

Nanotechnology's Potential for Detecting Heavy Metals in Water

Bhagyashree Meher

*Department of chemistry, Kalinga University, Naya Raipur, Chhattisgarh,
bhagyashreemeher40@gmail.com*

Priyanka Gupta

*Department of chemistry, Kalinga University, Naya Raipur, Chhattisgarh,
priyanka.gupta@kalingaunivrsity.ac.in*

Abstract

Organic and inorganic contaminants, toxic elements, and non-dissolving compounds are among the toxins found in sewage. Heavy metal ion contamination of effluent is seen as a severe ecological issue in modern civilization. This contaminant seriously threatens the planet. Consequently, it is necessary to develop new and cutting-edge systems and procedures for their eradication. The use of Nanoscience is practically ubiquitous in research and innovation. This also helps in the search for solutions to a variety of environmental issues, particularly water toxicity. It is getting more difficult to develop extremely sophisticated, innovative water remedies because the existing methods cannot keep up with the increased demand for reducing toxic metal concentrations in potable water and municipal wastewater. This research discusses four types of metalloid analysis methods based on nanotechnology: colorimetric, fluorescence, electrochemical, and bio-sensing technologies. This study aims to give academics and industry a current assessment and recommendations for developing nanotechnology and nanomaterials for identifying heavy metals in water.

Keywords: *Heavy metals, Water analysis, Biosensing technology.*

1. INTRODUCTION

The Greek word "nano," meaning "dwarf," is the source of the word nano. One billionth (10) of a meter, or approximately ten hydrogen atoms, is referred to as a nanometer. In many fields, including agriculture, food, the environment, and medicine, nanoscale offers numerous possibilities for discovering innovative features in processes, materials, or equipment [52].

For example, nanotechnology has promising utility in diagnostics, assessment techniques, antibacterial compounds, and cellular labeling for bioimaging. Additionally, they can be used to purify drinkable water, synthesize nano

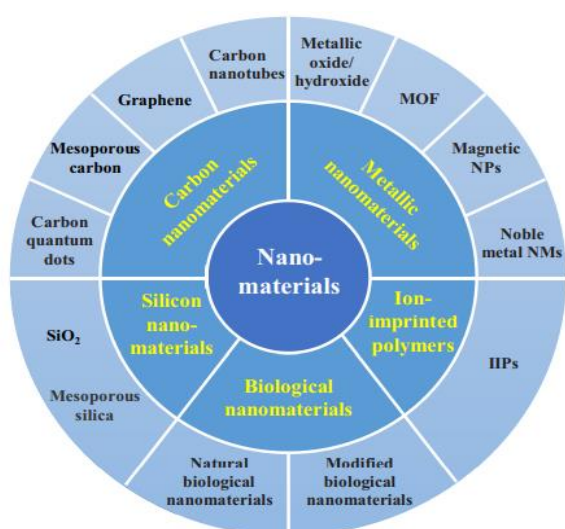
drugs for the therapy of several medical problems, and transport medicines. [25] [7] [44] It is a viable method for reducing the number of toxic substances, including drugs, microorganisms, and medicines, from sewage and water utilized for agriculture and the generation of drinkable water[1].

Nanotechnology is researched as a cost-effective, potential approach towards the efficient treatment of water and sewage impurities, including toxic metals, organic pollutants, and microorganisms. [14] [30] Several nanostructures have been used, according to various investigators. Nanostructured materials are oxide and

chalcogenide semiconductor photocatalysts, polymeric particles, zeolites, self-assembled monolayers on mesoporous supports, biopolymers, and metal-based nanoparticles. [4] [6] [43] In particular, nanoparticles of metal oxides such as titanium dioxide nanoparticles, ZnO NPs. Nanoparticles of iron oxide (and cerium oxide possess high sensitivity and photocatalytic characteristics against sewage and behave as extremely good sorbents for water treatment because of their sizeable surface area as well as their attachment to multiple functional groups [11].

Nanotechnology—in the form of nanoscales or nanoparticles coupled with regular methods—is becoming a threat to conventional remediation methods because of its performance in the water industry in eliminating contamination and minimizing toxins. [8] In fact, the removal of possibilities utilizing nanotechnology has greatly improved over the past 20 years, showing potential to enhance drinking and sewage treatment technologies beyond current methods and their boundaries.

Fig. 1. Schematic representation of different nanomaterials for sensing and Separation of metal ions



2. Heavy metals present in water

An element that is dangerous even in small amounts and has a higher density is referred to as a "heavy metal." Toxic metals in sewage have become a serious ecological problem in recent decades due to the massive impact these metals have on the environment and human health, even in trace amounts. Heavy metal contamination poses a considerable global impact due to its adaptability, collection, non-biodegradability, and tenacity. [45] [48]

Arsenic

Drinking water is the primary source of an organism's exposure to arsenic, and it has emerged as a global problem. Acute health issues brought on by prolonged arsenic exposure include central nervous system damage, kidney damage, liver failure of lungs, and dermal infection. Consuming arsenic-contaminated water regularly can also lead to vascular diseases like hypertension and have an impact on the skin's colour.[5][42][3][26].

Cadmium

Cadmium (non-degradable) ions mostly contain considerable toxicities and are ingested by organisms through food, making it difficult to remove and leading to biological harm. Additionally, it is a contaminant that negatively impacts human health in many ways, including inhibiting cell growth, causing infections in the bones, and damaging the lungs. The World Health Organization has declared that the maximum amount of Cd in blood should not exceed 0.005 mg/L due to all these health concerns[29].

Chromium

Amongst all toxic metals, chromium is one of the most dangerous toxins that are detrimental to a living thing, cancerous to humans, and non-

biodegradable. Various chromium structural forms have numerous effects on the ecological and toxicological characteristics of the metal. Chromium is released entering the ecosystem during industrial operations such as metals polishing, electrolysis, pigments and dyeing making, steel production, and tannery. The oxidized states of chromium do exist, though, and these are Chromium (III) and Chromium(VI) in water [51].

Nickel

Reaction kinetics, jewellery, batteries, metallurgy, resistance wires, and commercial components are just some of the items that use nickel. Because nickel is used so frequently, there are many ecological impacts. A dry cough, difficulty in breathing, uneasiness, diarrhea, skin rash, respiratory failure, intestinal pain, renal edema, and other adverse effects are caused by nickel. In order to prevent various health and ecological risks, the nickel metal recovery method must be appealing [13][40].

Lead

Lead is a toxic metal that is easily obtained in the human body. It causes cancer, mental

retardation, damage to the neurological system, and kidney disease in humans. The presence of lead poses greater risks to both plants and animals. As a result, numerous researchers from around the globe are currently concentrating on lead removal technology [46][10]

Mercury

The metal mercury can move through water systems and build up in ecosystems. It causes a variety of environmental issues because it is so prevalent in the environment to protect the environment and human health from mercury[61][62].

Fig 2:- Percentage of heavy metals used for various field[28]

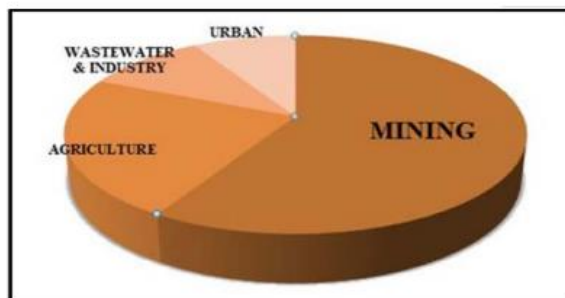


Table 1. World Health Organization and United States Environmental Protection Agency acceptable limit for certain heavy metal ions in sewage treatment [58].

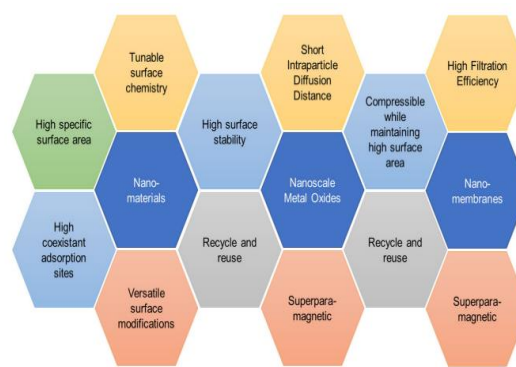
Heavy metal	Acceptable limit (USEPA)µg/l	Acceptable limit (WHO)µg/l	Impact on human beings
Copper	---	3000	Kidney failure, headache, diarrhea, liver problem
Zinc	---	5000	Stomach and intestinal disturbance, metal fume fever
Arsenic	----	500	Cancer and skin issue, bladder and long problem
Chromium	50	50	Lung problem, nasal and sinus cancer

Nickel	200	20	Lung cancer, cardiovascular disease Nasal cancer
Lead	6	10	Sleeplessness, abdominal pain, hypertension
Cadmium	10	3	Kidney disease, cardiovascular disease, caner

3. Nanoadsorbent

The best adsorbents are specialized nanomaterials called "nano adsorbents" due to their small size, extremely large surface area, enzymatic capacity, high sensitivity, easy to isolation, and various binding sites associated with different contaminants. The two key features that set nanoadsorbents apart from other materials are their inherent surface area and extrinsic chemical modification. Because to their extrinsic surface morphology, apparent dimension, and underlying constitution, nanoparticles exhibit unique physiological, chemical, and structural features. Elements like a wider coverage area, sorption behavior, chemical environment, element positioning on the surface, etc. all impact sorption in an aqua condition. Temperature, the kind of adsorbent and adsorbate, pH, the initial quantity of metals, interaction period, granular diameter, solid-liquid equilibria, and mass transfer velocities are a few more parameters that might affect adsorption. For usage as sorbent materials for absorbing the ions of heavy metals from sewage, nanoparticles must fulfill the essential characteristics: It must be highly specific and possess a strong sorption capability at low contamination levels. It must not be hazardous. 3) Adsorbents must be constantly reusable (4) Nanoparticles must enable it simple to remove contaminants that have been adsorb to their surface. [63]

Fig 2. Nanoparticles and their configurable surface characteristics



4. Nanotechnology-Based Heavy Metal Detection in Water

4.1. Nanomaterial-Improved Biosensing

(a)Magnetic Nanomaterial

Heavy metals can be found using sensors that combine magnetic nanoparticles with proteins. The majority of them are electrochemical detectors. One of the most popular magnetic nanomaterials is Fe₃O₄ NPs, which have a high surface volume ratio and magnetic characteristics. Fe₃O₄ has drawn a lot of attention due to its distinct catalytic and magnetic properties. Fe₃O₄-based nanomaterials can be used as a framework for DNA biosensing fabrication. The identification of Ag⁺ and Hg²⁺ with DNA-modified Fe₃O₄/Gold NanoParticless and a magnetized glassy carbon electrode was highly sensitive and specific. The method is effective for

analyzing silver ion (Ag^+) and Mercury ion (Hg^{2+}) levels in drinkable water, surface waters, etc. It can also be utilized to analyze various water samples[41].

(b) Gold and Silver Nanoparticles

A biological element that interacts with the target analytes (such as nucleotides, enzymes, or antibodies) is implemented in biosensors. The resulting biochemical modifications are typically converted into colorimetric and electrochemical signals that can be recognized by a sensor based on nanomaterials [47]. Good electrical conductivity, enzymatic biocompatibility, and catalytic abilities are all possessed by AuNPs. They could significantly enhance electrochemical biosensors' responsiveness, stability, and sensitivity. Technology for T- Hg^{2+} -T coordination can be utilized for finding Hg^{2+} [49].

4.2. Colorimetric Method

a) Nanozyme assisted colorimetric sensors

Nanozymes are artificial nanomaterials that simulate biological enzymes and can catalyze biological events. Nanozymes have the ability to detect low abundance heavy metal ions because they combine the catalytic capabilities of enzymes with those of nanoscale materials.[52,32]In contrast to conventional approaches, nanozymes' characteristics can be quickly developed and practically tuned to meet a variety of sensing demands[66].In some nanozymecatalyzed systems, the toxic heavy metal ions often have the function of actively participating with the catalyst surface or absorbing on the membrane of nanozymes to stimulate and decrease the enzymatic functionality. [56,36]

b) Localized surface plasmon resonance colorimetric sensors

It is commonly accepted that the localized surface plasmon resonance phenomenon causes metallic nanoparticles to produce a characteristic absorbance band at particular resonating frequencies. Using this property, metallic nanoparticles can be used to respond preferentially to different analytes, particularly heavy metal ions [24][69]. LSPR-based sensing technologies often employ silver, gold, and copper nanoparticles because of their unique optical, thermal, physical, and electrical properties properties[65][57]. Gold nanoparticles with exceptional stability and antioxidation have been designed for detecting heavy metal ions. [33].

4.3. Electrochemical Analysis by Nanosensors

(a)Semiconducting nanomaterial

The semi-conductor tin oxide (SnO_2) is well recognized, although SnO_2 nanoparticles tend to combine quickly, preventing them from performing to their full potential. In order to avoid the build-up of SnO_2 nanoparticles, rGO can act as a template. The utilisation of the synchronous and selective electrochemical processes involving Cadmium, Lead, Copper, and Mercury ion detection in water using rGO/ SnO_2 electrodes was reported. [60]

According to reports, porous silicon can be used as a nano scavenger to find traces of heavy metals in water.

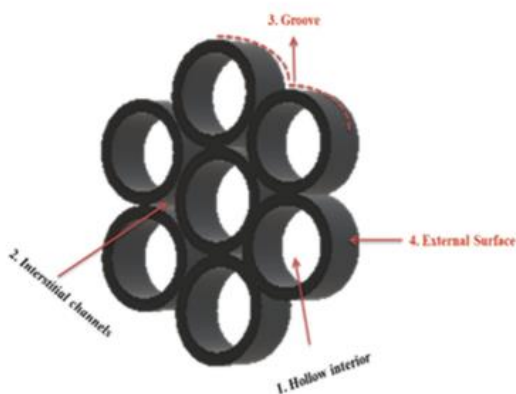
(b)Based upon carbon Nanomaterial

The three materials, graphene oxides, and graphene, reduced graphene oxide, all have been created as sophisticated nano-electrocatalysts for making electrochemical sensors since they can all adsorb heavy metal ions. Electrostatically attracted phytic acid and

in-situ bismuth film-coated graphene-based electrodes, respectively, were shown to have increased sensitivity to Pb^{2+} and Cd^{2+} [27][12]. A conductive polymer called polypyrrole (PPy) has the ability to be physically adsorbed on GO with high dispersion, which will improve electrode conductivity [31][9].

In water samples, various rGO-based electrodes have been used. Since its surface has functional groups, rGO has a significant affinity for water and a strong capacity for metal ions to bind to it [39]. The traces of Cd^{2+} and Pb^{2+} in drinking water were analyzed using Au electrodes that were coated in rGO that has been micro-patterned and electrodeposited [64].

Fig 3. Carbon nanotubes surface with a possible active adsorption location



4.4. Gold and silver nanoparticles used in the calorimetric analysis

(a) Silver Nanoparticles

According to various detection theories, heavy metal sensors based on modified AgNPs have

been proposed. These concepts include colour changes brought on by 1. Silver chloride precipitates development 2. Increased fluorescence intensity 3. Particle aggregation.

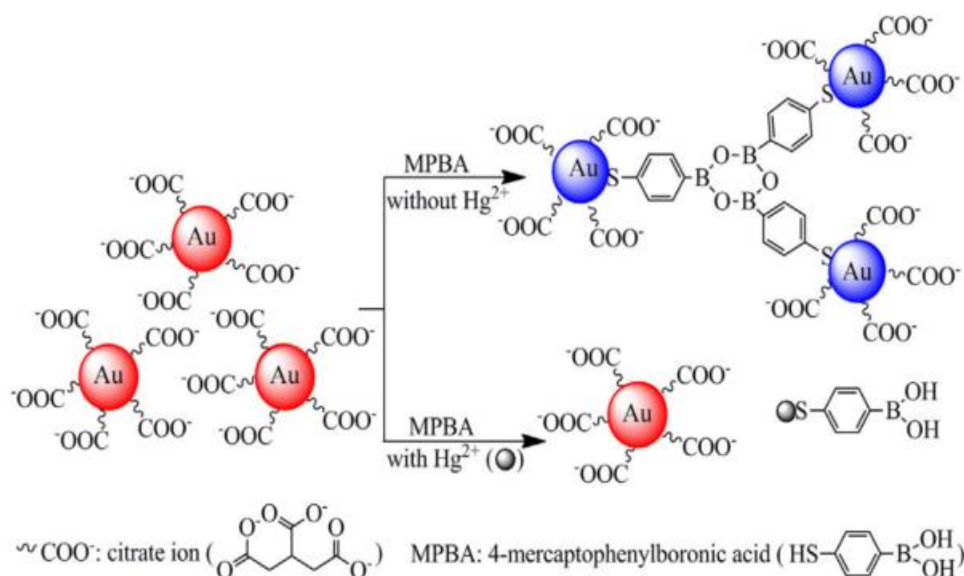
Poly (acrylic acid)-template silver Nano clusters can monitor mercury (Hg^{2+}) ions by initiating a specific type of fluorescence. AgNCs would glow more intensely when Hg^{2+} ions were present, causing an observable shift in colour of solution from purple to light red. Using samples of mineral water, river water, tap water, the technique has been shown to be useful [55].

(b) Gold Nanoparticles

Various toxic elements can be examined using the diffusion of Silver NanoParticles because they contain localized surface plasmon resonances (LSPR) present in AuNPs. [19]. A Hg^{2+} sensor made of 4-mercaptophenylboronic acid and Gold Nanoparticles have been developed. The AuNPs can be initially stabilized by covering them with negatively charged citrate ions, which promote electrostatic repulsion and inhibit formation [34].

In contrast to molecular diffusion, thiol-dependent aggregates of Au nanoparticles can be used to identify ions of heavy metals, including cobalt, lead, mercury and cadmium. [70] Furthermore, graphite-like nitride-doped carbon quantum dots (nanocomposite) can be employed as a sophisticated color-tuning indicator to track cadmium's common weak reactive metal ions.

Fig 4. Schematic representation 4-mercapto phenylboronic acid and Gold Nanoparticles of the colorimetric mechanism for Hg^{2+} detection [72]



5. Sensor-based Nanomaterials

a) Nanomaterial based electronic sensor

Because of their unique electrical abilities, nanomaterials have produced a large range of potential for the diagnosis of contaminants in water in addition to conventional techniques. Utilizing nanowires [2] [37] and carbon nanotubes [18] [58], a wide variety of electronic detectors, especially field effect transistor sensors, have been developed in the past ten decades. Due to their significant carrier mobility and strong sensitivity to electrical disturbances, nanomaterial-based field effect sensors generally exhibit a strong sensitivity and rapid response to water contaminants. These unique properties have made it conceivable to promptly detect water contaminants and get beyond conventional sensing techniques' drawbacks. Field effect transistor sensors recognize the concentration of water toxins depending on the conductance variation of the semiconducting component in the device once the contaminants attached to

the detecting component surface (for example, heavy metal ions and bacteria).

b) optical sensor

Optical chemical sensors have tremendous capability and can be used in many different ways to diagnose heavy metals. Chemical sensors, known as Optical chemical sensors, produce evaluative information in a transduction element using electromagnetic waves. The amount of the element can be determined from an optical feature that alters as a result of the specimen coming into contact with radiation. The interaction of an immobilized indicator with the sample causes variations in the optical response (transmission, absorption emission, lifetime, etc.), which forms the base of Optical chemical sensors operation[20].

(c) fluorometric biosensor

Fluorescence methods have been used with high specificity or extensive identification capabilities on a number of chemical

substances. [23]. Fast response rates, exceptional responsiveness, and specificity make fluorescence sensors effective tools for monitoring metal ions. Monitoring heavy metal ions using a fluorometric sensor dependent on nanoparticles is currently a significant scientific priority [15], [59].

6. Fluorescent Analysis

(a) Gold Nanocluster

Metal nanoclusters (NCs) are advantageous as potential fluorescent probes since they are low in toxicity, have a strong photoluminescence, and are biocompatible. [38] Fluorescent AuNCs typically have an organic ligand shell surrounding an inorganic gold core. [67] The core-shell arrangement might be altered in various ways to provide optical, chemical, and biological sensors with many uses. [22]. Since CQDs and AuNCs may both be activated by a single wavelength simultaneously, a dual-emission nanosystem of CDs and AuNCs was developed for the strong visual identification of Ag^+ in the presence of additional ecotoxicological metallic ions.

(b) Quantum dot

Fluorescence resonance energy transfer is an optical phenomenon in which energy is transferred from the donor fluorophore to the recipient fluorescence over a non-radiation path. Currently, attempts have been taken to develop nanomaterial-based fluorescence resonance energy transfer sensors. Carbon quantum dots exhibit better fluorescence properties and less toxic effects than traditional Quantum dots. Sulfur and nitrogen co-doped Carbon Quantum Dots (N, S-CDs) have a greater fluorescence quantum yield. [15] Fluorescence of N, S-CQDs can be "turned off" by Hg^{2+} , and Cr(VI) , respectively. Because of the high reactivity between Hg^{2+} and I, I- can

further "turn on" the Hg^{2+} -Carbon Quantum Dot system. In order to detect Hg^{2+} , Cr(VI) , and I- [54] in water samples, such have Carbon Quantum Dots been used.

7. Conclusion

In the past several decades, there has been a tremendous increase in heavy metal contamination of aqueous environments. Numerous nanostructures have unique physicochemical characteristics that make them a suitable alternative for pollutant assessment and water treatment. In this brief overview, the innovation of methodologies based on nanoparticles or nanostructured components in the recent decade towards monitoring heavy metal ions is highlighted. The technologies are further divided into four categories based on the identification mechanism: the EC method, the fluorescence detection method, and the spectrophotometric approach. In order to increase the sensibility, specificity, and functionality of methodologies, initiatives to produce heavy metal identification techniques based on nanoparticles were discussed. when trying to compare to traditional methodologies like AES, ICP-MS, ICP-OES, or AAS or technologies based on organic fluorescent chemicals. Nanomaterial-based sensing approaches are more advantageous than traditional methodologies because of their high LOD, lower expense, and ease of use in environmental applications. These strategies are generated from durable, affordable, compatible, and harmless inorganic compounds.

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