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RESEARCH PAPER

Spectrophotometric Detection of Mercury Using Lignosulphonic Stabilized Silver Nanopaticles (AGNP)

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Abstract: *Mercury, one of the common pollutants in water, is known to affect human health adversely upon exposure. It is released in water not only by various natural processes but also by human activities. Methods developed so far for the detection of mercuric ions in water have limitations like sensitivity range, complex setup, skillful operation etc. Silver nanoparticles, due to unique properties, have been explored by researchers to develop better detection systems. Stable silver nanoparticles can be easily synthesized by methods of green chemistry, its reaction with mercuric ion can be easily observed by changes in color and UV-Vis spectra. The absorbance data from UV-Vis spectra can also be used in quantifying mercury concentration. In this paper, stable silver nanoparticles synthesized using silver nitrate as precursor, sodium lignosulphonate (LS) as reducing and stabilizing agent under microwave radiation are explored for detection of mercuric ions in water. Formation of Ag nanoparticles was confirmed by UV-Vis band at 403.5nm. The intensity of this band showed a proportional decrease with increasing* Hg^{+2} *concentration.* Hg^{+2} *ions were detected by a distinct color change at higher concentration of* Hg^{+2} *also. The limit of detection (LOD) calculated from the observed absorbance data to be 0.7 ppm.*

Keywords: *Mercury, Silver nanoparticles, Lignosulphonic acid, Spectrophotometer.*

1 . INTRODUCTION

India, is one of the densely populated country in world. An estimated 70% of its available water is contaminated. It has been ranked 120 among 122 countries in the water quality index [1]. Millions of people die prematurely every year by consuming polluted water. Mercury is one of the pollutants in water and is known to be toxic to human [2-5] as it affects the central nervous system, kidney etc when consumed in excess. Amongst its various forms, mercury can be present as elemental mercury (Hg^0), inorganic mercury (Hg^{+2}) and methyl mercury in environment. The inorganic mercury is the most common form present in water. People receive it through contaminated water and food and at times by inhaling its vapors [6-7]. The accepted limit of mercury in water is very low. According to the World Health Organization (WHO), the permissible limit of Hg^{2+} in drinking water is 6 μg/L and it can create a serious health risks to human health when exposed beyond this limit [8]. Detection and monitoring of mercury is the most important aspect of prevention from mercury toxicity. Analytical approaches for its detection are based upon principles of spectroscopy [9-11], electrochemistry, chromatography [12] and colorimetry [13]. These methods require expensive instruments, specialized technical assistance and time consuming procedures. Even chemo-sensors with good selectivity and ability for naked eye detection of mercury face limitations like complex and time-consuming procedures, expensive equipment and elaborate setup.

Recently nanotechnology has been employed to develop methods to detect mercury. These methods are simple, efficient and cost effective. In most of the approaches, gold and silver nanoparticles in various stable forms have been employed. L-tyrosine stabilized gold nanoparticle has been used for the detection of mercury with sensitivity in the nanometer range [14-15]. Gold nanoparticles embedded paper electrode in another study has been found to show Hg^{+2} ion detection in the nanometer range successfully [16]. Silver nanoparticles (AgNp) have also been explored in various studies for the detection of mercury. Ease of synthesis and cost effectiveness are some of the advantages for silver nanoparticles [17]. In one of the study silver nanoparticles functionalized with 2-aminopyrimidine-4,6-diol (APD-AgNP) was synthesized and successfully used for colorimetric detection of mercury in aqueous solution with both naked eye and through the UV-visible spectrophotometer. In another study AgNP was synthesized using *Matricaria recutita* (Babunah) plant extract as reducing agent and the synthesized nanoparticle was proposed for detection of mercury. The AgNP showed a colour change from yellowish brown to colorless with increasing concentration of Hg^{2+} ions. Changes in intensity of UV visible band was also observed in the same order [18]. In another experiment chemical route was adopted for the syntheses of gelatin functionalize AgNP. The nanoparticle showed good results for colorimetric sensing of Hg^{2+} ions in solid, hydrogel network and on paper substrate [19].

It is evident that AgNPs have a great potential in detection of mercury. In this research we have developed a cost effective method with adequate sensitivity for the detection of mercuric ion in water by lignosulphonic acid (LS) stabilized AgNP. LS is a plant waste material and capable of synthesizing stable AgNP in aqueous medium [20]. The method of synthesis is purely based on principles of green chemistry, plant waste materials have been used for mercuric ion detection. Use of microwave has helped in synthesizing smaller AgNP in less time [21].

2. EXPERIMENTAL PROCEDURE

2. 1. Materials

Sodium salt of Lignosulphonic acid (LS), a plant byproduct, is purchased from sigma Aldrich, Germany, Mercurous chloride from nice chemicals. The chemicals are used as obtained and distilled water was used for preparation of solutions. All glassware is rinsed thoroughly with distilled water prior to use.

2. 2. Methods

LS stabilized AgNP was synthesized by method previously developed [22]. In short, the nanoparticles were synthesized by exposing the mixture of aqueous solutions of LS and silver nitrate to microwave radiation of 300W power for 2 minutes in a domestic microwave oven. Appearance of dark brown solution indicated the synthesis of AgNP. The obtained AgNP solution was mixed with mercurous chloride solution of various concentrations (1ppm, 2ppm, 3ppm, 4ppm, 5ppm, 10ppm, 15ppm, 20ppm, 25ppm) in 10 ml standard flask. Influence of AgNP on mercury ion was investigated using Schimadzu 2600 UV-Vis spectrophotometer between 280 to 420 nm wavelengths.

3. RESULT AND DISCUSSION

AgNP were synthesized as a result of silver ion reduction by the reducing groups present on the LS. The polymeric structure of LS is known to support the nucleation, growth and stabilization of nanoparticles. Microwave energy facilitates synthesis of nanoparticles of small and uniform size [23]. Upon exposing the silver nitrate and LS solutions to microwave radiation, a color change from light brown to dark brown for the mixture indicated synthesis of AgNP. The atomic silver then grows on the polymer surface as stable nanoparticle, the polymeric structure, in this case, supports nucleation and stabilization of silver nanoparticles. The characteristic plasmon resonance band at a wavelength of 403.5 nm [Fig1] confirmed presence of small sized silver nanoparticles [20]. Presence of absorption peak at 285nm in fig.1, indicates involvement of LS is in the synthesis and stabilization process [Fig2]. Presence of LS has also been verified by other characterization techniques and published earlier [22].

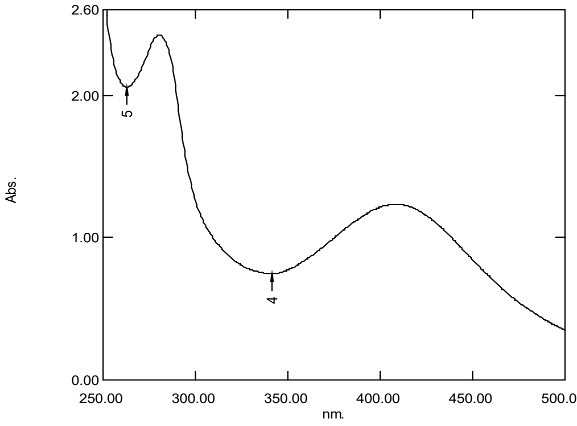

Fig 1: UV-Vis spectra of synthesized AgNP

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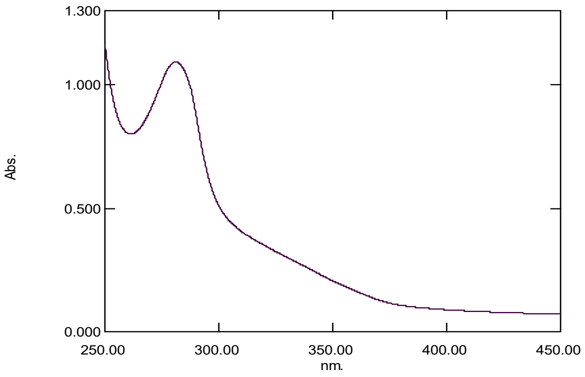

Fig. 2. UV-Vis spectra of LS

The standard potential for Ag^{+}/Ag and Hg^{+2}/Hg are + 0.80 V, and +0.85 V respectively. Thus, a redox reaction, as shown below, can establish between the atomic silver and mercuric ion in solution.

$$Ag + Hg^{2+}{}_{aq} \rightarrow Ag^{+}{}_{aq} + Hg$$

Therefore, when Hg^{2+} ion is added to the aqueous solution of AgNP containing atomic silver, above process gets initiated. This leads to reduction of mercuric ion to mercury and also aggregation and formation of silver amalgam. The aggregation leads to increase in particle size [24] which can be captured by a shift in the wavelength and absorbance of the SPR band by the UV-Vis spectrophotometer. A colour change can also be viewed through naked eye. It has been previously shown that this process is highly selective in nature and presence of metal ions like Na, K, Ca, Mg, Fe, Ni, Pb, Zn, Cr etc. does not interfere with mercuric ion detection in the concentration and wavelength study range of nanoparticles [25-27]. AgNP, therefore, are a suitable candidate for sensing the mercuric ions in the aqueous solution.

In this work, unmodified LS stabilized AgNP were used for the colorimetric estimation of mercury ions in water. The sensitivity of the process was evaluated by mixing different concentrations of mercuric ions with a fixed volume of AgNP solution. A gradual colour change from dark brown to light brown was also observed with increasing concentration of mercuric ions. A continuous reduction in absorbance as well as a slight blue shift in the wavelength was observed in the UV Vis spectra [Fig.3].

The change in absorption peak as observed indicates that redox reaction between the atomic silver on nanoparticle and mercuric ion in the solution is taking place. A higher standard potential value of mercury ($E^{o}_{Hg2+/Hg}$) as compared to silver ($E^{o}_{Ag+/Ag}$) prevents the occurrence of reverse reaction. An increase in absorption peak around 285nm with increase in mercuric ions concentration was also observed [Fig,3]. Possible reason for increase in the characteristic peak of LS could be release of polymer molecules involved in stabilization of nanoparticles. It is known fact that as the nanoparticles reacts with mercuric ions an aggregation of nanoparticles takes place.

The developed method was tested statistically

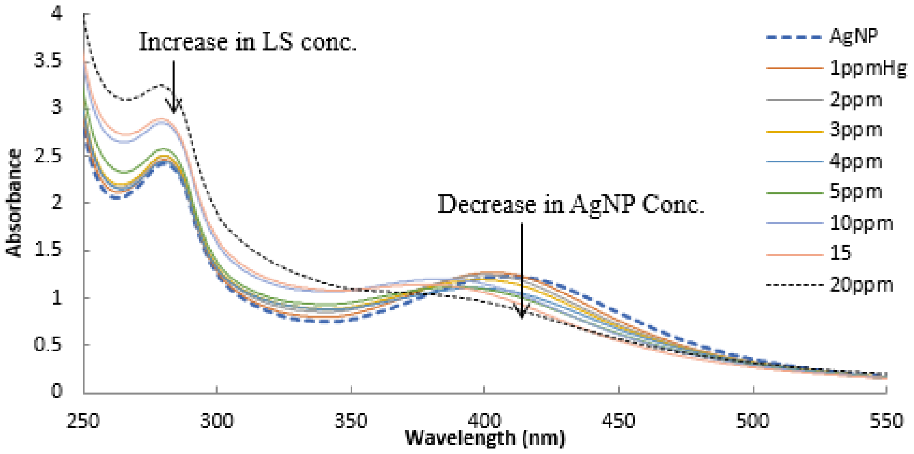

Fig. 3. Plot of intensity of absorbance at wavelength 409nm towards Hg^{2+} ion concentration.

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for its sensitivity using the absorbance data. The calibration curve plotted shows that the absorbance decreased linearly with the concentration of Hg [Fig 4]. It is also clear that the Beer Lamberts law is obeyed in the concentration range of 1-20ppm. The regression parameters for the curve are shown in the table 1 below.

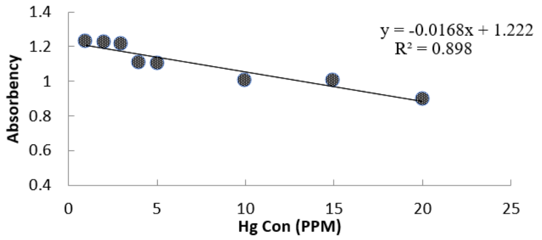

Fig. 4. A calibration curve was plotted with the obtained absorbance data

Parameter	Range
λmax,nm	403.5
Molar absorptivity, $Lmol^{-1}cm^{-1}$	$1.68x10^5$
Limit of detection,μg/ml	0.70
Limit of quantification, μg/ml	2.11
Sandell Sensitivity	0.0027
Regression Equation	
Intercept	1.2220
Slope	-0.0168
S_a	0.09980
S_b	0.00549

Table 1. Regression Parameters; Y=a+bX, where Y is absorbance and X is concentration (ppm), Sa is standard deviation of intercept and SE is standard deviation of slope.

The limit of quantification (LOQ) and limit of detection (LOD) showed a low value, indicating suitability for trace level detection of Hg. The molar absorptivity is calculated at $1.68x10^5$ showing a reasonably strong electronic transition. Further, the method is simple, free from complex reaction conditions and usage of any carcinogenic solvents.

4. CONCLUSIONS

In this paper, we have investigated the ability of LS stabilized AgNP for sensing Hg^{2+} ions in water. LS stabilized AgNP were synthesized by green method and used without modification for detection of mercuric ions. The AgNPs show good sensitivity towards the mercuric ions in water with an LOD of 0.7μg/ml. There is a decrease in absorption with addition of mercuric ions with a blue shift in λmax due to the aggregation of nanoparticles. The aggregation is also evident from the gradual release of LS in the solution with successive addition of mercuric ions. Sensing for higher concentration of mercuric ion was achieved by color change. Mercuric ions detection using AgNP is fast, highly sensitive with a lower LOD value and the method is easy to perform. Thus, the LS functionalized AgNP possess a good potential for sensor applications for the detection of mercuric ions in water.

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