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Silver nanoparticles (AgNPs) synthesis methods as heavy-metal sensors: a review

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Abstract

The quick and high-accuracy location of heavy metals is one of the principal prerequisites for reducing the environmental pollution. Therefore, the rapid and precise detection of heavy metals has become a primary problem for scientists worldwide. Among the different heavy metals, arsenic, cadmium, lead, mercury, and chromium (Cr) are highly toxic. Silver nanoparticles (AgNPs) have been created for the detection of heavy metals. The use of nanomaterials is promoted because of their solid adsorption, high electron energy, and biocompatibility, which are appropriate for heavy-metal sensor applications. This review focused on synthesis AgNPs by biological, chemical, and physical methods and their capability for detection of heavy metals by colorimetric methods included the practical and basic assessment of toxic heavy metals, and they are easily implemented on location, use simple instruments, and provide simple analysis results. In this review, we have provided the promising possibilities with new prospects and challenges for high efficiency and stability of AgNPs as a multi-sensor of heavy-metal ions with high-sensitive detection in tainted water bodies.

Keywords AgNPs · Heavy-metal ions · Sensor colorimetric · Environmental pollution

Introduction

The innovation in the use of nanoscience and nanomaterials in various field applications, including energy, optoelectronics, biomedicine, and biotechnology, has been reported (Zannotti et al. 2020). Nanotechnology is a part of such innovation, and it is applied in nanosized synthesis methodology. This rapidly developing and innovative technology has received interest over the last decade due to its historical backdrop of wide applications. Nanotechnology is a multi-disciplinary field with first uncovered. Characterization by nanotechnology is being prepared for control of nanoscale objects, where “nano” means one billionth of an actual unit. However, no settlement has been achieved regarding the meaning of nanotechnology (Kakakhel et al. 2021).

Nanoparticles (NPs) are natural substances used in nanotechnology (Magaye and Zhao 2012). The two types of NP sources can be inorganic or organic. AgNPs are inorganic NPs (Maaz 2018) with sizes in the 1–100 nm range. Investigations of AgNPs have focused on their unique physical, chemical, and biological properties. Their prevalence is mainly attributed to their form, composition, crystallinity, and structure of AgNPs, which is contrast with its mass structure (Syafiuddin et al. 2017), (Wang et al. 2015).

Metal NPs can be synthesized by chemical or physical methods. In general, bottom-up and top-down approaches, such as chemical reduction, have been used for the preparation of metallic NPs. The advantages of chemical and physical methods include their easy execution, large quantity production, and well-controlled particle interspacing; however, they also have disadvantages, such as the remarkably high cost, including those for the equipment and operation, and high energy consumption (Lin et al. 2021). Materials that are used for the synthesis of AgNPs using this chemical method are very toxic and hazardous in nature (Panja et al. 2021). Electrochemical methods are very intriguing because of their high performance in obtaining particles, which they attain by utilizing quick and direct techniques and controlling the molecular size effectively. Through

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these procedures, particles are not limited to the size and shape of a few compositions. In addition, such methods are eco-accommodating, that is, they steer away from the use of reducer specialists, which are occasionally toxic. The biological method is simple, environmentally friendly, and commercial, uses a single step method, and does not require elevated temperature, pressure, force, and harmful chemicals (Panja et al. 2021).

Over the period of years, various conventional analytical methods have been established for the detection of heavy metals at very low and ultra-low level employing different techniques such as liquid chromatography, UV-Vis spectroscopy, X-ray fluorescence spectroscopy (XFS), capillary electrophoresis (CE), microprobes (MP), anodic stripping voltammetry (ASV), atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) (Yu et al. 2022). However, these analytical tools suffer from several limitations including sample preparation, cleanup, pre-concentration processes, expensive instruments, and professional personnel on the other hand, facile, inexpensive, and easy implementation for the metal detection such as electrochemical colorimetric and fluorescence detection (Buledi et al. 2012, Aragay et al. 2011).

In recent years, nanomaterial-based sensors have shown great potential in detection of heavy metals due to their high surface reactivity, large surface area, strong adsorption capacity, high catalytic efficiency. Various nanomaterials like metal and metal oxide nanoparticles, polymeric nanomaterials, silicon, and carbon based nanomaterials have been used to design special nanosensors for the detection of toxic heavy metals. The enhanced sensitivity and selectivity of nanosensor is initiated by their large surface-to-volume ratio, high reactivity, size-dependent properties, and high degree of functionalization (Borah et al. 2015). For surface state, covalent functionalization, organic ligand, and nano-composite formation have large contribution to improve response selectivity and sensitivity in heavy-metal detection. The nanomaterials involved in chemical sensors have greatly enhanced their reproducibility and detection limit for selective determination of heavy metal (Kaur et al. 2015) (Buledi et al. 2020). Generally, electronic and optical properties of nanomaterials are highly considered to increase selectivity and sensitivity.

In addition, nanomaterials used in sensor fields have many advantages, such as ultra-high specific surface areas, easy functionalization, abundant active sites, and tunable electronic structure. Therefore, they are promising building blocks for constructing various sensors with excellent performances. The various types of sensors are including electrochemical sensors, fluorometric sensors, colorimetric sensors, electrochemiluminescence (ECL) sensors, photo-electrochemical sensors, and field effect transistor (FET)

sensors (Gan et al. 2018). In this review, many scientists globally were reported for colorimetric sensor silver (Ag)-based nanomaterials due to solid limited surface plasmon resonance absorption and interparticle distance, which affect to the optical properties. The colorimetric detection method has numerous advantages including efficient time and speed detection, high affectability, cost-viability, and user friendly. The surface state of NPs plays an essential role in the improvement of sensitivity of colorimetric sensors for heavy-metal particles. For example, AgNPs functionalized surface with small natural ligands to form bio-macromolecules demonstrated specific colorimetric detection of various heavy-metal particles (Wang et al. 2015).

One of the main causes of our environment's rapid degradation is the overexploitation of natural resources for heavy metals. Pb^{2+} , Cr^{3+} , Hg^{2+} , As^{3+} , and Cu^{2+} are the major heavy metals that have harmed the environment in recent years. As a result, numerous efforts have been exerted to quantify and detect heavy metals conventionally and analytically. However, advanced technologies are continuously being demanded for the detection of heavy metals in a user-friendly and sensitive manner, which resulted in the development of nano-based technology. Analytical devices, which are very sensitive, selective, and capable of working quickly, have become more effective due to the use of nanotechnology (Shrivastava et al. 2022).

Metals are naturally present in the earth's crust, but their composition and concentrations vary. Heavy metals pose a serious threat to the environment and human health. The rapid rise in heavy metals in the environment over the past ten years is attributable to the rise in mining and industrial activities. Metals can also be released from rocks by weathering, erosion, rainwater, soil, and other natural processes, which can significantly increase the release of toxic metals (Buledi et al. 2020). Mercury has deleterious effects on the human kidney, brain, and central nervous system. This element is volatile and predominantly exists as Hg^{2+} in water. The Hg^{2+} ion is highly toxic at low concentrations and can accumulate in ecosystems, in particular apex predators, causing several disorders and diseases. Meanwhile, lead (Pb) pollution has been associated with neurodevelopmental effects, and cadmium (Cd) is classified as a carcinogen. Arsenic intake causes dermal lesions, skin cancers, bladder, and lung cancers (Mensah et al. 2021, Li et al. 2013).

Mensah et al. (2021) reported efforts exerted for the improvement of the environment affected by heavy metals in water. Different inorganic NPs, including metals, metal oxides, and metal sulfides, have been applied successfully as nanoadsorbents for the treatment of water with high contaminations of heavy metals, that is, at concentrations greater than 100 mg L^{-1} , achieving high adsorption capacities up to 3449 mg g^{-1} . The synthesis method, selectivity, stability, regeneration and reusability, and adsorbent



separation from solutions are critical parameters that determine the quality of inorganic nanoadsorbents. Surface-functionalized nanoadsorbents possess high selectivity and capacity for heavy-metal removal from water at very low adsorbent dosages of less than 2 g L^{-1} , which make them better than conventional adsorbents in terms of environmental remediation.

Thus, we underscore the uses of AgNPs in sensors of heavy metals (Fig. 1), such as Pb^{2+} , copper (Cu^{2+}), manganese (Mn^{2+}), and mercury (Hg^{2+}). In this review, we specifically addressed the previously reported AgNPs for heavy-metal sensors with recent updates.

Materials and methods

AgNP synthesis methods

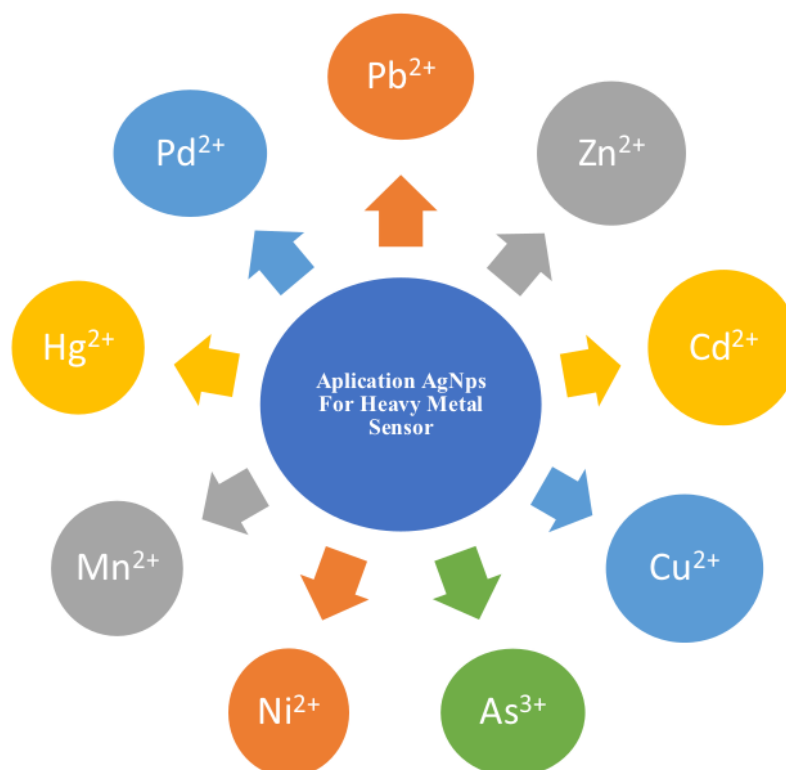
Synthesis of AgNPs using bottom-up approaches

As mentioned above, numerous types of silver nanostructures with distinctive properties have been used in various sensor applications, especially those regarding heavy metals (Lee and Jun 2019). The union of NPs has been utilized in

three distinct methodologies, including physical, chemical, and biological strategies. The physical and chemical synthesis methods, which point toward controlling the actual properties of particles, are presently utilized to create metal NPs.

The synthesis methods of metal NPs are mainly divided into top-down and bottom-up approaches (see Fig. 2) (Kalishwaralal et al. 2010). Method “top-down” is the mechanical crushing of mass metals with the resulting adjustment of the utilized colloidal NPs (Tao et al. 2006). Top-down approaches disincorporate bulk materials to generate the required nanostructures. These include physical and chemical synthesis methods. The physical synthesis of AgNP includes the evaporation–condensation approach and laser ablation technique. Both approaches can be used to synthesize large quantities of AgNPs with high purity and without the use of chemicals that release toxic substances and jeopardize the human health and environment. However, agglomeration is often a great challenge because capping agents are not used. In addition, both approaches consume high power and require relatively long synthesis duration with complex equipment, which all increase their operating cost (Lee and Jun 2019). The laser wavelength, time span of laser pulses, laser influence, ablation time duration, and effectual liquid medium with or without the surfactant are

15 Fig. 1 Schematic representation of AgNP applications for heavy-metal sensors



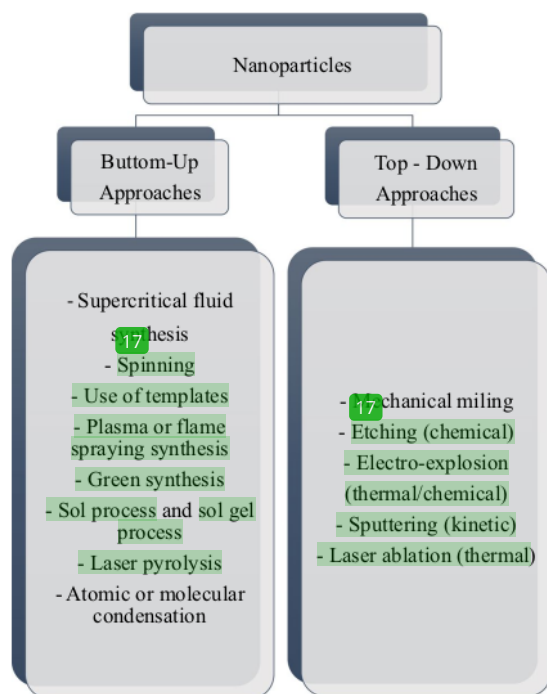


Fig. 2 Schematic illustration of two different routes in AgNP synthesis

the major parameters that influence the synthesized particles when using the laser ablation method (Shyam et al. 2020).

The AgNP synthesis is mainly achieved through chemical methods. Sodium borohydride, hydrazine hydrate, sodium citrate, and lithium aluminum hydride are the most commonly used reducing agents. Silver atoms (Ag^0) are formed due to the reduction of Ag^+ containing complexes, which may lead to the cluster formation due to agglomeration. Colloidal Ag particles emerge from these clusters. To avoid such issue, scientists use protective or capping agents (Shyam et al. 2020).

Different chemical and physical techniques, e.g., electrochemical strategy (Singaravelan and Bangaru Sudarsan Alwar 2015), phytochemical method (Narchin et al. 2018), and laser ablation (Ma 2019), have been utilized to combine AgNPs. The area of green synthesis has been investigated to use fundamental phytochemicals, such as amides, aldehydes, alkaloids, flavonoids, phenols, ketones, carboxylic acids, and ascorbic acids (Buledi et al. 2020).

Synthesis of AgNPs using top-down approaches

Figure 2 shows top-down methods, NPs are normally synthesized by evaporation and condensation and breakdown of bulk materials into fine particles via size reduction

using various lithographic techniques, e.g., grinding and milling (Khan et al. 2018a, b). This group includes the green synthesis method, which uses microorganisms or plants extracts. An intelligent strategy should be scaled up and climate friendly, combine great scope, and not require the use of toxic synthetic compounds. The green synthesis of NPs may be a granular perspective where the most response observed is drop. Biogenic incorporation is beneficial because of its natural reduction effect and the use of multiple physicochemical manufacturing methods. The unintentional production of large NPs free of impurities, size, and morphology has been reported by Gupta and Chauhan (2017).

In this regulatory race for AgNPs, the green biomimetic synthesis of plant-mediated AgNPs is considered the best innovation for the rapid manufacture of AgNPs, effectively meeting the extreme needs and interests of today's market and drives a decline in the business or aging of substances harmful to the environment, human well-being, and climate. Water hyacinth plant leaf extract was used for the colorimetric sensing of heavy metals (Zannotti et al. 2020); green synthesis was utilized to separate heavy metals from khat (*Catha edulis*) plant and effective in the detection of Hg^{2+} particles (Wang et al. 2015).

In addition, green synthesis principles put forward the need to evolve environmental technologies for the fabrication of nanomaterials. The biosynthesis of NPs, which is the combination of nanotechnology and biotechnology, has gained interest. Abundant reactants and starting materials used in chemical method reactions are toxic and potentially hazardous. Biomimetic approaches have been developed due to the increasing environmental concerns over harmful chemical methods. Green methods principles forced researchers to develop strategies involving biological methods where enzymes, microorganisms, and plant extract play a vital role in NPs formation. The biologically synthesized NPs exhibit tremendous interdisciplinary applications (Shyam et al. 2020).

NPs are created physically and chemically within a significant time frame. However, late advancements showed the primary job of microorganisms and biological systems occurring with metal NPs (Fig. 3).

As depicted in Fig. 3 and more detail can be seen in Table 1, metallic NPs can be obtained from cell or cell-free extracts of a variety of biological resources. The evaluation of NP preparation against green synthesis principles (see Table 1), such as the selection of a solvent medium, eco-friendly reducing agent, and nontoxic material for NPs stabilization, is the most important consideration. Plant extract reduces metal ions within a shorter period than microbial NPs, making plant-based NPs more stable and monodispersed. Microbial synthesis is one of the methods used for nanomaterial production (Kumar et al. 2020).



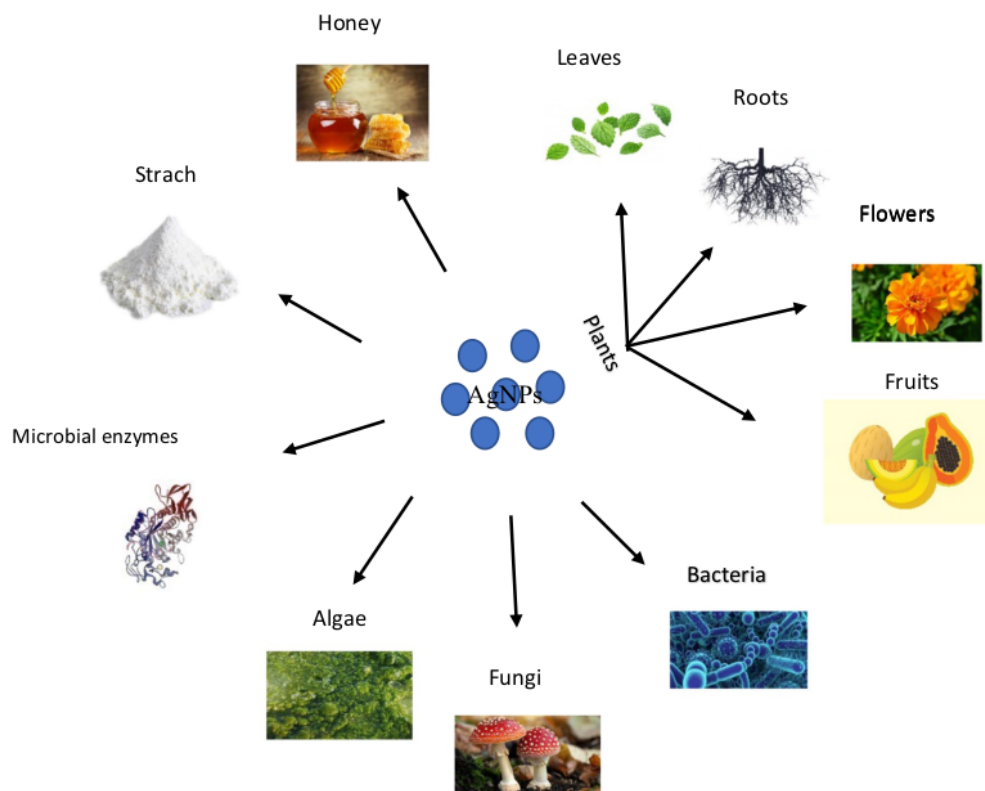


Fig. 3 Various types of green synthesis sources utilized for the arrangement of AgNPs

Table 1 Section green synthesis of AgNP detection of heavy metals

Metal NPs	Sources	Sources type	Heavy metal detection	References
AgNPs	Fruits	Watermelon (<i>Citrullus lanatus</i>)	Hg (II)	(Firdaus et al. 2021)
		Kokum fruit extract	Hg ²⁺	(Sangaonkar et al. 2020)
	Flowers	Durenta erecta (<i>D. erecta</i>)	Cr ⁶⁺	(Ismail et al. 2018)
		Mango (<i>Mangifera indica</i>)	As ³⁺	(Kolya et al. 2020)
	Roots	<i>Moringa oleifera</i>	Cr (II)	(Bindhu et al. 2020)
		<i>Bistorta amplexicaulis</i>	Hg ²⁺ Pb ²⁺	(Ahmed et al. 2020)
	Leaves	<i>Hyacinth</i>	Hg ²⁺	(Oluwafemi et al. 2019)
		<i>Acacia chundra</i>	Hg ²⁺	(Anto Judy et al. 2021)
		<i>Lantana camara</i>	Hg ²⁺ Cu ²⁺ Pb ²⁺ Mn ²⁺	(Aritonang et al. 2021)
	AgNPs	Bacteria	<i>Staphylococcus sciuri</i>	Cd
Fungi		<i>E. coli</i>	Fe ³⁺	(Princy et al. 2022)
Algae		<i>Porphyra yezoensis</i>	Cu ²⁺	(Xu et al. 2019)
Strach		<i>polyvinylpyrrolidone</i>	Hg (II)	(Al-Onazi and Abdel-Lateef 2022)

Results and discussion

Applications of AgNP in heavy-metal sensors

The chemical symbol of silver, Ag, comes from the Latin word “argentum,” which means “shiner” in proto-Indo-European. Silver is white, belongs to the noble element family, and has an atomic number of 47. AgNPs are an ideal candidate for a wide range of applications, including nanomedicine, nanobiotechnology, nanosensors, and electronic devices, due to their outstanding physicochemical properties and capability to exhibit surface plasmon resonance (SPR). Given their outstanding properties and low cost preparation, AgNPs attracted considerable attention in the field of sensor technology from an environmental standpoint (Hyder et al. 2022). Heavy metals are deleterious ecological toxins because they cause harmful impacts on living organic entities, including creatures, people, and plants. These metals persevere in the environment because they cannot be obliterated nor corrupted. The contamination by risky heavy-metal-based particles has been an expanding issue. Metal materials cause different medical conditions, such as those observed in the hematopoietic, gastrointestinal, kidney, and sensory systems (Duffus 2002).

Multiple detection technologies for the detection of heavy metals have been developed. Several analytical methods, including atomic absorption spectroscopy (AAS) (Tinas et al. 2018), have been used to monitor trace amounts of heavy metals in the environment. These methods include electrochemistry and atoms (Dali et al. 2018), voltammetry stripping (Luo et al. 2017), and ultraviolet-visible and fluorescence spectrometry (Zhao et al. 2017). These methods provide correct and accurate results, but they require a long operation time, skilled staff, expensive instruments, and proper handling. Therefore, a straightforward and delicate colorimetric method that effectively detects the target material by observing the change in color can be used to definitively address these issues (Zhai et al. 2019). Such a method can also be used in organic pesticides (Tang and Su 2018) and biomolecules (Hyder et al. 2021). Given that metal NPs have a large surface area, excellent optical properties, and high molar absorptivity and can be customized with a variety of stabilizing and capping agents, many metal NPs, including gold, silver, and copper can be used extensively for this purpose (Hyder et al. 2022).

These days, our current circumstance is the progressive manifestation of substantial metal poisons because of current farming practices and fast industrialization (Jumina et al. 2020). Regulatory authorities will decide essential standards for the safe consumption of these heavy metals.

Table 2 provides a list of different global and national regulatory authorities who determine and regulate these standards for the safe consumption of drinking water. The list also highlights the difference in threshold limits due to geographical variation and consumption limits of different populations in terms of drinking water (Shrivastava et al. 2022).

Given their great catalytic potential and reactivity, strong adsorption potential, and large surface area, nanomaterial-based colorimetric sensors have presented considerable promise in the detection of heavy metals in recent years. Various nanomaterials, specifically metal NPs, have been employed to construct distinctive types of colorimetric sensors for sensing of heavy metals. The improved selectivity and sensitivity of colorimetric nanosensors originates from their high degree of functionalization, great volume-to-surface ratio, size-dependent features, and high reactivity (Rasheed et al. 2022).

AgNPs' localized surface plasmon resonance (LSPR) properties contributed significantly to the field of colorimetric sensing as shown in Fig. 4. Although the stability of metal NPs is a major obstacle to their use in colorimetric heavy-metal sensing, different capping and stabilizing agents have been used to functionalize the metal surface of metal NPs. These capping agents prevent NPs from aggregating and increase their activity (Hyder et al. 2022).

Sensing of Mercury (Hg)

Mercury is a hazardous toxic material that can pollute the environment and is one of the most dangerous heavy-metal particles in metallic, inorganic, and natural forms (Wang et al. 2015). It is a common contaminant emitted from coal, gold mining companies, and volcanic emissions. Therefore, proficient procedures must be developed to enable the rapid observations of mercury in liquid frameworks (Yu and Tseng 2008). Hg is very stable and quickly accumulates in water bodies. Hg can be released to the surface and groundwater due to various industrial or natural activities, such as fossil fuels (especially from thermoelectric power plants), volcanic emissions, and agriculture (Abou El-Nour et al. 2010; Sharma et al. 2009). Water-soluble Hg^{2+} particles are one of the most stable and typical inorganic mercury compounds. In shallow conditions, this element can cause complicated issues in the regenerative, gastrointestinal, and cardiovascular systems (Şahin et al. 2020).

Hg^{2+} is harmful and can cause unfavorable impacts on human well-being and climate. Thus, numerous effective logical methodologies, including fluorescence spectrometry, have been created to enhance Hg^{2+} sensing. Colorimetric tests, electrochemical investigation, mass spectrometry (MS), and nuclear ingestion spectrometry. Although these strategies are sensitive and selective, they still have a few

Table 2 Maximum permissible limits of various heavy metals according to different regulatory authorities

Heavy Metal	WHO (mg L ⁻¹)	EPA (mg L ⁻¹)	FSSAI (mg L ⁻¹)	CODEX (mg L ⁻¹)	EU (mg L ⁻¹)	FDA (mg L ⁻¹)	Associated Health Risk	Reference
Hg	0.001	0.002	0.001	0.001	–	–	Tremors Insomnia and memory loss Kidneys	(Mukherjee et al. 2021), (Shrivastava et al. 2022)
Cd	0.003	0.005	0.003	0.003	0.005	0.005	Nausea, vomiting, and diarrhea Muscle cramps Salivation Liver injury	
As	0.01	0.01	0.05	0.01	0.01	0.01	Encephalopathy Thickening of the skin Diarrhea and heart disease	
Pb	0.01	0.015	0.01	0.01	0.01	0.005	Anemia and seizures Behavioral problems Intellectual disability	
Cr	0.05	0.1	0.05	–	0.05	0.100	Depression Anxiety and schizophrenia Kidney and liver diseases	
Cu	2	1.3	1.5	–	2.00	1.000	Vomiting Hematemesis, Hypotension Melena (black “tarry” feces)	
Ni	0.07	0.04	1.5	–	0.02	0.1	Chronic bronchitis Reduced lung function Allergy	

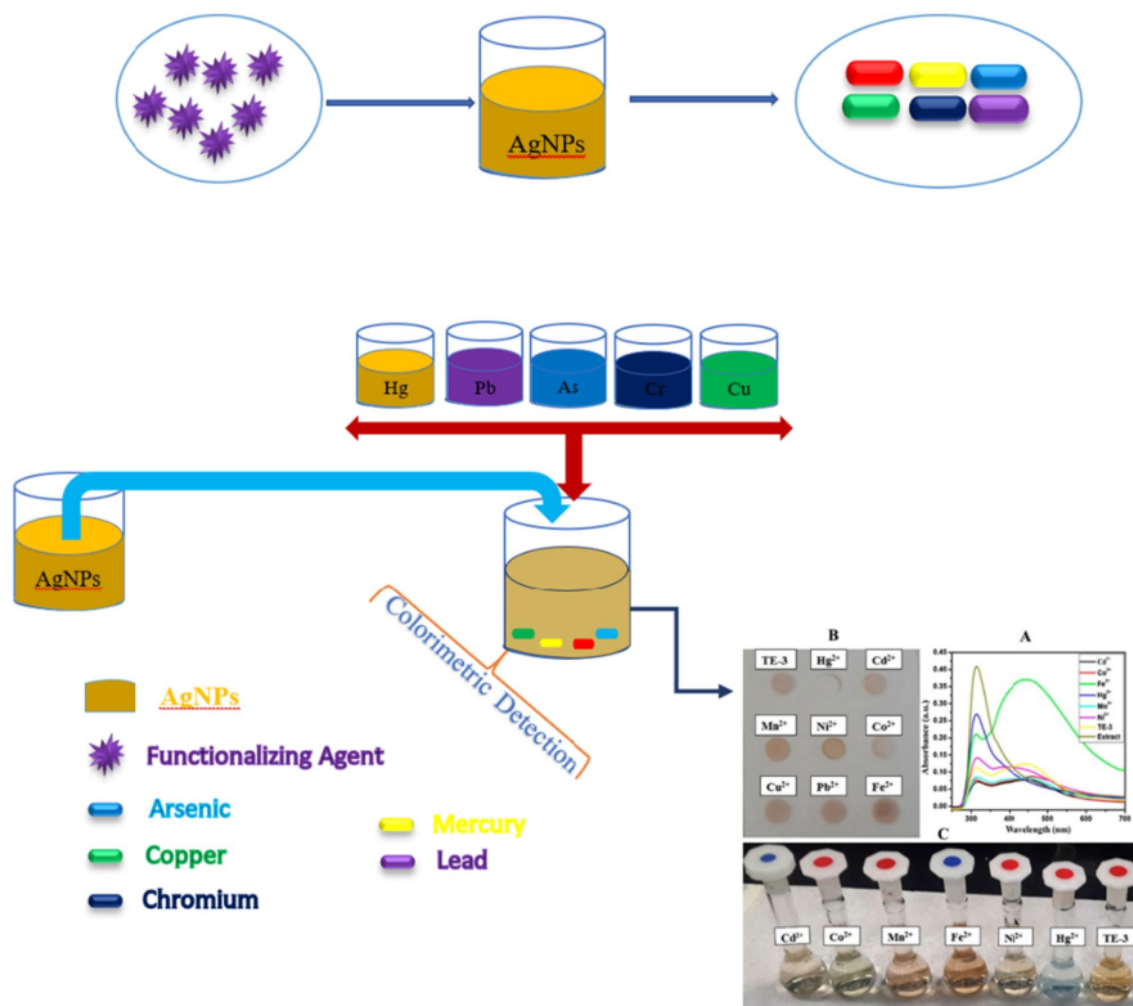
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FSSAI food safety and standards authority of India; WHO world health organization; CODEX codex alimentarius commission, a body under Joint FAO/WHO food standards program in Rome; EU European union; USFDA United State food and drug administration; EPA environmental protection agency

restrictions, such as being time-consuming and requiring the use of modern sample treatment, complex and costly instrumentation, or inapplicability in situ investigation. Accordingly, the advancement of a substitute productive, straightforward, and rapid insightful strategy for sensitive and selective recognition of Hg²⁺ is attracting the attention of researchers (Hao et al. 2020). Synthesis nanoparticles are shown to be used to develop new color sensors to detect Hg²⁺ ions selectively and easily in different media (Ullah et al. 2022).

AgNPs have drawn incredible attention for Hg sensor enhancement mainly because of their sensitivity, which affects micro-level Hg²⁺ concentration fixation changes. This conduct is related to the redox science of Hg²⁺ and Ag surface and the delicate science among metals and sulfur-containing capping agents used for AgNPs. In the two cases, the presence of Hg produces significant changes in the absorbance intensity and peak position of AgNPs. Surface influence plays the most important part in the stabilization and reactivity of AgNPs. Hence, ligand surface





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Fig. 4 Colorimetric sensing of heavy metal by AgNPs (Hyder et al. 2021; Kalam et al. 2018)

chemistry is used to tune their sensing properties (Zannotti et al. 2020).

Methyl mercury (CH_3Hg^+) is another form of Hg that bioaccumulates in inorganic tissues, poisoning the food chain (Mensah et al. 2021). Hg readily methylates to form the extremely toxic CH_3Hg^+ (Liu et al. 2022). CH_3Hg^+ , as the most toxic species of Hg, accounts for 95% of organic Hg and is of particular concern due to its bio amplification factors (106–107) in aquatic organisms via the food chain. Among Hg species, Hg^{2+} is only lower than CH_3Hg^+ in toxicity and can be converted into CH_3Hg^+ under anaerobic conditions in biological systems. Hence, different Hg species must be determined in addition to the total Hg to evaluate its toxicity in the environment (Zheng et al. 2018).

Consequently, surface ligands produce various properties and limitations of NPs, which will aggregate or disaggregate and cooperate with components and particles present in their environment. Surface ligands influence the detection against metal particles such as the altered selectivity and sensitivity of Hg^{2+} . Thus far, a limited number of studies reported the colorimetric identification of Hg^{2+} particles utilizing green synthesized unmodified AgNPs in liquid media. Numerous biomaterials from various plants, fruits, and leaves are utilized for the photoinduced green synthesis of AgNPs. A biomaterial was added as a stabilizing agent and applied in Hg^{2+} detection (Proposito et al. 2019). Citrus extracts from gum kondagog which are frequently used to decrease/settle the level of AgNPs, were applied as a direct colorimetric



sensor for the sensitive discovery of Hg^{2+} (Rastogi et al. 2014).

Sensing of Manganese (Mn)

Manganese is one of the significant resources, with more than 90% being used in the steel industry. China is the largest electrolytic metal Mn maker, producing approximately 1.40 million tons every year and representing over 97.0, paying little heed to the worldwide supply. In 2018, 49 electrolytic Mn metal ventures were recorded in China, with a limit of 2.26 million tons. Mn is one of the necessary minor components in the body, with functions involved in bone transformation phenomena, lipids, amino alkanolic corrosion, and carbohydrate metabolism. The average intake of Mn is in the range of 2 and 9 mg/day (for a mean 70 kg individual). Ordinarily, the brain contains a small amount of Mn, and the insufficiency and excess amount of Mn fundamentally influence its capacity (Nie et al. 2017).

Nonetheless, exaggerated exposure to Mn may cause manganese. An inebriated individual may suffer from depression, disposition swings, enthusiastic practices, and psychosis. Consequently, several optical methods for Mn^{2+} detection have been reported: AAS, inductively coupled plasma–atomic emission spectroscopy (ICP–AES), and ICP–MS. However, the significant parts of them require refined hardware and modern strategies, making them time-consuming and inconvenient to use. In this regard, the sensitive, selective, and straightforward detection procedure for detection of Mn^{2+} gains fundamental (Hu et al. 2014).

A few scientific methods for the detection of Mn^{2+} have been reported: ICP spectroscopy, AAS, and ICP–AES. Nevertheless, these methods need complex systematic processes and expensive equipment, making them inconvenient and time-consuming (Zhou et al. 2012). Colorimetric methods, which include unprecedented effects on the applications for metal ions, have drawn attention.

To date, different colorimetric sensors have been used for functional metal NPs. AgNPs are incredibly appealing due to their optical, electrical, and synthesis properties, especially in the field of location with detection. In addition, they will occasionally be perceived with unaided eyes for certain purposes. A fundamental disadvantage of the abovementioned methods is their sensitivity; accordingly, the sensitivity of a colorimetric sensor for detection can be developed (Hu et al. 2014).

Sensing of Lead (Pb)

The heavy-metal pollution in the air, soil, and water is a significant issue and a devastating danger for the humankind and the environment. The sources of heavy-metal contamination in the environment are petroleum, paper, plastic, coal,

and color enterprises. Certain metals, including Pb, Cu, Hg, and Cd particles, show toxicity in trace amounts. Pb is the second most toxic substance because of its wide use. Pb has been applied as an additional substance in fossil fuel, paint shades, electric stockpiling batteries, building development, projectiles, shot patch, and pills (Cheon and Park 2016).

Pb^{2+} is an exceptionally toxic heavy-metal ion that can cause genuine environmental and medical issues but is universally used in industries. Broad investigations have demonstrated that people, particularly youngsters, can experience extremely durable neurological harm and brokenness when displaying low blood levels of Pb. Until this point, no protected limit for Pb exposure has been recognized. In the brain, Pb-instigated harm in the prefrontal cerebral mantle, hippocampus, and cerebellum can cause the spread of neurologic problems. At the atomic level, Pb ions meddle with the administrative activity of calcium in cellular processes and disturb an assortment of intracellular biological activities (Noh et al. 2015).

The WHO suggested the value of $0.01 \text{ mg}\cdot\text{L}^{-1}$ as the most significant restriction of Pb^{2+} in drinking water. Low-level Pb exposure can cause neurological, conceptive, cardiovascular, and formative problems, kidney harm, muscle loss of motion, cognitive decline, and anemia (Cheon and Park 2016). Pb^{2+} is a risky metal material and a prominent eco-sphere modern pollutant. It has been pronounced as such because of the basic peril it induces, particularly in non-industrial nations worldwide. Human bones and delicate tissues can accumulate Pb^{2+} , which results in human organ debilitations; at an excessive level, such a condition will cause the body to terminate. Thus, the quantity of such poisonous metal particles in liquid conditions must be determined. Such a step is likewise essential in most applications, such as natural observation, control of normalized water quality, and reuse of water contaminated with Pb^{2+} (Khan et al. 2018a, b).

In this way, effortless strategies for the monitoring of Pb^{2+} levels in the environment are gaining significance. A sensitive method for the regular and adequate estimation of the Pb^{2+} concentration is critical in environmental assessment. Up to this point, the spread of scientific methods, including AAS, ICP–MS, fluorescence, and electrochemical methods, has accounted for the determination of Pb^{2+} particles. However, most of these procedures require complex instrumentation and general prepared settings. Henceforth, the advancement of a precise, quick, and helpful analytical method for the detection of Pb^{2+} remains a challenge for physicists (Noh et al. 2015).

Sensing of Copper (Cu)

Many heavy metals in the environment, climate, and living systems affect directly or indirectly the biota and humankind.



Cu is the third fundamental metal that causes changes in human bodies. However, the over-administration of Cu can harm the liver and kidney, expand imperative symptoms and respiratory rates, and damage the focal systema nervosum. Although Cu is a significant element, its concentration affects the physical body. Its bioaccumulation causes oxidative pressure and neurodegenerative infections. Thus, the WHO suggests that a close to 2 mg L^{-1} Cu concentration be permitted in beverages (Flores et al. 2017).

Cu^{2+} is a cation causing sizable fundamental changes in far-reaching industrial applications, such as in biological fields. Cu^{2+} additionally acts as a reactant cofactor in numerous metalloenzymes, including superoxide dismutase and tyrosinase. The sufficiency of Cu^{2+} may cause a few perilous illnesses. A high measure of Cu^{2+} inside the body can cause extreme conditions, such as gastrointestinal confusion to liver or kidney harm. Consequently, the specific detection of Cu^{2+} is an environmental and biological concern (Iftekhar et al. 2021).

Several developed methods have been broadly applied for the detection of Cu^{2+} particles; these methods include electrochemical sensing (Flores et al. 2017), ICP–AES (Shoae et al. 2012), and fluorescence analysis (Zhang et al. 2014). Fluorescence analysis has drawn expanding consideration because of its simplicity, minimal expense, high sensitivity, and selectivity. Moreover, these methods are inconceivably requesting and sensitive and include high working expenses, time-consuming pretreatment cycles, and considerable preparative or test sample analysis (Iftekhar et al. 2021). Therefore, fluorescent sensors for detecting Cu^{2+} have caught the interest of researchers. Together with fluorescent probes, NPs have raised an extensive scientific interest because they need to be generally applied inside the detection field for most analyses (Xu et al. 2019).

Sensing of Chromium (Cr)

Chromium is one of the essentially bountiful components usually present in earth, in the outside layer of rocks, soils, silt, plants. In nature, the chromite metal $[\text{FeCr}_2\text{O}_4]$ has two oxidation states: the trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) forms. The oxidation states vary in terms of their accessibility and harmfulness. Between Cr (VI) and Cr (III), the essential one is more poisonous considering its high solvency and portability in natural frameworks. Cr is expansive because of the applications in arranged enterprises, such as materials, color, calfskin, substance assembly, and metal finishing (Sharif et al. 2015).

Cr provides a quick result on physiological capacities and helps with the conventional digestion of different food sources, such as starch, protein, nucleic acids, and fat, and a critical ultra-follow supplement in the eating routine of people and creatures (Chamaraja et al. 2021). Low-level Cr^{3+} is

significant for ordinary physiological function. In this manner, a conspicuous part participates in lipid, protein, macromolecule, and glucose resistance digestion in humans. High convergences of Cr inside the body reach the DNA and break down tissue cells. Notwithstanding Cr's hazardous nature, different modern exercises consistently add Cr species to the environment, causing Cr contamination (Sharif et al. 2015).

Cr is a solid oxidizer that has a relationship with infections and the Cr content in human tissues and organs. Thus, it has been associated with certain medical problems, including persistent gastroenteritis, dermatitis, cancer, and septum perforation (Yokota et al. 2019). Cr ions are generally used in various economic applications, such as chrome plating, shade creation, calfskin tanning, landfill filtering, and impeccable handling. Cr^{6+} ions are prevalent in the environment and may be detected in normal water because of their vast scope of use in different industries (Kanagaraj et al. 2017).

Different novel nanotechnology-based colorimetric tests, including those dependent on label-free AgNPs (Elavarasi et al. 2014) and AgNPs capped with tartaric acid (Shrivastava et al. 2019), have been conducted for the detection of Cr^{6+} ions. However, scientific methods utilizing changed NPs have shown restricted selectivity and sensitivity in the detection of Cr^{6+} ions. For more detail about type of heavy metal detection, limit of detection (LOD) based on functionalizing agent, linear range, and particle size from various reference clearly can be seen in Table 2. The particle size of NPs was usually determined using transmission electron microscope (TEM) or scanning electron microscope (SEM), and crystallite size by quantitative analysis of X-ray diffraction (XRD) spectra (Ilyas et al. 2019), (Ilyas et al. 2021), (Tahir et al. 2021).

Challenges and future prospects

Over the past few decades, heavy-metal toxicity has become a serious threat to humans and the environment. Heavy metals are evident entities that have the potential to cause several dangerous health risks due to their long half-life, potential accumulation in various parts of the body, and non-biodegradability (Abdelsattar et al. 2022). Sensor-based methods for the detection of heavy/toxic metals have been developed.

AgNPs have emerged as promising nanotools for the detection of heavy metals. Their solidness, similarity to liquid media, simple surface functionalization, and scaling down has favored their application in detection and recognition, in contrast to the utilized traditional method. AgNPs give a formative stage to attainable and practical examination by conquering the typical procedures that incorporate extended conventions and refined instrumentation.

In the future, the research of nanocomposites and multifunctional NPs for heavy-metal sensors in the environment



Table 3 Performance of AgNPs with various functionalizing agents as a sensor for the detection of heavy metals using certain characteristics and synthesis methods

Metal	Functionalizing agent	Particle size (nm)	Linear range	LOD	Synthesis method	Analysis method	Reference
Hg ²⁺	Unmodified Ag NPs	–	25 × 10 ⁻⁹ –500 × 10 ⁻⁹ M	17 × 10 ⁻⁹ M	–	Colorimetric	Wang et al. (2010)
	Unmodified Ag NPs	–	10 ⁻¹⁰ × 10 ⁻⁶ M	2.2 × 10 ⁻⁶ M	Green synthesis	Colorimetric	Farhadi et al. (2024)
	Dendrimer-stabilized Ag NPs	12.1	0.01–10 ppm	–	Chemical	Colorimetric	Yuan et al. (2013)
	Citrate-Ag NPs	65.23	–	90.9 × 10 ⁻¹² M	Chemical	SERS	Ren et al. (2012)
	Small gel-Ag NPs	5.0	0.50–800 × 10 ⁻⁹ M	0.125 × 10 ⁻⁹ M	–	Colorimetric	Sun et al. (2014)
	4-mercaptopyridine-Ag NPs	–	1–100 × 10 ⁻⁹ M	0.34 × 10 ⁻⁹ M	Physical	Vibrational spectroscopic	Chen et al. (2014)
	Cysteine-Ag NPs	–	–	1 × 10 ⁻¹² M	Chemical	SERS	Wang et al. (2010)
	Polymethacrylic acid-Ag NPs	20	10 × 10 ⁻⁹ –20 × 10 ⁻⁹ M	< 10 × 10 ⁻⁹ M	Hydrothermal	Colorimetric	Liu et al. (2013)
	L-Tyrosine-Ag NPs	13	1–300 × 10 ⁻⁹ M	53 × 10 ⁻⁹ M	Green synthesis	Colorimetric	Annadhasan et al. (2014)
	Neem leaf extracts Ag NPs	20	0–140 × 10 ⁻⁶ M	< 1 × 10 ⁻⁶ M	Green synthesis	Colorimetric	Karthiga and Anthony (2013)
	Unmodified Au–Ag NPs	–	0.1–1.0 × 10 ⁻⁶ M	5.0 × 10 ⁻⁹ M	Chemical	Colorimetric	Li et al. (2014)
	Gln-His-Ag NPs	~ 10	1.0–500 × 10 ⁻⁶ M	0.9 × 10 ⁻⁶ M	Chemical	Colorimetric	Buduru et al. (2017)
	Citrate/L-cysteine AgNPs	2	–	3.0 × 10 ⁻⁶ (0.6 ppm)	Chemical	–	P. 28, osito et al. (2019)
	Gelatin /AgNPs	23	0.14–0.5 mg L ⁻¹	64.9 nM	Chemical	Colorimetric	Zannotti et al. (2020)
	Unmodified AgNPs	8.6	1.25 pM–125 nM	25 nM	Chemical (drop casting)	Colorimetric	Jeevika and Shankaran (2014)
	<i>Durio zibethinus</i> /AgNPs	97.37	10–50 nm	0–33 μM	Green synthesis	Colorimetric	Sengan et al. (2018)
	AgNPs/ MBO	~ 20	0–835 ppt	9.2 pM	Chemical	Colorimetric	Bhattacharjee et al. (2018)
	AgNPs/ MBI	~ 20	0–2760 ppt	46 pM	Chemical	Colorimetric	Bhattacharjee et al. (2018)
	AgNPs/ MBT	~ 20	0–3294 ppt	92 pM	Chemical	Colorimetric	Bhattacharjee et al. (2018)
	AgNPs/ 2-aminopyrimidine-4,6-diol	18	10–50 μM	0.35 μM	Chemical	Colorimetric	Prasad et al. (2018)
AgNPs/ starch	15.4 ± 3.9	4.5–2500 nM	4.5–2500 nM	Physical	Colorimetric	Vasileva et al. (2017)	



Table 3 (continued)

Metal	Functionalizing agent	Particle size (nm)	Linear range	LOD	Synthesize method	Analysis method	Reference
Pb ²⁺	PVA/ AgNPs	–	0.2–1.4 ppm	0.1609 mg L ⁻¹	Green synthesis	Colorimetric	Taufiq et al. (2021)
	37 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione AgNPs	10	0.1–0.6 µg mL ⁻¹	0.06 µg mL ⁻¹	Chemical	Colorimetric	Noh et al. (2015)
	Green synthesized-AgNPs	20	0.5–25 µM	0.1 µM	Green synthesis	Colorimetric	Khan et al. (2018a, b)
	Paper-AgNPs/PVA	22.5	241 nM–4.8 µM	96 nM	Green synthesis	Colorimetric	Shrivastava et al. (2019)
	Gluc-Ag NPs	–	9.57 ± 2 nm	0.203 × 10 ⁻⁶ M	Chemical	Colorimetric	Choudhury and Misra (2018)
	(AgNPs/ dithizone)	14	0.5–10 µg/L	62 0.64 µg/L	Chemical	Colorimetric	Roto et al. (2019)
	16 AgNPs/ 3,4-dihydroxy-L-phenylalanine	20	65–125 µM	81 µM	Green synthesis	Colorimetric	Cheon and Park (2016)
	AgNPs/ L-Tyrosine	17 ± 2	16–100 nM	16 nM	Green synthesis	Colorimetric	Annadhasan et al. (2014)
	16 AgNPs/ 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione	10	1.2–7.3 µM	96.5 nM	Physical	Colorimetric	Noh et al. (2015)
	AgNPs/ Gluconate	9.57 ± 2	0.5–2.0 µM	0.203 × 10 ⁻⁶ M	Chemical	Colorimetric	Choudhury and Misra (2018)
Mn ²⁺	(TMB)-(PEI)/AgNPs	–	20 nM to 1 µM	1 nM and 200 nM	Chemical	Colorimetric	Zhang et al. (2022)
	4-MBA-MA-AgNPs	–	5 × 10 ⁻⁷ mol/L to 1 × 10 ⁻⁵ mol/L	50 nM	Chemical	Colorimetric	Zhou et al. (2012)
	Clove-AgNPs	25	0.4–2.0 µM	0.2 µM	Chemical	Colorimetric	Joshi et al. (2016)
	P ₃ O ₁₀ ⁵⁻ -AgNPs	–	0.05–20 µM	0.1 µM	Chemical	Colorimetric	Gao et al. (2013)
	Na ₄ P ₂ O ₇ -HPMC-AgNPs	15	11.8 to 12.7 µM	0.5 µM	Chemical	Colorimetric	Wu et al. (2015)
	CA-AgNPs	~ 1	0–0.8 µM	5 nM	Chemical	Colorimetric	Qi et al. (2017)
	NTTA-AgNPs	11	0.05–10 µM	0.5 µM	Chemical	Colorimetric	Wei et al. (2018)
	AgNPs/ L-Tyrosine	8.2 ± 2	16–500 nM	16 nM	Green synthesis	Colorimetric	Annadhasan et al. (2014)



Table 3 (continued)

Metal	Functionalizing agent	Particle size (nm)	Linear range	LOD	Synthesize method	Analysis method	Reference
Cu ²⁺	4-MBA AgNPs	~10	1 × 10 ⁻⁷ –1 × 10 ⁻⁴ M	2.5 × 10 ⁻⁸ M	Chemical	Colorimetric	Zuo et al. (2011)
	PADs AgNPs	10	7.8–62.8 mM	7.8 nM	Physical	Colorimetric	Ratnarathorn et al. (2012)
	AgNPs / gelatin hydrogels	–	1 × 10 ⁻⁸ –1 × 10 ⁻⁴ M	1 × 10 ⁻⁷ M	Chemical	Colorimetric	Jeevika and Shankaran (2014)
	Trehalose–AgNPs	0.23	1.92 nM	0.817–5.66 μM	Chemical	–	Maruthupandi and Vasimalai (2021)
	Cdots–AgNPs	33.8 ± 3.4	0.005–1 μM	4.81 nM	Physical	Colorimetric	Wei et al. (2019)
	Flow-batch/Ag NPs/ Na ₂ S ₂ O ₃ /Cu ²⁺	25 ± 5	0.5–35 μg/L	0.24 μg/L	Chemical	Colorimetric	Peng et al. (2017)
	R-PE-AgNPs	8	0 μM to 100.0 μM	0.0190 μM	Green synthesis	Colorimetric	Xu et al. (2019)
	(DNA-Ag NCs)	2	5.0–125.0 (μM)	0.500 μM	Chemical	Colorimetric	Liu et al. (2012)
	AgNPs 2-aminothiopheny	5.5	0.0005–50.0 (μM)	0.0005 μM	Physical	Fluorescent	Tharmaraj and Pitchumani (2013)
	Chitosan-capped AgNPs	20	3.33–40.0 (μM)	0.0103 μM	Chemical	Colorimetric	Zuo et al. (2011)
	DSP-AuNPs / AgNPs	–	1.0–1000 nM	0.48 nM	Chemical	Electrochemical	Cui et al. (2014)
	AgNPs/ casein-peptide	20 ± 2	0.08–1.44 μM	0.16 μM	Physical	Colorimetric	Ghodake et al. (2018)
	AgNPs/ 3,4-dihydroxy-L-phenylalanine	20	65–125 μM	94 μM	Green synthesis	Colorimetric	Cheon and Park (2016)
	AgNPs/ Riboflavin	20	5–100 μM	1.12 nM	Green synthesis	Colorimetric	Basiri et al. (2017)

will be real-time directed toward the location of numerous analytes during a solitary go with improved affectability and handiness. Furthermore, nanochips are being pushed for improvement, wherein NPs are immobilized into tiny chip-like materials and utilized for detector applications. This venture may open new vistas for the creation of a “lab to chip” strategy for the sensitive detection of metal ions in tainted water bodies. Third, the origination of a novel innovation that licenses possible recognition and evaluation of metal particles in defiled samples will help in screening and limit environmental toxicity, subsequently providing protection to humans and government assistance. A consensus among physicists, scientists, and researchers will help in the assembly and commercialization of these entertainers, which may work with the usage of various tests in the laboratory and field for metal identification.

Conclusion

This paper investigated the synthesis and functionalization of AgNPs, which can be used as a sensor for heavy metals (Cu²⁺, Hg²⁺, Cr²⁺, Pb²⁺, Mn²⁺, and As²⁺), using different synthesis methods (chemical, physical, and biological). In conclusion, endeavors were explored to create nanomaterial-based sensors for the detection of heavy metals for further development of the sensitivity, selectivity, and execution of gadgets. Better affectability and selectivity in the detection of heavy metals are accomplished when using nanomaterials as sensors. Physical and chemical methods have the advantage of high surface-to-volume ratio of high-functionality nanomaterials used in the detection of heavy metals. On the other hand, biological method-based sensors from steady, economical, biocompatible, and nontoxic inorganic reagents



offer the best results due to their high limit of detection, low cost, and accessible applications. For advances and developments in detection of heavy-metal ions using these nanosensors were poses incredible improvement challenges.

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Declarations

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