Silver Nanoparticles as a selective probe for Mercury Ions: A Review

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Abstract
Nanochemistry is a significant area which involves the synthesis, design, and manipulation of particle structures with dimensions ranging from 1 to 100 nanometres. It is now one of the major concerns of pharmaceutical and biological researchers. The current study discusses recent advances in the use of silver nanoparticles (AgNPs) as a selective sensor for qualitative and colorimetric quantitative detection of mercury ions. The synthesis of significant noble metal AgNPs is described as a novel, low-cost, quick, and simple method for detecting mercury ions. Due to the seriousness of mercury toxicity to our cells, AgNPs may be successfully employed for the detection of ecologically harmful mercury ions in a wide variety of aqueous practical samples using a colorimetric approach. As a result, as provided in this review with extensive details regarding this analytical approach, it might be utilized to monitor mercury ions via AgNPs in a variety of practical samples.

Keywords: Mercury ions, Silver nanoparticles, Colorimetric detection, Selective sensing, Naked-eye

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Introduction

Nanotechnology is a relatively new discipline of science and technology that involves the creation, refinement, and application of nanostructures [1]. It involved the creation, characterization, and/or manipulation of components with a length of around 1-100 nm in one of their dimensions. The chemical and physical characteristics of the resultant materials alter substantially from macro scale components when particle size is reduced [2]. Nanoparticles (NPs) have been studied in a variety of sectors in recent years, including healthcare, the environment, chemical production, cosmetics, electronics, chemical manufacture, water management, catalysts, mechanics, optics, and sensors [3]. Biological, physical, and chemical approaches are now used to synthesize NPs [4].

The two most common methods for producing metal nanoparticles (MNPs) are top down and bottom up. The first (top down) strategy is well-known in the fields of physics and engineering, where NPs are created from bulk components, whereas the second (bottom up) approach attempts to prepare NPs from metal component solutions. The bottom-up technique is more popular in chemistry [5]. NP has played a key role in the creation of nano-biosensors [6]. MNPs have unique properties and applicability in a wide range of industries; these characteristics are related to Surface Plasmon Resonance (SPR) [7]. As a result of the interaction between NPs and the analyte, which alters the strength and/or location of the absorption spectrum and is usually perceived as a color change seen by the naked eye, they are qualified to operate as colorimetric sensing for mercury ions (II) [8].

Using of "eco-friendly" nanotechnology in order to develop selective and sensitive detection techniques of analytical and biological approaches has become gradually remarkable [9, 10], especially, sensors that are used in colorimetric methods have a distinct advantage because of their high selectivity, simplicity and rapidity [11, 12].

Advantages and disadvantages AgNPs

The silver metal was subjected to cutting-edge engineering techniques in order to create ultrafine particles with a length scale of nanometres (nm). AgNPs have piqued interest as promising therapeutic agents due to their unique characteristics and biocompatibility [13-16]. Table 1 shows that AgNPs have numerous advantages and few downsides [17-19].

<table>
<thead>
<tr>
<th>Table 1- Main advantages and disadvantages of AgNPs</th>
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<tbody>
<tr>
<td><strong>Main advantages of AgNPs</strong></td>
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<tr>
<td>✓ The possibility of high-scale production of AgNPs.</td>
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<td>✓ Easily to synthesized via different methods.</td>
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<td>✓ Used as biosensor materials and in drug delivery</td>
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<tr>
<td>✓ AgNPs can be freeze-dried, so lyophilized powder can be obtained.</td>
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<tr>
<td>✓ AgNPs possess long-term stability.</td>
</tr>
</tbody>
</table>

Synthesis methods for AgNPs

The production of AgNPs may be accomplished using a variety of chemical, physical, and biological approaches [20-22], as shown in Table 2.
Table 2-Synthesis methods (chemical, physical and biological) for AgNPs

<table>
<thead>
<tr>
<th>Types of approaches</th>
<th>Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical methods</td>
<td>✔ The chemical reduction</td>
</tr>
<tr>
<td></td>
<td>✔ The Micro-emulsion technology</td>
</tr>
<tr>
<td></td>
<td>✔ The UV initiated photo-reduction</td>
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<tr>
<td></td>
<td>✔ Photoinduced reduction</td>
</tr>
<tr>
<td></td>
<td>✔ Electro-chemical</td>
</tr>
<tr>
<td></td>
<td>✔ The Irradiation, include:</td>
</tr>
<tr>
<td></td>
<td>☑ Microwave assisted synthesis</td>
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<tr>
<td></td>
<td>☑ Radiolysis</td>
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<tr>
<td></td>
<td>☑ γ-ray irradiation</td>
</tr>
<tr>
<td></td>
<td>✔ Using polysaccharides and some polymers</td>
</tr>
<tr>
<td></td>
<td>✔ The Tollens technique</td>
</tr>
<tr>
<td></td>
<td>✔ The Pyrolysis technique</td>
</tr>
<tr>
<td>Physical methods</td>
<td>✔ electrochemical cell technique</td>
</tr>
<tr>
<td></td>
<td>✔ Arc-discharge technique</td>
</tr>
<tr>
<td></td>
<td>✔ laser ablation</td>
</tr>
<tr>
<td></td>
<td>✔ Evaporation-condensation method</td>
</tr>
<tr>
<td>biological methods</td>
<td>✔ Using bacteria, fungi, yeast, algae, as well as plants</td>
</tr>
</tbody>
</table>

Chemical and physical synthesis techniques for AgNPs have various drawbacks, such as being dangerous and expensive. To address these issues, green biosynthesis of NPs has sparked a lot of attention in recent years since it is an environmentally benign, low-cost method that can be used in a variety of applications. Many researchers in this sector are concerned about this crucial method [22-25].

Mercury and environmental pollutants

Another notable aspect of nanotechnology, which is still in its early stages, is the ability to prevent environmental harm as well as safeguard individual health against various dangerous chemicals and ions [26].

Mercury (Hg) is a metal having an oxidation state of "zero," Mercury (0), that may be found in a liquid metal form or as a vapour. Mercury (I) is found as inorganic salts when the oxidation state equals "one." The mercuric state, Mercury (II), is found as inorganic salts or organometallic complexes when the oxidation state is equal to "two." Because of its capacity to travel freely and quickly through and across our live cell membranes, dimethylmercury, Hg(CH3)2, is the most deadly molecule among these groupings [10].

The mercury ion, Hg (II), is prevalent and widely dispersed in our environment, and it is one of the most common contaminants used in agriculture, industry, and medicine. Hg (II) is also non-essential and extremely damaging to human systems. If it is discovered in our drinking water, even in trace amounts, it accumulates mostly in the kidneys and may cause lasting harm to cardiac cells and the neurological system [26-28]. Mercury poisoning is defined as levels in the blood that are between 30–40 ng/mL for pregnant women and 100 ng/mL for adults.

In view of this, mercury could be known as a persistent pollutant, because it does not break down in the environment. The human consuming fish and shellfish is the significant way of mercury exposure, because of accumulation of methyl-mercury over the food web [10].

As a result, increased emphasis must be placed on the selective detection of extremely minute amounts of mercuric ions in various biological fields and wastewater; moreover, all contaminated components must be analyzed in order to monitor mercuric levels. Drinking water must also have fewer than 2 parts per billion (ppb) of mercury ions, as required by the
World Health Organization (WHO) and the Environmental Protection Agency (EPA) [29, 30]. Many researchers have developed and explored a selective/sensitive approach for detecting mercury ions (II) in aquatic environments without the need for expensive apparatus [31-34]. The use of AgNPs to detect mercury ions is demonstrated in this review (II). Even though it is an incredibly important requirement for detecting a specific analyte, the reversibility experiment for sensing mercury ions (II) utilizing AgNPs has remained unexplored till now [31].

**Mercury detection analytical techniques**

Multiple analytical techniques have been used to detect mercury levels in various environmental analytes; several of these techniques require a complex test pre-treatment procedure, skilled technicians, are expensive, time-consuming, and exhausting processes, while others are low-cost with rapid detection and simple analytical methods, which have advantages and remain a challenge to analytical chemists, as shown in Table 3.

<table>
<thead>
<tr>
<th>Expensive Analytical techniques</th>
<th>Low-cost Analytical techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔ Cold vapor atomic fluorescence (CV-AFS) [34]</td>
<td>✔ Silver nanoparticles (AgNPs) [12]</td>
</tr>
<tr>
<td>✔ Inductively coupled plasma mass spectrometry (ICP-MS) [35]</td>
<td>✔ Gold nanoparticles (AuNPs) [47]</td>
</tr>
<tr>
<td>✔ Direct mercury analyzer (DMA) [36]</td>
<td>✔ Carbon nanoparticles (CNPs) [48]</td>
</tr>
<tr>
<td>✔ Ion chromatography (IC) [37]</td>
<td>✔ Silver nanoprisms (AgNPRs) [49]</td>
</tr>
<tr>
<td>✔ High performance liquid chromatography (HPLC) [38]</td>
<td></td>
</tr>
<tr>
<td>✔ Atomic fluorescence spectrometry (AFS) [39]</td>
<td></td>
</tr>
<tr>
<td>✔ Fluorescence sensor [40]</td>
<td></td>
</tr>
<tr>
<td>✔ Conjugated polymers [41]</td>
<td></td>
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<tr>
<td>✔ Ratiometric [42]</td>
<td></td>
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<tr>
<td>✔ Oligonucleotides [43]</td>
<td></td>
</tr>
<tr>
<td>✔ Proteins [44]</td>
<td></td>
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<tr>
<td>✔ Bioluminescent bacterial sensors [45]</td>
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<tr>
<td>✔ Electrochemical sensing [46]</td>
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</tbody>
</table>

Some analytical methods that detect analytes by changing color have the potential to be easily implemented in the field of quantitative and qualitative analysis via colorimetric detection or naked-eye detection. Because of the higher attenuation coefficients and the inter-particle distance-dependent optical feature, colorimetric approaches employing AgNPs have shown to be promising methods for monitoring mercury detection in elevated polluted settings [47, 50]. Because of its distinctive properties, such as particular optical characteristics in the visible spectrum, AgNPs have sparked a lot of interest in the field of colorimetric sensors. AgNPs, in particular, are particularly advantageous due to their inexpensive cost and a 100-fold increase in SPR of the absorption band compared to AuNPs of the same size [51, 52].

Recently, the main possible way had been proposed and indicated a decreased absorbance and SPR shift due to interaction between AgNPs and mercury ions (II) [53]. According to first proposed mechanism, surface coating of Hg° ions are takes place on AgNPs, which produce a decreasing in the absorbance and made a small shift in SPR, while the other mechanism confirm the production of amalgam between both AgNPs and Hg ions. The second mechanism seems more acceptable than its predecessor as the differences in electro-chemical potentials between mercury ions (II) equal =0.85 V, and AgNPs equal=0.8 V, are much smaller to makes mercury ions (II) and AgNPs having the ability to chemical interaction.
through the so-called under-potential deposition (UPD), which leads to formation of amalgam[53, 54].

In addition, the structure and particle arrangement, as well as the interaction of Ag° as NPs with mercury ions (II), are all factors that contribute to the color transformation phenomenon. In a reduction-oxidation process, Ag° and mercury ions (II) interact in a stoichiometric ratio of 2:1 to form Hg° and Ag+, as opposed to bulky scale. Nonetheless, at the nanoscale (less than 32 nm, with a ratio of Ag: Hg of 1:1.25), Ag° was not oxidized straight to solution, but mercury ions (II) were reduced from solution (water) onto the surface of AgNPs to form solid amalgams Ag-Hg [55]. Furthermore, the water molecules might be activated, on the surface of AgNPs, to work as a reducing agent for mercury ions (II) to produce too small quantity of Hg° that may lead to the production of Ag-Hg amalgam [56].

The existence of oxidation-reduction chemistry combining AgNPs (Ag°) and mercury ions (II) to form AgHg mixture by NPs etching, as well as high sensitivity of AgNPs localized SPR, as well as cost-effective manufacture, are all factors to consider. Furthermore, UVVis spectrophotometric measurement, which deals with particular optical characteristics with localized SPR in the visible spectrum (350–800 nm), has been employed to monitor AgNPs conveniently [30]. Some researchers believe AgNPs have a spherical form, with a blue-shift in absorbance caused by a color change from yellow to colorless [57]. In another work, non-spherical AgNPs were employed to create a blue hue [58]. Firdaus et al. [10] suggest the colorimetric detection of mercury ions (II) by a reduction-oxidation process (upper one) and AgNPs aggregation (lower one) that occurs after a long period of storage without mercury ions (II) in the mixture, as illustrated in Figure 1.

![Proposed mechanism shows of mercury ions (II) colorimetric detection using AgNPs through redox reaction (higher one) and AgNP aggregation (lower one) [10].](image)

**Interfering ions’ effect**
The targeted analyte with highly selective detection in presence of another similar ion is an essential characteristic of a sensor behavior to use in analytical fields and it's a major aspect for a colorimetric sensor [51, 59]. Some researchers synthesized AgNPs using starch as stabilizing agent to form a yellowish color and gradually became colorless with elevating of mercury ions (II)[60]. Many investigations [60–62] have shown that AgNPs have a high
selectivity for mercury ions (II) and no interferences with cations or anions. However, numerous researchers have demonstrated the selectivity of AgNPs against various cations such as transition metals, alkalis, and alkali earths; however, only a few have mentioned the conjugate anion type, with the exception of one report that mentions acetate, chloride, and sulfate as counter ions for cations selectivity testing [56]. Thus, it was easy to characterize mercury ions (II) from the other metal ions using naked-eye assay.

Conclusion
Nanotechnology is expected to play a significant role in the development of analytical fields for the identification of various environmental contaminants. As a result, we demonstrated and reviewed the latest literature on mercury ions detection through AgNPs: a new low-cost, quick technology that may be done with the naked eye. The presence of Hg(II) ions in combination with other ions will re-oxidize Ag(0) of AgNPs to generate Ag(I) ions, changing the hue of AgNPs to colorless in linear fashion as the amount of Hg(II) increases.

When more modern technology is not readily accessible, the sophisticated technique's robust detection process can be used as a useful test for qualitative and quantitative mercury detection in water, biological, and other environmental samples. It's worth noting that AgNPs can be used to selectively detect mercury (a sensor) in the presence of other metal ions.

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Conflicts of interest
There is no conflict of interest regarding the publication of this paper to declare.

References:


[34] H. Bagheri and A. Gholami," Determination of very low levels of dissolved mercury(II) and methylmercury in river waters by continuous flow with on-line UV decomposition and cold-vapor atomic fluorescence spectrometry after pre-concentration on a silica gel-2-mercaptobenzimidazol sorbent," Talanta., vol. 55, no. 6, pp. 1141-1150, 2001.


