weathering, can lead to heavy metal production [2]. Even anthropogenic effects like industrial waste, discharge from sewages and drains, and use of fertilizers can lead to the higher emergence of heavy metals[3]. These heavy metals may affect plant and human health in various aspects, as described below. In humans, the use of heavy metals may disrupt the body's metabolic functions in several ways. They may cause disturbances in body functioning by accumulating in essential organs such as the kidney, heart, and liver[4]. In plants, these metals enter through roots. Their accumulating and absorbing power depends on many key elements such as moisture, pH, temperature, and organic matter. Heavy metals are highly toxic. They cause phytotoxicity in plants which has an adverse effect on plant growth, yield depression accompanying reduced nutrient uptake, and disturbance in plant metabolism [5].

Certain essential heavy metals, such as Zinc (Zn) and Copper (Cu) contribute to biological activities in the human body. As excess of everything is bad; hence, when present in higher concentrations, these metals may become toxic while some other metals like Cadmium (Cd) and Lead (Pb) even at lower concentrations are hazardous toxins[6]. The threshold limits of a few metals in wastewater recommended by the World Health Organization (WHO) are given in Table 1[7].

Heavy Metal	Threshold Limit (in ppm)
Cadmium (Cd)	0.003
Lead (Pb)	0.01
Chromium (Cr)(hexavalent)	0.05
Nickle (Ni)	0.02

Table 1: Threshold limits for certain heavy metals

Various conventional techniques such as Atomic Absorption Spectroscopy (AAS), Anodic Stripping Voltammetry (ASV), UV/Vis Spectroscopy, Liquid Chromatography, X-ray Fluorescence Spectroscopy (XFS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Capillary Electrophoresis (CE) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) are used to detect heavy metals, although these techniques have selectivity and sensitivity for the entire information; however, they possess certain drawbacks, such as monotonous preparation of the sample, calibration, and pre-concentration techniques, require a professionally skilled person with great knowledge, costly equipment's, and greater analysis time [8], [9], [10], [11]. An easier, cost-effective, and advanced method i.e., the use of fluorescent chemosensors for the detection of heavy metals[12]. Due to high catalytic activity efficiency, huge surface area, and excellent absorption capacity sensors based on nanomaterials have greater potential to detect heavy metals more efficiently[13].

1. Nanomaterials

Nanomaterials are materials whose size or at least one of the dimensions lies in the range of 1-100 nanometers[14]. The breakthrough in 1985 and 1991 with the evolution of C₆₀ and carbon nanotubes respectively served as a real stimulus for the advancement of nanomaterials this made scientists more eager and keener to explore the uses of these materials[15]. These materials have distinctive physical and chemical properties such as conductivity, composition, light absorption, emission properties, ductility, magnetism, and size which makes them more appealing [16]. With advancements in nanotechnology, nanomaterials have been meticulously designed and forged for heavy metal detection[17]. Graphene-based, Gold or Silver or Copper nanoparticles, Carbon dots, and Metal nanoclusters are some of the frequently used nanomaterials for heavy metal identification[18]. Plants and microbes have the ability to gather and absorb metal ions from their surroundings, making them suitable candidates for the production of nanomaterials[19].

2. Functionalization of nanomaterials

To understand the full potential of a nanomaterial, it is necessary to functionalize it, which can simply be achieved by two methods i.e., Direct Functionalization (which may include covalent, noncovalent, inorganic, and functionalization by heteroatom doping) and Indirect Functionalization (Grafting). It may induce conductivity, hydrophobicity, hydrophilicity, and corrosion resistance to the nanomaterial[20], [21]. Surfaces of certain conventional nanomaterials (like nano-silica, metallic nanoparticles, and carbon-based nanomaterials, etc.) have been modified and are explored to determine their viability for solid-phase metal adsorbents[22]. For example, W. Yantasee *et al.*, and her team developed a new dispersible sorbent that can be magnetically collected and has a high capacity and selectivity for heavy metals (like Pb, Ag, Cd, Cu, and Hg) by functionalizing the Iron(II, III) oxide(Fe₃O₄) nanoparticles with Dimercaptosuccinic Acid (DMSA) [23].

Similarly, Maleki *et al.* and his team functionalized the magnetic nanoparticle (Fe₃O₄) with the Polyamidoamine dendrimers (PAD) for the detection of Lead (II) and Cadmium (II) ions even in trace amounts (i.e., having detection limit around 0.17 ng mL⁻¹ and 0.21 ng mL⁻¹ respectively). As compared to other dendrimers, polyamidoamine dendrimers are particularly used for the detection of heavy metals present in water (like rivers, lakes, and wastewater) because they possess structural uniformity and numerous functional terminal groups [24].

Frost *et al.* used a very cost-effective and highly sensitive (having LOD 25ng/L) method for the selective determination of lead (II) ions in aqueous samples by citrate-functionalized gold nanoparticles [25], likewise Mehta *et al.* also used gold nanoparticles but functionalized it with chitosan dithiocarbamate, which in turn forms complex only with Cd²⁺ ions present inside wastewater (making it sensitive and selective for Cd²⁺ even at a low volume of sample i.e., up to 63nM) [26]. Also, for the selective detection of Cu²⁺ in aqueous samples, gold nanoparticles functionalized with β-cyclodextrin were used by Bindhu *et al.*, which in turn-maintained particle size and controlled aggregation of the AuNPs [27].

Functionalized Fluorescent Nanomaterials

Various fluorescent nanomaterials, such as quantum dots, gold nanoparticles, carbon dots, Fe₃O₄ nanoparticles, and TiO₂ nanoparticles, are employed for detecting trace amounts of heavy metal ions. These detections are achieved through the mechanisms of fluorescence enhancement or quenching. The core principle of fluorescence-based detection hinges on the

interaction between the metallic targets and the nanomaterials. This interaction can significantly alter the fluorescent properties of the nanomaterials, resulting in observable changes such as shifts in fluorescence wavelength, fluorescence quenching or enhancement, ratiometric fluorescence output, and changes in anisotropy. These alterations provide a sensitive and effective means of identifying and quantifying heavy metal ions in various samples. [28] [29].

3.1 Carbon Dots:

In 2004, Xu et al., while purifying the carbon nanotubes, accidentally obtained a fluorescent carbon nanoparticle, later which was named “Carbon Dots” by Sun et al in the year 2006.[30], [31] Carbon dots are nanosized fluorescent carbon compounds with one dimension smaller than 10 nm, that can be obtained from a variety of carbon materials, including carbon nanotubes, graphene, graphite, and fullerenes[32]. They exhibit tremendous properties such as good biocompatibility, unique optical properties, inertness, low cytotoxicity, excellent photoluminescence emission, great aqueous stability, facile synthesis, etc, and also have an appropriate band gap to act as fluorescent materials, which macroscopic carbon materials lack [30], [31], [33], [34]. Carbon dots (CDots) are characterized by their pronounced luminescence and compact size, comparable to that of traditional Quantum Dots (TQDs). Furthermore, C Dots possess distinctive advantages, including elevated conductivity, low toxicity, and favorable aqueous dispersibility, which are typically not present in TQDs [35].

Carbon dots have emerged as a highly cost-effective option for heavy metal sensing due to their straightforward one-step synthesis process, which utilizes affordable carbon raw materials. Bhatt et al. demonstrated an innovative green synthesis route for fluorescent carbon dots using ascorbic acid and urea. The synthesized carbon dots exhibit a surface rich in functional groups such as hydroxyl, amide, and carboxyl, as verified by IR and XPS analyses. These functional groups interact with metal ions, forming network structures or aggregates that result in fluorescence quenching. This property enables the carbon dots to selectively detect Hg^{2+} and Cu^{2+} ions in aqueous media, with impressive limits of detection at 250 nM and 200 nM, respectively. The high sensitivity, coupled with the eco-friendly and cost-effective synthesis, underscores the potential of carbon dots in advanced environmental monitoring and heavy metal detection [36].

Similarly, Song et al. achieved the synthesis of biocompatible fluorescent carbon quantum dots via a hydrothermal reaction, utilizing wool keratin as a precursor. Their study unveiled a selective fluorescence quenching effect induced by Fe^{3+} and Cr^{6+} ions. Notably, among these ions, carbon dots exhibited heightened sensitivity towards chromium ions, establishing them as a preferential choice for chromium ion detection in chromium-rich electroplating wastewater. The influence of iron on this sensitivity was observed; however, this effect can be mitigated through the addition of acid. [37].

This groundbreaking work aligns with recent advancements in analytical methodologies, exemplified by the study conducted by Xiao et al.. 2020, and their collaborators. They introduced an innovative Android application, the SBR-App, designed to streamline the conversion of fluorescence changes (ΔI) into digital signals, facilitating the generation of comprehensive reports and the display of quantitative results. Employing a fluorescent detector integrated with smartphones and a microassay based on fluorescent carbon dots, this smartphone-based system demonstrated highly sensitive and specific simultaneous detection

of Hg^{2+} , Pb^{2+} , and Cu^{2+} ions in aqueous media, particularly in samples collected from the Pearl River. Renowned for its cost-effectiveness, reliability, ease of use, and portability, this smartphone-based system plays a pivotal role in establishing a comprehensive monitoring system for water drainage and pollution [38].

In a similar vein, P. Paneerselvam et al., 2018, synthesized fluorescent carbon dots using *Coccinia indica*, with self-passivated CDs exhibiting selectivity for Hg^{2+} ions having a detection limit 3.3 Nm. Meanwhile, passivated CDs functionalized with different organic precursors (like: L-cysteine (N, S), ethylene diamine (N), and glycine (N, O)) displayed selectivity for ferric ions (Fe^{3+}), lead ions (Pb^{2+}), and copper ions (Cu^{2+}) with lower limits of detection of 6.2, 0.27, 0.045 μM , respectively. This diversification in selectivity, coupled with varying detection limits, underscores the versatility and applicability of fluorescent carbon dots in environmental monitoring [39].

Similarly, Ramamurthy et al., 2017, expanded the scope of fluorescent carbon dots synthesis by utilizing waste-expanded polystyrene (EPS). The resulting multi-functionalized fluorescent CDs demonstrated remarkable sensitivity and selectivity for Au^{3+} ions with a detection limit of 53 Nm, further illustrating the potential of these nanomaterials in advancing analytical methodologies for heavy metal ion detection [40].

In line with these studies, Han et al. (2019) developed a highly selective and sensitive fluorescent sensor for the detection of Hg^{2+} ions, presenting a significant contribution to the field of heavy metal ion detection. Their sensor utilized carbon dots functionalized with sulfhydryl (HS-CDs), which, when interceded with Ag^+ ions, produced brown aggregates of silver-thioate precipitates, resulting in fluorescent quenching. However, upon the addition of Hg^{2+} ions, fluorescence was regained due to the energy traps provided by the amino (NH_2) groups when amalgam was formed. This amalgamation process decreased the presence of unbound Ag^+ and Hg^{2+} ions, thereby limiting their capacity to re-bind with carbon dots and preventing fluorescence quenching [41].

3.2 Quantum Dots:

Quantum dots often referred to as “Artificial atoms” were initially identified within a glass matrix by Alexey Ekimov in the year 1981. Four years later, Louis Brus successfully synthesized the first colloidal semiconductor nanocrystalline. In 1998 Mark Arthur Reed gave the significant term “Quantum Dots” to precisely elucidate photoluminescent nanostructure consisting of fully quantized energy states [42]. For something to be referred as quantum dots, Cayueka et al., mentioned a condition that the quantum confinement effect must be present. This made carbon nanodots, graphite quantum dots, and carbon quantum dots distinguishable as CNDs do not have any impact to the confinement [43]. Quantum dots exhibit good performance, including light stability, facile surface modification, and optical tunability, making them promising for use in heavy metal detection [44].

Recent advancements in the functionalization of quantum dots have significantly improved the detection capabilities for various heavy metal ions in environmental monitoring. Zhu et al. pioneered the functionalization of CdS quantum dots with L-cysteine, achieving an enhanced fluorescence for the detection of silver ions with a detection limit of 5.0×10^{-9} mol/L. These CdS quantum dots exhibit superior stability against photobleaching compared to single organic fluorophores, thereby minimizing blinking and improving their practical application in sensing technologies. Similarly, Zhao et al. expanded the utility of quantum dots by functionalizing

CdS/CdSe quantum dots with dithizone. This functionalization decreased fluorescence intensity via the fluorescence resonance energy transfer (FRET) mechanism, which was subsequently reversed upon the addition of Pb^{2+} ions present in wastewater or soil. The system demonstrated excellent sensitivity, high selectivity, and a broad detection range from 0.01 nmol L^{-1} to $20 \text{ } \mu\text{mol L}^{-1}$, with a remarkable detection limit of $0.006 \text{ nmol L}^{-1}$. This approach highlights the efficacy of quantum dot-based sensors in detecting lead ions in complex environmental samples. Building on these innovations, Z. Liu et al. developed a sensitive and selective method for detecting Cu^{2+} ions in wastewater by functionalizing CdTe/CdS quantum dots with glyphosate. The functionalized quantum dots exhibited increased fluorescence intensity, which was quenched upon sensing cupric ions. This method achieved a detection limit of $1.3 \times 10^{-3} \text{ } \mu\text{g mL}^{-1}$, demonstrating high sensitivity and specificity for Cu^{2+} detection. [45] [46] [47].

Additionally, Guo et al., 2020, utilized a highly selective turn-off fluorescent method for the detection of mercury ions using molybdenum disulfide (MoS_2) quantum dots functionalized with 3-aminobenzeneboronic acid (APBA). These functionalized MoS_2 quantum dots exhibited outstanding thermostability, photostability, and salt tolerance, making them highly suitable for industrial wastewater applications. The fluorescence intensity of the MoS_2 quantum dots decreased linearly with increasing Hg^{2+} concentration, observed in the range of 0.005 to $41 \text{ } \mu\text{mol L}^{-1}$, and demonstrated a remarkably low detection limit of 1.8 nmol L^{-1} . This study underscores the potential of functionalized MoS_2 quantum dots in providing reliable and precise detection of mercury ions in challenging environmental matrices [48].

Likewise, Doong et al., 2016 used graphene quantum dots functionalized with dopamine, where the catechol moiety of dopamine, having bright blue fluorescence, interacts specifically with Fe^{3+} . This interaction leads to highly sensitive and selective detection, with a detection limit of 7.6 nM . Similarly, Anh et al. distinguished their approach by doping graphene quantum dots with nitrogen atoms to enhance quantum yield up to 41.9%, and subsequently adding sulfur atoms to create N, S-GQDs. These doped graphene quantum dots demonstrated exceptional selectivity towards Hg^{2+} ions, achieving a detection limit at nanomolar levels (0.14 nM) in wastewater and water [49][50].

Collectively, these studies highlight the tremendous potential of functionalized quantum dots in enhancing the detection and monitoring of heavy metal ions in various environmental matrices. By integrating innovative synthesis methods and functionalization techniques, researchers have developed highly sensitive, selective, and versatile sensors that address critical challenges in environmental monitoring and heavy metal ion detection.

3.3 Metal nanocluster and nanoparticles

Nanoclusters have a restricted size distribution and at least one of their dimension lies in the range of 1 to 10 nanometers. The discrete as well as size-tunable electronic transitions produced by the special confinement of free electrons in metal nanoclusters which further resemble some molecular characteristics like fluorescence and distinct charging behaviours[51]. These clusters are comprised of 100 atoms however, when the size exceeds 1000 or more then they are referred to as “nanoparticles”[52]. Lately, fluorescent metal nanoclusters functionalized using polymers, biomacromolecules (protein and DNA), and thiol-ligands have gained greater interest in sensing probes due to their attractive core-shell structures which possess significant Stokes shifts ($>100\text{nm}$) and extremely small size ($<2\text{nm}$) [53]. However, metal nanoparticles

(like Silver, Copper, and Gold) help in the colorimetric detection of heavy metals as they demonstrate characteristics like localized plasmon resonance (LSPR), but stability was the prior issue faced by these nanoparticles, which was then resolved by functionalizing them using stabilizing as well as capping agents, including vitamins, polymers, acids, and amino acids. These agents not only increase their activity for a longer time but also inhibit their aggregation[54].

Recent advancements in the utilization of functionalized gold nanoclusters have significantly enhanced the selective detection of heavy metal ions. For instance, Zhang et al. (2013) developed an innovative, eco-friendly fluorescence probe for the detection of copper ions (Cu^{2+}) in aqueous samples. This probe, based on glutathione-protected gold nanocomposites, achieved a detection limit of 86 nM, showcasing its high sensitivity and potential for environmental applications. [55] Building on this approach, Wang et al. (2020) designed a sophisticated fluorescent colorimetric sensor specifically for cadmium ion (Cd^{2+}) detection, achieving a remarkably low detection limit of 33.3 nM. This sensor utilized the same glutathione-protected gold nanocomposites, which exhibit orange fluorescence that is quenched by the presence of Cu^{2+} ions. The innovative aspect of this design involved the integration of ethylenediamine-functionalized graphene oxide, which provided a stable blue emission as a background reference. The presence of Cd^{2+} ions induced the aggregation of Cu^{2+} -glutathione gold nanocomposites, leading to a color change from blue to red due to the orange emission from the aggregated nanocomposites. [56].

Similarly, Huang et al. (2006) proposed a simple yet effective method for the detection of mercury ions (Hg^{2+}) in aqueous media, leveraging the fluorescence quenching efficiency of gold nanoparticles and Rhodamine B in the presence of Mercury(II) ions. Initially, Rhodamine B exhibits high fluorescence, but its fluorescence decreases when attached to gold nanoparticles due to fluorescence resonance energy transfer (FRET). When Hg^{2+} ions are introduced, they interact with the gold nanoparticles, causing the ejection of Rhodamine B and the subsequent restoration of its fluorescence, thus acting as a "turn-on sensor." The gold nanoparticles were functionalized with thiol ligands such as MPA, MSA, and HCys to enhance selectivity towards Hg^{2+} ions, achieving a detection limit of 2.0 ppb. [57].

Despite these significant advancements, certain challenges remain, particularly in the context of Hg^{2+} detection. These methods often face drawbacks such as the formation of irreversible mercury compounds, complex probe material fabrication, and interference from other metal ions. Addressing these issues, Tan et al. (2013) utilized a DNA-based approach with a mercury-specific aptamer (MSD) rich in thymine to functionalize gold nanoparticles. In the presence of mercury ions, the fluorescence of the fluorescein (FAM) was quenched due to the formation of a T- Hg^{2+} -T duplex. This assay achieved a detection limit of 16 nM and allowed for the detection of Hg^{2+} in the range of 0.02-1.0 μM , demonstrating improved selectivity and sensitivity. Further refining the detection techniques, Feng et al. (2011) employed gold nanoparticles functionalized with SH-DNA, which selectively interacted with mercury ions due to the formation of cytosine- Ag^+ -cytosine base pairs. This interaction produced a scattered light "turn-on" signal that was subsequently turned off by cysteine, which dissociated the base pairs.

However, this method had a relatively high detection limit of 50 nM. To enhance sensitivity, Wang et al. (2018) introduced a technique based on fluorescence polarization for detecting Silver(I) ions, achieving a lower detection limit of 9.5 nM. The complex formation (C-Ag⁺-C) led to fluorescence quenching, offering a more sensitive approach for heavy metal detection. [59], [60].

In addition to these advances, Zhang et al. (2016) established a highly sensitive sensor for detecting Cr(VI) ions using fluorescent Ag nanoclusters functionalized with polyethyleneimine. This sensor had an impressive detection limit of 0.04 nM and could detect concentrations ranging from 0.1 nM to 3.0 μM. Detection occurred through fluorescence quenching due to electron transfer from the silver nanocluster to chromium ions, as well as the formation of hydrogen bonds between Cr(VI) and the free amino groups of the polyethyleneimine surrounding the nanocluster. Furthermore, this method can detect Cr(III) ions, which are oxidized to Cr(VI) using H₂O₂, making it applicable for detecting Cr(III) and Cr(VI) ions in environmental and drinking water samples.

Burratti et al. (2019) also contributed to this field by using UV radiation to generate poly(methacrylic acid) (PMAA) functionalized silver nanoclusters, which were subsequently used to detect Pb²⁺ ions with a detection limit of 60 nM. When lead ions entered the solution, they interacted with the COOH groups of the nanocluster based on the strength of their ion-dipole interactions, resulting in fluorescence enhancement. Replicating the experiment with ten times the concentration of colloidal solution instead of twenty times, the detection limit increased to 800 nM, suggesting that the overall approach was more accurate at lower lead ion concentrations, making it applicable to actual water samples. [62], [63].

Vasimalai et al. (2012) produced three types of Ag nanoparticles functionalized with mercaptothiadiazole (AMT, DMT, and MMT). Of these, the DMT-AgNPs exhibited greater stability and increased fluorescence intensity. Upon addition of Hg²⁺ ions, the fluorescence intensity further increased. Using spectrofluorimetry and DMT-AgNPs, they developed a selective detection system for Hg²⁺ ions with an extremely low detection limit of 1.0 pg/L. However, this method led to the aggregation of nanoparticles as the emission intensity decreased. Bhatt et al. (2016) addressed this issue by using Calix pyrrole octa hydrazide (CPOH) Ag nanoparticles, which did not aggregate upon addition of Hg²⁺ ions. Instead, fluorescence increased due to charge transfer from Hg²⁺ to CPOH. Similarly, Kongor et al. (2018) employed a core structure comprising Calix pyrrole tetrahydride (CPTH) functionalized Ag nanoparticles for the sensitive and selective detection of Cu²⁺ ions through a fluorescence quenching process. [64], [65], [66].

Expanding on these advancements, Makwana et al. (2016) synthesized octamethoxy resorcin arene tetrahydrazide (OMRTH) functionalized Ag nanoparticles for the selective and sensitive detection of Cd²⁺ ions. This detection method operates through a "turn-off" mechanism, achieving sensitivity at concentrations as low as 10⁻⁸ M. The successful development of these OMRTH functionalized Ag nanoparticles was verified by the transformation of the solution's color from colorless to yellow, highlighting the potential for practical applications in environmental monitoring and water quality assessment. [67].

3.4 Metal-Organic Framework:

Metal-organic frameworks(MOFs) are a promising new type of porous materials comprising of metal nodes and organic linkers. They also exhibit a substantial porous area, encompassing approximately 90 % free space, and are characterized by tunable pores and such properties make them prominent for use in chemosensing. Remarkably, it has been documented that the highest recorded surface area for MOFs is 7000 m²/g, a figure that surpasses those of other porous materials[68], [69], [70].

In a notable study by Ming et al. (2019), an amino-functionalized metal-organic framework (Cu-MOF) was synthesized using a solvothermal method with 2-amino terephthalic acid. This innovative Cu-MOF initially exhibited a distinct blue fluorescence at 430 nm. However, upon exposure to ferric ions (Fe³⁺) in aqueous media, the fluorescence intensity gradually decreased, resulting in a quenching effect. This method demonstrated significant superiority over previous approaches for detecting ferric ions, achieving a detection limit of 0.5 μM. Furthermore, the Cu-MOFs effectively detected ferric ions in real water samples. [71].

In a compelling study by An et al. (2021), an amino-functionalized metal-organic framework (MOF-5-NH₂) was developed for the specific and sensitive detection of Cu²⁺, Pb²⁺, and pyrophosphate (PPi) in water samples. The detection limits for these analytes were impressively low, at 0.057 μmol L⁻¹ for Cu²⁺, 0.25 μmol L⁻¹ for Pb²⁺, and 0.32 μmol L⁻¹ for PPi. Comparative analysis revealed that the MOF-5-NH₂ significantly outperformed a probe based on NH₂-BDC (2-amino terephthalic acid), which had higher detection limits of 11.78 μmol L⁻¹ and 83.77 μmol L⁻¹ for Cu²⁺ and Pb²⁺, respectively. Notably, Cu²⁺ and Pb²⁺ were found to quench the fluorescence of the MOF-5-NH₂ probe, whereas the presence of PPi restored fluorescence due to its strong affinity with Cu²⁺, preventing electron transfer. [72]

In a significant study by X. X. Peng et al. (2020), a metal-organic framework (MOF), UiO-66-(COOH)₂, was functionalized with Tb³⁺ ions to create a selective and sensitive sensor for Cu²⁺ ions in aqueous media. This innovative sensor exhibited a remarkably low detection limit of 0.23 μM and a rapid response time of just one minute. The detection mechanism is based on the decrease in luminescence caused by the interaction of Cu²⁺ ions with carboxylate groups in the Tb³⁺-functionalized MOF, which diminishes the energy transfer efficiency from the ligand to the Tb³⁺ ion. This method also allows for visual observation of Cu²⁺ detection under ultraviolet light, enhancing its practical applicability in real-world scenarios. [73]

Similarly, Chen et al. (2019) developed another advanced MOF for copper ion detection with an impressively low detection limit of 0.068 nM. They created a probe by integrating UiO-66(OH)₂ into the structure of a porphyrin MOF (PCN-224). In this setup, the green light emitted by UiO-66(OH)₂ served as a reliable reference to adjust for environmental variations, while the red light from PCN-224 indicated the presence of Cu²⁺ ions. The interaction of Cu²⁺ with the MOF led to a quenching of the fluorescence intensity emitted by PCN-224, facilitating rapid and specific detection of copper ions. This dual-emission strategy not only enhanced sensitivity but also improved the accuracy of the detection in complex environmental samples. [74]

Wang et al. (2017) conducted a comprehensive investigation on the utilization of metal-organic frameworks (MOFs) for the sensitive and selective detection of Fe²⁺ ions in aqueous media.

They employed two distinct MOFs, $[\text{Zr}_6\text{O}_4(\text{OH})_8(\text{H}_2\text{O})_4(\text{L}_1)_2]$ (referred to as BUT-14) and $[\text{Zr}_6\text{O}_4(\text{OH})_8(\text{H}_2\text{O})_4(\text{L}_2)_2]$, each functionalized with different ligands, namely 5',5''-bis(4-carboxyphenyl)-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4''''-dicarboxylate and 4,4',4'',4'''-(4,4'-(1,4-phenylene)bis(pyridine-6,4,2-triyl))tetra benzoate, respectively. While both MOFs possessed similar structures, BUT-15, modified with a pyridine nitrogen atom, exhibited enhanced detection capabilities for Fe^{2+} ions compared to BUT-14. The detection limits for Fe^{2+} ions were determined to be 212 ppb and 16 ppb for BUT-14 and BUT-15, respectively. Notably, BUT-15 demonstrated superior efficiency in detecting Fe^{3+} ions due to the presence of lone pair electrons, which facilitated stronger interactions with the target ion, resulting in a lower detection limit.

In the realm of MOF-based sensing mechanisms, fluorescence quenching can occur through various mechanisms, including the dismantling of MOF structures due to the intrusion of metal ions, ion exchange between metallic centers of the framework and targeted cations, and establishment of strong interactions between the embedded luminophores within MOFs and newly introduced metal ions. While previous studies utilized lanthanide and MIL-53 MOFs for Fe^{3+} ion detection via ion exchange mechanisms, Wang et al. demonstrated that their approach, relying on strong interactions between luminophores and metal ions, facilitated rapid and selective detection of Fe^{3+} ions in water systems. This was validated through meticulous analysis utilizing inductively coupled plasma (ICP) techniques. [75].

Conclusion:

In conclusion, heavy metal contamination in water poses significant health and environmental hazards, originating from natural and human activities. Traditional detection methods have limitations, including complexity and cost. However, emerging techniques, such as fluorescent chemosensors and nanomaterial-based sensors, offer promising solutions. Functionalization of nanomaterials enhances their performance. Thus, this paper highlights the effectiveness of functionalized fluorescent nanomaterials, including carbon dots, quantum dots, metal nanoclusters, metal nanomaterials, and metal-organic frameworks, in detecting heavy metal contamination in water. These advanced technologies offer rapid, sensitive, and cost-efficient methods crucial for safeguarding human health and the environment from the hazards of heavy metal pollution.

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