Colorimetric Detection of Mercury Using Silver Nanoparticles: A Review

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Abstract. Manufacturing nanometals that use natural materials as bioreductant media is still a significant concern due to their environmentally friendly properties. The use of silver nanoparticles prepared using plants or organic materials. They are used for the rapid detection of sustainable mercury ions. The use of these natural materials is capable of producing stable nanoparticles and environmentally friendly nanoparticle synthesis. In this paper, we will report the synthesis of silver nanoparticles with various types of reducers and stabilizers, mechanisms, and nanoparticle characterization for applications of colorimetric sensors of mercury ions in water pollutants. The aim is for the reader to obtain comprehensive information about the ability of the silver nanoparticle as a colorimeter sensor.

1 Introduction

Industrial growth, population growth, and human activity directly affect environmental damage, one of which is environmental pollution. Industrial sector pollution contributes pollutants to water bodies. Many types of environmental pollutants today are directly impacting us, such as pesticides, dyes, and heavy metals. Some of the strategies that have been tried are a breakthrough combination of bioremediation techniques and nanotechnology. [1]

Heavy metals, such as mercury, are often dangerous and have an impact on human health [2]. Mercury is the only liquid metal at room temperature. These metals are very evaporative and change their chemical shape into other toxic compounds. Mercury is also known to be a toxic element that can cause large-scale contamination and adversely affect human health. Still, the complexity of the bio-geochemical cycle of the elements makes it difficult to determine environmental and human health risks accurately. Mercury enters the body, destroys body tissues, and has the potential to harm the brain, nerve tissue, and endocrine system. [3]

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Mercury in its elemental form can be found in the form of inorganic salts or as organometallic compounds, depending on its oxidation state [4]. Among these, mercury dimethyl ($Hg(CH_3)_2$) is the most dangerous molecule as it has the ability to move freely in tissues. In protecting the environment from mercury contamination, scientists have used many techniques including Atomic Absorption Spectrophotometry (AAS)[5], Atomic Absorption Fluorescence Spectroscopy (AFS)[6], plasma-induced atomic emission microwave (MIP-AES), pairing plasma time spectrophotometric (ICP-MS [7]), UV-Vis spectrum photometry, high-performance liquid chromatography (HPLC) .All of the above methods use state-of-the-art technology, and sophisticated equipment, and are time-consuming.[4]

Nanoscience is a field that includes metal nanoparticles (MNPs) that have optical properties that are bound to very different sizes at both the mass and atomic levels. Among noble metal nanoparticles, silver nanoparticles (AgNPs) have properties for metal interactions. The use of MNPs, especially AgNPs, to detect heavy metals using economical methods [8] A detection method that is simpler, faster, does not require a long time, is simpler, has a lower cost, and requires high sensitivity One thing that is currently being developed is heavy metal detection using nanoparticles. Several studies have explored whether silver nanoparticles can be used as colorimetric sensors for the heavy metal mercury. Silver nanoparticles synthesized using the green chemistry concept have also been carried out by Kittiya et al. The use of ginger-stabilized silver nanoparticles (Gin-AgNPs) uses a more environmentally friendly method that utilizes AgNO3 and a natural ginger solution [9]. Silver nanoparticles are used as a sensor to detect the heavy metal mercury, which is characterized by a change in the brown color of the crust to a colorless solution.[10]

1.2 Mechanism of silver nanoparticles as colorimetric sensors

Silver nanoparticles (AgNPs) are still of particular interest regarding their synthesis and fabrication using green synthesis, as well as their applications in various fields. Application of silver nanoparticles as antibacterial [11], antioxidant [12], and anti-cancer [13]. The development capabilities of nanoparticles are very extensive due to their unique properties and characteristics. Nanoparticle sizes ranging from 1-100 nm have unique properties that can be manipulated and produce advantages [14]. Apart from that, the medical use of silver nanoparticles is also being explored in the development of the detection of heavy metal pollution, especially mercury [15]

Nanoparticle synthesis begins with the addition of a reductor to a solution of the silver nitrate precursor [16]. Chemical reductors or natural reductors will reduce silver ions to silver nanoparticles. The biological silence that helps reduce silver not only acts as a reductor but also as a stabilizer[17]. Nanoparticles stabilized by organic compounds that also act as reductants in silver nanoparticle synthesis were developed as colorimetric sensors to detect metals like mercury. This is explained by the ability of silver nanoparticles to interact with Hg^{2+} through a redox reaction that can be seen directly through color changes [3]. The sensitivity of silver nanoparticles to detecting mercury ions is very promising [15]. The color change from yellow to silver nanoparticles synthesized with gingerol turn colorless when mercury compounds are added according to Hg^{2+} concentrations.

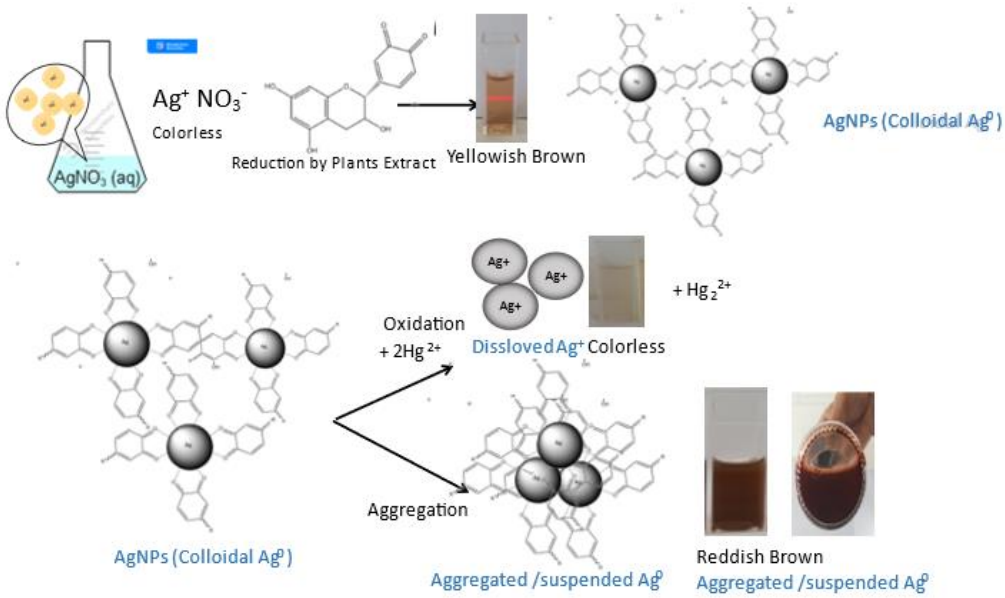

Fig. 1. Illustration The mechanism of AgNPs stabilized by organic compounds used for the detection of mercury. Indicates detection of mercury (II) ions using AgNPs through redox reactions (higher) and $AgNO_3$ aggregation (lower)[4], [16]

According to other viewpoints, the mechanism of silver nanoparticles as colorimetric sensors was proposed by Zhengquan Yan et al. [18] and Safana Ahmed [19], where the surface coating of HgO into AgNP resulted in a decrease in absorption and SPR shift, while other mechanisms confirmed the production of amalgam between AgNPs and Hg ions. The amalgam mechanism is more likely to be accepted because the electrochemical potential difference between mercury ions (II) with 0.85V and AgNPS with 0.8V is much smaller, allowing Mercury (II) and AgNP to resist chemical interactions leading to amalgam formation.

The interaction of Ag^0 nanoparticles and mercury (II) is an important component that contributes to the phenomenon of color variables, in addition to particle structure and arrangement. Hg-Ag forms an amalgam solid during the oxidation-reduction interaction. Hg0 and Ag+ are formed as a result of a 2:1 stoichiometric interaction. The presence of a reduction oxidative reaction that combines AgNPs (Ag0) and mercury ions (II) to form a nanoporous Ag-Hg mixture, as well as the high sensitivity of SPR, determine the condition. Some researchers believe that spherical-shaped AgNPs with spectral wavelengths in the 350-480 nm range [9,19] exist.

1.3 Instrumentation for characterization of silver nanoparticles stabilized by the concept of green synthesis

1.3.1 Spectrofotometry UV-VIS

Silver nanoparticles are synthesized using the concept of green synthesis. Using organic compounds from plants as reducers and stabilizers to enhance the properties of silver nanoparticles Nanoparticles are characterized to see the absorption of nanoparticles' colloid solutions at certain wavelengths; the absorbent spectrum shows the characterization of a strong surface plasmon resonance tape (SPR) at 420 nm. It is also the same research that has been found in some previous studies [20,21].

In describing the interaction of silver nanoparticles, the absorption peak decreases when the mercury solution interacts with silver nanoparticles, which is shown by a change in yellow or brownish yellow as the colloid color of the nanoparticle changes to a lame or uncolored color. This indicates that there has been a redox reaction characterized by a decreased peak SPR absorption of nanoparticles. It was previously that silver potentially detects Hg^{2+} because silver nanoparticles have surface plasmon resonance properties which can change through surface modifications such as size, shape, composition, and dielectric constant systems. [22]

Change of color when AgNPs interact with Hg^{2+} due to the presence of hydrogen bonding Hg^{2+} to the stabilizer on the surface of the nanoparticles. This is due to the loss of stability of organic compounds such as the secondary metabolites of phenolic, flavonoid, polyphenol, and others that become nanoparticle stable. Loss of stabilizing ability due to phenolic compound content that can form composite complexes with heavy metals through interaction between the hydroxy group of heavy metals[10,22,23]

In a study of silver nanoparticle synthesis with gingerol acting as a reducer and stabilizer, this component contains a hydroxyl cluster. The addition of Hg^{2+} to a silver nanoparticle colloid solution that is closed by gingerol leads to an electro-ionic interaction between the surface of the nanoparticle and $Hg^{2+,}$ followed by a redox reaction on the AgNPs surface. The redoxy reaction occurs spontaneously, with the potential reduction of the standard silver and silver ions ($Ag/Ag^{+)}$ being 0.8 V lower than the standard potential $Hg^{+1/}Hg$, which is only 0.85 V [1] [2]; it will form an Ag-Hg amalgam. When Hg^{2+} will react with the silver nanoparticles; the size of the nanoparticle will become large and produce the formation of the Hg^{+} ion, instead forming an Hg-AgNP amalgam with the surface merged, and this SPR amalgam will cover an AgPs surface that does not see any real change in the color of the node.[23][24,25]. The occurrence of this color change indicates that the Ag available in the suspension has been oxidized completely with the addition of mercury. In addition, the Hg-opened Ag that is available in a colloidal suspension causes a blue shift, which absorbs a larger SPR than the AgNPs SPR.

1.3.2 Fourier Transform InfraRed (FT-IR) Spectrometry

Fourier transform infrared (FT-IR) silver nanoparticle synthesis results need to be known properties and structure as well as target compound components through characterization. Besides, through characterization, we know the development of the generated application. Fourier transform infrared (FT-IR) is used to analyze the function clusters contained in a

material. In silver synthesis green studies, the FT-IR analyzer is used to find out what function groups are present in bioactive compounds in plant extracts as well as how they change after reaction with precursors.

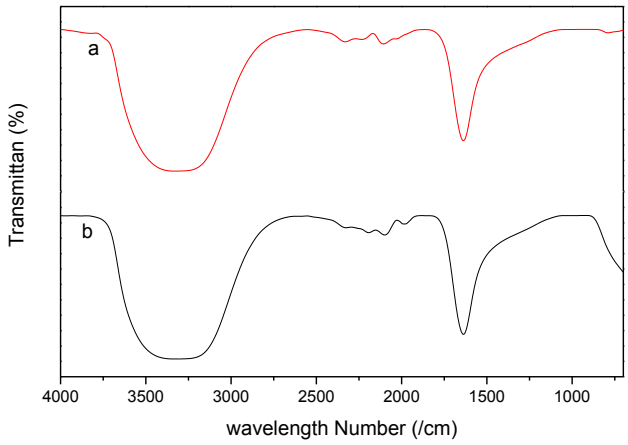

Fig. 2. 1 FTIR spectrum of obtained from **a**. The mangrove aqueous extract of rhizophora stylosa, and **b**. green synthesized AgNPs [11,26,27]

1.3.3 X-Ray Diffraction (XRD)

XRD is widely used to study the lines of the crystal structure by giving the degree of crystallinity. The crystal structure is known from comparing the distance between the crystal field (d) and the peak intensity of the fraction with the standard data. Through XRD analysis, it is possible to determine the dimension of the grid d, that is, the gap between the fields in the crystalline structure. Constructive and de-distructive interference patterns will result in a difraction pattern that meets the Bragg equation. Each material has a specific and distinctive difractogram pattern that describes its characteristics.

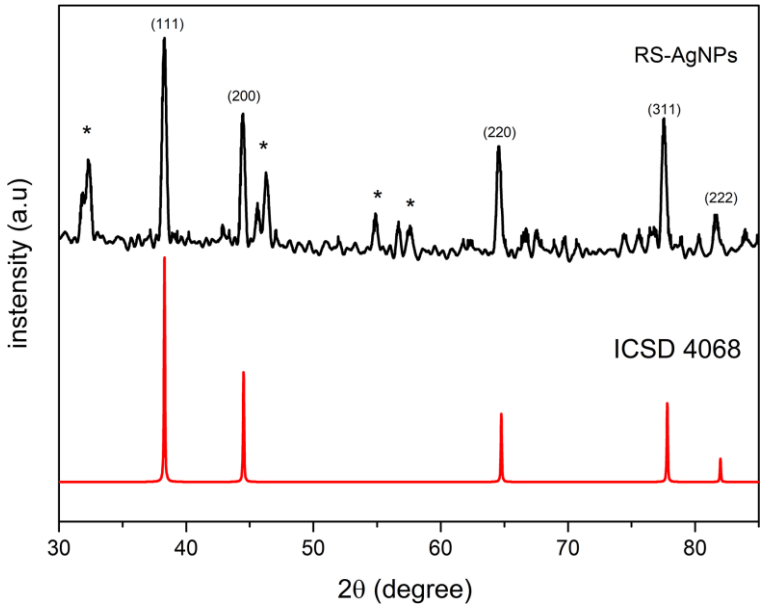

Fig. 3. X-ray diffraction of Rhizophora stylosa mediated silver nanoparticles [11]

1.3.4. Transmission Electron Microscopy (TEM)

It is a microscopic technique that provides information about morphology, crystalline structure, defects, crystal phase composition and microstructure magnetically. Particle sizes of AgNPs are shown in TEM characterization with various variations of shapes such as spherical [28–30] whereas in some references of sphericals, hexagonal, pentagonal and trigonal forms are found in AuNPs synthesis [31,32]

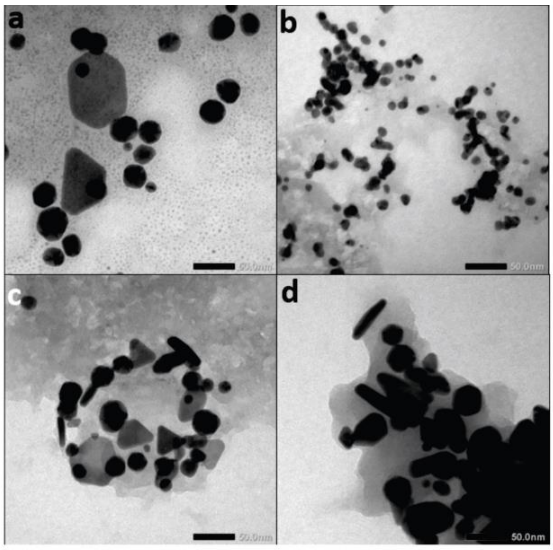

Fig. 4. TEM Image of Gold Nanoparticles [33]

1.3.5 ZETA POTENSIAL/ DLS

The silver formed by PSA aims to determine the size of the particle. analyzes the size distribution of particles based on the maximum size produced in a certain sample volume percentage. The advantage of using this device is its accuracy and reproducibility, which are within ±1% and capable of measuring ranging from 0.02 nm to 2000nm. PSA uses the Dynamyc Light Scattering (DLS) method by using an infrared blast that is fired at the sample so that the samples will react to produce a Brown movement, which is the random movement of very small particles in the liquid as a result of a collision with molecules present in liquid matter. This is the movement that is then analyzed by the instrument; the smaller the size of the molecule, the faster it moves. [34,35]

When exposed to laser rays, the particles in the solution spread light at varying intensities. This method is based on light's interaction with particles in suspension. DLS is trustworthy for particle sizes ranging from 20 to 200 nm. Because DLS measures the size in the solution where the particles are in Brown motion, the sizes obtained are relatively larger than those obtained from TEM and SEM.[36]

1.4 Silver Nanoparticles' Role in Detecting Mercury Pollution

The development of nanotechnology offers great opportunities for solving health and environmental problems. The morphology, function, and size of nanoparticles can be optimized to improve particle performance. In the context of sensors, the performance of nanoparticles can be improved by modifying surfaces, increasing sensor sensitivity, selectivity, and simplicity. A lot of silver nanoparticles have been used in the detection of heavy metals like mercury. It's because of its unique physical and chemical properties. It has a morphology that is unmodified, an absorption that can be domesticated, and a ratio of the surface area to the volume that is domesticable so that it can detect analytics [10].

Many colorimetric sensors have been found in the detection of mercury. The differences occurring from stabilizers or capping agents are present in the formation of nanoparticles if synthesized using cosnep grren synthesis. In general, the working principle of the colorimetric sensor of silver nanoparticles is based on the optical aspect when in contact with the analytic. Extensive research has been undertaken by various research groups over the last few decades to develop mercury ion sensors that are highly sensitive in aqueous solutions. As the extent of detection of heavy metals such as mercury on silver nanoparticles continues to develop, some studies will be described as follows:

The synthesis of silver nanoparticles (AgNPs) and gold nanoparticles (AuNPS) has been used as mercury pollutant sensors [19,22,24]. The detection of heavy metals by silver and gold nanoparticles can be observed by a color change that can be seen visually with UV-Vis spectroscopy. The SPR properties of these metal nanoparticles depend heavily on the size, shape, coating or ligan material, and distance between the particles.

Research was conducted by Lei Zan et al. [37], where silver nanoparticles are capped with cytosine triphosphate as a visual detection of mercury (II) and chromium (III). The interaction of AgNPs with the addition of Mercury (II) ions causes the formation of a layer of mercury on the AgNP surface, which causes the absorption of SPR from AgNPS to decrease, undergo a slight blue shift, and cause the yellow color to fade, with a

concentration limit of Hg^{2+} 0.125 μM in a drinking water sample. The interaction between silver nanoparticles and Hg(II) ions produces Hg atoms by reducing the Hg(II) and Ag-Hg nanoalloy ions. This is because the cohesion energy for Hg is lower than that of Ag. Hg, which is capable of diffusion into the silver surface, resulting in a blue shift and a decrease in the absorption tape.

In addition, the study was conducted by Imdad Ali et al. [38]. Investigation of mercury detection in tap water using silver nanoparticles synthesized with triazole Conjugated silver nanoparticles called benzotriazol (BT-AgNPs) are synthesized using chemical reduction methods. The nanoparticles were tested as colorimetric sensors on the Hg^{2+} compound. The addition of mercury decreased the intensity of absorption and showed a change in the color of the solution from yellow to uncolored. The nanoparticles show sensitivity to concentrations of Hg^{2+} with a detection limit of 0.33 μM. The synthetic nanoparticle is used as a water detection probe for the Hg^{2+} ion.

2 Conslusion

Nanotechnology is a promising technology in a variety of chemical aspects, with superior particle sizes of 1-100 nm and beneficial characteristics both physically and chemically. This potential develops a message path to the field of specialized analysis of the identification of environmental pollution. A new technology with a low cost, fast, simple, and high sensitivity capable of detecting heavy metals The presence of Hg(II) ions in combination with other ions will re-oxidate Ag(0) from AgNPs to produce Ag(I) ions, changing the color of AgNP's to uncolor with an increased concentration of the Hg ion. With this simple technology, it can detect the presence of mercury ions qualitatively and quantitatively in both water, biological material, and other environments.

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