



Identification of heavy metal ions from aqueous environment through gold, Silver and Copper Nanoparticles: An excellent colorimetric approach

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ABSTRACT

Heavy metal pollution has become a severe threat to human health and the environment for many years. Their extensive release can severely damage the environment and promote the generation of many harmful diseases of public health concerns. These toxic heavy metals can cause many health problems such as brain damage, kidney failure, immune system disorder, muscle weakness, paralysis of the limbs, cardio complaint, nervous system. For many years, researchers focus on developing specific reliable analytical methods for the determination of heavy metal ions and preventing their acute toxicity to a significant extent. The modern researchers intended to utilize efficient and discerning materials, e.g. nanomaterials, especially the metal nanoparticles to detect heavy metal ions from different real sources rapidly. The metal nanoparticles have been broadly utilized as a sensing material for the colorimetric detection of toxic metal ions. The metal nanoparticles such as Gold (Au), Silver (Ag), and Copper (Cu) exhibited localized plasmon surface resonance (LPSR) properties which adds an outstanding contribution to the colorimetric sensing field. Though, the stability of metal nanoparticles was major issue to be exploited colorimetric sensing of heavy metal ions, but from last decade different capping and stabilizing agents such as amino acids, vitamins, acids and polymers were used to functionalize the metal surface of metal nanoparticles. These capping agents prevent the agglomeration of nanoparticles and make them more active for prolong period of time. This review covers a comprehensive work carried out for colorimetric detection of heavy metals based on metal nanoparticles from the year 2014 to onwards.

1. Introduction

Nanotechnology is the field of science that has significantly reached at remarkable achievements and developments during the past few decades (Al Sharabati et al., 2021; Aykan, Karaman, Karaman, Necip, & YOLA, 2021; Karimi-Maleh et al., 2022; Karimi et al., 2022). Nanoscience has made several types of materials at the nanoscale level (Karimi-Maleh et al., 2011; Khand et al., 2021; Orooji et al., 2021; Salmanpour et al., 2018; Tajik et al., 2021a, 2021b). Nanoparticles have

a broad range of components that consist of particulate substances that have one dimension below 100 nm (Laurent et al., 2008). They can be categorized into various classes based upon their properties, forms and magnitude. They possess different groups like fullerenes, metal NPs, ceramic NPs, polymeric NPs. Nanomaterials have exceptional properties due to the large surface to volume ratio (I. Khan, Saeed and Khan, 2019). The metal nanoparticles are precisely made up of their precursor salts. Significant scientific attention has been focused on the production and application of metal nanoparticles. As metal nanoparticles possess

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various shapes and sizes that permit many researchers to bear their fascinating applications in many fields such as sensors, electronics biotechnology, catalysis and optical devices. Due to their top distinctive and exciting localized plasmon resonance surface (LSPR), metal nanoparticles, especially gold (Au), silver (Ag), and copper (Cu) had drawn fabulous responses than the other metals (Zhu et al., 2008). Precisely metal NPs such that gold, silver, and copper, size in between 10 and 60 nm show LPRS band at about 520 nm, 400 nm, 570 nm with splendid purple, yellow and red colloidal color (Eustis and El-Sayed, 2006; Shu et al., 2015; Smitha et al., 2008; S.-H. Wu and Chen, 2004). When the metal NPs' size decreases to the nanoscale, a rugged UV-Visible excitation band peak is detected due to the combined oscillation showing band electrons at the metal surface. Unlike the ordinary UV-Visible band, this LPRS of metal NPs is the nanoscale size characteristics and exhibits extreme sensitivity toward the arrangement and structure of the nanomaterials (Tatsuma, 2016). The LPRS property of metal NPs intensely depends upon their interparticle distance among the aggregated metal NPs; thus, the metal absorption LPRS allowed to be used as an analytical tool for colorimetric detection and optical characteristic of different chemical species with low cost and enhanced sensitivity (H. K. Sung, Oh, Park and Kim, 2013). Metal NPs can be synthesized by chemical or physical methods, commonly bottom-up and top-down approaches have been used for the preparation of metal NPs like chemical reduction (Mondal et al., 2007), solvothermal (Jang et al., 2007), vacuum vapour deposition (Zongwen Liu & Bando, 2003), electrochemical (Raja et al., 2008), biosynthesis (Ahmad et al., 2003; Dhas et al., 1998; Mandal et al., 2006) etc. There has been an extensive release of heavy metal ions in the environment that severely affects human beings and aquatic life. Some of the heavy metals, like lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), and chromium (Cr) are highly toxic and pose dangerous effects on human health even at trace level. These toxic heavy metals can cause many health problems such as brain damage, kidney failure, immune system disorder, muscle weakness, paralysis of the limbs, cardio complaint, nervous system, etc. (Jamil Ahmed Buledi, Amin, Haider, Bhangar and Solangi, 2020; Ha et al., 2017; Kim et al., 2016). The main source of their entrance into waterbodies are from various industrial discharge such as, metal plating and finishing, plumbing, petrochemical, pesticides, burning of coal, battery manufacturing, painting and paper industries etc. The acceptable limit of heavy metal ions such as lead, cadmium, mercury, arsenic and chromium ions in drinking water according to World Health Organisation (WHO) is around 0.01, 0.003, 0.00, 0.05 and 0.5 mg/L, respectively (Chowdhury et al., 2016).

Numerous analytical techniques have been employed to monitor the heavy metals at the trace amounts in the environment, such as atomic absorption spectroscopy (AAS) (Tinas et al., 2018), spectrofluorimetric (SF) (Zhihong Liu, Wang, Mao and Cai, 2000), atomic emission spectrometry (Rao et al., 2002), electrochemistry (Dali et al., 2018), stripping voltammetry (Luo et al., 2017), inductive coupled mass spectrometry (ICP-MS) (Ohira et al., 2015; Peš et al., 2008), surface enhanced-Raman scattering spectroscopy (Ji et al., 2015), Fluorescence, and UV-visible spectrometry (C. Dong et al., 2016; Zhao et al., 2017a; Zhao et al., 2017b). These techniques are proper and accurate but require lengthy sample preparation, skilled staff, costly instruments, adequate handling and time expanding procedures. Therefore, these issues can be conclusively retaliated using an easy and delicate colorimetric method that can effectively detect the target material by observing a change in color (Zhai et al., 2019). Such colorimetric methods can be used for the sensing of noxious gases (Tang and Sun, 2018), organic pesticides (Bala et al., 2015; Bala et al., 2018a, 2018b), and also for biomolecules (Bala et al., 2018a, 2018b; Hyder et al., 2021). For this objective, many metal nanoparticles like gold, silver, and copper can be used broadly for the colorimetric biosensing of different targets since these metal NPs have a high surface area, superb optical properties, high molar absorptivity and their surfaces can be customized with different stabilizing and capping agents as well. These stabilizing and

capping agents can keep metal nanoparticles active for long period of time. Moreover, if the cost and the stability issue of metal nanoparticles is resolved, the life span, future and their sensitivity can be easily sustained. (Bajaj et al., 2018; Jamil A Buledi et al., 2021; Panhwar et al., 2021; Schwartzberg et al., 2006). Beside, the sensing properties and applications there are numerous industrial applications of metal nanoparticles according to their low cost as compared to the other materials. In addition, amongst the metal nanoparticles Au NPs are broadly used in the biotechnology and biomedical field because they absorb light very strongly and their absorption maxima can be altered from visible to the near infrared region where tissue absorb weakly. The metal NPs are highly sensitive to light and hence are broadly applied as naked eye sensor for targeted analytes.

2. Colorimetric sensing of heavy metal ions through AuNPs

Gold is a chemical element with the symbol Au, derived from the Latin word aurum and having atomic number 79. Chemically, gold is the transition element of group 11 element. The oxidation number of Au varied from -1 to $+5$ but mostly (Au^{+1}) and (Au^{+3}) dominates its chemistry. With the progress of nanoscience, noble metals have got great attention in recent years due to their distinct photoelectric and physicochemical properties. Among precious metal NPs, Au NPs have attracted much attention from researchers involving spectral study because of their high value of molar absorptivity (2.7×10^8 – 3.7×10^9 $M^{-1} cm^{-1}$ in the region of UV-visible (Kreibig and Genzel, 1985). Depending on the size of the AuNPs, the agglomerated AuNPs exhibit red to blue shifts, respectively (H. Li and Rothberg, 2004). Au NPs can be successfully prepared via chemical as well as physical method and can be modified with the different stabilizing agents to prevent further oxidation and aggregation. Au NPs can be used for the colorimetric assay for the detection of toxic heavy metal ions. The colorimetric method is an easy low cost, can be used without expensive instruments, while the analyte can be monitored through the visual color change (F. Wang et al., 2013).

The Au NPs have been synthesized via chemical methods using diglycolic acid as a capping agent and stabilizing agent. Various analytical tools characterized the successfully prepared Au NPs, and the size of synthesized NPs was determined to be around 30 nm, and the UV-visible peak observed at 520 nm manifested wine-red color, which confirms the successful preparation of AuNPs. The fabricated NPs were applied for the colorimetric detection of Cr (VI), with high sensitivity and linear dynamic range from 0.332 ppb to 0.1 ppm, with LOD found to be 0.32 ppb. The proposed method was based on the LPRS (Zhang et al., 2019). In another study (Yu et al., 2017), prepared the Au NPs through the chemical method and effectively functionalized them with mercaptosuccinic acid (MPC). The successfully prepared Au NPs were applied for different characterization analytical techniques, which determined the average size of synthesized NPs around 17–28 nm. Subsequently, the prepared material was used for the colorimetric determination of Cr^{3+} , and the LOD was estimated as 0.04 μM through UV-visible spectroscopy. Moreover (Sang et al., 2018), synthesized the Au NPs by the chemical method, and the surface was customized with a zwitterionic amino acid to control size and functionality. The size and morphology of NPs were determined by analytical tools that reveal that the average size was about 13 nm, and red color was observed for prepared NPs. The successfully prepared Au NPs were used for simultaneous colorimetric detection of Cr^{3+} and Pb^{2+} ions. The limit of quantification and limit of detection was found to be 20–30 μM and 1–2 μM for Cr^{3+} and Pb^{2+} ions, respectively. In addition (Yu et al., 2016), have synthesized the gold nanoparticles through hydrothermal processes and the surface was modified with Glutathione to reduce the particles size and increase their stability. The size was investigated through various analytical tools, which were found to be 20.6–1.4 nm. The synthesized NPs exhibited wine red color and when agglomerated with Pb^{2+} ions, the color changed from wine red to yellow and then finally attained purple color which confirm the colorimetric determination of Pb^{2+} ions. The LOD

was observed as 15 nm and 13 nm visually and instrumentally. Furthermore (Qiu et al., 2019), have carried out the synthesis of AuNPs via chemical method in which 3-mercaptopropionic acid and 4-amino benzo-18-crown-6 (3-MPA-abc) were used as functionalizing and stabilizing agent to enhance the surface area of particles. The size of the particles was examined by different analytical instruments and the average size of NPs was observed around 13 nm. The successfully synthesized material was used as colorimetric probe for the detection of Pb^{2+} ion with low LOD 50 nM while linear relationship was about 0.9934.

While in another experimental study (Dehghani et al., 2019) prepared the Au NPs with chitosan as a capping as well as reducing agent. Different analytical tools were used to characterize the surface morphology and the size of the prepared material, which revealed the ultra-small size of about 1–2 nm. The synthesized material was successfully applied for the colorimetric sensing of Pb^{2+} ions. The LOD was found to be 16 nM, and the linear range was from 25 nM to 1 μ M, respectively. Moreover (Lei et al., 2019), successfully synthesized AuNPs by using pyridine-formaldehyde as functionalizing as well as reducing agents to limit the size and enhance the stability. The Au NPs were examined through numerous analytical instruments to study the surface morphology and size of prepared particles, which was about 17.8 nm. The synthesized particles were efficiently applied for the selective colorimetric sensing of Pb^{2+} ion. The LOD was found about 4 to 1 μ M. The color changed rapidly when the solution of metal nanoparticles interacted with the solution of lead, which was observed by the naked eyes and with the instrument as well. Besides this (Yun et al., 2016), have synthesized Au NPs via chemical reduction method, Denzyme and molecular beacon (MB) were exploited as the reducing as well capping agent for the surface modification and to increase the reactivity of gold metal particles. The prepared material was characterized by several analytical techniques to determine the size of particles which was examined to be 30 nm. The successfully prepared material was used for the colorimetric determination of Pb^{2+} ions while the Linear range was from 0.05 to 5 nM with low limit of detection of 20 pM. In addition (Priyadarshini and Pradhan, 2017), employed valine as both capping and the stabilizing agent during the synthesis of gold NPs. The Au NPs were synthesized by previously reported work. The prepared particles were studied through different techniques to define the size of NPs, which was found to be 26.69 ± 2.64 nm. The fabricated nanomaterials were successfully employed for the colorimetric sensing of Pb^{2+} ion with the minimum limit detection 30.5 μ M. The valine capped Au NPs were highly sensitive to detect Pb^{2+} ions. Herein (Ratnarathorn et al., 2015), effectively-prepared Au NPs through the hydrothermal method capped and reduced by maleic acid. The AuNPs were examined via different analytical tools which determined the size of gold metal particles around 20 nm. Maleic acid capped gold NPs were used for as colorimetric probes for determination of Pb^{2+} ion. The linear range was from 0.0 to 10 μ g/L⁻¹ and the LOD was found to be 0.5 μ g/L⁻¹. The maleic acid modified Au NPs particles were very sensitive and selective for the recognition of Pb^{2+} ion. Additionally, (L. Xu et al., 2019) have synthesized gold NPs via the chemical method and modified them by using poly diene dimethyl ammonium chloride (PDDA) through the aptamer process. The gold nanoparticles' surface morphology and size were determined by various analytical techniques, which manifested microscopic morphology for prepared nanoparticles. The gold nanoparticles were then successfully applied for the colorimetric detection of Cd (II) having linear range 1–400 ng/mL while LOD was found to be about 1 ng/mL respectively. Similarly (Qiu et al., 2019), reported a work related to Au NPs that have been engineered by the previously stated method. The 3-mercaptopropionic acid and 4-aminobenzo-18-crown-6 or (3-MPA-abc), used as the capping as well reducing agent for the gold nanoparticles. Both entities modified the surface of gold particles and reduced the size. Prepared nanoparticles were characterized via many analytical tools, that defined characteristics of synthesized material used for the colorimetric detection of Cd (II) ion. The linear relationship $R^2 = 0.9917$ and

LOD was found to be 20 nM. The gold particles showed quick and fast response toward the Cd (II) ions. However (Leng et al., 2013), fabricated Au NPs manipulated with hexadecyl trimethyl ammonium bromide (CTAB) and dithizone both were used as capping and stabilizing agent. The physical and chemical characteristics of engineered nanoparticles were confirmed by analytical techniques, while the size of AuNPs was observed to be 15 nm. The well-defined nanoparticles were successfully applied for the colorimetric sensing of Cd (II) ion. The limit of detection was calculated to be 10^{-5} M.

Furthermore (Mehta et al., 2015), have synthesized Au NPs through chemical method. Chitosan-dithiocarbamate was used as the modifier and stabilizing agent to control the size of particles. Several analytical tools confirmed the synthesized particles to investigate the shape and the average size of nanoparticles which were found to be around ~15 nm. The prepared particles were successfully applied to determine Cd^{2+} by colorimetric assay probes, which demonstrated the Linear range from 50 to 500 μ M while LOD was found as 63 nM. The chitosan-dithiocarbamate -Au NPs were extremely highly sensitive and selective for Cd^{2+} ions. In addition (A.-J. Wang et al., 2013), synthesized the 5-mercapto-1,2,4, triazole based functionalized Au NPs by chemical reduction method, reduced and stabilizing via chelation process. The carefully capped and stabilized Au NPs have been examined by different analytical tools to determine the average size of particles about 19 nm. The modified Au NPs were subjected to the colorimetric detection of Cd^{2+} ion through the color change from red to blue, which indicated the agglomeration of cadmium ions with gold particles. The LOD was observed at about 30 nM. This color change was monitored by naked eyes as well by a UV-visible spectrophotometer. Besides, this (Y.-M. Sung and Wu, 2014) experimented with the proficient synthesis of Au NPs via chemical reduction method modified and capped by di-(1H-pyrrol-2-yl) methanethione which reduced the particles size and stabilized them for many months. The gold nanoparticles have been examined by several analytical techniques that reveal particles' size around 13 nm. The successfully capped Au NPs were used for colorimetric detection of Cd (II) ions. The limit of detection was observed to be 16 nM, the color of the solution changed from red to blues which confirmed the detection of cadmium ion by UV-visible spectrometer. Furthermore (Boruah and Biswas, 2018), utilized polyethylene glycol functionalized Au NPs prepared by the hydrothermal reduction process. The manipulated gold nanoparticles were employed for the colorimetric detection of AS (III) ion, which has a limit of detection 5 ppb and linear range from 5 ppb to 20 ppb. In addition (Gong et al., 2017), exploited the citrate functionalized AuNPs prepared via chemical reduction method. Various analytical tools studied the citrate-based gold nanoparticles to determine the size of particles, the overall size of a prepared material was 13 nm. The successfully synthesized material was employed for the colorimetric sensing of As (III). The color altered from wine red to blue which confirmed the agglomeration of detectable ions with gold nanoparticles. The low limit detection 1.8 ppb was observed by UV-visible spectrometry. Moreover (T. Yang, Zhang, Yang, Wang and Chen, 2018), prepared Au NPs by citrate-based reduction method and functionalized with a peptide, which acted as a reducing and stabilizing agent. Peptide-based Au NPs were confirmed via different analytical techniques, which manifested the average size of particles at around 13.87 nm. The well-defined Au nanoparticles were deployed for the colorimetric determination of As (III) ion with a low limit of detection 54 μ M (μ g/L⁻¹). The functionalized nanoparticles were very selective for arsenic (III) ions. Furthermore (Zhan et al., 2014), reported the aptamer-based Au NPs prepared through a reported method. The average size of fabricated NPs was found to be 15 nm. The successfully prepared Au nanoparticles were employed for the colorimetric sensing of As^{3+} ion with a linear range from 1.26 to 200 ppb and LOD was calculated as 1.26 ppb. Herein (Lakatos et al., 2015), demonstrated a procedure of S-Layer functionalized Au NPs prepared via reported work. The Au NPs were carefully characterized by several analytical techniques to check the size of prepared particles which was found around 20 nm. The

well-organized Au NPs were applied for the colorimetric detection of As (V) with a limit of detection of 1.7 μM and a linear range of 24 ppb. The color change from burgundy red to blue with aggregated Au NPs. Moreover (Daware et al., 2018), manifested an experiment for AuNPs fabricated via citrate-based reduction method functionalized with the Hexane dithiol and Rhodamine. Various analytical tools were used to investigate the morphology and size of Au NPs functionalized with HDT and RB, the average size of particles was observed about ~ 17 nm. The successfully prepared gold nanoparticles were used for the colorimetric sensing of Hg^{2+} ion. The linear range was 1–60 ng/mL^{-1} with the detection limit 1 ng/mL^{-1} (1 ppb). In addition (D. Huang et al., 2019), have engineered Au NPs through citrate-mediate method functionalized with the dithioerythritol (DETL) which was employed as capping and stabilizing agent. The well-defined Au NPs were applied for the colorimetric investigation of Hg^{2+} ion. The detection limit was found to be 24 nM with two linear range 0.1–0.5 and 0.5–5 μM , respectively. Moreover (Xie, 2018), has utilized AuNPs prepared via the citrate-mediate-based method and capped with trithiocyanuric acid (TMT). The TMT-Au NPs were characterized via several analytical tools, which revealed the average size of particles is about 13 nm. The successfully prepared Au NPs were employed for colorimetric detection of Hg^{2+} ion with low LOD of 2.8 nM while the linear range from 5×10^{-9} to 1×10^{-6} M. The TMT-Au NPs were highly sensitive and selective for mercury (II). Likewise (Xie, 2018), exploited AuNPs prepared via a citrate-based method modified with aminopropyltriethoxysilane (APTES). APTES-Au NPs were confirmed by numerous analytical techniques that determine the size of particles about 13 nm. The successfully prepared nanoparticles were effectively applied for the colorimetric determination of Hg^{2+} ion with LOD of around 10 nM and linear range from 0 to 92.3 nM accordingly. The APTES-based Au NPs were selective toward the mercury (II) ion. Furthermor (P.-C. Yang, Wu and Lin, 2018) have employed Au NPs prepared by chemical reduction method capped with 2-[4-(2-hydroxyethyl) piperazine-1-yl] ethansulfonic acid (HEPEs) on the surface of Au NPs. HEPEs-Au NPs were checked by different analytical techniques to investigate the morphology and size of particles. The overall size was 42.5 ± 0.7 and 38.4 ± 3.3 nm with mercury and without Hg^{2+} .

The fabricated nanoparticles were used for the colorimetric detection of Hg^{2+} ions. The LOD was calculated to be 0.7 nM with a linear range from 1.0 nM to 100 μM . Moreover (Kong et al., 2017), have prepared Au NPs by the previously reported method. The synthesized nanoparticles were carefully capped and stabilized with Mercapto phenylboronic acid (MPBA) to prevent the agglomeration. The synthesized Au NPs were examined by various analytical techniques to determine the size of particles, the overall size of Au NPs was found 16 ± 1 nm. MPBA-based Au NPs were used for colorimetric sensing of Hg^{2+} ions. The LOD was found to be 37 nmoldm^{-3} with a linear range from 0.08 to 1.25 $\mu\text{mol dm}^{-3}$. Herein, (Zhao et al., 2017a; Zhao et al., 2017b) synthesized citrated-mediate Au NPs via the reported procedure. The Au NPs were characterized by different analytical tools that revealed the average size of particles around 15 nm. The manipulated gold particles were employed for the colorimetric detection of Hg^{2+} ions. The linear range was set from 0.5 to 10 nM while the limit of detection was calculated to be 0.26 nM. Furthermore (Kumar and Anthony, 2016), experimented Au NPs synthesized by chemical reduction method and capped with different capping agents to stabilize them. The overall size of Au NPs was about 5–10 nm. The successfully prepared material was effectively applied for the colorimetric detection of Hg^{2+} ions. The LOD was observed to be about 10^{-9} M. Similarly (Sener et al., 2014), performed an experiment for the synthesis of Au NPs through the citrate-mediate method and functionalized with Lysine amino acid on the surface of Au NPs. The Lysine-capped Au NPs were characterized by several analytical techniques which confirmed the average size of gold particles at about 24.5 ± 3.7 nm. The Au NPs were employed for the colorimetric detection of Hg^{2+} ions. The limit of detection was found to be 2.9 nM with linear range from 1 nM to 1000 nM respectively. Detection of heavy metal ions through AuNPs is given in Table 1. The colorimetric detection process of heavy metal ions by Au NPs is shown in Fig. 1.

2.1. Silver metal nanoparticles for heavy metal ion detection

Silver is a chemical element with symbol Ag derived from Latin word Argentum, proto-Indo-European means shiner and white, having atomic

Table 1
Colorimetric sensing of Heavy metals via Gold nanoparticles.

MNPs	Functionalized	Detection	Size	LOD	References.
AuNPs	Diglycolic acid	Cr(VI)	30 nm	0.32 ppb	Zhang et al. (2019)
AuNPs	Mecptosuccinic acid	Cr^{3+}	$17 \pm 2.28 \pm 5$ nm	0.4 μM	Yu et al. (2017)
AuNPs	Zwitterionic amino acid	Cr^{3+}	13 nm	1.2 μM	Sang et al. (2018)
AuNPs	Gluthathione	Pb^{2+}	20.6 ± 1.4 nm	15 nM	Yu et al. (2016)
AuNPs	(3-MPA-abc)	Pb^{2+}	13 nm	50 nM	Qiu et al. (2019)
Au/PtNPs	Chitosan	Pb^{2+}	1–2 nm	16 nM	Dehghani et al. (2019)
AuNPs	Pyridine-formaldehyde	Pb^{2+}	17.80 nm	4–1 μM	Lei et al. (2019)
AuNPs	Molecular Beacon and DNAzyme	Pb^{2+}	30 nm	20 pM	Yun et al. (2016)
AuNPs	Valine	Pb^{2+}	26.69 ± 2.64 nm	30.5 μM	Priyadarshini & Pradhan (2017)
AuNPs	Maleic acid	Pb^{2+}	20 nm	0.5 $\mu\text{g/L}^{-1}$	Ratnarathorn et al. (2015)
AuNPs	PDDA	Cd^{2+}	–	1 ng/mL	(L. Xu et al., 2019)
AuNPs	(3-MPA-abc)	Cd^{2+}	13 nm	20 nM	Qiu et al. (2019)
AuNPs	CTAB and dithioine	Cd^{2+}	15 nm	10^{-5}	Leng et al. (2013)
AuNPs	Chitosan and dithiocarbamate	Cd^{2+}	15 nm	63 nM	Mehta et al. (2015)
AuNPs	5-mecrapto-1,2,4-trizole	Cd^{2+}	19 nm	30 nM	(A.-J. Wang et al., 2013)
AuNPs	di-(1H-pyrrol-2-yl) methane	Cd^{2+}	13 nm	16 nM	(Y.-M. Sung and Wu, 2014)
AuNPs	Polyethylene glycol	As^{3+}	–	5 ppb	Boruah & Biswas (2018)
AuNPs	Citrate	As^{3+}	13 nm	16 nM	Gong et al. (2017)
AuNPs	Peptide	As^{3+}	13.87 nm	54 μM	(T. Yang et al., 2018)
AuNPs	Aptamer	As^{3+}	15 nm	1.26 ppb	Zhan et al. (2014)
AuNPs	S-layer	As^{5+}	20 nm	1.7 μM	Lakatos et al. (2015)
AuNPs	HDT and RB	Hg^{2+}	~ 17 nm	1 ng/mL^{-1}	Daware et al. (2018)
AuNPs	DETL	Hg^{2+}	–	24 nM	(D. Huang et al., 2019)
AuNPs	TMT	Hg^{2+}	13 nm	2.8 nM	[62]
AuNPs	APTES	Hg^{2+}	13 nm	10 nM	Xie (2018)
AuNPs	(HEPEs)	Hg^{2+}	38.4 ± 3.3 nm	0.7 nM	(P.-C. Yang et al., 2018)
AuNPs	MPBA	Hg^{2+}	16 ± 1 nm	37 nmoldm^{-3}	Kong et al. (2017)
AuNPs	Citrate	Hg^{2+}	15 nm	0.26 nM	(Zhao et al., 2017a; Zhao et al., 2017b)
AuNPs	Various capping agents	Hg^{2+}	5–10 nm	10^{-9}	Kumar & Anthony (2016)
AuNPs	Lysine	Hg^{2+}	24.5 ± 3.7 nm	2.9 nM	Sener et al. (2014)

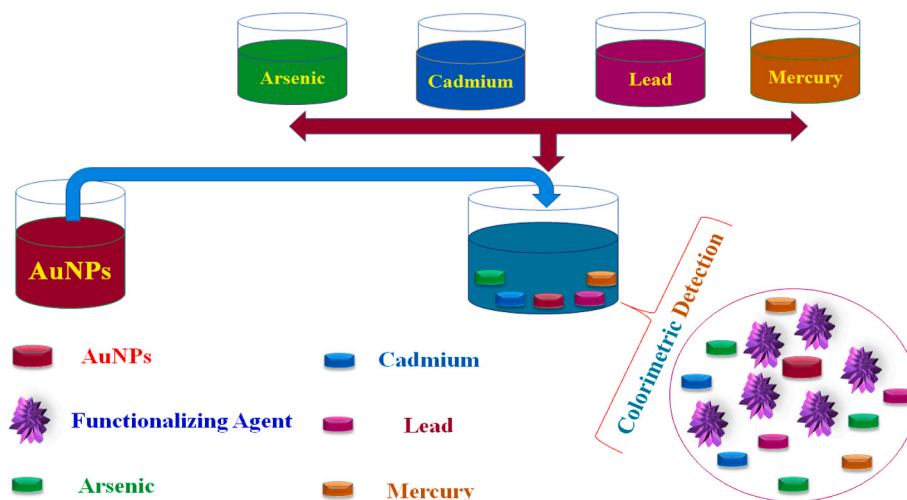


Fig. 1. Colorimetric sensing of heavy metal ions by Au NPs.

number 47 belongs to noble element family. Ag NPs possess outstanding physicochemical properties and can show surface plasmon resonance and become an ideal candidate for various types of applications, e.g. nanomedicine, nanobiotechnology, nanosensors, and electronic devices. From an environmental perspective, the Ag NPs got great attention in sensor technology because of their low-cost preparation method and outstanding properties (Proposito et al., 2016). The Ag NPs are usually manipulated with different capping and stabilizing agents to avoid them from aggregations.

Herein (Choudhury and Misra, 2018), synthesized Ag NPs via chemical reduction method and coated them with gluconate, which acted as a capping as well stabilizing agent for them. The gluc-Ag NPs were characterized by different analytical tools to investigate the crystallinity and size of particles. The average size of Ag NPs was found around 9.57 ± 2 nm with a spherical shape. The successfully prepared particles were employed for the colorimetric sensing of Pb^{2+} ions. The LOD was found to be $0.2029 \mu\text{M}$ with LOQ of $0.6763 \mu\text{M}$. In another study (Roto et al., 2019), have engineered Ag NPs by hydrothermal method using dithizone as capping and reducing agent to protect the surface and control the particle's size. The synthesized Ag NPs exhibited the size of about 35–50 nm. The prepared nanoparticles were employed for the colorimetric detection of Pb^{2+} ion. The LOD was $0.64 \pm 0.044 \mu\text{g/L}$ with a limit of quantification of $2.1 \pm 0.15 \mu\text{g/L}$ and linear range $0.00282 \pm 0.004 \mu\text{g/L}$. Moreover (Xing et al., 2018), have prepared Ag/Au bimetallic NPs by the chemical reduction method, using sodium citrate and tannic acid as reducing and capping agents. The engineered bimetallic particles were examined through various analytical techniques, which revealed the average size of particles about 26 and 59 nm Ag and Au. Meanwhile, the prepared material was applied for the colorimetric detection of Pb^{2+} ions under the linear range from 3 to 180 nM and the Limit of detection was found to be 1.4 nM. In addition (Cheon and Park, 2016), synthesized Ag NPs via chemical reduction method while using PolyDOPE functionalizing and reducing agent. The average size of PolyDOPE based Ag NPs was about 20 nm. The manipulated material was employed for the colorimetric detection of Pb^{2+} ions. The LOD was calculated to be $9.4 \times 10^{-5} \mu\text{M}$. Similarly (Qi et al., 2012), have prepared Ag NPs through chemical reduction method functionalized with Iminodiacetic acid. The analytical techniques tools determined the size of IDA-A NPs of about 7–10 nm. The fabricated Ag NPs were subjected to Pb^{2+} ions with lowest possible LOD 13 nM.

Moreover (Anambiga et al., 2013), have followed a chemical reduction method to synthesise Ag NPs by using glutathione as capping and reducing agent. The GHS-Ag NPs were examined via several analytical techniques to determine the crystalline nature of nanoparticles with a face-centred cubic structure. The successfully prepared

nanoparticles were used for colorimetric probes for Pb^{2+} ion. The LOD was calculated to be 10^{-9} M. Furthermore (Y. Dong, Ding, Jin and Zhu, 2017), prepared Ag NPs by the reported method with chalcon carboxylic acid used as capping and stabilizing agent. The manipulated Ag NPs were examined through various analytical techniques to confirm the successful synthesis of Ag NPs. The Ag NPs were used to determine the colorimetric sensing of Cd^{2+} ion. The limit of detection was 0.13 μM . Similarly (P. Huang, Liu, Jin, Wu and Wan, 2016), synthesized Ag NPs via chemical reduction, using 1-amino-2-naphthol-4-sulfonic acid as reducing and functionalizing agents to modify the surface of Ag NPs. The prepared Ag NPs were analyzed by various characterization tools to investigate the size and crystallinity of Ag NPs. The size of the particles was around 12 and 28 nm. The synthesized material was applied for the colorimetric detection of Cd^{2+} ion, with a limit of detection of 87 nM. Besides, this (Mehta et al., 2016), fabricated Ag NPs by chemical method, using 5-sulfoanthranilic acid dithiocarbamate modified and capping agent for surface modification of Ag NPs. AgNPs were confirmed through numerous analytical techniques to determine the size and morphology of Ag NPs. The overall size was around 20 nm while the synthesized material was employed for the colorimetric sensing of Cd^{2+} ion. The low LOD of 5.8 μM with a linear range concentration of Cd^{2+} ion from 10 to 100 μM . Furthermore (Jin et al., 2015a, 2015b), engineered Ag NPs via the chemical method utilizing 5-sulfosalicylic acid as a capping agent for Ag NPs. The Ag NPs were characterized by different analytical tools to investigate the size and morphology of Ag NPs. The well-defined particles were employed the colorimetric detection of Cd^{2+} ion. The minimum LOD of 3 nM was calculated for Cd^{2+} ions. In a similar case (He et al., 2019), developed and designed a simple and excellent colorimetric sensing assay by utilizing Polyvinylpyrrolidone (PVP) functionalized Ag NPs to determine the hexavalent Cr^{6+} ions. The synthesized Ag NPs were examined via different analytical techniques to investigate the size and morphology of particles. The size of particles was observed about 17.80 nm. The functionalized Ag NPs were successfully aggregated with Cr^{6+} ions and the color change was monitored with naked eyes. The LOD was 34 nM with a linear range from 1.0×10^{-7} to 2.4×10^{-6} respectively. The colorimetric detection mechanism of heavy metal ions through AgNPs is displayed in Fig. 2.

Furthermore, an easy, simple and excellent colorimetric detection method has been reported by (Kailasa et al., 2018) by using citrate functionalized Ag NPs. The Ag NPs have been investigated by numerous analytical tools to determine the size. Overall particle size around 20 nm was found. The Ag NPs aggregated with Cr^{3+} ions, which have been observed by naked eyes. The linear range set from 1.0 to 50.0 μM and with a limit of detection 0.52 μM . The Ag NPs were also successfully applied for a real water sample to monitor Cr^{3+} ions. Moreover (Joshi

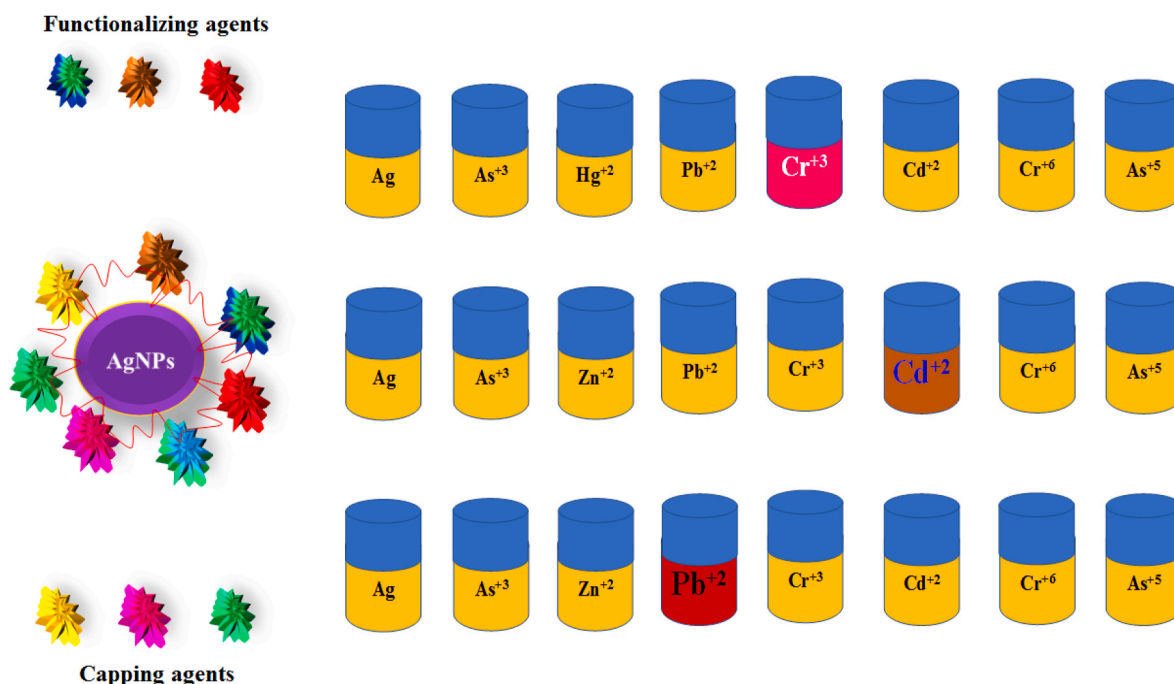


Fig. 2. Colorimetric sensing of toxic heavy metals functionalized Ag NPs.

et al., 2016), synthesized Ag NPs functionalized with 3,4-dihydroxy phenylalanine used as capping and stabilizing agent for the selective colorimetric sensing probe for Cr^{6+} ions. The Ag NPs were aggregated with Cr^{6+} ions, which verified through the color change from dark yellow to reddish-brown. The low limit of detection 0.01 ppm was detected. Furthermore (Shrivastava et al., 2016), prepared AgNPs via the reported method and functionalized them with tartaric acid, which acted as stabilizing and capping agent to customized Ag NPs surface. The colorimetric sensor has detected the Cr^{3+} and Cr^{6+} ions. The linear range from 5 to 100 $\mu\text{g/L}^{-1}$ and 10–100 $\mu\text{g/L}^{-1}$ with a limit of detection 2 $\mu\text{g/L}^{-1}$ and 32 $\mu\text{g/L}^{-1}$ respectively. The developed method was applied to determine chromium ions in groundwater samples, industrial wastewater, and vegetable samples. In addition this (Jin et al., 2015a, 2015b), prepared Ag NPs by chemical reduction using 4-amino hippuric acid as functionalizing and coating material to modify the Ag NPs' surface. The Ag NPs size was calculated around 13.3 nm. In the presence of HAP-based Ag NPs, the Cr^{3+} ions change the color from red to violet or blue. The linear range set from 5.0- to 120 μM with a limit of detection 1.17 μM . The colorimetric assay was also applied for the real sample to determine Cr^{3+} ions. Also (Sharif et al., 2015) engineered Ag NPs via previously reported method. Ag NPs were functionalized with Isonicotinic acid to cap and stabilize them. The Ag NPs aggregated with Cr^{3+} ions successfully and the color changed from yellow to red along with the significant change in the absorption band. The Cr^{3+} ions concentration ranged from 1×10^{-6} to 5×10^{-5} M with LOD 4.5×10^{-7} M accordingly. Although (Elavarasi et al., 2014), have manipulated Ag NPs with citrate-capped for the modification of Ag NPs. The successfully prepared particles were applied for colorimetric detection of Cr^{3+} and Cr^{6+} ions, respectively. The average particle size was about 10–20 nm with a spherical shape. The linear range from 500 to 5000 ppb was observed. The proposed sensor exhibited simultaneously colorimetric assay for the Cr^{3+} and Cr^{6+} ions.

However (X. Wu, Xu et al., 2013), have synthesized Ag NPs via chemical reduction method functionalized with ascorbic acid to modify Ag NPs. The facile and easy method was designed for the colorimetric sensing of Cr^{6+} ions. The detection ranged from 7.0×10^{-8} to 1.84×10^{-6} with the limit of detection 5×10^{-8} M. The developed sensor was selective and sensitive Cr^{6+} ions. Likewise (Y. Xu, Dong, Jiang and Zhu,

2013), synthesized Ag NPs by chemical reduction method using Tartrate acid as a capping agent for Ag NPs. The prepared Ag NPs were confirmed by various analytical techniques that revealed particles' crystallinity and size in the nano range. The manipulated particles were used for the colorimetric detection of Cr^{3+} ions. The LOD was 0.06 μM with a linear range from 0.1 to 0.17 μM . The tartrate capped Ag NPs were also applied for the colorimetric sensor of Cr^{3+} ions in real samples as well. Similarly (Ravindran et al., 2012), have prepared Ag NPs via chemical reduction method without modifying Ag NPs' surface. The synthesized Ag NPs were well dispersed with spherical shape and size between 10 and 15 nm. The unmodified Ag NPs were successfully applied for the colorimetric sensor for Cr^{6+} ions. The Limit of detection was found to be 0.1 nM with a linear range concentration of Cr^{6+} ions from 10^{-3} – 10^{-4} M or (50 mg/L to 50 ng/L). Moreover (Toshev et al., 2019), fabricated Ag NPs through chemical reduction method functionalized with citrate. The Ag NPs were examined by different analytical tools that revealed that particles were well dispersed with spherical crystallinity and size around 1.8–8 nm. The well-dispersed Ag NPs were employed for the colorimetric probe to determine As^{3+} ions. The limit of detection was found as 6 ppm with a linear range from 6 to 14 ppm. Likewise (Boruah et al., 2019), engineered Ag NPs via chemical reduction method and modified with PEG, which acted as a capping and stabilizing agent. The synthesized material was investigated by numerous analytical techniques that confirmed that Ag NPs were in nano range and well dispersed. The Ag NPs were applied for the colorimetric sensor for arsenic (III). The detection of As^{3+} ions was seen through naked eyes by changing of color from yellow to bluish which indicated that Ag NPs aggregated with As^{3+} ions successfully. The limit of detection found as 1 ppb with the concentration of arsenic (III) ions ranging from 5 to 13 ppb. In another study (Divsar et al., 2015), synthesized aptamer-based Ag NPs via chemical reduction method. The Ag NPs were characterized by analytical techniques that revealed particles with a spherical shape with size 12 ± 3 nm. The Ag NPs were used for the colorimetric detection of arsenic (III) ions, having a limit of detection 6 $\mu\text{g/L}^{-1}$ with a linear range from 50 to 700 $\mu\text{g/L}^{-1}$. Nevertheless (Sakthivel and Sekar, 2020), have prepared Ag NPs via wet chemical method and used isonicotinic acid hydrazide as the functionalized and reducing agent. The Ag NPs were confirmed by different analytical tools that gave information about the

morphology and size of particles, while the overall size of particles was around 34.64 and 536.02 nm. The Ag NPs were applied for the colorimetric probe to detect Hg^{2+} ions with the limit of detection 0.18 nM. The INH-Ag NPs were also utilized for the determination of Hg^{2+} ions in real water samples. Similarly (Amirjani and Haghshenas, 2019), have synthesized Ag NPs by the chemical reduction method. By using citrate as a capping and stabilizing agent. The synthesized Ag NPs were applied successfully for the colorimetric sensing of Hg^{2+} ions. The limit of detection was found 4 nmolL⁻¹ with a linear range of 10 nmolL⁻¹ to 50 nmolL⁻¹. The citrate-based Ag NPs were also used for the industrial discharge of Hg^{2+} ions. Furthermore (Annadhasan et al., 2019), engineered Ag and Au NPs by chemical reduction method by using phenylalanine conjugated cholic acid as a capping and functionalizing agent. The Ag and Au NPs were characterized by different analytical tools that revealed the average size of particles around 16.5–21.4 nm with a spherical shape. The Cphe- Ag, and Au NPs were exploited as colorimetric sensors for Hg^{2+} ions. The low LOD of 7 nM was obtained with a linear range from 25 nM to 50 nM. The Cphe-capped Ag and Au NPs showed excellent selective nature towards the Hg^{2+} ions. The particles were also applied to real water samples to determine Hg^{2+} ions. Also (U. Khan et al., 2018), synthesized the Ag NPs via chemical reduction method by using thiamine as a stabilizing and functionalizing agent. The average size of silver particles was around 13.0 nm. The thiamine-based Ag NPs were utilized for the colorimetric sensing of Hg^{2+} ions. When thiamine-capped Ag NPs were aggregated with Hg^{2+} ions, the rapid color change was observed from yellow to violet-blue. The low detection limit has been observed as 5 nM with a linear range of Hg^{2+} ions from 1×10^{-8} to 5×10^{-6} M. The developed colorimetric sensor was also applied in real water samples for the detection of mercury (II) ions (Shiva Prasad, Shruthi and Shivamallu, 2018). have prepared Ag NPs via hydrothermal reduction method. 2-aminopyridine-4,6-diol used as a functionalizing and stabilizing agent. The silver metal particles were investigated through different analytical tools, which revealed that the average size of silver particles around 10–40 nm with spherical

morphology. The Ag NPs were used for the colorimetric sensing of Hg^{2+} ions. The color turned from pale brown to deep yellow due to chelation that was ensued between APD- Ag NPs and Hg^{2+} ions. The limit of detection was observed around 0.3 μM . Likewise (S. Li et al., 2018), synthesized Ag-Cu bimetallic nanoparticles by chemical reduction method by using citrate as a capping and stabilizing agent. The average size of the particles was around 9.0 ± 8.0 nm. The Ag-Cu NPs were applied to the colorimetric sensor for Hg^{2+} ions. The minimum limit of detection 0.51 nM was obtained; the colorimetric sensor was also used for the determination of Hg^{2+} ions in real water samples. Furthermore (Vasileva et al., 2017), fabricated Ag NPs by the chemical reduction method by utilizing starch as capping agent and D-glucose as the reducing agent. The prepared Ag NPs have been examined thoroughly with different analytical techniques, which revealed the average size of silver particles around 15.4 ± 3.9 nm with a spherical shape. The synthesized material was successfully employed for the colorimetric probe for Hg^{2+} ions. The limit of detection $0.94 \mu\text{g/L}^{-1}$ with two concentration ranges was obtained from 0.9 to $12.5 \mu\text{g/L}^{-1}$ and 25–500 $\mu\text{g/L}^{-1}$ respectively. In other case (Jeevika and Shankaran, 2016), prepared Ag NPs via chemical reduction method, by using geltain as protecting and stabilizing agents to modify the Ag NPs' surface. The Ag NPs were analyzed via various analytical tools which revealed the minimum size of geltain-based silver particles at about 8.3 nm. The geltain-modified silver particles were successfully applied as colorimetric assay for the detection of Hg^{2+} ions. The low limit of detection 25 nM was observed. Herein, (L. Li, Gui and Li, 2015) have synthesized Ag NPs via chemical reduction method. The lysine was used as protecting and capping agent for the Ag NPs. The prepared material having an average size around 1 nm. The lysine-modified Ag NPs were utilized for the colorimetric sensing of Hg^{2+} ions. The low LOD of 25 nM with linear concentration range of Hg^{2+} ions from 1 nM to 30 nM were obtained. Table 2 displays the detection of heavy metal ions via Ag NPs.

Table 2
Ag NPs based colorimetric sensing of Heavy metals.

MNPs	Capping agent	Detection	Size	LOD	References.
AgNPs	Glucanate	Pb ²⁺	9.57 ± 2 nm	0.2029 μM	Choudhury & Misra (2018)
AgNPs	Dithiazone	Pb ²⁺	35–50 nm	0.64 ± 0.044 $\mu\text{g/L}^{-1}$	Roto et al. (2019)
Ag/AuNPs	Citrate and Tannic acid	Pb ²⁺	26 and 59 nm	1.4 nM	Xing et al. (2018)
AgNPs	PolyDOPE	Pb ²⁺	20 nm	$9.4 \times 10^{-5} \mu\text{M}$	Cheon & Park (2016)
AgNPs	Iminodiacetic acid	Pb ²⁺	7–10 nm	13 nM	Qi et al. (2012)
AgNPs	Glutathione	Pb ²⁺	–	10^{-9} M	Anambiga et al. (2013)
AgNPs	Chalcon carboxylic acid	Cd ²⁺	–	0.13 μM	(Y. Dong et al., 2017)
AgNPs	1-amino-2-naphthol-4-sulfonic acid	Cd ²⁺	12–28 nm	87 nM	(P. Huang et al., 2016)
AgNPs	5-Sulfonicanthranilic acid dithiocarbamate	Cd ²⁺	20 nm	58 μM	Mehta et al. (2016)
AgNPs	5-Sulfosalicylic acid	Cd ²⁺	–	3 nM	Jin et al., 2015a, 2015b
AgNPs	PVP	Cr ⁶⁺	17.8 nm	3 μM	He et al. (2019)
AgNPs	Citrate	Cr ³⁺	20 nm	0.52 μM	Kailasa et al. (2018)
AgNPs	3,4-dihydroxyphenylalanine	Cr ⁶⁺	–	0.01 ppm	Joshi et al. (2016)
AgNPs	Tartaric acid	Cr ³⁺ and Cr ⁶⁺	–	2 $\mu\text{g/L}^{-1}$ and 32 $\mu\text{g/L}$	Shrivastava et al. (2016)
AgNPs	4-amino hippuric acid	Cr ³⁺	13.3 nm	1.17 μM	Jin et al., 2015a, 2015b
AgNPs	Isonicotinic acid	Cr ³⁺	–	4.5×10^{-7} M	Sharif et al. (2015)
AgNPs	Citrate	Cr ³⁺ and Cr ⁶⁺	10–20 nm	–	Elavarasi et al. (2014)
AgNPs	Ascorbic acid	Cr ⁶⁺	–	5×10^{-8} M	(X. Wu et al., 2013)
AgNPs	Tartrate acid	Cr ³⁺	–	0.064 μM	(Y. Xu et al., 2013)
AgNPs	Unmodified	Cr ⁶⁺	10–15 nm	0.1 nM	Ravindran et al. (2012)
AgNPs	Citrate	As ³⁺	1.8–8 nm	6 ppm	Toshev et al. (2019)
AgNPs	PEG	As ³⁺	–	1 ppb	Boruah et al. (2019)
AgNPs	Aptmar	As ³⁺	12 ± 3 nm	6 $\mu\text{g/L}^{-1}$	Divsar et al. (2015)
AgNPs	Isonicotinic acid	Hg ²⁺	34.64 and 536.02 nm	0.18 nM	Sakthivel & Sekar (2020)
AgNPs	Citrate	Hg ²⁺	–	4 nmol/L ⁻¹	Amirjani & Haghshenas (2019)
AgNPs	Phenylalanine	Hg ²⁺	16.5–21.4 nm	7 nM	Annadhasan et al. (2019)
AgNPs	Thiamine	Hg ²⁺	13 nm	5 nM	(U. Khan et al., 2018)
AgNPs	2-amino pyridine-4,6-diol	Hg ²⁺	10–14 nm	0.3 $\mu\text{M/L}$	Shiva Prasad et al. (2018)
Ag/CuNPs	Citrate	Hg ²⁺	9.0 ± 8.0 nm	0.51 nM	(S. Li et al., 2018)
AgNPs	Starch	Hg ²⁺	15.4 ± 3.9 nm	0.94 $\mu\text{g/L}^{-1}$	Vasileva et al. (2017)
AgNPs	Geltain	Hg ²⁺	8.3 nm	25 nM	Jeevika & Shankaran (2016)
AgNPs	Lysine	Hg ²⁺	–	25 nM	(L. Li et al., 2015)

3. Copper metal nanoparticles and colorimetric detection of heavy metals

Copper is a chemical element with symbol Cu derived from Latin word (Cuprum) and atomic number 29. It is soft, malleable and ductile with very high thermal and electrical conductivity. Cu NPs have many applications in the field of nanotechnology such as catalysts, antimicrobial, colorimetric sensing, etc. Cu NPs have remarkable optical, electrical, conductivity properties as compared to the other precious metals like Au, Ag and Hg. The main disadvantage of Cu NPs is that it easily oxidized and form copper oxide. Therefore, to overcome this problem, many researchers developed various methods to produce Cu NPs by using inert atmosphere and capped with different capping and stabilizing agents (Jana et al., 2000; Siegel and Hu, 1999; Vanden Bout, 2002). The Cu metal also exhibits the localized surface plasmon resonance like Au and Ag. The Cu NPs produced at low cost and can be extensively used for colorimetric detection of heavy metals ions (Rycenga et al., 2011).

Herein (Sengan and Veerappan, 2019), fabricated Cu NPs by chemical reduction method and used N-myristoyltaurine as a capping and stabilizing agent. The synthesized Cu NPs were successfully applied for the colorimetric determination of Hg^{2+} ions. The limit of detection was calculated to be 0.1125 μM . Similarly (Q. Li et al., 2019), have synthesized Cu NPs by thermal reduction method in which citrate was employed as capping and reducing agent. The prepared Cu NPs characterized via different analytical techniques, which revealed an average size around 3.6 ± 4.0 nm. The synthesized Cu NPs were effectively employed for the colorimetric sensing of Hg^{2+} ions. The limit of detection 0.185 μM with a linear range from 0.050 μM to 10.000 μM were obtained. The citrate capped Cu NPs were also applied in the tap water for the detection of Hg^{2+} ions. Likewise (Ghobashy and Mohamed, 2018), have prepared copper nanostructures via chemical reduction method functionalized and reduced by polyacrylic acid/polyvinyl alcohol and ascorbic acid. The Cu NPs were characterized through numerous analytical techniques that showed an average size of around 8 nm. The synthesized material was used for the colorimetric detection of Hg^{2+} ions with low LOD of 10^{-5} M. Additionally (Lin et al., 2016), have engineered Cu NPs through chemical reduction method, and D-penicillamine utilized as capping while ascorbic acid as a reducing agent. The DPA-Cu NPs were used as colorimetric probe for Hg^{2+} ion with a limit of detection around 32 nM and limit of quantification 1.0–30 μM . The Cu NPs have been functionalized with various capping and stabilizing agents. The detection mechanism of heavy metal ions via effectively capped/stabilized Cu NPs is exhibited in Fig. 3.

(Megarajan et al., 2016) synthesized Cu NPs via chemical reduction method. N-lauryltrimine used as a stabilizing agent, while ascorbic acid

as a reducing agent. The Cu NPs were investigated with different analytical techniques that revealed the size and crystallinity of Cu NPs. The prepared Cu NPs were applied for the colorimetric sensing assay for Hg^{2+} ions. The limit of detection was found as 0.13 μM with a linear range from 0 to 25 μM , respectively. Moreover, (Soomro et al., 2014), synthesized Cu NPs by chemical reduction method. The L-cysteine used as protecting and stabilizing agents. The average size of Cu NPs was around 34 ± 2 nm. The L-cysteine capped Cu NPs were employed for the colorimetric sensing of Hg^{2+} ions with LOD 4.3×10^{-8} mol/L⁻¹ with a linear dynamic range from 0.5×10^{-5} – 3.5×10^{-6} mol/L⁻¹ for Hg^{2+} ions. In a similar case (R. Liu et al., 2019), prepared Cu NPs via hydrothermal method by using metallothionein as a capping agent. The metallothionein capped Cu NPs were applied for the colorimetric determination of Hg^{2+} ions. The limit of detection was found as 43.8 nM with a linear dynamic range from 97 nM to 2.325 μM for Hg^{2+} ions. However (Chakrapani et al., 2014), have developed an easy and facile synthesis method for Cu NPs with casein as a stabilizing agent. The size of the prepared particles was about 35–80 nm. The casein capped Cu NPs were applied for the colorimetric detection of Hg^{2+} ions with LOD in the ppb range. In another study (Laghari et al., 2019), prepared Cu NPs via chemical reduction method and utilized ranolazine used as capping and stabilizing agents. The average size of fabricated nanoparticles was around 40 ± 2 nm with a spherical shape. The Ranolazine-capped Cu NPs were successfully applied for the colorimetric sensing probe for As^{3+} ions. The low limit of detection of 1.6×10^{-8} M was observed with a linear ranging from 3.0×10^{-7} to 8.3×10^{-6} M. Likewise (R. Liu et al., 2019), have synthesized Cu NPs by the hydrothermal method by using Metallothionein as a reducing and capping agent. The prepared Cu NPs were examined via numerous analytical tools to reveal the size and morphology of Cu NPs in the nano range. The MT-based Cu NPs were employed for colorimetric sensing of Pb^{2+} ions. The LOD of 140 nM with a linear dynamic ranges from 707 nM to 96 μM were observed for Pb^{2+} ions. Table 3 displays the colorimetric determination of heavy metal ions through Cu NPs. Amongst metal nanoparticles mentioned above e. g. gold and Ag NPs, the CuNPs have numerous advantages such as easy preparation, long term stability, cost effectiveness, wide dynamic range, and high sensitivity in naked eye sensors. The Cu NPs are excellent replacement of Au NPs and Ag NPs because Cu NPs exhibit same kind of properties as the Au NPs and Ag NPs. Moreover, Cu NPs have low cost fabrication process than the Au and Ag NPs, and have wide range of applications in the different areas such as catalysis, fuel cell, antimicrobial etc.

4. Conclusion

The present review covers a previously reported work on the

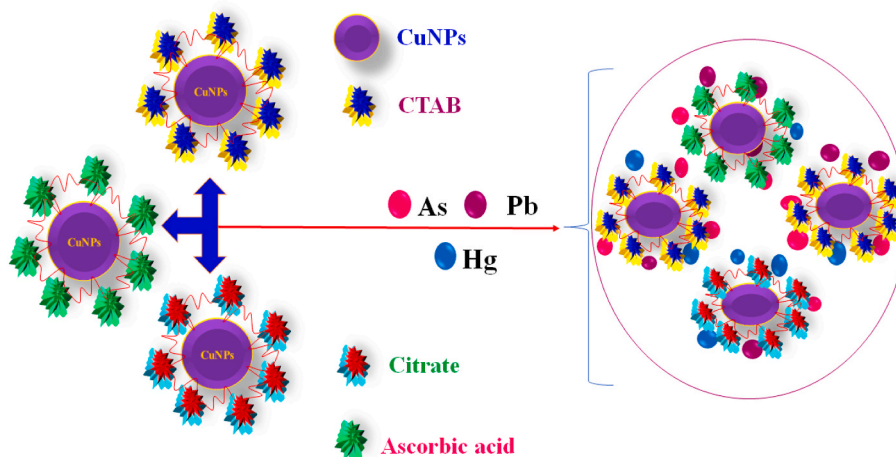


Fig. 3. Colorimetric sensing approach of Cu NPs for heavy metal ions.

Table 3
Copper nanoparticles as a detection probe for Heavy metal sensing.

Metal NPs	Capping agent	Detection	Size	LOD	Reference
CuNPs	N-mristoyltaurine	Hg ²⁺	–	0.1125 μM	Sengan & Veerappan (2019)
CuNPs	Citrate	Hg ²⁺	3.6 ± 4.0 nm	0.185 μM	(Q. Li et al., 2019)
CuNPs	Polyacrylic/polyvinyl alcohol	Hg ²⁺	8 nm	10 ⁻⁵ M	Ghobashy & Mohamed (2018)
CuNPs	D-penicillamine	Hg ²⁺	–	32 nM	Lin et al. (2016)
CuNPs	N-lauryltrimine	Hg ²⁺	–	0.134 μM	Megarajan et al. (2016)
CuNPs	L-cysteine	Hg ²⁺	34 ± 2.1 nm	4.3 × 10 ⁻⁸ mol/L ⁻¹	Soomro et al. (2014)
CuNPs	Metallothionein	Hg ²⁺	–	43.8 nM	(R. Liu et al., 2019)
CuNPs	Casein	Hg ²⁺	35–80 nm	Ppb range	Chakrapani et al. (2014)
CuNPs	Ranolazine	As ³⁺	40 ± 2 nm	1.6 × 10 ⁻⁸ M	Laghari et al. (2019)
CuNPs	Metallothionein	Pb ²⁺	–	140 nM	(R. Liu et al., 2019)

chemical synthesis of metal nanoparticles, e.g. Au, Ag, and Cu nanoparticles, using various functionalizing, reducing, and stabilizing agents. By the incorporation of different stabilizing and capping agents, the size and morphology of metal nanoparticles can be easily controlled and their aggregation can also be prevented. The nanoscale metal nanoparticles exhibited an excellent sensing capability for heavy metal ions through colorimetric detection approaches as naked eye sensors. Till now different traditional analytical tools have been used for the determination of heavy metal ions but due to certain pitfalls such as expensiveness, required trained personels and exhaustive sample preparation, the reseachers focused to develop different detection method using metal nanoparticles. Doubtlessly, still there are many gaps in the preparation of metal nanoparticles such as less stability, low sensitivity and selectivity for the targeted analyte. However, by incorporation of functionalizing agents, these problems can be tackle out effectively. The metal-based nanostructures shown an exceptional response as sensing materials for the determination of toxic metals. That can lead to save the environment from upcoming challenges regarding heavy metal pollution.

Authors contributions

Ali Hyder: Writing – formatting of the review article, Jamil A. Buledi: Drafting and literature review, Muhammad Nawaz: Data collection/editing drafting, Dhani Bux: Tabulation and language checking, Zia-ull Hassan Shah: language check, Hongjun Lin, editing and Yasin Orooji, Mehmet Lütfi Yola, Hassan Karimi-Maleh, Amber R. Solangi: Conceptualization/Supervision/editing/correcting draft/Submission/Correspondence to the Journal.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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