

Synthesis of Capsicum Annum L Capped Gold Nanoparticles and their Application in Sensor

Pirah Siyal¹, Sirajjuddin¹, Syed Tufail H. Sherazi¹

¹National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Pakistan

Abstract: Different research studies have been performed to synthesize metallic nanoparticles using different techniques. The green synthesis method of nanoparticles or the "eco-friendly method" is one of these methods that have got great attention. The commonly used sources for the green fabrication of nanoparticles are extracts of plants, leaves, fungi, and microorganisms. Green synthetic methods are easier, cheaper, environmentally sustainable and can result in the manufacture of Nano objects with regulated size and shape. In the present study, AuNPs were synthesized by using green bell pepper or Shimla Mirach extract as reducing as well as capping agent after mixing with aqueous HAuCl₄ as precursor and NaOH used as accelerating agent to speed up the reaction. Synthesized gold nanoparticles were confirmed through the color change from yellow to ruby red. The optimization study included a variety of parameters such as plant extract concentration, sodium hydroxide, chloroauric acid, and solution pH to achieve a blue-shifted spectrum. The surface Plasmon resonance band was controlled at 519 nm. Synthesized gold nanoparticles have been characterized by UV / Vis spectroscopy, FT-IR, AFM, ZPA, and DLS to check the stability, morphology, crystallinity, and size of nanoparticles. Synthesized nanoparticles were successfully applied as colorimetric sensor for detection of selected metal ion Fe²⁺. The linear range of Ferrous ion was 3.3-8 ppb based on increase in absorption intensity with R² value of 0.987 using UV-Vis spectrophotometer. The sensor was successfully applied to real water samples regarding the detection of Fe²⁺.

Keywords: Capsicum; SEM; AuNPs; gold; nanoparticles

I. INTRODUCTION

Because of their usual electrical, magnetic, and catalytic properties, metallic nanoparticles are commonly used. They are vital for tuning size, shape, mono-dispersity, and morphological properties [1]. Among these metal nanoparticles, gold (Au) metal gained much attention due to its unique size and shape and has fascinated mankind since discovery [2]. In ancient Roman times, Gold Nanoparticles were used for the decorative purpose of the staining glass [3]. In 1857, Faraday first noticed that 'gold solution contains tiny metallic particles.' He conducted a study on the optical properties of the thin film synthesized from the dried gold nanoparticle (NPs) solution. He further found that upon applying and removing pressure on the film resulted in color alternations (changed from bluish-purple to green by applying pressure). Later on, similar observations were quantified and studied in detail by Mulvaney [4]. In 1908, Mie described the theory about the absorption and scattering of metal NPs with prime focus on gold sols [5]. Because of Surface Plasmon resonance (SPR) effects, Gold Nanoparticles (AuNPs) contain rare optical properties. It is an optical phenomenon induced by electromagnetic wave interaction and metal conduction of electrons. [6].

Several synthesis methods are developed to produce gold nanoparticles, including chemical, physical, and biological approaches. The Physical and chemical methods used in gold nanoparticles synthesis can be associated with the production of toxic compounds with harmful effects on human health [7]. The use of plant extracts for nanoparticles synthesis has an advantage over physical and biological methods because green synthesis is environmentally friendly, less time consuming, readily available, and cost-effective [8]. Various parts of plants including leaf, stem, shoot, petal, fruit, and peel, are used in a plant extract-based green synthesis as fresh or dried materials. The obtained green extract contains reducing and capping materials that are necessary to reduce the metallic ions. Additional green approaches used to make gold nanoparticles (AuNPs) include microorganism-based methods, honey-mediated green synthesis, and plant-based intracellular manufacture of metal nanoparticles [9]. Raj et al. [10] documented green synthesis of AuNPs through *Acmella oleracea*, synthesized AuNPs were used for colorimetric sensing of Cysteine. Kumar et al. [11] demonstrated the *Croton bonplandianum* (AEC) mediated gold nanoparticles and the detection of glutathione by colorimetric sensor from human blood serum. Similarly, Boruah et al. [12] found that *Mangifera indica* leaf extract synthesized Au NPs are used for the colorimetric detection of As (III).

Metals play a vital role in controlling most of the human body's biochemical and physiological processes. Ferrous ion (Fe²⁺) is a major hemoglobin element that transports oxygen to each and every part of the body. Hemoglobin deficiency can result from physiological and pathological conditions such as iron deficiency anemia, methemoglobinemia, damage to the liver and kidneys, diabetes and heart disease. Hence, it is essential to develop methods and tools for detecting trace iron contents in the samples with higher accuracy and precision. Various methods are reported for iron ion detection such as Inductively Coupled Plasma Mass Spectroscopy (ICPMS), derivative Spectrophotometry, Atomic Absorption Spectrometry (AAS), Fluorescence, and Voltammetry. Most of these methods are however complex, time-consuming, expensive, use a wide range of samples and reagents.

Metal nanoparticles, including gold (Au) nanoparticles, are commonly used for chemical detection of different metal ions through colorimetric sensors. The colorimetric analysis is preferred for the investigation of heavy metal ions in aqueous solution as it is an economical quick method compared to others. The colorimetric process relies on the color variations associated with surface plasmon absorption, depending on the size and shape of the nanoparticles. [13-16].

In the present study, we developed a highly sensitive, selective, and facile approach for the detection of the Fe²⁺ ion using Green Bell pepper (*Capsicum Annum L.*) (commonly known as Shimla Mirch) synthesized gold nanoparticles (CAL-AuNPs). The synthesized CAL-AuNPs were characterized through Scanning electron microscopy, Atomic force microscopy, UV-vis spectroscopy, Zeta potential analysis (ZPA), Dynamic light scattering (DLS) and X-ray diffraction spectroscopy. The prepared CAL-modified gold (Au) NPs were used as a nano-sensor probe for colorimetric detection of Fe²⁺ content in different water samples.

II. MATERIALS & METHODS

A. Chemicals

Tetra chloroauric acid trihydrate (HAuCl₄·3H₂O) was purchased from MERCK (Germany) NaOH from DAEJUNG; HCl from Sigma-Aldrich, and green bell pepper were purchased from Local market of Hyderabad, Pakistan. While metal ions including Ni²⁺, Ca²⁺, Hg²⁺, Be²⁺, Ba²⁺, Zn²⁺, Mg²⁺, Cd²⁺, Cu²⁺, Co²⁺, Cr²⁺, Pb²⁺, Zn²⁺ and Fe²⁺ were purchased from Sigma-Aldrich.

B. Gold Solution Preparation

By the mixing 0.025 M of tetra chloroauric acid trihydrate (HAuCl₄·3H₂O) in 100 ml Milli-Q water and further 20 mL (0.5 mM) solution was diluted to 100 ml and the gold solution was prepared

C. Preparation of Extract

The extract was prepared by weighing 2 gm of thoroughly washed green bell pepper (Fig. 1), mashed in a mortar pestle, and transferred to 100 mL Erlenmeyer flask with Milli Q water (100 ml). The extract was simmered at 100 °C for 15 minutes, and then the extract was filtered by Whatman™ filter paper no:1, pore size 125 mm. The extract was then processed for further use at 4 °C.

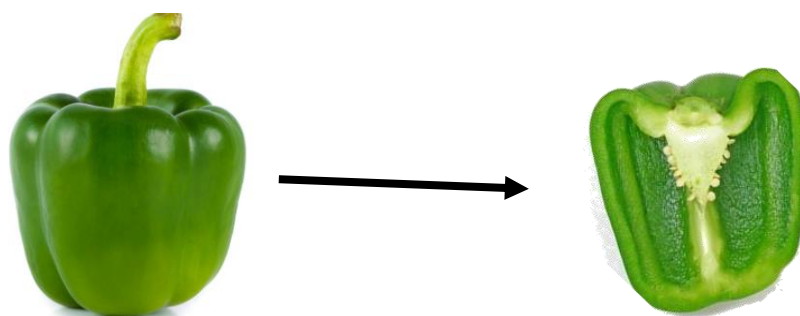


Fig. 1. Green Bell Pepper (*Capsicum Annum L.*) or Shimla Mirch

D. Synthesis of CAL-AuNPs

In a typical experiment, four different parameters were used to optimize CAL-AuNPs synthesis protocol. Variation in the concentration of the gold solution, extract sodium hydroxide, stirring time as well as pH. Gold salt, extract, and NaOH was optimized at six different concentrations with 0.5 mM HAuCl₄ aqueous solution. For the typical reduction of Au³⁺ to Au⁰, 400 μL of the gold solution, 200 μL of extract and 150 μL of NaOH was added in clean glass vial and volume makeup to 10 ml with Milli Q water and then at 100 °C sample was placed on a hot plate for about 40 minutes or until the ruby red color emerges. The visual evidence of color exchange and ruby red color formation suggested AuNP formation.

E. Colorimetric response of Fe²⁺ to CAL-AuNPs solution

The solution (3 mL each) of synthesized CAL-AuNPs was added 100-230 μL of Fe²⁺ solution to get a final concentration range of 3.3 to 8 ppb Fe²⁺. Around 2 to 3 minutes later, each solution was applied to a quartz cell to record the UV-Vis response to a blank solution. The corresponding absorbance changes at 519 nm were reported with each addition of Fe²⁺ solution in the form of LSPR spectra against a blank solution. The color change from ruby red to violet was observed, allowing for visual differentiation of Fe²⁺ ion.

F. Analysis of real water samples for Fe²⁺ detection

From various areas of Hyderabad and Jamshoro Sindh, Pakistan, samples of water were collected. These samples of water were filtered through a Whatman™ filter paper 1, pore size 125 mm and transferred to a vial before the analytical analysis is completed. As there was no change of the AuNP signal by inserting a blank run, in the respective water sample Fe²⁺ solution was prepared. Then, a sufficient volume of 100 μL of Fe²⁺ was combined with 3 mL of CAL-AuNPs, which resulted in a marked increase in absorbance intensity. In order to obtain a linear array, the shift in absorbance values versus the addition of various Fe²⁺ concentrations, obtained in the calibration curve, was plotted.

G. Characterization Studies

The initial CAL-AuNPs characterization was carried out by model lambda 35 from Perkin-Elmer Lambda 356 UV-Vis spectrophotometer within the spectral range of 400–800 nm with quartz cuvettes. The UV-visible spectrum of the resulting solutions was recorded. FTIR spectral studies of AuNPs and green bell pepper (*Capsicum annuum L.*) were carried out through Perkin-Elmer: Model (Nicolet 5700) from the Thermo Scientific (Beijing, China) using the KBr disc method, to confirm the interaction of AuNPs with the biomolecules of green bell pepper fruit extract. The shape and size of the CAL-AuNPs were detected by microscopy of atomic force (model 550, Agilent, Santa Clara, CA, USA) and electron scanning (model JSM-6380LV, JEOL Ltd., Tokyo, Japan). Information regarding the stability and size to volume ratio analyzed by Dynamic light scattering and Zeta potential analysis (Malvern: Model ZETASIZER Nano-ZS). A digital camera was used to capture colloidal CAL-AuNP images for visual colorimetric detection of Fe²⁺.

III. RESULTS

3.1 Optical Characterization of CAL-AuNPs

Surface plasmon resonance (SPR) frequencies of metallic nanoparticles, for instance, Ag, Cu, and AuNPs are present within the visible range of electromagnetic spectrum [17]. With sizes ranging from 10 to 60 nm, these nanoparticles showed LSPR bands between 400 nm, 570 nm and 520 nm with the solutions of yellow, purple, and ruby red. It is also observed that metal nanoparticle's size and geometric shape have a significant impact on their optical characteristics [18]. Hence UV-Visible spectroscopy was used as a primary technique for initial characterization of CAL-AuNP. In neutral aqueous media, the CAL-AuNPs were synthesized using green bell pepper (*Capsicum annuum L.*) fruit extract as both a reduction and a capping agent.

Key parameters for AuNPs formation, such as the concentration of accelerating agent, green bell pepper extract along with pH and stirring time were optimized by UV-Vis spectrometry. Under the optimized conditions, CAL-AuNPs were synthesized by 200-600 μL of 0.5 mM precursor Au salt, 150 μL of 0.1 mM of NaOH as accelerating agent and 200 μL of green bell pepper diluted to the mark with 10 ml Milli Q water and heated on a hot plate on 100 °C for about 40 minutes. After combining the fruit extract and gold chloride solution, the color change was observed after 20 min. The production of gold nanoparticles was completed within 40 minutes of initiation of the reaction. The visual evidence of color change and ruby-red color formation confirms the formations of AuNPs, as in Fig 2a. A quantity of 400 μL of 0.5 mM gold chloride was thus chosen as the optimal concentration, as it results in a blue-shifted peak that appeared at 519 nm.

For the fabrication of CAL-AuNPs, the effect of pH in the 4–11 range was observed. The pH analysis was adjusted by the addition of specific volumes from 0.1 M solutions of NaOH and HCL as needed. The study shows that CAL-AuNP's most blue-shifted surface plasmon absorption band was occurred at 519 nm at pH 7, compared with red-shifted wavelengths produced at other pH values by AuNPs. The time study of synthesized gold nanoparticles was recorded at various time intervals (up to 30 days), as shown in Figure 2b. The data show that for more than four weeks there has been no change in Lambda (λ) max or color.



Fig 2a: Synthesized Ruby red colored CAL-AuNPs

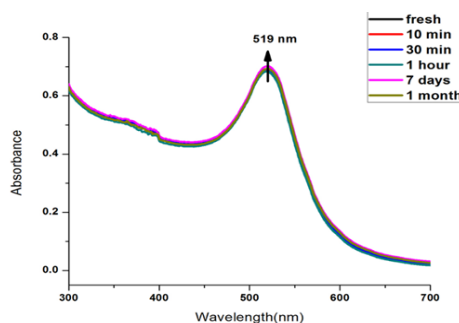


Fig 2b. Time-dependent study of CAL-AuNPs showing stability for the period of 1 month.

3.2 Fourier-transform infra-red (FT-IR) spectroscopy

The interaction of Au metal with *Capsicum annum L.* biomolecules of fruit extract was examined through FT-IR spectroscopy. Figure 4 contained the IR spectra recorded for pure green bell pepper fruit extract (black) and CAL-Au NPs (red), respectively. Within green bell pepper extract, different functional groups showing characteristic signals based on their particular mode of vibration. The FTIR spectrum shows some major peaks appeared at 3432.6 cm⁻¹, 3409.4 cm⁻¹, 2925.9 cm⁻¹, 1640.3 cm⁻¹, 1063.4 cm⁻¹ and 593.2 cm⁻¹. The FT-IR spectra confirmed the dominated strong absorbance bands in the region at 3409.4 cm⁻¹ shows N-H stretch – amides, alcohols, 3432.6 cm⁻¹ NH₂, and N-H groups and 2935.9 cm⁻¹ shows C-H stretching band. Whereas the peaks at 1640.3 cm⁻¹ show C = O stretch – amides and it also demonstrates the oxygen group attachment of Carbonyl functionalities that are responsible for gold nanoparticles capping; C – N– stretching vibration of aliphatic amines appeared at 1063.4 cm⁻¹ and the band appearance at 593.2 cm⁻¹ shows the association of gold nanoparticles with *capsicum annum L* biomolecules. [19-21].

Table 1: FT-IR data shows the main functional groups of *Capsicum annum L.* capped AuNPs

Main Functional Groups	Vibration Frequency
N-H stretching	3432.6 cm ⁻¹
NH ₂ and N-H stretching	3409.4 cm ⁻¹
C-H stretching	2925.9 cm ⁻¹
C=O stretching	1640.3 cm ⁻¹
C-N stretching	1063.4 cm ⁻¹
R-CH group	593.2 cm ⁻¹ .

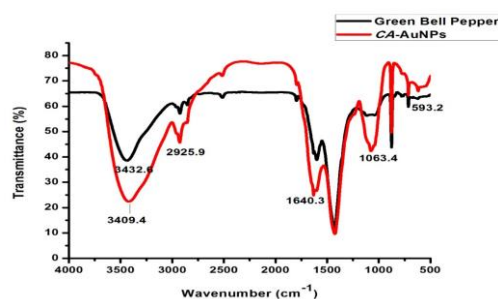


Figure 3. FTIR spectrum of green bell pepper fruit extract (black) and green bell pepper capped AuNPs (red).

3.3. Zeta Potential Analyzer (ZPA) and Dynamic Light Scattering (DLS)

Synthesized *Capsicum annum L.* capped gold nanoparticles were used for the Zeta potential analysis and Dynamic light scattering for determination of surface charge and charge to volume ratios of prepared gold nanoparticles. The Zeta Potential of *capsicum annum L.* mediated AuNPs was found by Zeta Potential Analyzer (ZPA). Zeta potential provides the information about the surface charge and stability of the synthesized AuNPs in suspension. The higher the zeta potential values, the higher will be the stability of synthesized nanoparticles due to the aggregation of nanoparticles. In general, zeta values in the range 20-30 mV or higher, are considered stable. So here (Fig. 4a) shows the Zeta (z) potential measurements for the *capsicum annum L.* capped gold nanoparticle at ambient temperature was found to be -43.2mV which confirms the great stability of nanoparticles and it also shows the interaction of AuNPs with fruit extract of *capsicum annum L.* The negative zeta potential value obtained for the currently prepared nanoparticles indicates that a negative charge has been generated on the surface of CAL-AuNPs and could be useful in the detection of metal ions of particular interest.

(a)

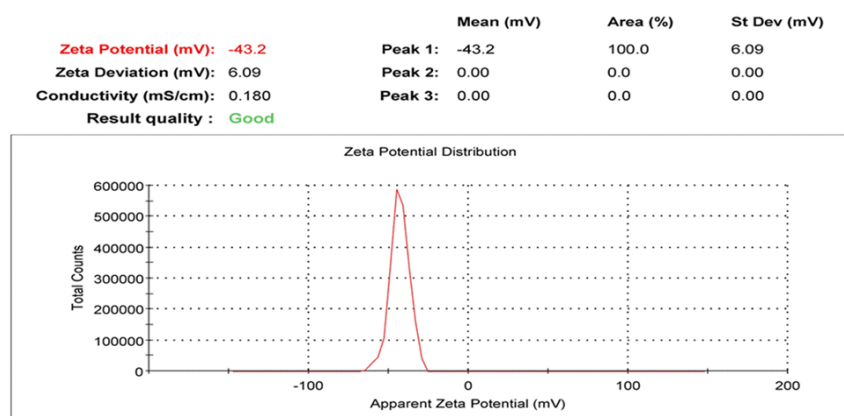


Fig. 4a. Zeta potential distribution of Green Synthesized Gold Nanoparticles.

Dynamic light scattering is a method widely used to research the scale of nanoparticles in the nano-range colloidal suspensions.

DLS is used to calculate light scattering as a function of time. **Fig. 4b** shows the particle size variation of the synthesized *CAL*-AuNPs which is measured by using Dynamic Light Scattering (DLS) instrument. DLS pattern for the size distribution of *CAL*-AuNPs shows that the size arranged between 17.50 Decca nanometer. This also confirms the smaller size of gold nanoparticles and also shows mono-dispersivity in aqueous solution [22-24].

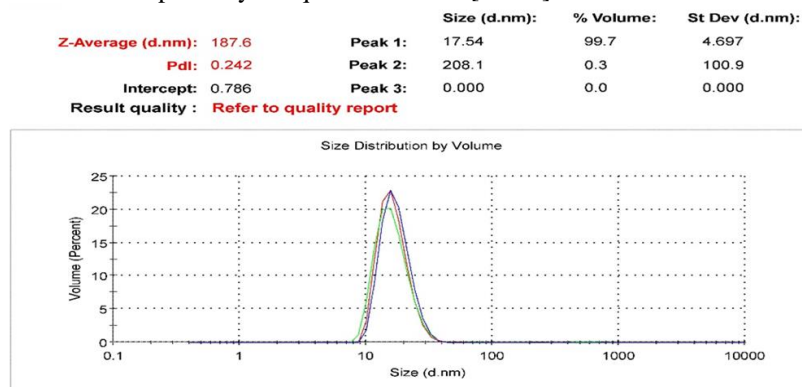


Fig. 4. (b) Size distribution of Green Synthesized Gold Nanoparticles

3.4. Atomic force microscopy (AFM) Studies

Synthesized *CAL*-Au nanoparticles were analyzed to check the average size and shape of the sample through atomic force microscopy. AFM studies were conducted to evaluate the size and roughness of the synthesized *CAL*-AuNPs. AFM directly inspect the 3-dimensional material surface in the nanoscale. AFM does not need sophisticated samples preparation; surface modification and it also gives non-destructive information about the sample material' morphology. AFM imaging technique can also investigate visual morphological changes based on nanoparticles that are stable, dispersed and aggregated. It is evident from Figure 5(a) that the green synthesized *CAL*-AuNPs are spherical and monodisperse with an average particle size of 5.5 nm between the 3 to 12.5 nm range as shown in Fig 5(b) [25-27].

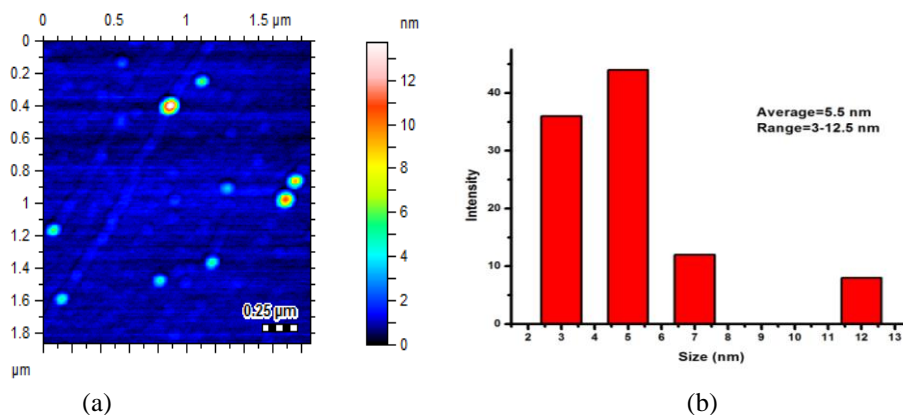


Fig. 5(a). AFM image of *CAL*-AuNPs, 5(b) average size distribution bar diagrams of AuNPs within 3-12.5 nm range.

3.5. Colorimetric Assay for Fe^{2+} Ion

When Fe^{2+} was added to synthesized *CAL*-AuNPs, the interaction of *CAL*-AuNPs with Fe^{2+} (ferrous ion) was investigated by a colorimetric variation from ruby red to violet was noted (Figure 6). The respective spectrum of *CAL*-AuNPs (black curve in Figure 6) revealed that after the addition of Fe^{2+} absorption was increased with a red-shifted wavelength (red curve in Figure 6).

Colorimetric change of color from ruby red to violet occurs, which indicates the spectral property of *capsicum annum L.* capped AuNPs was changed from blue-shifted band to red-shifted band with increased intensity. Upon the addition of Fe^{2+} , a change in size with an increase in absorption intensity can be expected due to aggregation in the aqueous solution associated with the formation of Au-Fe alloy [28].

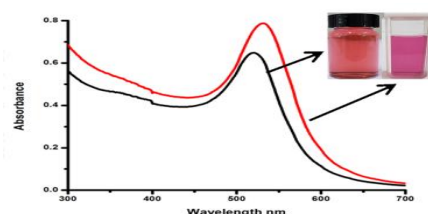


Fig.6. UV-Visible spectrum for *CAL*-AuNPs (black curve) and the interaction of *CAL*-AuNPs with Fe^{2+} (red curve). Inset reveals color changes according to UV-Vis spectral results.

3.6. Analytical Response of Colorimetric Assay

Quantitative data were obtained in the UV-Visible spectral range of 400–800 nm by adding Fe²⁺ to synthesized CAL-AuNP (Figure 7a). For a well-defined calibration plot, the shift in absorbance (ΔA) against concentration was plotted to get the concluding result. The sensor showed a highly linear response between 0.3 to 8 ppb (Figure 7b). The coefficient of correlation (R^2) was 0.9872, the detection limit (LOD), and the quantification limit (LOQ) were 0.5 ppb and 1.69 ppb, respectively, confirming the higher sensitive nature of the developed sensor that can be used successfully even in diluted samples. The value of LOD was calculated by $LOD=3\times\sigma/Slope$, whereas standard deviation of three blank signals is represented by σ .

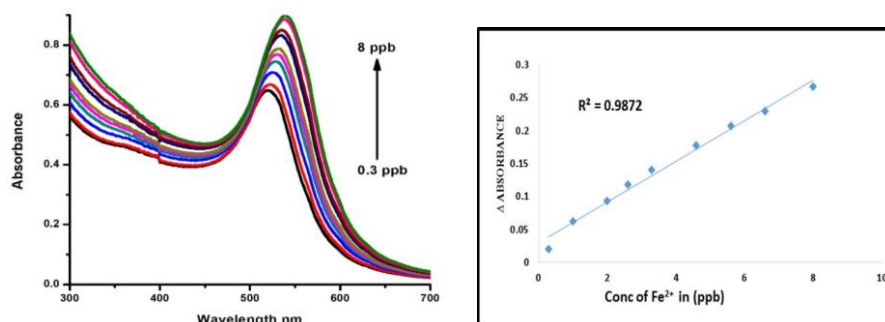


Fig. 7. (a) Increase in absorbance as Fe²⁺ concentration increases. (b) Plot of Linear regression between Δ absorbance versus Fe²⁺ concentration.

Table 2 shows the comparative data for the detection of various sensors recorded based on the detection limit and the distance obtained by this process and other techniques. Obviously, in this study, the AuNPs used to detect Fe²⁺ have a lower LOD, a simpler protocol, quick analysis and more economical nature than other approaches. Practically, the lower LOD represents the developed sensor's better sensitivity. The results clearly show that the newly developed sensor is more sensitive than all the Fe²⁺ + sensors mentioned.

Table 2: Comparative data revealing a colorimetric Fe²⁺ sensor with specific nanomaterials.

<i>Detection Probe</i>	<i>Method</i>	<i>Range (ppb)</i>	<i>LOD (ppb)</i>	<i>Ref</i>
1. MnO ₂ nanosheet	Colorimetric	55845 ppb	16.8 ppb	[29]
2. Gold nanoclusters (AuNCs)	fluorescence	4.47ppb	1.34 ppb	[30]
3. AuNPs	Colorimetric	0.79-69.8 ppb	0.63 ppb	[31]
4. AuNPs	Colorimetric	7.3-63104.9 ppb	59.2 ppb	[32]
5. AuNPs	Colorimetric	1 to 11 ppb	1.2 ppb	[33]
6. CAL-AuNPs	Colorimetric	3.3-8 ppb	0.5 ppb	Present work

3.7. Determination of Fe²⁺ in real water samples

In this context, water samples of different types were collected from different Jamshoro areas, and Hyderabad was tested for Fe²⁺ + assay using the developed CAL-Au NP-based sensor. Samples are processed in the experimental section according to the method described. For the measurement of Fe²⁺ in various water samples, the linear plot was used (Figure 8b). The Fe²⁺ + values were estimated in the range of 3.2-3.4 ppb, with recovery ranging from 97.56% to 104.3%, as shown in Table 2. The test strongly supports our developed Fe²⁺ ion sensor for every type of water sample as mentioned in our study.

Table 3: Determination of Fe²⁺ through a developed sensor in real water samples were collected from different areas of Jamshoro and Hyderabad, Sindh, Pakistan

S. No	Sample	Actual (ppb)	Added (ppb)	Total (ppb)	Determined (ppb)	Recovery (100%)
1.	Tape Water	0	0	0	0	-
2.	Milli Q Water	0	0	0	0	-
3.	Distill Water	0	0	0	0	-
	Distill Water (Spiked)	0	0.66	0.66	0.65	101
		0	1.66	1.66	1.67	99.4
		0	2.66	2.66	2.63	101

IV. CONCLUSIONS

In summary, a simple, efficient, economical and environmentally friendly method for the synthesis of AuNPs through capsicum annum L -AuNPs solution was used as a highly sensitive and selective optical sensor for the colorimetric sensing of Fe²⁺ through changes in LSPR band. The presence of ferrous ion (Fe²⁺) can be monitored by naked eyes and UV-visible spectrophotometer at room temperature. When Fe²⁺ is applied to the solution CAL-AuNPs, the mechanistic route specifies the aggregation associated with the formation of Au-Fe alloys. The influence of different metal ions has also been investigated. This method displays high Fe²⁺ ion selectivity and sensitivity over other metal ions as well as Ferric (Fe³⁺) ion. The sensor developed was successfully used to detect Fe²⁺ in real water samples from different locations in Jamshoro and Hyderabad Sindh, Pakistan. This is the first report for the colorimetric detection of Fe²⁺ via CAL-AuNPs. This method provides a new, economical and simple technique that can be applied in the study of environmental water samples.

Abbreviations and Acronyms

- i. CAL-AuNPs: *Capsicum Annum L.* Gold Nanoparticles
- ii. FT-IR: Fourier Transform Infrared Spectroscopy
- iii. DLS: Dynamic Light Scattering
- iv. ZPA: Zeta Potential Analysis

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