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Sensitive Determination of Mercuric Ion Using Silver Nanoparticles Functionalized With *Nymphaea Stellata* Extract

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ABSTRACT: Nowadays novel methods are employed for the detection of heavy metals using nanoparticles. In this article we adopted green synthesis of silver nanoparticles functionalised by the plant extract (*NymphaeaStellata*). The presence of phytochemicals in the leaf extract acts as reducing and stabilising agents for the synthesis of nanoparticles. The nanoparticles showed selectivity towards Hg^{2+} under the presence of various common ions like Pb^{2+} , Ca^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} , Cu^{2+} , Na^{2+} , Fe^{2+} , Zn^{2+} and sensitivity with a limit of detection of 0.05 μM . The power of the sensor system is employed in the analysis of Hg^{2+} in real water samples like bottled drinking water, tap water, lake water, and river water are estimated to be good.

KEY WORDS: NymphaeaStellata, Silver nanoparticles, Mercuric ion, Spectrophotometry

I. INTRODUCTION

Heavy metal pollution is a global problem and emerging threat to the environment and humanity. Heavy metal ions in water bodies, vegetables, meats and grains may exist in different chemical forms or binding modes. The determination of heavy metal ions has gaining prime importance because high doses of heavy metal ions can cause a series of toxic effects such as coughing, gastrointestinal bleeding, Bowen's disease, cardiac hypertrophy, hypertension, convulsions and cancer.

Metal toxicity can also occur due to other heavy metals such as chromium, mercury, cadmium, lead, aluminium, antimony, beryllium, thallium etc., Among these mercuries is considered to be more toxic and the safest limit of mercury to human is 0.002mg. Now a day's nanoparticles are synthesized in this way. Mercury is an element that occurs naturally throughout our solar system. It is liquid at room temperature. It is used in some thermometers, dental amalgams, fluorescent light bulbs, some electrical switches, mining and some industrial processes. It is released into the air when coal and other fossil fuels are burned. It is zero oxidation state Hg^0 exists as vapour or as liquid metal, its mercurous state Hg_2^{2+} exists as inorganic salts, and its mercuric state Hg^{2+} may form either inorganic salts or organomercury compounds; the three groups vary in effects. Toxic effects include damage to the brain, kidney, and lungs. Mercury poisoning can result in several diseases, including acrodynia (pink disease), Hunter-Russell syndrome and Minamata disease. Symptoms of elemental mercury when it is inhaled are, Tremors, Emotional changes, Insomnia, Weakness, Muscle atrophy, Disturbances in sensation, Headaches.

Mercury in its various forms is particularly harmful to fetuses as an environmental toxin in pregnancy, as well as to infants. Women who have been exposed to mercury in substantial excess of dietary selenium intakes during pregnancy are at risk of giving birth to children with serious birth defects. Mercury exposures in excess of dietary selenium intakes in young children can have severe neurological consequences, preventing nerve sheaths from forming properly. In human body, mercury enters the blood stream and attacks the blood-brain barrier where neurological disease can cause from mercury stimulated toxicities. Higher exposure of mercury can also affect kidney, respiratory failures and death. It exists in three forms based upon its toxicity. Metal nanoparticles have received great attention due to their unique optical and chemical properties. In recent years there has been great progress for the application of



nanomaterials as sensors for toxic chemicals and biomolecules. Nanomaterials such as gold and silver nanoparticles have been actively investigated for their possible sensing applications of both biochemicals and toxic chemicals [1].

In metal nanoparticles have been widely used for the chemical sensing and biosensing relying on their unique size dependent and interparticle distance dependent absorption spectrum. However, AgNP have some advantages over AuNPs they possess higher extensive coefficient, bio compatibility, stability, ease of preparation. Silver is an indispensable element in our daily life. This element and its compounds and alloys are extensively used in the production of photographic film or paper, jewelry, mirrors, dental fittings and other electrical and electronic applications. Because of its bacteriostatic properties, it also plays an important role in the processing of drugs, foods, beverages, polymeric materials and in filters and other equipment's to purify water. In many countries, silver impregnated filters are used for drinking water preparation.

For instance, the micro bacterial activity of different metal nanoparticles such as silver colloids are closely related to their size; that is the smaller the silver nuclei, higher the antibacterial activity. Moreover, the catalytic activity of silver nanoparticles is also dependent upon the size, shape, physical and chemical parameters and environment. Thus, the control over the size and shape is a paramount task for the researchers. Generally, specific control of shapes and size can be achieved by varying the synthetic methods, reducing agents and stabilizers [2].

In this method, silver nanoparticle is synthesized using *NymphaeaStellata* extract. It is an important and well-known medicinal plant, widely used in Ayurveda and siddha systems of medicines for the treatment of diabetes, inflammation, liver disorders and hepato protective. *Nymphayola* steroid isolated from the flowers used as antidiabetic activity. All parts of the plant contain the alkaloid Nymphaeum. This alkaloid is toxic to frogs and produce tetanus like symptoms. Calcarine has been found in leaves and stem. The plant contains several flavonoids such as Kaepmferols, Quercetins and Myricetins. They also contain Glycoside, Nymphalin which has a digitalis like action upon the heart. Nymphaeine have a mild sedative and Spasmolytic action. They are also used to treat diarrhea, stomach-ache and headache. The slightly bitter juice of the leaves is used in the treatment of gonorrhea. The juice possesses mildly narcotic properties and rubbed in the forehead to treat fever.

Several methods for the determination of mercury ions at the trace quantity level have been proposed. They include coupled plasma-optical emission spectrometry (ICP-OES), microwave-induced plasma (MIP), electrothermal atomic absorption spectrometry (ET-AAS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma-mass spectrometry (ICP-MS), solid-phase extraction (SPE), high-performance liquid chromatography, cloud point extraction (CPE), and stripping voltammetry. However, these methods have several disadvantages such as high costs and are not easily adaptable for online monitoring, long analysis time, requirement for sample pretreatment, low sensitivity and selectivity that makes them unsuitable for routine analysis. On the other hand, spectrophotometry method has now attracted much attention for many researchers with the advantages of excitation signals being non-destructive, low detection limit, sensitivity, selectivity, low cost and less time consuming [3].

In the present work, EA-AgNP has been utilized for detection of Hg^{2+} in various aqueous environment.

II. MATERIALS AND METHODS

2.1 Materials:

Silver nitrate (99.99%) was purchased from Merck Company. All other analytical grade of high purity chemicals was also purchased from Merck Company. All aqueous solutions were prepared using ultra purified water obtained from Millipore Milli Q – water system.

2.2. Instrumentation

2.2.1 UV-Visible Spectroscopy:

UV-visible spectra were recorded using Perkin-Elmer Lambda 50 was employed for the measurement of green synthesized AgNP. UV-vis spectra of the leaf extract and AgNP were scanned by using a quartz cuvette having an optical path length of one cm and were run in the range from 200 to 800 nm.

2.2.2 Fourier Transform Infrared Spectroscopy:

FTIR spectra of leaf extract and synthesized AgNP were recorded in the wavenumber between 400–4000 cm^{-1} with a resolution of 4cm^{-1} for the analysis of functional groups.

2.2.3 Dynamic Light Scattering:

The size of NPs was resolved by DLS spectroscopy of the suspension of AgNP

2.2.4 Zeta Potential Measurement:

Zeta potential and particle size distribution were determined with Zeta sizer (ZEN 3600- size range 0.3–10 μm with He-Ne laser light).

2.3 SYNTHESIS OF NS-AgNP

2.3.1 Preparation of the Extract:

The fresh leaves were collected and washed thrice with tap water and then with distilled water. The washed leaves are then soaked in distilled water and then heated at 80°C with stirring at 1000rpm for 2 hrs. The extract is then filtered with Whatman filter paper.

2.3.2 Preparation of Silver Nanoparticles:

All glassware used in the preparation of colloidal AgNP were cleaned with freshly prepared aqua regia and rinsed thoroughly with water. (*Caution: aqua regia is a powerful oxidizing agent and it should be handled with extreme care*). The colloidal solution of NS functionalized AgNP were prepared by the following procedure.

1mM (0.0016987 g) of silver nitrate was weighed and made up to the mark in the 100mL standard measuring flask. 1ml of AgNO_3 (1 mM) was added into 89 mL of water in 500 ml beaker with constant stirring. To this solution, 10 mL of NS extract was added, and the stirring was continued for another 30 min. The green colour solution turns into yellow immediately after the final addition, indicating the formation of AgNP. This is possible that the compounds present in the extract reduces the silver from (Ag^{+1}) to (Ag^0).

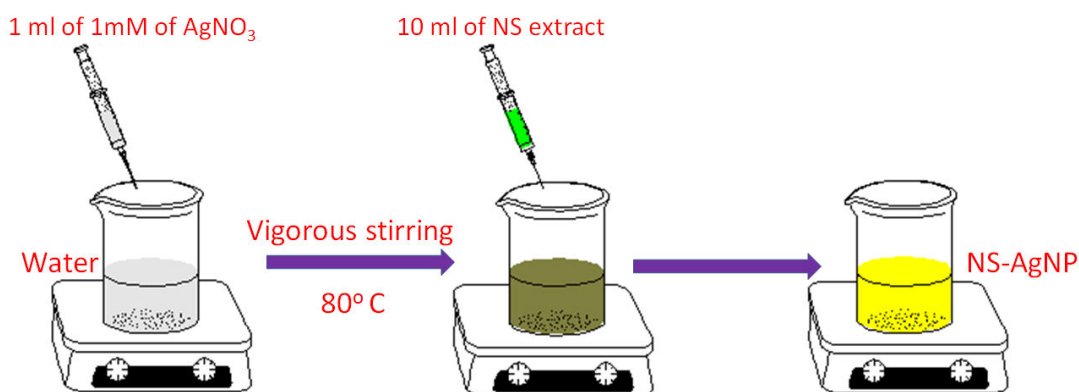


Figure.1 Schematic representation of Synthesis of NS-AgNP

2.4 SAMPLE PREPARATION FOR THE DETECTION OF MERCURY

For selectivity analysis, 100 μL each of 1 μM solutions of the chosen eleven metal ions, namely, Pb^{2+} , Ca^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} , Cu^{2+} , Na^{+} , Fe^{2+} , Zn^{2+} and 2 mL of NS-AgNP were added, allowed to stand for 10 min and then subjected to spectrophotometric analysis. 100 μL of known concentration of mercuric chloride solution was taken in a series of 10 mL flasks. 2 mL of NS-AgNP suspension was added to each of them and allowed to stand for 10 min. 2 mL of each of the mixtures was transferred to a quartz cuvette and the absorbance was measured in the range of 200–800 nm against water as a blank. For sensitivity analysis, six different concentrations of Hg^{2+} were chosen and they were: 0.01 μM to 1 M.

III. RESULTS AND DISCUSSION

3.1 UV-Visible Analysis:

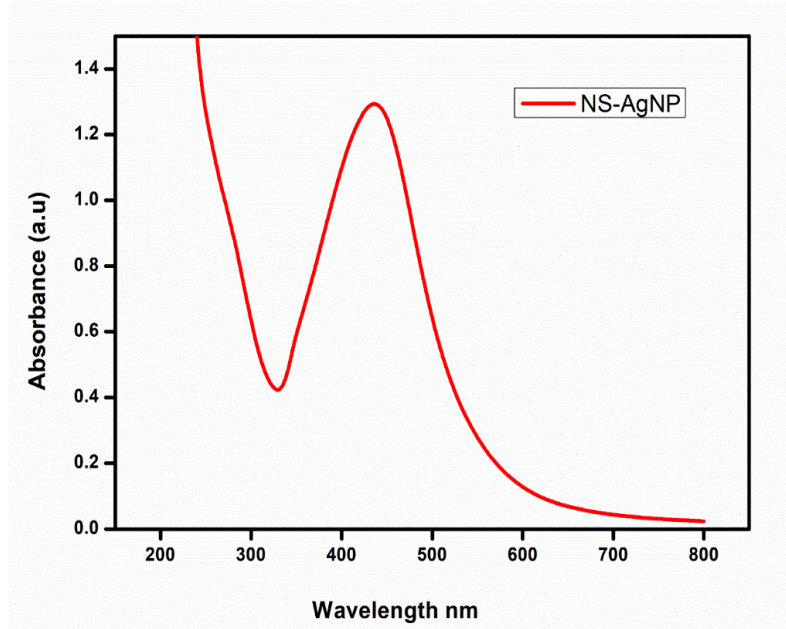


Figure.2 UV-Visible spectra of as-synthesized silver nanoparticles using plant extract (*Nymphaea Stellata*)

Metal nanoparticles have free electrons and the combined vibration of electrons of metal nanoparticles in resonance with the light wave gives rise to a surface plasmon resonance (SPR) band. The UV-visible spectrum of the as-prepared NS stabilized AgNP shows a strong SPR band at 436 nm [4] which suggest that the silver ions from Ag^{+1} to Ag^0 nanoparticles, shown in fig 2

3.2 FT-IR Analysis:

FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range are measured as wave numbers typically over the range $4000 - 600 \text{ cm}^{-1}$. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and crosslinks involved, all of which will have characteristic vibrational frequencies in the infra-red range.

The several functional groups in the compounds of *Nymphaea Stellata* were observed at 3423 cm^{-1} (broad), 2946 cm^{-1} , 2852 cm^{-1} , 1657 cm^{-1} , 1458 cm^{-1} , 1378 cm^{-1} and 1050 cm^{-1} , 907 cm^{-1} which corresponds to $-\text{OH}$, $-\text{NH}$, $-\text{CH}$, $-\text{C}=\text{O}$, $-\text{COOH}$, $-\text{NH}_2$ groups of steroids, flavanoids, alkaloids, tannins and sugars etc., are shown in Fig 3. The phytochemicals in the leaf extract are potent reducing and stabilising agents and they are confirmed by phytochemical tests [5].

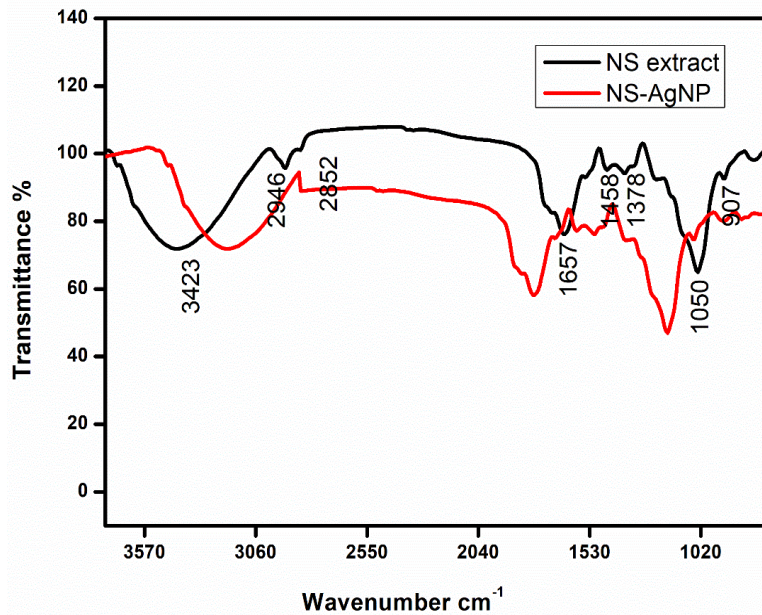


Figure.3 FTIR spectra of the plant extract (*Nymphaea stellata*) and as-synthesized NS-AgNP

The FTIR of the synthesized NS-AgNP was also taken to confirm that the amine groups, aldehyde, and hydroxyl groups in the extract can bound with Ag^{+1} ions with the changes in transmittance after the formation of AgNP. This shows that the leaf extract are responsible for reducing and stabilising the AgNP by preventing agglomeration.

3.3 DLS Analysis:

It is a technique in that can be used to determine the size distribution profile of small particles in suspension or polymers in solution. All the molecules in the solution are being hit with the light and all the molecules diffract the light in all directions. The diffracted light from all the molecules can either interfere constructively or destructively. This process is repeated at short time intervals and the resulting set of speckle patterns are analyzed by an auto correlator that compares the intensity of light at each spot over time. The average size of the silver nanoparticles functionalized with *Nymphaeastellata* extract was found to be 45.4nm [6] are shown in fig 4.

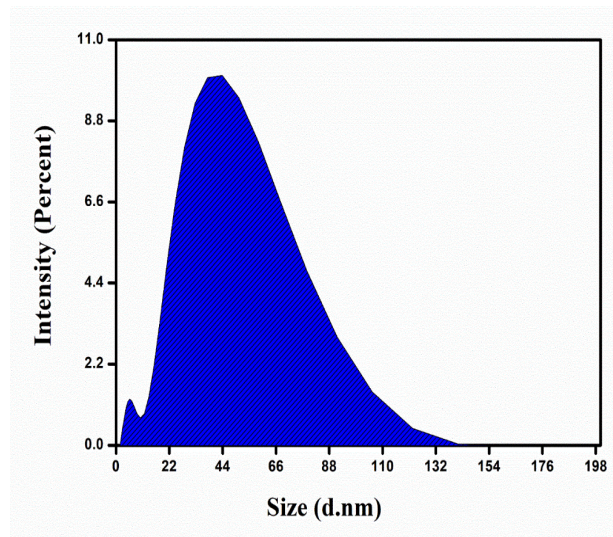


Figure.4 Particle size analysis (DLS) of synthesized NS-AgNP.

3.4 Zeta Potential Analysis:

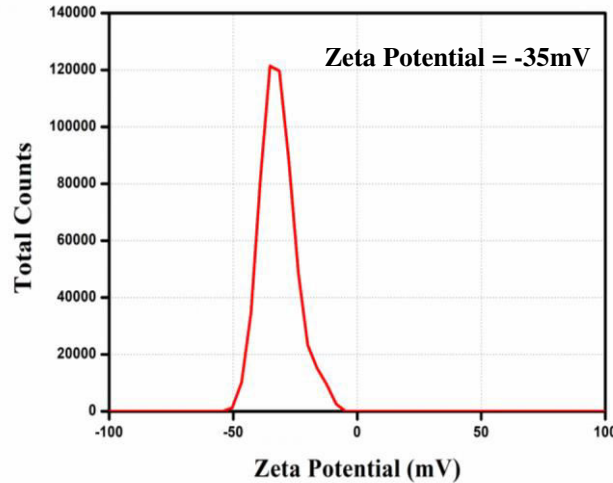


Figure.5 Stability of the NS-AgNP by zeta potential.

The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. Zeta potential can be determined by electrophoretic phenomena or electrokinetics. The stability of the synthesized NS-AgNP was measured as -35 mV which indicate the nanoparticle has high degree of stability [7].

3.5 Selective and Sensitive Detection of Hg (II) Ion Using NS-AgNP by Spectrophotometric Method:

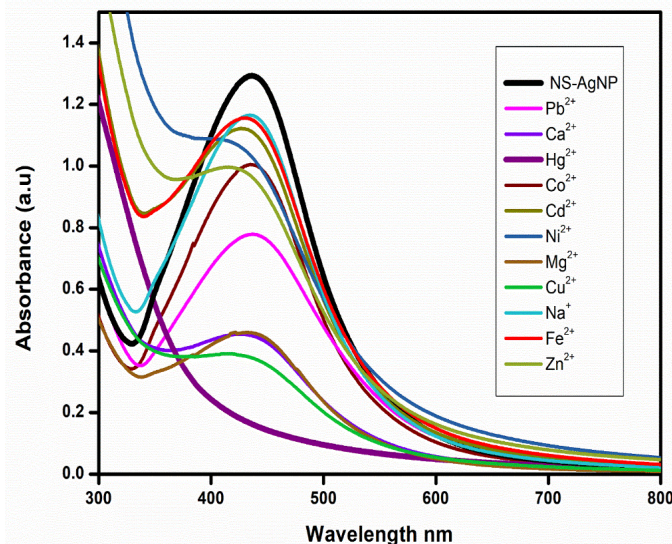


Figure.6 UV-Visible spectra of synthesized NS-AgNP 1 M of different metal ions

The absorption shows maximum for the yellow coloured NS-AgNP was at 436 nm in the absence of mercuric ions. The colorimetric detection of different metal ions like Pb²⁺, Ca²⁺, Hg²⁺, Co²⁺, Cd²⁺, Ni²⁺, Mg²⁺, Cu²⁺, Na⁺, Zn²⁺ were carried out by mixing with NS-AgNP, shown in fig 6. It is found that when mercuric ions are mixed with Ag nanoparticles, it changes its colour from yellow to colorless [8]. This shows that individual characteristics peaks are



obtained for each metal ions, but on the addition of mercuric ions, a linear plot obtained. This means that the synthesized AgNP are selective towards Hg (II) ions.

Fig. 7 shows UV-Visible spectrum for NS-AgNP with different concentrations of Hg²⁺. Incremental addition of Hg ions from 0.01μM to 1M caused a gradual blue shift in the absorption maximum of AgNP, indicating the deposition of mercuric ions around the surface of AgNP.

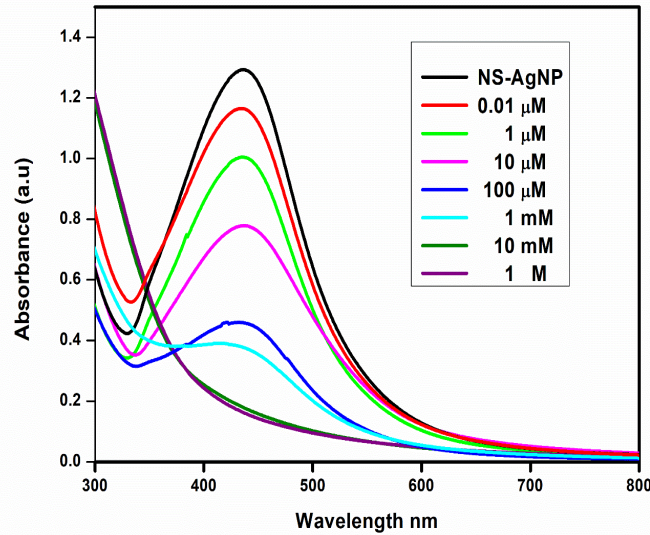


Figure.7 UV-Vis spectra of NS-AgNP with different concentrations of Hg²⁺.

The added mercuric ions began to occupy the surface of the silver nanoparticles. With an increase in the concentration of Hg (II), the inter-particle distance between AgNP and the metal progressively reduced, leading to the formation of an amalgam [9]. This amalgamation would have led to the decrease in excitation energy of silver Nano aggregates, thus at a high Hg (II) ions Concentration of 1 M, extensive amalgamation and aggregation lead to a change in the colour of the medium from yellow to colorless.

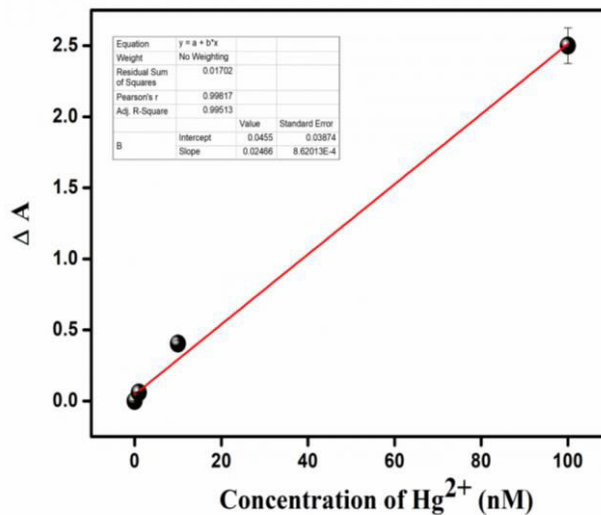


Figure.8 linearity assay at different concentration of Hg²⁺ ions

A good linear relationship was achieved in fig 8, and Hg(II) Concentration within the range of 0.01 μ M to 1M Hg(II), indicating that this NS-AgNP sensor system was valid for the quantitative determination of Hg(II) at low concentration [10].

Limit of Detection (LOD) can be calculated by the following equation

$$\text{LOD} = 3.3 \times \text{Standard deviation of the regression line} / \text{slope}$$

This study has established a lower detection limit for spectrophotometric analysis of Hg²⁺ in aqueous medium as 0.05 μ M Nano molar, using *Nymphaea stellata* functionalized silver nanoparticles as sensor.

3.6 Mechanism for Ag-Hg amalgam

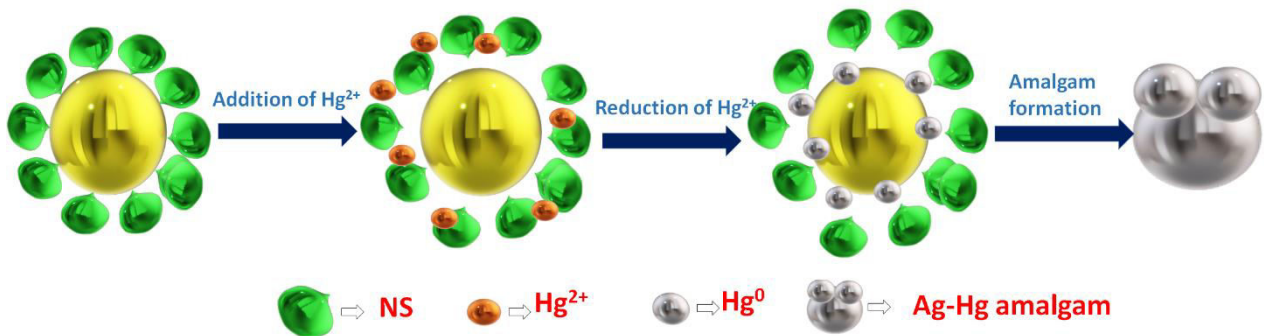


Figure.9 Schematic representation of mechanism for Ag-Hg amalgam formation

The possible mechanism of the interaction involves, the reduction potential of Hg²⁺ (+0.86) is higher than Ag⁰ (+0.80), thus the spontaneous redox reaction occurred between Hg and Ag, in which Ag⁰ was partially converted to Ag⁺ confirmed by the color of solution changed from yellow to colourless. Hg-Ag amalgam formed between mercury atoms with surface silver atoms, Due to the interaction with AgNP with Hg, surface charge of the nanoparticle was decreased, leading to their aggregation and destabilization of nanoparticle that were confirmed by DLS and Zeta potential analysis[11].

3.7 DLS Analysis and Zeta Potential Analysis for Ag-Hg amalgam formation

The aggregation of gold nanoparticles was further confirmed by DLS and zeta potential measurements. The DLS measurements revealed a gradual change in the particle size distribution with increasing concentration of Hg²⁺. The size of NS-AgNP was shown to change from 45.4 to 120 nm in the presence of 1 μ M of Hg²⁺ indicated in fig 10. Zeta potential value for NS -AgNP in presence of 1 μ M Hg²⁺ was -17.36 mV in fig 11. A change from -35 mV for pure NS-AgNP to -17.36 mV in the silver-mercury amalgam revealed that the stability of the nanoparticles diminished due to the aggregation and amalgamation [12].

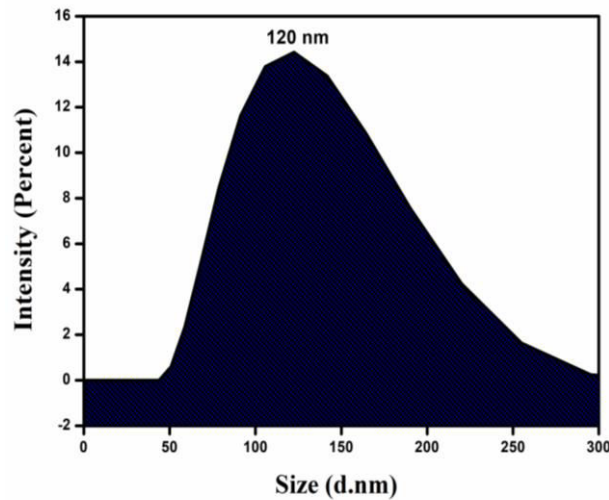


Figure.10 DLS of NS-AgNP in the presence of Hg²⁺

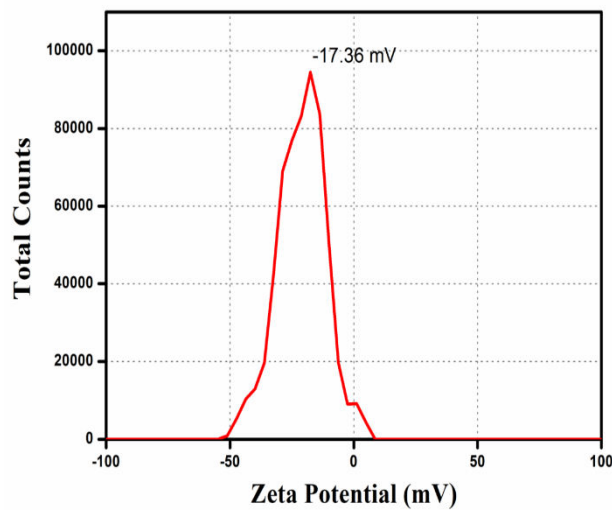


Figure.11 Zeta Potential of NS-AgNP in the presence of Hg²⁺

3.9 Real Sample Analysis

The application of the proposed method was evaluated by determining Hg(II) in bottled drinking water, river water collected from koovam river, Adyar, lake water collected from Chengalpattu lake and tap water samples collected from Anna University, Chennai in the period of January 2019. The obtained results are given in Table 1. The water samples collected from river, lake and tap were used without previous treatment and known amounts of Hg (II) were spiked with a standard stock solution. The recovery of 96%, 100.1%, 106% and 104.5% were obtained and good agreement and Hg (II) was obtained between spiked and measured analyte amounts.

The average amount of mercury was detected, and it is found to be present in polluted river water and lake water whereas less in tap water [13].

Table 1 DETERMINATION OF Hg²⁺ IN REAL WATER SAMPLES USING NS-AgNP

Samples	Hg ²⁺ added ($\mu\text{M L}^{-1}$)	Hg ²⁺ determined ($\mu\text{M L}^{-1}$)	Recovery %	Average amount of mercury present
Drinking water	0.01	0.0096 \pm 0.0002	96	Not detected
Tap Water	0.01	0.01001 \pm 0.0004	100.1	0.02 pg/L
Polluted Lake Water	0.01	0.0106 \pm 0.0003	106	0.12 ng/L
Polluted River Water	0.01	0.01087 \pm 0.0019	108.7	0.17 ng/L

The mercury is not present in bottled drinking water. The spectra of NS-AgNP in different environments indicated that the sensor system was not only sensitive, but also selective towards mercury, even in the presence of heterogeneous pollutants in water samples.

IV. CONCLUSION

Ag nanoparticles were synthesized using *Nymphaeastellataplant* extract. These synthesized nanoparticles are highly selective for Hg²⁺ ions among the interference of common ions like, Pb²⁺, Ca²⁺, Hg²⁺, Cd²⁺, Ni²⁺, Co²⁺, Mg²⁺, Cu²⁺, Na⁺, Fe²⁺, Zn²⁺. Sensitivity is also achieved on increased addition of Hg²⁺ ions from 0.01 μM to 1M which resulted in amalgamation and agglomeration. The interaction of Ag nanoparticles and Hg²⁺ ions was measured using UV-Vis spectrophotometer. It was found that absorbance intensity of Ag nanoparticles decreases from 436nm to 427nm as Hg²⁺ ions combine with nanoparticles, which shows the colour changes from yellow to colorless. We believe that Ag nanoparticles synthesized at ambient condition can be used for easy detection of Hg²⁺ ions.

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