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# Facile Synthesis and Characterization of Silver Nanoparticles Based Sensors for Colorimetric Detection of Mercury Ions

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**ABSTRACT:** Metals contamination is one the severe form of water pollutions. Mercury contamination is most hazardous among them and poses great threat to environment. It is need of hour to develop analytical methods for detection of even trace levels of mercury concentration in water sources. Highly sensitive and discriminatory colorimetric sensing platforms for $Hg^{2+}$ ions are recorded for this purpose. Herein, we report the fabrication of functionalized silver nanoparticles (AgNPs) with protocatechuic acid (PCA). UV-Vis spectrophotometry confirmed the development of PCA-AgNPs. Transmission electron microscopy (TEM) was used to observe the shape and size distribution of PCA mediated AgNPs. The average diameter size was observed to be 11 nm and almost spherical in shape. Powder X-Ray diffractometry proved face centered cubic crystal of Ag. These PCA-AgNPs have been used for metal sensing. When $Hg^{2+}$ solution was mixed with PCA-AgNPs solution, there was an apparent color transition from light brown to almost colorless. UV-Vis spectrophotometric measurements have confirmed this color transition. At 395 nm there was substantial decrease in the absorption band and new peak emerged at 550 nm . PCA-AgNPs exhibited reasonable sensitivity for $Hg^{2+}$ in the concentration range of $1 \times 10^{-7}$ to $5 \times 10^{-5}$M. This sensor was also tested in presence of many other metals to check the competing effect of other metals, but it showed no color change thus suggesting high sensitivity for mercury ions. This method also showed satisfactory percentage recoveries with different water samples.

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## I. INTRODUCTION

Nanotechnology is the science to produce different materials on nano scale for potential use. The technology ensures scientific innovations in many areas including medicines, consumer products, energy, materials, and manufacturing. Particles between 0.1 and 100 nm in size are commonly referred to as NPs, with completely different physiochemical characteristics compared to their major counterparts[1]. With the broad variety of biological and medical uses for NPs, innovative diagnostics provides a very extensive collection of nanoparticle items of varying sizes and surface properties to meet the research and industrial growth needs. NPs are extensively used in fields such as; Biosensors, agents of photography and contrast enhancer, targeted and managed mechanisms for drug distribution, tech for tissues and implants, hyperthermia as well as photodynamic care, antibacterial compounds and immunoassay[2? –5]. Heavy metal emissions that can harm global sustainability is one of the serious environmental issues.

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A simple, rapid, economical and on spot assay is urgently needed to monitor the presence of metallic ions in the environment and waterbodies where Hi-Tach instrumentation analysis is not feasible. Localized surface plasmon resonance (LSPR) is a vital optical property of silver NPs exhibiting different colours in the visible vicinity of the electromagnetic spectrum depending on their shape, size and aggregation conditions. LSPR provides an excellent platform for the development of an ingenious, economical, visual readout assay for on-site monitoring of various analytes. Thus, several efforts have been made to create portable devices to track heavy metals in the environment. Performance of sensor is improved due to adding nanomaterials and nanostructures because they are sensitive and more sensitive. They also have capability of clear detection. In addition, small molecules are mixed with inorganic materials as a molecular recognition probe to selectively bind heavy metals[6]. By natural and mechanical means, heavy metals are damaging the world. This metal ion may have significant consequences on human health and the atmosphere, so the amount of highly toxic metal ions needs to be controlled. In marine environments, $Cu^{2}$ $^{+}$.$Hg^{2+}$,$Fe^{2+}$,$Fe^{3+}$ and many other heavy metals induce contamination. . Various methods are used to detect these metal ions including mass spectrometry, optical methods, and electrochemical methods. Gnanaprakasam et al. produced AuNPs in a different way. They synthesized particles on low graphene oxides. The AgNPs based on mPEGylated luteolin composite was used to detect $Hg^{2+}$ ions[7]. Green silver NPs using Euphorbia geniculata leaf extract were employed in investigations on catalytic degradation of methyl orange dye and optical sensing of $Hg^{2+}$[8]. $Hg^{2+}$ is one of the most harmful metal ions that can destroy multiple human organs, which can cause extreme effects and a deterioration in health[9]. Therefore, the development of responsive and selective methods to track the occurrence of $Cu^{2+}$ ions and $Hg^{2+}$ is of considerable significance for public health and environmental safety. Several strategies for detecting $Cu^{2+}$ and $Hg^{2+}$ ions have been demonstrated so far. Most of them are chromosomal sensors sensors activated by chemo dosimeters and fluorescent chemosensors[10,11]. Functionalized metal NPs (MNPs) of gold (AuNPs) and silver (AgNPs) have attracted interest for their effective sensing ability towards $Hg^{2+}$ detection due to their high extinction coefficients and distance-dependent optical properties. Many reports are available on the usage of AuNPs for colorimetric detection of Hg (II) ion .Although, AuNPs have made marked progress in $Hg^{2+}$ detection, due to their high cost AgNPs are cost-effective when compared to AuNPs and have higher extinction coefficients , which make them much better candidates for colorimetric detection of $Hg^{2+}$ ions.

In green synthesis methods, NPs are being syntheiszed in vivo by plants, algae, yeast, fungi, and bacteria[12]. The biological components that stabilize NPs other than phytochemicals are primarily proteins, enzymes, carbohydrates, and sometimes-entire cells that enable NPs to interact with other biomolecules and enhance interactions with microbes, increasing antimicrobial activity[13]. The structure of NPs is influenced by the concentration and kind of biological entities in addition to organic reducing agents [[14]. Additionally, the growth, medium, characteristics, including pH , temperature, salt concentration, and exposure period, substantially influence the size and form of NPs[15]. Plants or their extracts exhibit the finest biological properties because they are widely accessible and appropriate for mass-producing NPs. Their waste products are environmentally acceptable, in contrast to some microbial extracts[16]. Normally plant extracts containing many compounds are used as reducing and stabilizing agents without isolating all potential compounds. Therefore, it is hard to identify which compound actually acted as reducing or stabilizing agent. Thus, the potential of individual compounds cannot be investigated. The easy ionization properties of phenolic groups have been exploited in the synthesis of Ag-NPs in the past. For example, 2-d assemblies of Ag-NPs were prepared by the spontaneous reductions of silver ions by pentadecylphenol Langmuir monolayers. Organic phenolic ligands based on amino acids exhibited versatile coordination behaviour with different metal ions that resulted in the formation of intriguing structures including helical supramolecular structures in the solid state. It was hypothesized that utilization of compounds with carboxyl or hydroxyl moieties like plant phenolics in the Ag-NPs synthesis would provide metal ions interacting surface functionality for developing selective colorimetric sensor for toxic metal ions. In this manuscript, we report the synthesis of AgNPs based on protocatechuic acid (PCA). PCA can be isolated from the stem bark of Boswellia dalzielii[17] and from leaves of Diospyros melanoxylon[18]. It is a major metabolite of antioxidant polyphenols found in green tea. PCA is antioxidant and anti-inflammatory. PCA extracted from Hibiscus sabdariffa protected against chemically induced liver toxicity in vivo. In vitro testing documented antioxidant and anti-inflammatory activity of PCA, while chemical markers and histological assessment measured liver protection in vivo. Since PCA that is also actually from plant origin and possess a safe profile can solely be investigated for not only Ag ions reduction but also other heavy metal ions in aqueous solutions. It makes it a suitable candidate for the green synthesis of such probes. Functionalities present in its structure and proven safety profile attracted our attention to use it. Moreover, its potential as a reducing and stabilizing agent has not been exploited which also directed us to use it[19]. Therefore, it makes sense to use plant extracts-based AgNPs or direct use of isolated compounds such as Protocatechuic acid (PCA) to synthesize AgNPs that could independently detect heavy metal ions as electrochemical sensor components.

Here in this study, we aim to investigate the potential of PCA for the synthesis of silver NPs based colorimetric assay for recognition of toxic metal ions.

## II. MATERIALS AND METHODS

### A. MATERIALS

One of the main chemicals for fast and easy synthesis of AgNPs is 3,4-dihydroxy benzoic acid also known as Protocatechuic acid (PCA) and was purchased from Sigma Aldrich. Silver precursor used for AgNPs was silver nitrate ($AgNO_3, 99.9\%$) obtained from Alfa Aesar. Milli-Q water was used during all experimental procedures. Heavy metal chlorides or nitrates were used as source of metal ions and purchased from Sigma Aldrich too. The pH of solutions was maintained in narrow range and prevented from fluctuations using sodium hydroxide ($NaOH, 0.01M$).

### B. SYNTHESIS OF PCA-AGNPS

$AgNO_3$ solutions of concentrations 50,75 and 100 mM were prepared using Milli-Q water. Then a concentrated aqueous solution of PCA was prepared, the solubility was aided by small amount of ethanol. For a few hours, equivalent volumes (2 mL) of $AgNO_3$(50mM) and PCA solutions were mixed and incubated in the dark. To improve the performance of PCA-Ag NPs, the mixture was then put in bright sunlight. The development of PCA-Ag NPs was observed as the mixture changed color. Similarly, other concentrations of $AgNO_3$ ( 75 and 100 mM ) were also separately combined with equivalent amounts of PCA aqueous solutions to investigate the impact of the concentration of Ag ions on PCA- Ag NP formation. Each solution was then centrifuged for 20 min at 10000 rpm to extract NPs.

### C. MEASUREMENTS

UV-Vis spectroscopy of PCA-Ag NPs was made on UV-1700 PharmaSpec double beam spectrophotometer (Shimadzu, Japan). The spectra were recorded with ultra-fast scanning at resolution of 1 nm in the range of $200-800$ nm.

FTIR spectrum of nanoparticles was recorded in transmittance mode in the spectral region of 4000-400 $cm^{-1}$ using a resolution of $\leq 1$ $cm^{-1}$ and 8 co-added scans on an IR Prestige 21 spectrophotometer (Shimadzu, Japan). The samples were dried before analysis. The presented spectrum was baseline corrected and normalized.

Philips 420 transmission electron microscope was used to capture micrographs of PCA-Ag NPs at an acceleration voltage of 120 kV . For this purpose, PCA- Ag NPs solution was centrifuged to isolate Ag NPs. Method of drop casting on a carbon-coated Cu TEM grid was used to prepare TEM samples. X-Ray diffraction pattern of PCA-Ag NPs was performed by using the Bruker D8 Discover X-Ray diffractometer. Diffraction patterns were acquired at room temperature in Bragg-Brentano geometry. The goniometer scanned at 0.012° for peak resolution in the scanning range $10° \leq 2\theta \leq 80°$.at a 0.5scan/ step.

### D. COLORIMETRIC DETECTION OF METAL IONS

The $Hg, Pb$ and Cd solutions were prepared by dissolving the necessary amounts of their salts in Milli-Q water. All these solutions were kept in caped flasks before detection studies. The colorimetric detection ability of PCA-Ag NPs was assessed by mixing equal volumes (1 mL) of each metal solution with PCA-Ag NPs suspension. A selective sensing ability of PCA-Ag NPs was observed. As soon as the light brown colored PCA-Ag NPs suspension was mixed with $Hg^{2+}$ aqueous solution, it turned colorless instantly depicting a distinct behavior towards $Hg^{2+}$. Whereas no significant color change was observed when PCA-Ag NPs suspension was mixed with $Pb^{2+}$ and $Cd^{2+}$ solutions.

Practical application of this method was checked on tap water and mineral water samples. Then detection limit of this method was checked using different samples with various metal ion concentrations.

## III. RESULTS AND DISCUSSION

### A. FORMATION OF PCA-AGNPS

Polyphenols and polyhydroxy compounds have been reported as potential reducing and capping agents for silver to fabricate AgNPs. 3,4-Dihydroxy benzoic acid also known as Protocatechuic acid (PCA) was exploited as potential reducing agent due to its structural functionalities. When $AgNO_3$ solution was prepared it was colorless and showed visible color change on addition of reducing agents. In a typical experiment, solution of $AgNO_3$ turned dark yellow after incubating for couple of hours. On increasing the incubation time, the color became intense and it appeared dark brown after 8h. This change in colour was the indication of Silver nanoparticles formation due to reduction of silver ions by PCA. Fig. 1 shows the synthetic scheme for fabrication of PCA mediated Ag-NPs.

### B. Characterization

Surface plasmon resonance of AgNPs resulted in more intense color change. Peak absorbance ($\lambda_{\max}$) of colloidal mixture was noticed at 460 nm by scanning it on UV-Vis spectrometer. Fig. 2 shows effect of time and sunlight on the formation of Ag-NPs. This outcome further supported the development at 460 nm of silver nanoparticles. The accretion of silver nanoparticles in the mixture was continuously observed at frequent intervals (every 2 hours) by UV-Vis spectrophotometry.

On increasing the incubation time of mixture, no shift in $\lambda_{\max}$ was observed as depicted by Fig> 3, however increase in absorbance value was observed.

Effect of Ag ion concentration on time dependent absorbance is also given in Fig. 4 - 6. A significant number of silver nanoparticles were produced up to 8 h of reaction time since the absorbance value increased linearly. Because of saturation in the formation rate, the reaction is completed after 12 h of observation.

It was also observed that formation of AgNPs was directly proportional to concentration of Ag ions since the 100 mM solution of $AgNO_3$ showed absorbance value of approximately 2 indicating the maximum concentration of AgNPs formed after 10 h time period. Figure 6 explain the UV-Visible spectra of PCA mediated $Ag-NPs$ using different concentrations of Ag ions ( 50,75 and 100 mM ) at different reaction times.

### C. FTIR SPECTROSCOPY

FTIR spectrum of PCA-AgNPs is shown in Fig. 7. The weak peak at 3567 $cm^{-1}$ indicates $O-H$ stretching depicting most of the PCA molecules have deprotonated and reduced Ag+ ions.

The peaks at 2918 and 2851 $cm^{-1}$ show C-H asymmetric and symmetric stretchings. Carbonyl stretching of acid carbonyl appeared at 1740 $cm^{-1}.C=C$ stretching of aromatic ring appeared at 1543 $cm^{-1}$ while C H bending appeared at 1420 $cm^{-1}$. The peak at 1245 $cm^{-1}$ represents C-O stretch of carbonyl carbon with oxygen of acidic OH . Peak at 719 shows metal oxygen stretching.

### D. Powder X-Ray Diffractometry

PXRD confirmed the crystalline structure of the newly synthesized PCA-AgNPs in the $2\theta(10^\circ < 2\theta < 80^\circ)$ range. Figure 8 demonstrates the X-ray diffraction pattern of PCA-AgNPs. The 111, 200, 220 and 311 crystal phases of face centered cubic AgNPs appeared at $29.18^\circ, 44.61^\circ, 65.02^\circ$ and $76.93^\circ$, respectively. The peaks verified that spherical Ag NPs were produced.

A number of Bragg reflections are observed for the PCA-AgNPs, which may be indexed based on the fcc structure of silver and is shown in Table I. The XRD pattern thus clearly shows that the AgNPs formed by the reduction of $Ag^+$ions by the PCA are crystalline in nature. From the calculated d spacing values corresponding to each $2\theta$ values, it appears that the (101), (111), (200), (220) and (311) lattice spacing are broadened as compared to the bulk form and this phenomenon is more pronounced in case of the (111) planes. In addition to the Bragg peaks representative of fcc silver nanocrystals (JCPDS: International Center for Diffraction Data, PCPDFWIN v. 1.30, 31-1238) corresponding to the lattice planes (101), (111), (200) and (220), respectively. This estimation confirmed the hypothesis of particle monocrystallinity. The sharpening of the peaks clearly indicates that the particles are in the nanoregime. The XRD pattern thus clearly shows that the silver nanoparticles are crystalline in nature. The average crystallite size of PCA-AgNPs was determined to be 27.74 nm . A comparable particle size has alos been reported[27–29].

### E. Transmission Electron Microscopy

Important topographic parameters like size, shape, and morphology of PCA-AgNPs were investigated using high resolution TEM. Figure 9 depicts TEM Micrographs of PCA mediated AgNPs captured at different magnifications. Almost spherical shape of AgNPs was confirmed by the images. The diameter size distribution was in the range of $8-16$ nm with maximum frequency of 11 nm .

A circular diffraction outline was observed in SAED pattern of these PCA-AgNPs, signifying the crystalline nature of the particles. The diffraction rings can be indexed according to the face-centered cubic (FCC) structure of silver. The lattice planes (200), (220), and (311) constructed three rings due to reflections from of FCC silver, respectively. A similar SAED pattern obtained with green Ag-NPs is also reported in literature[30]. Size distribution of Ag-NPs is given in Fig. 10.

A comparison of Ag-NPs synthesized using green methods is tabulated in Table II. The tabulated data

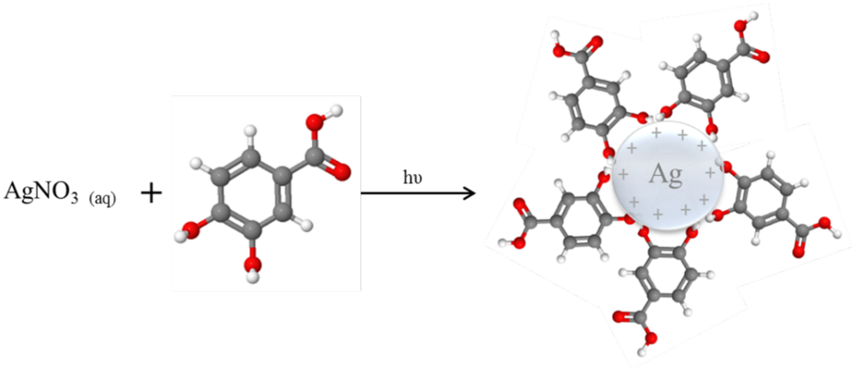

FIG. 1: PCA mediated facile synthesis of AgNPs.

TABLE I: Lattice spacing values calculated from the $2\theta$ values obtained from the XRD pattern of green AgNPs.

| Sr. No. | $2\ \theta$ Degree Position | Lattice Planes (hkl) | Crystallite size D (nm) |
|---|---|---|---|
| **1** | 32.52 | 101 | 27.14 |
| **2** | 38.37 | 111 | 21.40 |
| **3** | 44.09 | 200 | 27.94 |
| **4** | 64.70 | 220 | 30.48 |
| **5** | 77.69 | 311 | 31.73 |

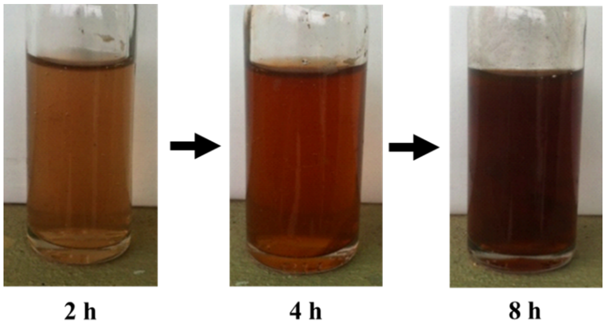

FIG. 2: Time and light dependent color change in PCA mediated AgNPs suspensions.

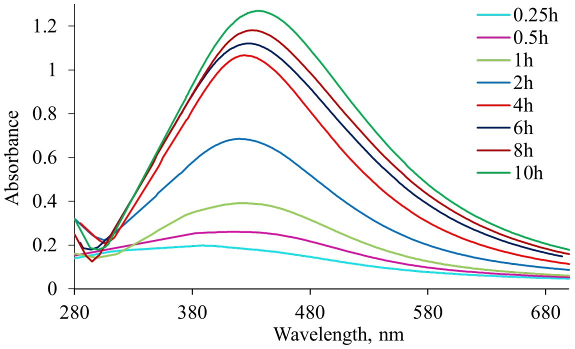

FIG. 3: UV-Visible spectra of AgNPs (50 mM) prepared in PCA at different reaction times at moderate temperature.

reveals that PCA mediated Ag-NPs possesses similar attributes like those reported in literature.

### F. Hg2+ SENSING Activity of PCA-AGNPs

The PCA-AgNPs suspension functions as a colorimetric sensor. In the suspension of PCA-AgNPs, equivalent amounts of metal salt solution $\left(Hg^{2+}, Cd^{2+} \text{ and } Pb^{2+}\right)$ have been introduced for the identification of various metal ions. There was an immediate discoloration of silver nanoparticle solution after adding $Hg^{2+}$ solution. Whereas no colorimetric change in color was found on addition of $Cd^{2+}$ and $Pb^{2+}$ solutions indicating selective colorimetric detection of $Hg^{2+}$. Colorimetric difference in $Hg^{2+}$ ions solution before and after adding sensor is given in Fig. 11. This was also confirmed by UV-Vis spectroscopy. Different amounts of $Hg^{2+}$ ions in the solution were applied and variations in absorption were observed. The colorimetric detection is shown in Fig. 12.

It was observed that $HgCl_2$ added even in small amount it reduces the intensity of absorption. As we increase the concentration of $Hg^{2+}$ the absorbance peak

TABLE II: A comparison of AgNPs synthesized by green methods[20].

| Sr. No. | Biomaterial | Species | Precursor | Location (Intra/Extra) | Size (nm) | Morphology | Reference |
|---|---|---|---|---|---|---|---|
| 1 | Fungus | Humicola sp. | $AgNO_3$ | Extracellular | 5-25 | Spherical | [21] |
| 2 | Fungus | Endophytic fungus Penicillium sp. | $AgNO_3$ | Extracellular | 25-30 | Spherical | [22] |
| 3 | Bacteria | Escherichia coli DH5a | $AgNO_3$ | Extracellular | 10-100 | Spherical | [23] |
| 4 | Bacteria | Bacillus methylotrophicus | $AgNO_3$ | Extracellular | 10-100 | Spherical | [24] |
| 5 | Plant leaves | Excoecaria agallocha | $AgNO_3$ | – | 20 | Crystalline Spherical | [25] |
| 6 | Plant leaves | Phyllanthus niruri | $AgNO_3$ | – | 30-60 | Crystalline Spherical | [26] |
| 7 | Phytocompound | PCA | $AgNO_3$ | – | 8-16 | Crystalline Spherical | Present study |

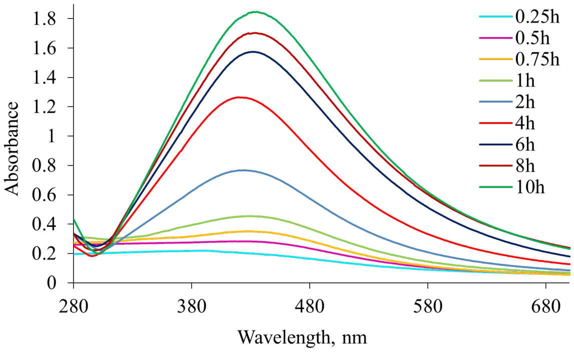

FIG. 4: UV-Visible spectra of AgNPs (75 mM) prepared in PCA at different reaction times at moderate temperature.

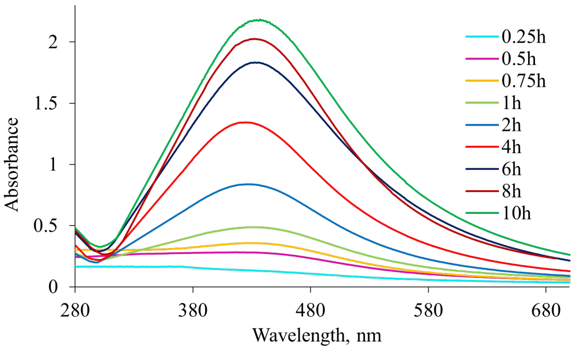

FIG. 5: UV-Visible spectra of AgNPs (100 mM) prepared in PCA at different reaction times at moderate temperature.

decreases gradually. The process to detect $Hg^{2+}$ by suspension of Ag-NPs was explained by two metal ions, $Hg^{2+}$ and $Ag^{+}$. They have distinct reduction potentials, such as $Hg^{2+}$ reduction potential is +0.85 V , while $Ag^{+}$reduction potential is +0.80 V.

The possible mechanism for the selective recognition of $Hg^{2+}$ can be explained based on redox reaction taking place at the surface of the AgNP , due to the differences in the standard potential of 0.8 V $\left(Ag^{+}/Ag\right)$ and 0.85 V $\left(Hg^{2+}/Hg\right)$. Upon addition of $Hg^{+2}$ to the colloidal AgNPs suspension, the presence of organic capping agents on the surface of AgNPs stimulates electrostatic-ionic attractions between the NPs and $Hg^{2+}$. The added mercury reacts with the $Ag^{0}$ core by redox reaction and displaces the capping agents present on the surface of the AgNPs. Flavonoids, carbohydrates, amino acids, and their derivatives are present in plant extracts and are known to form complexes with heavy metal cations. In the present study PCA is acting as ligand for metal ions. As a result of these redox reactions taking place between $Ag^{0}$ and mercury, $Hg^{2+}$ gets reduced to $Hg^{0}$ on the nanoparticle surface and $Ag^{0}$ oxidized to $Ag^{+}$. As the AgNP are converted to $Ag^{+}$ions by added mercury, the colloidal solution becomes colorless. The result demonstrates that the accessible $Ag^{0}$ in the colloidal suspension has been completely oxidized by the added quantity of mercury. Colorimetric detection of $Hg^{2+}$ (at minimum detectable concentration) was also undertaken over a wide pH range ( pH 3 to 8 ) to sense the presence of $Hg^{2+}$ in water under different physiological conditions. To adjust the pH of the solution, an aqueous NaOH solution was used. Moreover, there was no change in effectiveness of Ag nanoparticle suspension throughout the whole range of pH for

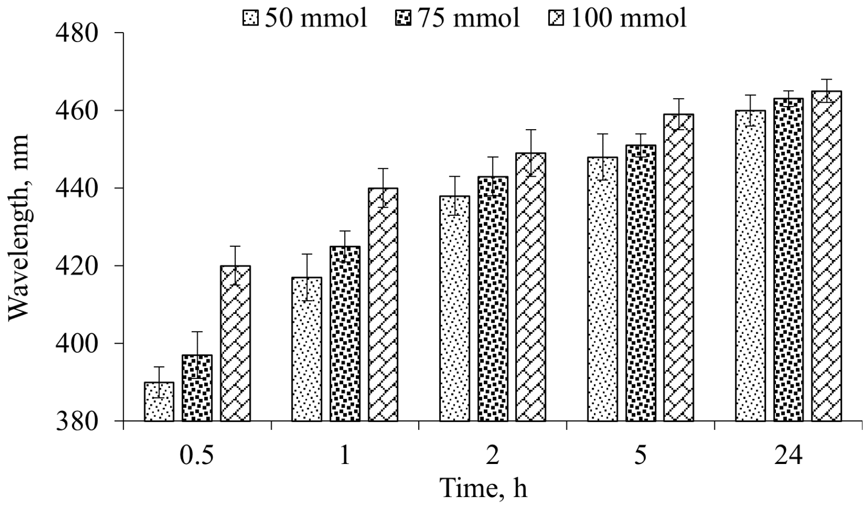

FIG. 6: UV-Visible spectra of PCA mediated AgNPs (50, 75 and 100 mM) at different reaction times at moderate temperature.

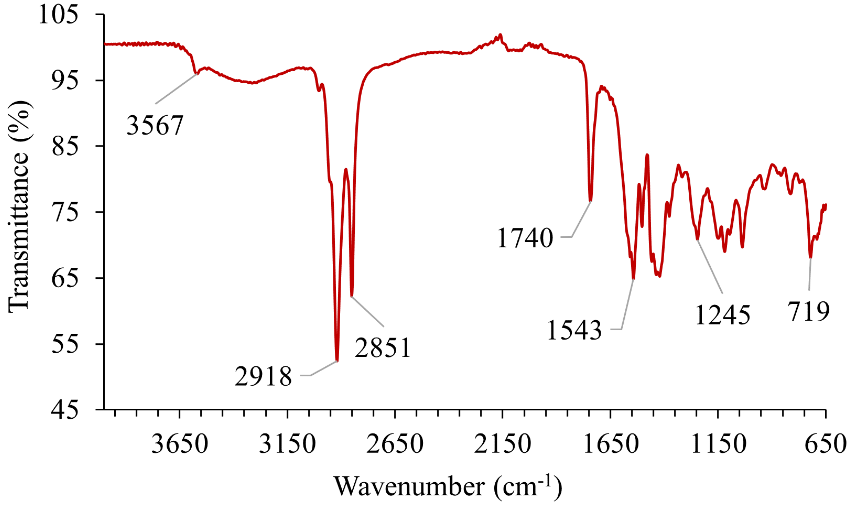

FIG. 7: FTIR spectrum of PCA mediated AgNPs.

detecting $Hg^{2+}$ ions. Thus, these silver nanoparticles protect the environment by reducing pollution caused by hazardous mercury by detecting them easily.

## IV. CONCLUSION

In present era, the green synthesis process is being widely used for preparation of metallic nanoparticles because it is a simple and inexpensive method. And of its importance lies in its eco-friendly nature which is biodegradable and can also be carried out at room temperature. During this research work we prepared silver nanoparticles using silver nitrate solution and PCA. The hydroxyl groups of PCA reduced the silver ions and stabilized the particles in the mixture. It was observed that the shape of synthesized nanoparticles was almost spherical with an average diameter of about 11 nm. The Ag nanoparticles most remarkably demonstrated the ability to sense harmful $Hg^{2+}$ ions selectively in a wide range of pH . Hence these nanoparticles can be used for detecting toxic $Hg^{2+}$ ion in water and protecting the atmosphere from mercury contamination.

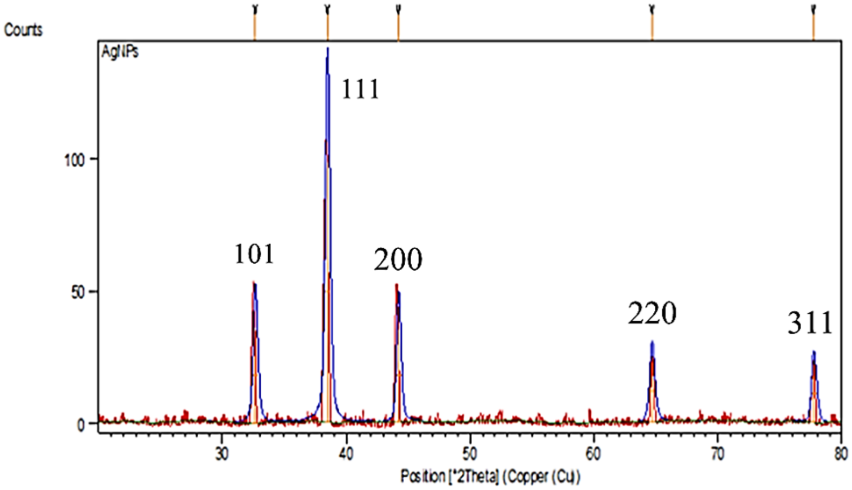

FIG. 8: XRD pattern obtained for AgNPs synthesized using sweat basil leave extract.

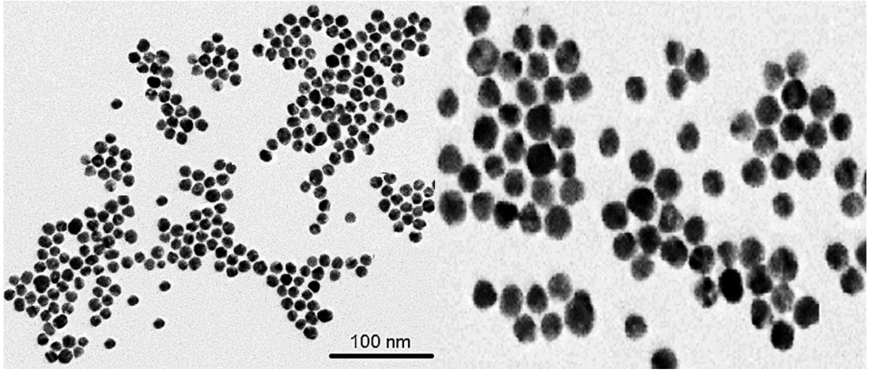

FIG. 9: TEM images of PCA mediated AgNPs.

## DECLARATION OF COMPETING INTEREST

The authors have no conflicts to disclose.

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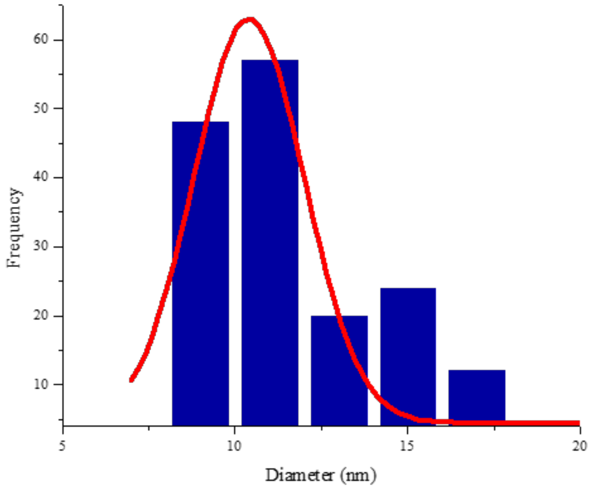

FIG. 10: Size distribution of PCA mediated AgNPs (100 mM).

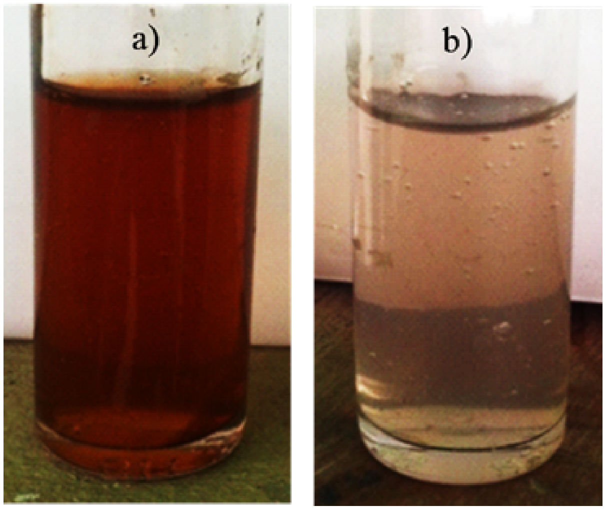

FIG. 11: Color change in PCA mediated AgNPs suspensions; a) before addition of $Hg^{2+}$ solution b) after addition of $Hg^{2+}$ solution.

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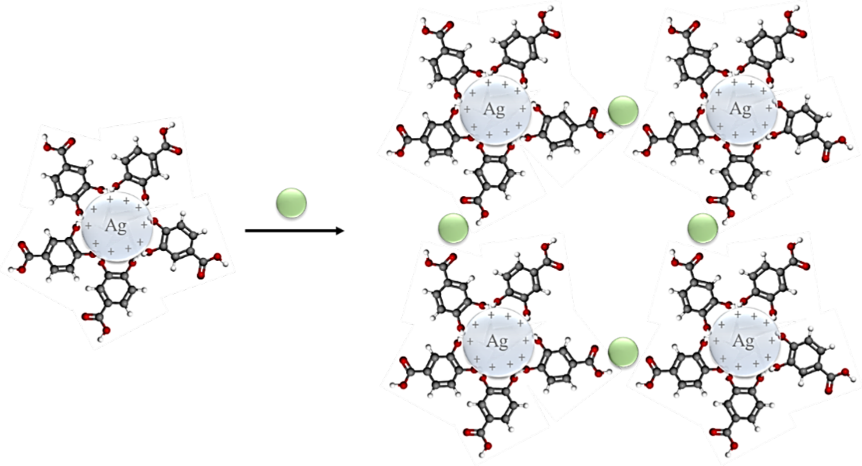

FIG. 12: PCA – AgNPs color change mechanism on addition of $Hg^{2+}$ solution.

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