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Colorimetric Sensing of Mercury in Aqueous Solutions Using Silver Nanoparticles Prepared from *Synadenium glaucescens* Root Aqueous Extract [†]

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Abstract: Mercury contamination from various anthropogenic activities has been a recent global problem. Thus, developing cheap and efficient techniques for sensing mercury is significant for protecting humans and other organisms. The sensing of mercury using silver nanoparticles fabricated using phytochemicals extracted from *Synadenium glaucescens* roots (SYR) is reported. The successful synthesis of silver nanoparticles (SYR-AgNPs) was confirmed by a strong plasmon resonance in the UV-Vis spectrum at 420 nm due to oscillations of electrons in the silver nanoparticles. The potential use of fabricated silver nanoparticles for the sensing of mercury ions from aqueous solutions was investigated. The prepared silver nanoparticles displayed a high selectivity for detecting mercury against other divalent metal ions (Hg^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, and Pb^{2+}). The addition of mercury changed the SYR-AgNPs' color to colorless, and the observed change in color was proportional to mercury concentration. The application of silver nanoparticles for the sensing of mercury displayed a detection limit of 11.3 µM. Therefore, the findings in the current study indicate that the prepared SYR-AgNPs can serve as a potentially sensitive and selective readily available method for sensing mercury ions in environmental samples. The method can be useful in advancing the application of green technology for sensing heavy metals from environmental samples.

Keywords: silver nanoparticles; *Synadenium glaucescens*; Plasmon Surface Resonance; mercury sensing

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1. Introduction

Mercury is a toxic and hazardous element that naturally occurs in environments such as soil and rocks. The element causes various adverse effects in humans and animals, even in small concentrations. The metal emanates from natural processes such as soil erosion and volcanic eruptions. Human activities, such as coal burning and artisanal gold mining, can also significantly contribute to mercury accumulation in aquatic environments [1]. The aqueous mercuric ion (Hg^{2+}) is the most stable form of mercury that is found in different environments and can be converted to a more bio-accumulative form (methylated mercury). Thus, developing a selective and sensitive method to detect the stable form of mercury (Hg^{2+}) from household, environmental, and industrial wastes is significant for protecting public health.

Several techniques, such as cold vapor integrated quartz crystal microbalance, gas chromatography-triple quadrupole mass spectrometry, electrochemical sensors, mercury analyzers, fluorescence and atomic absorption spectroscopy, and atomic fluorescence spectroscopy, have been reported for the effective detection of mercury [2]. However, most of the techniques require sophisticated instruments and trained personnel. Consequently, developing simple, rapid, and accurate methods for sensing mercury ions in aqueous solutions is becoming highly significant. Silver nanoparticles prepared using plant extracts to detect mercury ions have gained considerable recent attention as one of the simple and cheap alternatives [3–5]. In this technique, silver ions combine with phytochemicals to impart a plasmon resonance behavior useful for sensing mercury ions. Phytochemicals such as polyphenols, flavones, terpenoids, carboxylic acids, ketones, aldehydes, and amides were found useful for this purpose [6].

Synadenium glaucescens belongs to a family known as *Euphorbiaceae*. This plant's roots are used to treat various diseases, such as toothache, cough, tuberculosis, sexually transmitted diseases and symptoms caused by the human immunodeficiency virus [7]. The roots are also reported to be a good source of secondary metabolites, such as terpenoids, steroids, alkaloids, flavonoids, anthraquinones, tannins, coumarins, and glycosides [8]. Similar compounds from other plant extracts have been reported to be useful for the synthesis of silver nanoparticles suitable for various applications [8]. However, information on using the phytochemicals from this widely used plant to prepare silver nanoparticles suitable for sensing mercury ions is still limited. Thus, the application of silver nanoparticles prepared from the aqueous extract of the roots of *Synadenium glaucescens* for the detection of mercury ions from aqueous solutions is reported in the current study.

2. Materials and Methods

2.1. Materials

$AgNO_3$ (99.9%) was purchased from Sigma-Aldrich, Dorset, UK. *Synadenium glaucescens* roots (SYR) were used as a source of phytochemicals.

2.2. Methods

2.2.1. Preparation of Plant Extract

SYR were collected from the Sokoine University of Agriculture, Solomon Mahlangu campus grounds. The collected roots were washed with tap water to remove dirt and dried in an oven at 60 °C for 48 h. Dried roots were ground to powder and stored in polyethene bags. The extraction of phytochemicals was performed by boiling the powder (10 g) in distilled water (200 mL) and the filtrate obtained was used to synthesize silver nanoparticles.

2.2.2. Synthesis of SYR-AgNPs Nanoparticles

Silver nanoparticles were prepared using optimized conditions of 0.02 M $AgNO_3$ (50 mL), extract (10 mL), pH 8, temperature of 60 °C, and time of 70 min. The success of the synthesis was confirmed by a color change and measurement of a sample solution using UV-Vis spectrophotometry over the wavelength range of 300–800 nm.

2.2.3. Application of SYR-AgNPs Nanoparticles for Sensing Mercury

The specificity of a silver nanosensor for the detection of mercury ions from an aqueous solution was investigated using selected divalent metal ions (Hg^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Ni^{2+}, and Pb^{2+}). In this case, a sample solution (750 µL) containing mercury (200 mg/L) was mixed with 150 µL in a 5 mL volumetric flask and diluted with distilled water. The resulting solutions were scanned using UV-Vis spectrophotometry in the 300–800 nm wavelength range.

SYR-AgNPs were used to determine the detection limit for sensing mercury ions. The sample solution made of different concentrations of mercury, 20 mg/L, 1, 0.1, 0.01, and 0.001, were treated with 100 µL of silver nanoparticles. The resulting solution was visually examined and then measured using UV-Vis spectrophotometry.

3. Results and Discussion

3.1. Synthesis of SYR-AgNPs Nanoparticles

The UV-Vis spectrophotometry measurement is a useful confirmatory test for forming silver nanoparticles [9]. Reports indicate that spherical silver nanoparticles show a surface plasmon resonance (SPR) extending in the wavelength range of 350–500 nm with maximal absorption at around 410 nm [10]. Therefore, the technique was used to confirm the formation of silver nanoparticles in the current study. The findings (Figure 1) showed a symmetrical absorption peak at 420 nm, confirming the formation of silver nanoparticle suspensions. The appearance of the SPR absorption band was attributed to the mutual vibrations of electrons in nanoparticles in resonance with light waves [9]. The appearance of the SPR absorption band at 420 nm was also reported in other prepared silver nanoparticles [11,12]. The appearance of the symmetrically shaped surface plasmon resonance in the spectrum suggests that the prepared silver nanoparticles were spherical with a uniform distribution. Thus, the results indicated that the silver nanoparticles were successfully fabricated. The application of the silver nanoparticles for the detection of mercury ions was performed in subsequent experiments.

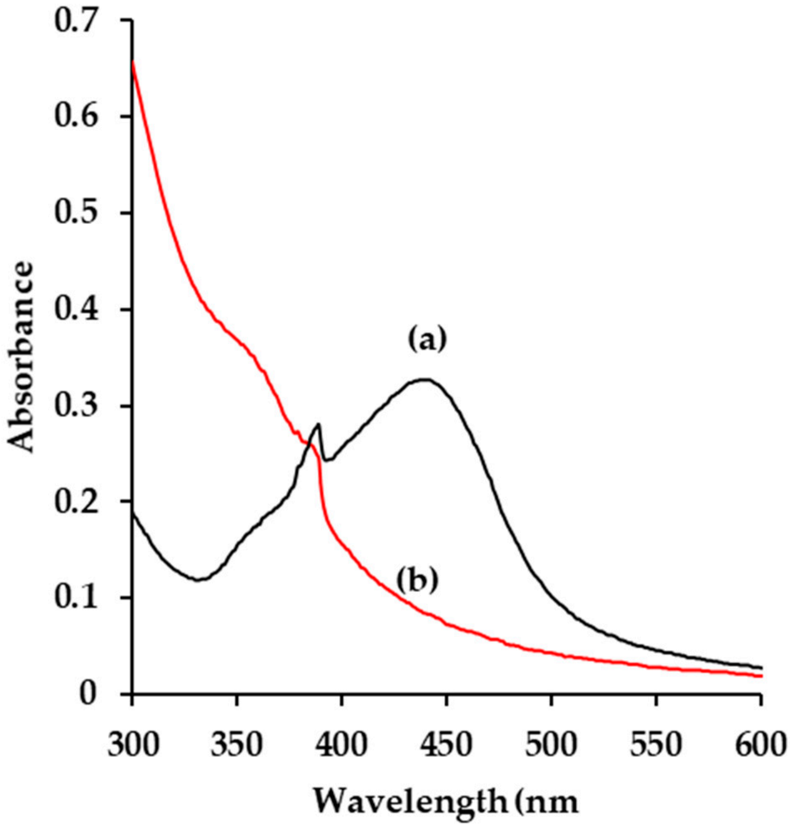
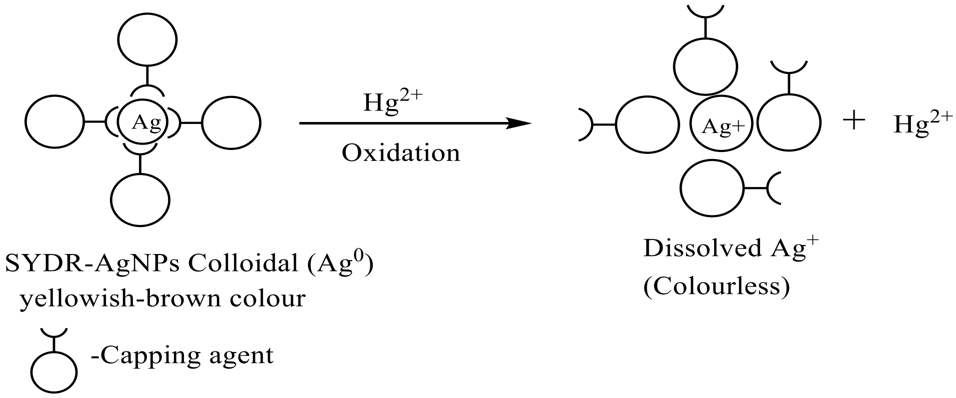


Figure 1. UV-vis spectral of prepared SYDR-AgNPs (a) and SYDR root extract (b).

3.2. Selectivity

The fabricated SYDR-AgNPs were used for sensing divalent metal ions in an aqueous solution. The visual observation (Figure 2a) indicated that adding mercury ions resulted in the decolorization of silver nanoparticles, forming a colorless solution. The observation was possibly attributed to the disintegration of silver nanoparticles caused by the oxidation of metallic silver to Ag (I), turning the mixture colorless (Figure 2b). Consequently, the resultant Ag (I) ions combined with Hg (II) to form the Ag-Hg nanoalloy. Thus, the calorimetric detection of Hg by silver nanoparticles was based on applying the redox reaction.

(**a**)



(**b**)

Figure 2. (**a**) Color change due to the detection of Hg^{2+} using fabricated SYDR-AgNPs to produce colorless Hg- SYDR-AgNPs. (**b**) Schematic illustration of a proposed mechanism for the calorimetric detection of mercury ions using SYDR-AgNPs through a redox reaction.

The selectivity was also investigated using the UV-Vis spectrophotometric measurement. The results (Figure 3) indicated that the fabricated silver nanoparticles were sensitive to most of the investigated divalent metal ions, as characterized by changes in the absorbance. However, a remarkable difference in absorption was observed in the presence of mercury ions. The decrease in absorption due to mercury ions was possibly attributed to the spontaneous oxidation of metallic silver that originated from the electrochemical difference between mercury metal ions and Ag(0) [13]. Mercury has a higher reduction potential (+0.85 V) compared to Ag (0) (+0.8 V), which makes mercury an excellent oxidizer. A similar decrease in the absorption of silver nanoparticles in the presence of mercury was previously reported by others [14]. The preliminary findings indicated that the synthesized silver nanoparticles showed high selectivity and specificity to mercury ions. Thus, the subsequent experiments involved the use of nanoparticles to detect different concentrations of mercury ions.

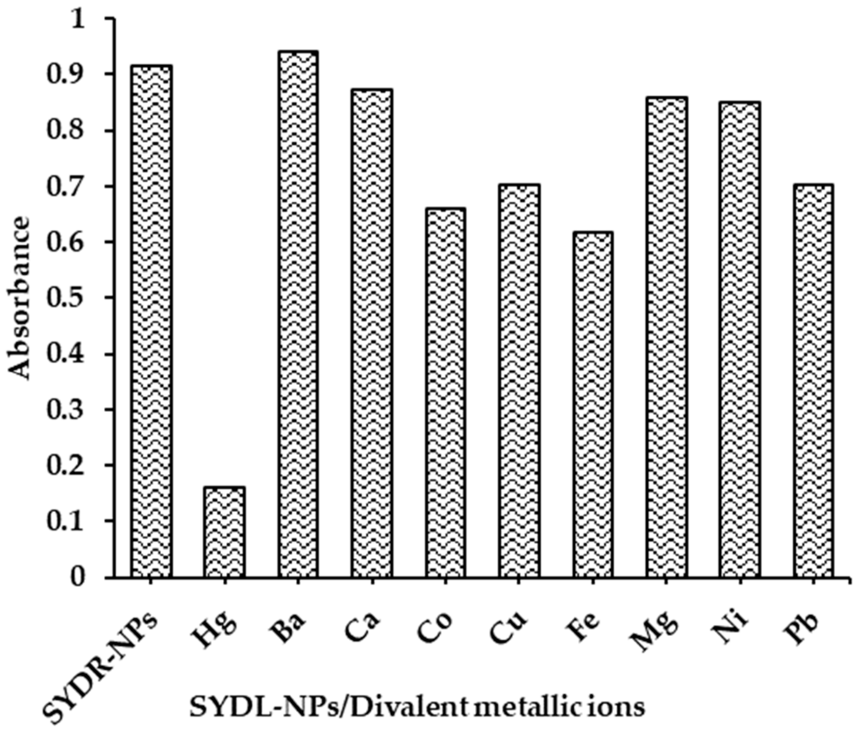


Figure 3. Selectivity of SYDR-AgNPs against various divalent metallic ions.

3.3. Sensitivity

The sensing method was evaluated for its sensitivity against different concentrations of mercury ions present in the aqueous solution. The results indicated that the color intensity of the fabricated silver nanoparticles decreased with increasing concentrations of mercury ions (Figure 4). Using a small mercury concentration caused less Ag to be reduced to Ag (I), resulting in a slight color change. The change in color intensity with the mercury concentration is a possible indicator that the prepared silver nanoparticles were useful for quantifying mercury ions. Similarly, the UV-Vis spectral (Figure 5a) indicated that the surface plasmon absorption band decreased with increasing mercury concentration. Consequently, the plotted calibration curve (Figure 5b) indicated that the response changed linearly with mercury concentration and the determined linearity coefficient ($R^2 = 0.985$) was close to 1. The observation indicated that the prepared silver nanoparticles can be applied to determine mercury ions present in aqueous solutions quantitatively. The limit of detection (LoD) of 11.3 µM was determined using Equation (1). The obtained LoD was compared with other reported silver nanoparticles (Table 1). The findings indicated that the LoD value determined in the current study was better than using silver nanoparticles made from *Vachellia xanthophloea* and similar to silver nanoparticles from *Trigonella foenum-graecum* L. leaves [15]. However, LoD values better than that obtained in this study were also available in the literature. The observed differences in LoD values were likely caused by the nature of the extract used to prepare the silver nanoparticles. Thus, more investigations are required on the applications of the fabricated silver nanoparticles (SYDR-AgNPs) for detecting mercury ions from actual samples.

$$\text{LoD} = \frac{3(\text{standard deviation of slope})}{\text{slope of calibration curve}} \quad (1)$$

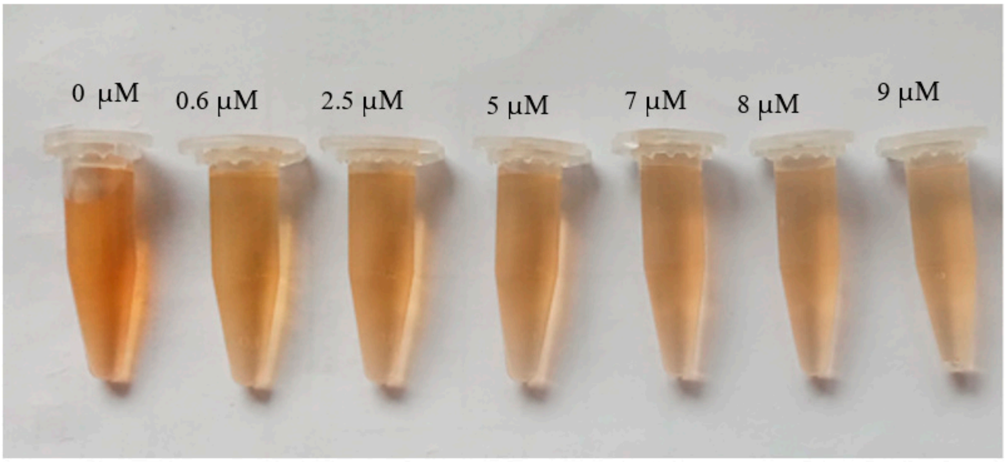
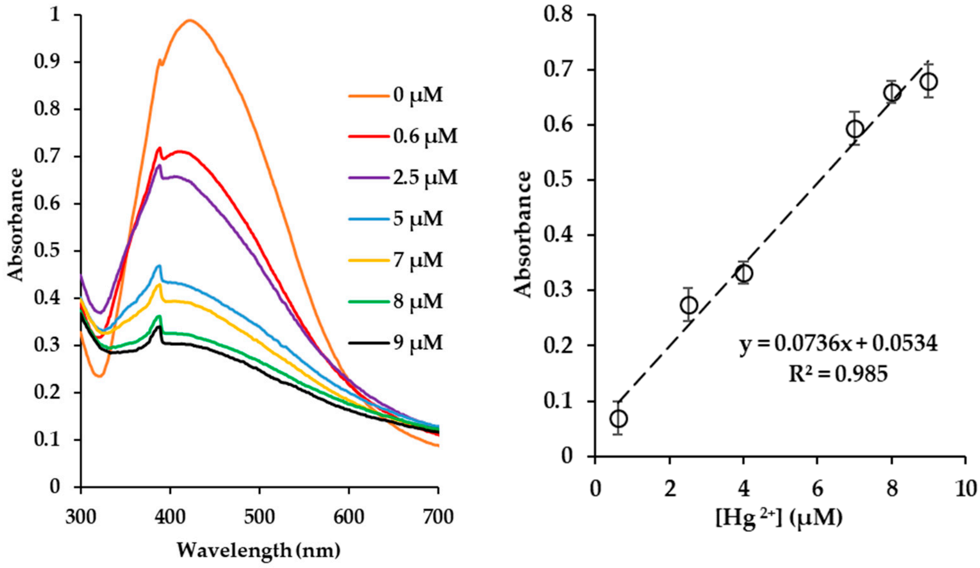


Figure 4. Color changes with different concentrations of mercury.

Table 1. Comparison of performance of SYR-AgNPs with previously reported silver nanoparticles.

Chemical/Extract Used	LoD (µM)	Sensitivity	Reference
Vachellia xanthophloea	22	0.0086	[12]
Synadenium glaucescens	11.3	0.073	This study
Trigonella foenum-graecum L. leaves	11.17	0.1166	[15]
Chlorophyll	2.7	0.0097	[16]
Aminobutyric acid	2.37	0.113	[17]
Bistorta amplexicaulis	0.8	0.0038	[18]
Coffea canephora fruit skin	0.195	0.03876	[19]



(**a**) (**b**)

Figure 5. Sensitivity plot (**a**) and calibration curve (**b**) prepared for sensing mercury ions in the aqueous sample.

4. Conclusions

SYDR-AgNPs were successfully fabricated and applied for preliminary sensing of mercury ions in aqueous solutions. The successful synthesis of SYDR-AgNPs was indicated by the appearance of a maximal absorption band at 420 nm in the UV-Vis spectrum. The fabricated SYDR-AgNPs showed a response to all tested divalent metal ions (Hg^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, and Fe^{2+}). However, a remarkable selectivity in the absorption was observed in the presence of mercury ions. The use of SYDR-AgNPs for the detection of different concentrations of mercury showed a linear response with a linear coefficient of 0.985. The LoD value determined using a slope from the calibration curve was 11.3 μM. The findings from this study indicate that the prepared SYDR-AgNPs can be effective for sensing mercury ions from an aqueous solution. However, more investigations on using the SYDR-AgNPs for sensing mercury from environmental samples are required to demonstrate their applicability. Thus, the silver nanoparticles studied in the current study can serve as a potential simple, low-cost, and rapid technology for sensing mercury ions from environmental samples to protect different organisms.

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