

Green Synthesis of Silver Nanoparticle in Calotropis Procera Flower Extract and its Application for Fe²⁺ Sensing in Aqueous Solution

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Abstract:- The silver nanoparticles (AgNPs) was synthesized in Calotropis procera extract. The synthesized AgNPs were characterized by UV-vis spectroscopy, dynamic light scattering (DLS) and transmission electron microscopy (TEM). DLS and TEM analysis of the synthesized AgNPs clearly showed the nanoscale particle size distribution having spherical shaped morphology. The color change and spectral shift in absorption spectrum after addition of Fe²⁺ ion to AgNPs solution develop a simple and quick method for quantitative determination of Fe²⁺ from aqueous solution without any interference from excipients. The selective adsorption of Fe²⁺ ions over the nano particle surface and mechanism of binding was supported by Langmuir adsorption plot, zeta sizer and absorption titration results. The results suggest that the synthesized AgNPs to be used as an ideal, eco-friendly nano probe for selective and sensitive detection of Fe²⁺ ion in aqueous medium based on adsorption studies. The present method successfully applied for the quantitative analysis of Fe²⁺ ion in samples collected from local area having limit of detection 4.29 µg/mL. The method offers a simple, selective, economical approach for quantitative detection of Fe²⁺ in environmental samples without any pretreatment.

Keywords: Calotropis procera, Silver nanoparticles, Fe²⁺ ion detection, Environmental sample analysis, Green synthesis.

Introduction:

Recently, metal nanoparticles received much importance in the nanotechnology field due to their noteworthy properties such as optical, magnetic and catalytic activity. Nanosensors, optoelectronics, nanodevices, absorbents, information storage are the key areas for the application of metal nanoparticles [1-3]. Metal nanoparticles can be synthesized by various methods such as electrochemical, sonochemical, chemical reduction, microwave irradiations [4-6]. Use of toxic chemicals as reducing and capping agents in chemical synthesis restricts the direct application of metal nanoparticles in aqueous media due to discharge of wastes leading to environmental pollution. Up to date, most of the synthetic physicochemical methods were reported for preparation of metal nanoparticles using organic solvents and toxic reducing agents like thiophenol, mercapto acetate, sodium borohydride [7-10], which are highly reactive and has potential environmental and biological risks. With the increasing interest in minimization or elimination of such kinds of hazardous chemicals, the method development based on biological, biomimetic and biochemical

approaches is desirable. Microorganisms, plants and enzymes are employed as environmentally benign materials to use in the synthesis of metal nanoparticles [11-12]. Synthesis of metal nanoparticles using part of plant extracts was found valuable process as compared to microbes due to several advantages viz. simple process, easily available, safe to handle and easily scaled up. Reduction rate and stabilization of nanoparticles can be increased by the presence of various phytochemicals in plant extract which can act both as capping and reducing agents. Therefore, biological approach has advantages over physicochemical methods because of its clean, non-toxic chemicals, environmentally benign solvents, and user-friendly nature [13-15].

Now a days, plant (leaf, flower, seed, tuber, and bark) extract mediated biological process for the synthesis of silver nanoparticles has been extensively explored as compared to other bio-inspired processes [16-17]. A range of plant extracts have been investigated for their ability to synthesize silver nanoparticles. Ananda Babu *et al.* reported the synthesis of silver nanoparticles using *Calotropis procera* flower extract at room temperature [18]. In

addition, the report is also available on the synthesis of silver nanoparticles using soy (*Glycinemax*) and curry (*Murraya Koengii*) leaf extracts [19-20]. Similarly, neem (*Azadirachta indica*) and mango (*Mangifera indica*) leaf extracts were effectively utilized for the synthesis of silver nanoparticles [21-22]. Apart from silver nanoparticles, plant extract mediated biological processes are also explored for the synthesis of gold and palladiumnanoparticles [23-24]. The *Calotropis procera* (*CP*), is a desert plant known as Madar in GreecoArab medicine and is widely distributed in tropical and subtropical Africa and Asia. The different parts of the plant are used in Indian traditional medicine for the treatment of painful muscular spasm, dysentery, fever, rheumatism, asthma and as an expectorant and purgative. *CP*, is a plant with good enough quantities of latex i.e. milky liquid, when any mechanical damages, their tissues are broken and secrete the milky latex, consisting of several biologically active compounds, including proteins, amino acids, carbohydrates, lipids, vitamins, alkaloids, resins, and tannins. Predominantly, milky latex contains several alkaloids of interest such as calotropin, catotoxin, calcilin, gigatin etc [25-26]. To the best of our knowledge, biological approach using milky latex of *Calotropis procera* has been used for the first time as a reducing material as well as surface stabilizing agent for the synthesis NPs. The stem and leaf extracts of *Calotropis procera* did not produce nanoparticles of appreciable size.

Silver nanoparticles receive enormous scientific, technological, and commercial attention due to their unique size and shape dependent properties. Extensive research has been devoted to explore the applications of silver nanoparticles in different fields including healthcare/ biomedical, sensors, spectroscopy and catalysis [18, 27-28]. One of the challenging tasks in the synthesis of nanostructured materials is the precise control of size and shape. Especially, silver nanoparticles exhibit drastic variation in their physicochemical properties with the size, shape, and their conjugation with other organic/ biological substances. Among the biological processes that are based on part of plant extracts are extensively investigated due

their eco-friendly protocol and better morphological control. Using “green” methods in the synthesis of silver nanoparticles has increasingly become a topic of interests as conventional chemical methods are expensive and require the use of chemical compounds/organic solvents as reducing agents [29]. The present study reports the utilization of *Calotropis procera* (*CP*) flower extract as reducing agent to synthesis silver nanoparticles (AgNPs). Characterization of synthesized AgNPs was done by UV–Vis spectroscopy, DLS, and TEM analysis. We found that latex of the plant *CP*, a multifarious plant having many remedial properties, can act as both reducing and capping agent in the NPs synthesis. This motivated us to further explore the synthesis of AgNPs using *CP* flowers. We found remarkable shortening in the reaction time and NPs of reduced diameter as compared to conventional heating method. The approach is a green route for the rapid *CP* stabilized AgNPs synthesis as no hazardous chemicals.

Experimental:

Reagents

All chemical reagents were of analytical reagent grade and used as received without further purification. Silver Nitrate (AgNO_3) was procured from Sigma Aldrich, Mumbai (India). The metal salts used were purchased from S. D. Fine-Chem Ltd (Mumbai, India). The stock solution of Fe^{2+} was prepared using ferrous sulphate. The 2-3 drops of dilute solution of hydroxylamine hydrochloride was added to Fe^{2+} ion solution to avoid its oxidation into Fe^{3+} state. Doubly distilled water was used throughout the experiments. The flowers of *Calotropis Procera* were obtained from local campus.

Characterization Techniques:

UV–visible spectra were recorded on a UV-3600 Spectrophotometer (Shimadzu, Japan) in respective solvents. The size of the nanoparticles was measured using a Malvern Zetasizer (nano ZS-90) equipped with a 4 mW, 633 nm He–Ne Laser (U.K.) at 25° C under the fixed angle of 90° in disposable polystyrene cuvettes.

The morphology of NPs was assessed by transmission electron microscope (TEM) (Technai G2 F30).

Synthesis of silver nanoparticle

The experimental procedure for the preparation of silver nanoparticles includes use of the *Calotropis procera* flowers. The purpose of using flowers of *Calotropis procera* is to stabilize the prepared nanoparticles in aqueous solution [30] and to develop a negative zeta potential over the nanoparticles surface which could be useful to explore its use in the sensing of metal ion detection. About 20g *calotropis procera* flowers were taken washed thoroughly with double deionized water and boiled in beaker containing 100mL double distilled water for 10-15 min. The hot solution was kept at room temperature to settle down and was filtered through Whatmann No.1 filter paper. The obtained filtrate was diluted to 250mL and stored in a refrigerator. 10 mL of the flower extract was injected in 100mL of 1 mM $AgNO_3$ solution and kept stirr for 12 hours. The change in color was noted and which was preliminary test toward formation of *Calotropis procera* stabilized silver nanoparticles (CP-AgNPs) solution. The resultant aliquots were stored in a freezer at $4^{\circ}C$ to avoid aggregation of nanoparticles into larger size. The schematic diagram for the formation of CP-AgNPs is shown in Scheme 1.

reduction process of silver ions in aqueous solution resulting in CP-AgNPs. The UV-Vis spectra of prepared CP-AgNPs shows broad absorption band peaking at 450 nm. The color of solution supports the absorption wavelength in the visible range.

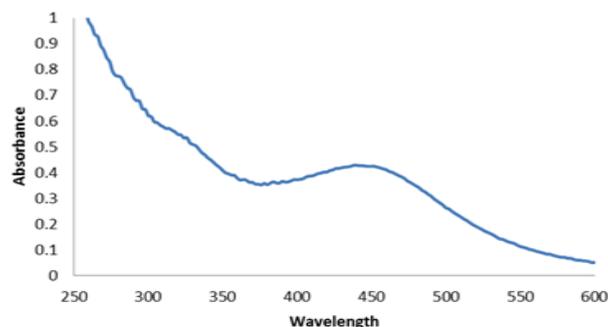
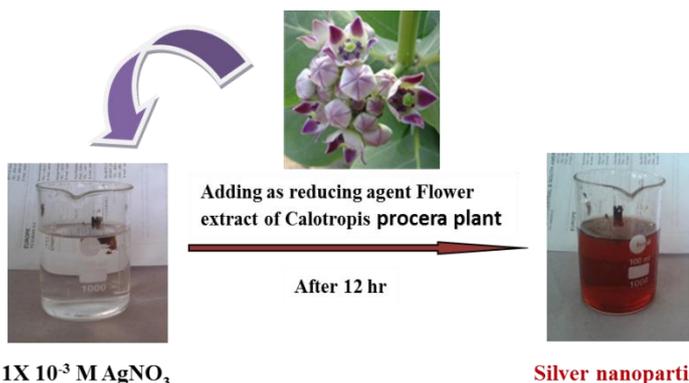


Fig.1 UV-visible absorption spectrum with maximum wavelength 450 nm of synthesized CP-AgNPs in aqueous solution

Dynamic light scattering

Fig. 2 shows the typical size and particle size distribution of the synthesized CP-AgNPs measured using Dynamic Light Scattering equipment. The average hydrodynamic diameter of well-dispersed CP-AgNPs is seen to be of 37 nm shows monodispersivity in aqueous solution. **Fig. 3** shows Zeta (ζ) potential measurements for the nanoparticle and was found to be -22.8mV which confirms the stability of nanoparticles at ambient temperature. The zeta potential in between the range +25 to -25 mV indicates the high and best stability for the prepared nanoparticles [31]. The obtained negative zeta potential for the present nanoparticles indicates that negative charge was developed over the surface of CP-AgNPs and which could be useful to explore its use in the metal ion detection of particular interest. The particle size distribution and size of CP-AgNPs obtained from the Transmission Electron Microscope (TEM) technique shown in **Fig. 4** supports the results obtained by DLS technique.



Scheme 1 Synthesis route for CP-AgNPs

Result and Discussion:

UV-Visible spectroscopy analysis

Fig. 1 shows UV- visible spectra of *Calitropis Procera* stabilized silver nanoparticles (CP-AgNPs). The colour change in the reaction mixture was responsible for the bio-

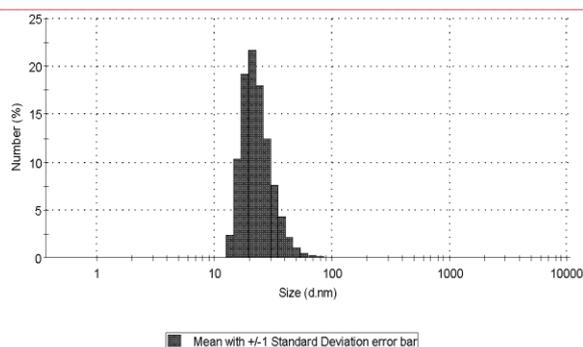


Fig.2 Particle size distribution of CP-AgNPs obtained using DLS equipment

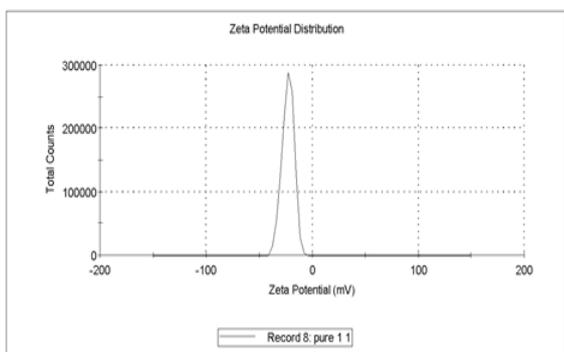


Fig.3 Zeta potential of CP-AgNPs

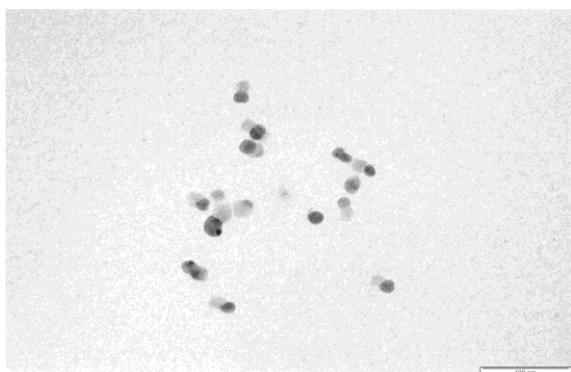


Fig. 4 Microphotograph of CP-AgNPs obtained by TEM
Selectivity of CP-AgNPs towards Fe²⁺ ion

The negative zeta potential of CP-AgNPs confers the negative charge over the surface of nanoparticles which could be responsible to bind the oppositely charged ion or positively charged metal ion due to the adsorption and electrostatic attraction between oppositely charged ions. The aqueous solution of CP-AgNPs was tested against the different metal ions viz. Cu²⁺, Pb²⁺, Ni²⁺, Zn²⁺, Ca²⁺, Na⁺, K⁺, Co²⁺, Hg²⁺, Fe²⁺ and Al³⁺ solution of 20 µg/ mL concentration. **Fig.5** shows absorption spectra of CP-AgNPs in absence and presence of different metal ion solution

tested. The present probe CP-AgNPs show high selectivity response for the Fe²⁺ ion solution over other metal ions solutions. The drastic change in absorbance of CP-AgNPs with blue shift in wavelength maxima due to addition of Fe²⁺ solution reveals the electrostatic interaction between oppositely charged surface of CP-AgNPs and Fe²⁺ ion solution. The color change in the CP-AgNPs with successive addition of Fe²⁺ solution was observed and indicates the strong complexation between CP-AgNPs and Fe²⁺ ion showing increase in absorption value. Neither significant color changes, nor shift in absorption maxima were observed upon addition of the other cations indicates the strong interactions were observed only with Fe²⁺ ion.

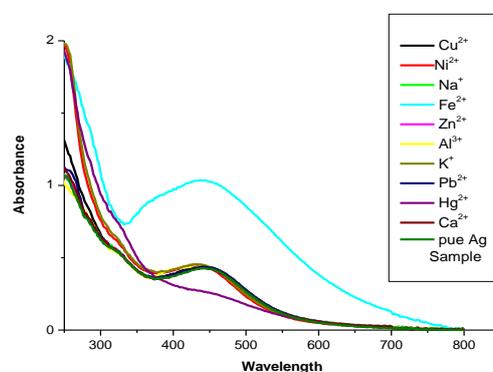


Fig.5 Absorption intensity of the CP-AgNPs solution shows selectivity for Fe²⁺ compared with other interfering metal ions

The color change behavior with addition of different metal ion solution is shown in **Fig.6**. The study explores the use of synthesized CP-AgNPs as a highly selective and sensitive optical and colorimetric probe for Fe²⁺ ion in aqueous media.

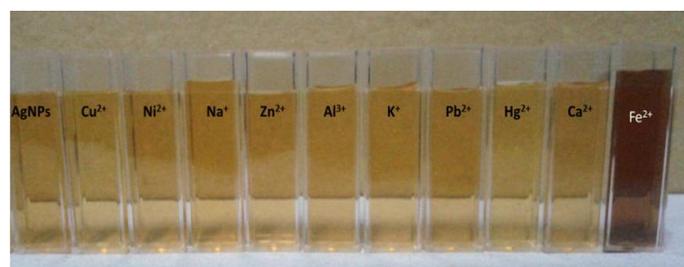


Fig.6 The photographic images of the CP-AgNPs solution in the presence of different ions

Absorption titration with Fe²⁺

At ambient temperature, the absorption spectra of the CP-AgNPs with increasing amounts of Fe²⁺ were recorded. The results are shown in Fig. 7 indicates slight blue shift in absorption maxima of CP-AgNPs and increase in absorption value with incremental addition of Fe²⁺ ion solution over the linear range of 2 to 40 µg/mL Fe²⁺ ion solution.

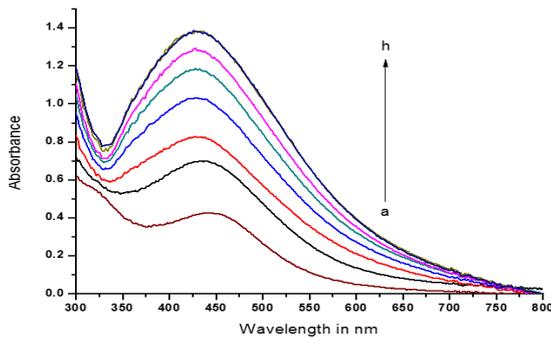


Fig.7 Absorption spectra of the synthesized CP-AgNPs solution with various concentrations of Fe²⁺ (a : 0 µg/mL, b: 2 µg/mL, c: 5 µg/mL, d: 10 µg/mL, e: 15 µg/mL, f: 20 µg/mL, g: 30 µg/mL and h: 40µg/mL)

The experimental data well fitted in linear plot relationship shown in Fig.8 and Fig. 9. The obtained results shows excellent linearity in the calibration graph (A-A₀) at wavelength 438 nm against concentrations of Fe²⁺ with a correlation coefficient of 0.9731 within the range 2-20 µg/mL of Fe²⁺ addition. Fig. 8 shows equilibrium calibration curve for the present study and reveals that beyond addition of 20 µg/mL Fe²⁺ ion solution, there is equilibrium state formation in between the interaction of Fe²⁺ and CP-AgNPs.

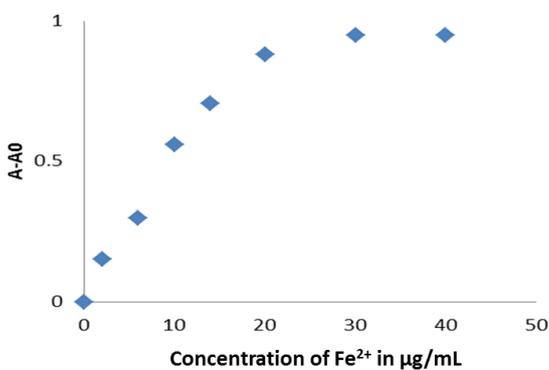


Fig.8 Equilibrium curve for (A-A₀) of the CP-AgNPs solution at 438 nm and different Fe²⁺ concentration

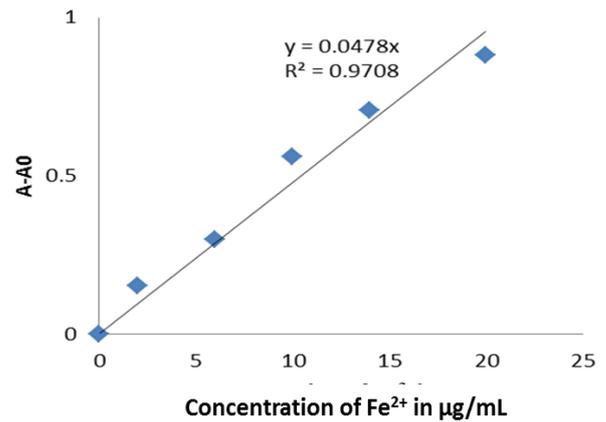


Fig 9 Linearity of (A- A₀) values with increasing concentration of Fe²⁺ solution to CP-AgNPs

Mechanism of binding between CP-AgNPs and Fe²⁺ ion

Fe²⁺ ions are believed to be adsorbed and bind with the negatively charged surface of CP-AgNPs. The interaction occurs due to electrostatic forces of attraction between them. The mechanism of binding was discussed on the basis of the Langmuir adsorption concept [32-34]. The rate of binding of Fe²⁺ ion to the nanoparticle surface (R_b) is proportional to their concentration (C) in the analyte solution and the fraction of available binding sites is 1-θ; where θ is defined as the fraction of occupied sites.

$$R_b = K_b \times C(1 - \theta) \tag{1}$$

Similarly, the rate of desorption of bound Fe²⁺ from the nanoparticle surface depends only on the fraction of the occupied binding sites and is expressed as,

$$R_d = K_d \times \theta \tag{2}$$

At equilibrium, the rate of binding is equal to rate of desorption

$$K_d \times \theta = K_b \times C(1 - \theta) \tag{3}$$

where, K_b and K_d are the binding and desorption constant of Fe²⁺ ions. The above equations can be solved as function of their ratio as,

$$B = \frac{K_b}{K_d}$$

$$\theta = \frac{BC}{1 + BC} \tag{4}$$

The fraction of occupied binding sites (θ) is related to the ratio of the absorption signal obtained (A) at given Fe^{2+} concentration and the maximum absorption intensity (A_0) without Fe^{2+} solution and is expressed as,

$$\theta = \frac{A}{A_0} = \frac{BC}{1 + BC} \quad (5)$$

The equation can be linearized to take the form,

$$\frac{C}{A} = \frac{1}{BA_0} + \frac{1}{A}C \quad (6)$$

Equation 6 is the linear form of the Langmuir adsorption equation.

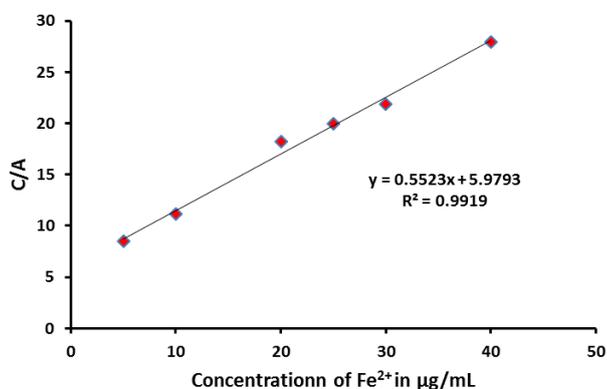


Fig 10 Langmuir adsorption plot for C/A as function of concentration of Fe^{2+} solution

The linearized plot of C/A vs. concentration of Fe^{2+} ions added (C) is shown in **Fig.10**. The adsorption equilibrium constant, B, is the Langmuir binding constant (K) given by the slope and the intercept of the linear plot. Hence, according to the Langmuir adsorption description, the binding of Fe^{2+} on the surface of the nanoparticles can be examined by the plot of C/A as a function of concentration

(C) of the Fe^{2+} ion solution added and as per the expectation this plot is linear as shown in **Fig. 10**. The coefficient of linear fit is 0.9919 and the Langmuir binding constant K is $1.0826 \times 10^4 M^{-1}$. The adsorption results led to consider that the spectral changes in absorption spectra of CP-AgNPs with addition of Fe^{2+} ion solution from 450 nm to 438 nm is because of the binding of adsorbed Fe^{2+} on the nanoparticle surface. In addition to this, the results of the DLS-Zetasizer support the adsorption of Fe^{2+} ion on the nanoparticle surface.

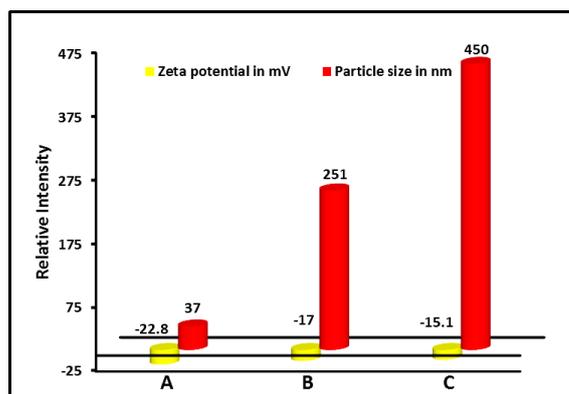


Fig. 11 Bar diagram of variation of zeta potential and particle size distribution for CP-AgNPs with increasing concentration of Fe^{2+} ion solution

The bar diagram in **Fig. 11** shows variation of the zeta potential and the size of CP-AgNPs in the presence of the Fe^{2+} solution. It can be seen that the negative zeta potential of the nanoparticle/water interface decreases successively from -22.8 mV to -17.0 mV and -15.1 and the particle size increases from 37 nm to 251 nm and 450 nm upon addition of 20 $\mu g/mL$ and 40 $\mu g/mL$ solutions of Fe^{2+} ions respectively. It is also supported by the TEM image in absence and in presence of Fe^{2+} ion with nanoparticles and shown in **Fig.12**.

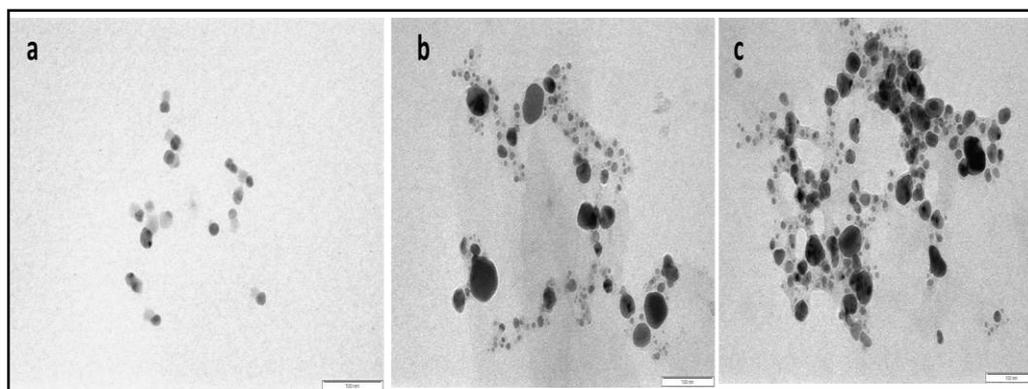
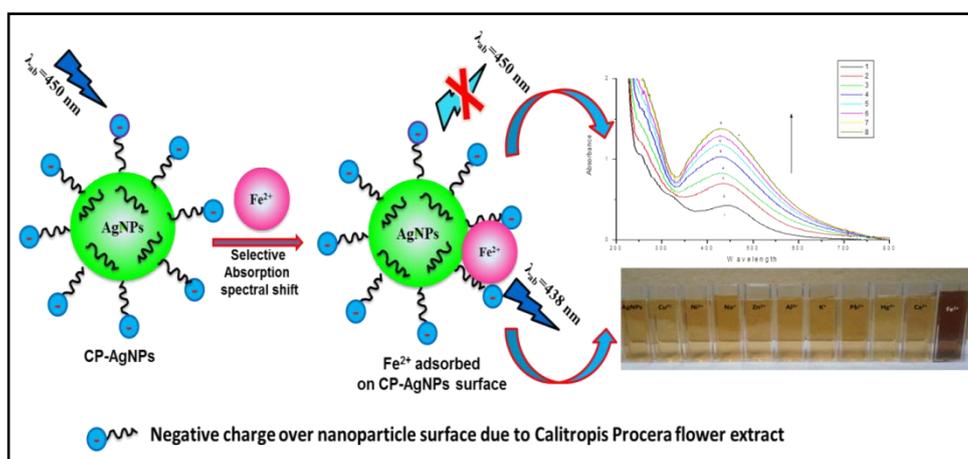


Fig. 12 TEM images of CP-AgNPs without (a) and with (b and c) Fe^{2+} ion solution

These observations suggested that the adsorption of Fe^{2+} ions over the negatively charged surface of nanoparticles increases the possible absorption unit in CP-AgNPs- Fe^{2+} complexation and introduces naked eye color change

behavior. The plausible mechanism based on Fe^{2+} ion adsorption on the surface of CP-AgNPs is graphically represented in Scheme 2.



Scheme 2 Plausible mechanism of binding between CP-AgNPs and Fe^{2+}

Determination of Fe^{2+} from environmental water samples:

To demonstrate the potential use of developed colorimetric nano probe to analyse the environmental water samples for the Fe^{2+} content using standard addition method. The water samples collected from Shivaji University, Kolhapur campus. The water samples were boiled for few minutes to settle down the aggregate particles and impurities. The samples were then filtered through filter paper (Whatman no. 41) to remove suspended impurities. After that the water samples were spiked with standard Fe^{2+} at two different concentration levels and further diluted within the working

linear range and analyzed with the method proposed via a standard addition method. The accuracy and reliability of the method were further ascertained by recovery results for spiked samples. The obtained results are summarized in Table 1, which shows good consistency between the expected and experimental found values. These results demonstrate that the designed nano probe is successfully applied for the quantitative determination of Fe^{2+} in environmental water samples without interference of other ingredients present in the matrix.

Table: 1: Detection of Fe^{2+} in water samples from different water sources using a standard addition method (n = 3)

Water sample studied	Amount of Fe^{2+} added in ppm	Total Fe^{2+} found (n=3) In ppm	Recovery of Fe^{2+} added (%)	RSD (%)	Relative Error (%)
Tap water from Dept. of Chemistry	20	20.614	103.068	0.293	0.031
Drinking water from Dept. Of Chemistry (SUK)	20	19.913	99.563	0.409	-0.437

Conclusion:

A simple biological reduction method used to synthesize AgNPs which have the ability to detect Fe^{2+} over ten other tested cations in aqueous solution. The synthesized CP-AgNPs was characterized by using DLS, TEM and UV-visible spectroscopy techniques. The present nano probe was found to be efficient and selective probe for naked dye detection of Fe^{2+} ion in aqueous medium. The ground state complexation between CP-AgNPs and positively charged Fe^{2+} ion was confirmed on the basis of results obtained in the absorption titration. The strong binding constant of complex formation between CP-AgNPs and Fe^{2+} was evaluated using Langmuir adsorption plot. The addition of increasing amounts of Fe^{2+} , increases the absorption intensity of AgNPs and a visible color change from yellow to brown. The obvious color change induced by Fe^{2+} can be easily observed by the naked eye. This study reports a selective method for the detection of Fe^{2+} in aqueous solution and can open a new cost-effective, rapid and simple detection method for Fe^{2+} ion from environmental samples without further pretreatment.

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References:

- [1] Mamonova, I. A., Babushkina, I. V., Norkin, I. A., Gladkova, E. V., Matasov, M. D., Puchinyan, M. D. (2015) Biological Activity of Metal Nanoparticles and Their Oxides and Their Effect on Bacterial Cells. *Nanotech. Russia.*, **10**, 128-134.
- [2] Das, S., Dhar, B. (2014) Green synthesis of noble metal nanoparticles using cysteine-modified silk fibroin: catalysis and antibacterial activity. *RSC Adv.* **4**, 46285-46292.
- [3] Subhankari, I., Nayak, P. L. (2013) Antimicrobial Activity of Copper Nanoparticles Synthesised by Ginger (*Zingiber officinale*) Extract. *World J. Nano Sci. Tech.* **2**, 10-13.
- [4] Feldheim D. L., Foss, C. A. (2002) *Metal nanoparticles: synthesis, characterization, and applications.* Marcel Dekker, New York.
- [5] Irvani, S., Korbekandi, H., Mirmohammadi, S. V., Zolfaghari, B. (2014) Synthesis of silver nanoparticles: chemical, physical and biological methods. *Res. Pharm. Sci.* **9**, 385-406.
- [6] Makarov, V. V., Love, A. J., Sinitsyna, O. V., Makarova, S. S., Yaminsky, I. V., Taliany, M. E., Kalinina, N. O. (2014) Green Nanotechnologies: Synthesis of Metal Nanoparticles Using Plants. *Acta Naturae*, **6**, 35-44.
- [7] Shukla, V. K., Singh, R. P., Pandey, A. C. (2010) Black pepper assisted biomimetic synthesis of silver nanoparticles, *J. Alloy. Compd.* **507**, L13-L16.
- [8] Singh, R. P., Shukla, V. K., Yadav, R. S., Sharma, P. K., Singh, P. K., Pandey, A. C. (2011) Biological approach of zinc oxide nanoparticles formation and its characterization, *Adv. Mat. Lett.* **2**, 313-317.
- [9] Mohanpuria, P., Rana, K. N., Yadav, S. K. (2008) Biosynthesis of nanoparticles: technological concepts and future applications. *J. Nanopart. Res.* **10**, 507-517.
- [10] Parashar, U. K., Saxena, S. P., Srivastava, A. (2009) Bioinspired synthesis of silver nanoparticles, *Dig. J. Nanomater. Biostruct.* **4**, 159-166.
- [11] Nair, B., Pradeep, T. (2002) Coalescence of nanoclusters and formation of submicron crystallites assisted by *Lactobacillus* strains. *Cryst. Growth Des.*, **2**, 293-298.
- [12] Willner, I., Baron, R., Willner, B. (2008) Growing metal nanoparticles by enzymes. *Adv. Mater.*, **18**, 1109-1120.
- [13] Chauhan, R., Kumar, A., Abraham, J. (2013) A Biological Approach to the Synthesis of Silver Nanoparticles with *Streptomyces* sp JAR1 and its Antimicrobial Activity, *Sci. Pharm.* **81**, 607-621.
- [14] Kulkarni, N., Muddapur, U. (2014) Biosynthesis of Metal Nanoparticles: A Review, *J. Nanotech.* <http://dx.doi.org/10.1155/2014/510246>
- [15] Pantidos, N., Horsfall, L. E. (2014) Biological Synthesis of Metallic Nanoparticles by Bacteria, Fungi and Plants. *J. Nanomed. Nanotechnol.* **5**, 233.
- [16] Chindambaram, J., Saritha, K., Maheswari, R., Sayed Muzammil M. (2014) Efficacy of Green Synthesis of Silver Nanoparticles using Flowers of *Calendula Officinalis*, *Chemi. Sci. Trans.* **2**, 3-5.

- [17] Haverkamp, R.G. (2007) Pick your carats: nanoparticles of gold-silver-copper alloy produced *in vivo*. J. Nano. Res. **9**, 697-700.
- [18] a) Babu, S. A., Prabu, H. G. (2011) Synthesis of AgNPs using the extract of Calotropis procera flower at room temperature. Mater. Lett. **65**, 1675-1677; b) Mason, C., Vivekanandhan, S., Misra, M., Mohanty, A. K. (2013) Switchgrass (*Panicum virgatum*) Extract Mediated Green Synthesis of Silver Nanoparticles, World Journal of Nano Science and Engineering, **2**, 47-52
- [19] Vivekanandhan, S., Misra, M., Mohanty, A. K. (2009) Biological Synthesis of Silver Nanoparticles Using *Glycine max* (Soybean) Leaf Extract: An Investigation on Different Soybean Varieties, J. Nanosci. Nanotech. **9**, 6828-6833.
- [20] Christensen, L., Vivekanandhan, S., Misra, M., Mohanty, A. K. (2011) Biosynthesis of Silver Nanoparticles Using *Murraya Koenigii* Leaf: An Investigation on the Effect of Broth Concentration in Reduction Mechanism and Particle Size. Adv. Mat. Lett. **2**, 163-167.
- [21] Shankar, S. S., Rai, A., Ahmad, A., Sastry, M. (2004) Rapid synthesis of Au, Ag, and bimetallic Au core-Ag shell nanoparticles using Neem (*Azadirachta indica*) leaf broth, J. Colloid Int. Sci. **275**, 496-502.
- [22] Philip, D. (2011) *Mangifera Indica* Leaf-Assisted Biosynthesis of Well-Dispersed Silver Nanoparticles, Spectrochim. Acta Part A: Mol. Biomol. Spectro. **78**, 327-331.
- [23] Narayanan, K. B., Sakthivel, N. (2010) Phytosynthesis of gold nanoparticles using leaf extract of *Coleus amboinicus* Lour. Mat. Charact. **61**, 1232-1238.
- [24] Petla, R. K., Vivekanandhan, S., Misra, M., Mohanty, A. K., Satyanarayana, N. (2012) Soybean (*Glycine Max*) Leaf Extract Based Green Synthesis of Palladium Nanoparticles. J. Biomat. Nanobiotech. **3**, 14-19.
- [25] Song, J. Y., Kim, B. S. (2012) Rapid biological synthesis of silver nanoparticles using plant leaf extracts. Bioprocess. Biosyst. Eng. **32**, 79-84.
- [26] Vishwa Nath V. (2014) The Chemical Study of Calotropis, International Letters of Chemistry, Physics and Astronomy, **1**, 74-90.
- [27] a) Kim, J. S., Kuk, E., Yu, K. N., Kim, J. H., Park, S. J., Lee, H. J., Kim, S. H., Park, Y. K., Park, Y. H., Hwang, C. Y., Kim, Y. K., Lee, Y. S., Jeong, D. H., Cho, M. H. (2007) Antimicrobial effects of silver nanoparticles, Nanomedi. **3**, 95-101. b) Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramirez, J. T., Yacaman, M. J. (2005) The bactericidal effect of silver nanoparticles. Nanotech. **16**, 2346-2353; c) Jones, C. M., Hoek, E. M. V. (2010) A Review of the Anti-bacterial Effects of Silver Nanomaterials and Potential Implications for Human Health and the Environment, J. Nano. Res. **12**, 1531-1551.
- [28] a) Murphy, C. J., Gole, A. M., Hunyadi, S. E., Stone, J. W., Sisco, P. N., Alkilany, A., Kinard, B. E., Hankins, P. (2008) Chemical sensing and imaging with metallic nanorods. Chem. Comm. **5**, 544-557; b) Haes, A. J., Haynes, C. L., McFarland, A. D., Schatz, G. C., Van Duyne, R. P., Zou, S. (2005) Plasmonic Materials for Surface-Enhanced Sensing and Spectroscopy, MRS Bulletin, **30**, 368-375; c) Jiang, Z. J., Liu, C. Y., Sun, L. W. (2005) Catalytic Properties of Silver Nanoparticles Supported on Silica Spheres. J. Phy. Chem. B. **109**, 1730-1735.
- [29] Philip, D. (2010) Green synthesis of gold and silver nanoparticles using *Hibiscus rosa sinensis*, Physica E. **42**, 1417-1424.
- [30] Lyklema, (1995) Fundamentals of Interface and Colloid Science, Elsevier, Wageningen.
- [31] a) Mahajan, P. G., Bhopate, D. P., Kolekar, G. B., Patil, S. R. (2015) N-methyl isatin nanoparticles as a novel probe for selective detection of Cd²⁺ ion in aqueous medium based on chelation enhanced fluorescence and application to environmental sample. Sensors and Actuators B, **220**, 864-872.; b) Mahajan, P. G., Bhopate, D. P., Kolekar, G. B., Patil, S. R., (2016) FRET Sensor for Erythrosine Dye Based on Organic Nanoparticles: Application to Analysis of Food Stuff. J. Fluoresc., **26**:1467-1478.
- [32] Hou, J., Wang, L., Li, D., Wu, X. (2011) A rigid conjugated pyridinylthiazole derivative and its nanoparticles for divalent copper fluorescent sensing in aqueous media. Tet. Lett. **52**, 2710-2714.
- [33] Mahajan, P. G., Desai, N. K., Dalavi, D. K., Bhopate, D. P., Kolekar, G. B., Patil, S. R. (2015) Cetyltrimethylammonium bromide capped 9-anthraldehyde nanoparticles for selective recognition of phosphate anion in aqueous solution based on

fluorescence quenching and application for analysis of chloroquine. *J. Fluoresc.* **25**, 31–38.

- [34] Mahajan, P. G., Bhopate, D. P., Kamble, A. A., Dalavi, D. K., Kolekar, G. B., Patil, S. R. (2015) Selective sensing of Fe²⁺ ions in aqueous solution based on fluorescence quenching of SDS capped rubrene nanoparticles: application in pharmaceutical formulation, *Anal. Methods.* **7**, 7889-7898.