

Preparation of Spherical Gold Nanoparticles Capped by *Fragaria ananassa* (Strawberry) Fruit Extract and their Catalytic Activity for Degradation of Industrial Dyes

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The prospect of developing new approaches in the assembly of noble metal nanoparticles and its functions has been garnering intense interest among researchers in various fields. The green synthesis method is an evolving trend as it is environment benign and aids in large-scale formation of nanoparticles. The versatile properties of green synthesized gold nanoparticles (AuNPs) like surface plasmon resonance, stability and morphology are examined by UV-visible spectroscopy (UV-Vis), dynamic light scattering (DLS), zeta potential (ZP) and high resolution transmission electron microscopy (HRTEM) studies at pH 7. Fourier transform-infrared (FT-IR) analysis confirms the pivotal role of anthocyanins and polyphenols in *Fragaria ananassa* (strawberry) fruit extract for the capping of AuNPs. The size of gold nanoparticles is in the range of 10 to 40 nm and they exhibit greater negative value of zeta potential. The catalytically active AuNPs follow the pseudo-first order kinetic model and takes 10 min for rapid degradation and adsorption of methylene blue dye from aqueous solution. These results confirm that *Fragaria ananassa* has a remarkable function in the plant-mediated synthesis of AuNPs and thus can emerge as a positive platform to convert water pollutants into harmless molecules.

Keywords: Adsorption, Gold nanoparticles, Surface Plasmon Resonance, *Fragaria ananassa*, Psuedo-first order Kinetic model.

INTRODUCTION

The textile industry being a diverse and substantial sector generates maximum employment, boosts the economic growth in many of the developing countries. The extensive usage of organic dyes as colouring agents for fabrics, paper, plastics and leather are one of the main reasons for environmental pollution. A large discharge of chemicals like detergents, oils, stain release agents and bleaching agents can cause rampant waste of water resources [1]. Various processes like sedimentation, oxidation and filtration have been earlier reported for water purification to remove the majority of the contaminants present in it [2]. The development of new strategies in designing unique photocatalysts like tuning the specific surface area, morphology, pore structure and volume of nanoparticles have been a primary aim of several studies [3]. Gold nanoparticles emerges to be a prospective material for photocatalysis under visible light harnessing as it can decompose organic dyes, inorganic chemicals, estrogens, phenols and pesticides from

aqueous solutions in a relatively short time interval of time when matched to other conventional water refining methods [4].

Synthesis of metal nanoparticles using plant extracts are attaining greater impact by researchers, since the metabolites in plants can have a significant influence on the reduction and stabilization of the nanoparticles [5,6]. Green synthesis of gold nanoparticles using citrus fruits [7], pear [8], plum [9], *Nepenthes khasiana* leaf extract [10] and *Cinnamomum zeylanicum* leaf broth [11] have been earlier reported.

In the present study, a novel attempt has been made to synthesize stable gold nanoparticles (AuNPs) using *Fragaria ananassa* fruit extract. This fruit is cultivated worldwide and belongs to the family of Rosaceae and genus *Fragaria*. Fresh strawberries have a high content of ascorbic acid, ellagic acid, quercetin and pure compounds of anthocyanins (cyanadin-3-glucoside, pelargonidin and pelargonidin-3-rutinoside), flavanols and phenolic acids such as hydroxycinnamic acid and hydroxybenzoic acid [12]. The as-synthesized AuNPs

possess good fermi-potential, strong light adsorption characteristics, large surface area making it an excellent pathway for photocatalytic activity. Methylene blue is a synthetic dye and largely used for dyeing cotton, silk and wood. An emphasis on the reduction of methylene blue to Leuco methylene blue in the presence of sodium borohydride is made to assess the catalytic activity of gold nanoparticles.

EXPERIMENTAL

Chloroauric acid ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$) was procured from Loba Chemie, Pvt. Ltd. Mumbai, India. *Fragaria ananassa* fruits were collected from Mahabaleshwar city, India. The aqueous solutions were prepared using double distilled deionized water for all the experimental work.

Preparation of gold nanoparticles: Aqueous fruit extract was prepared by soaking 20 g of fruit in 50 mL of deionized water for 2 h. The soaked fruit was then crushed with an electric blender following filtration using Whatmann filter paper (Grade 1). For synthesis procedure, 1 mM of 50 mL solution of $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ was added to 1.2 mL of aqueous fruit extract at room temperature ($32 \pm 1^\circ\text{C}$). The appearance of a colour change from pale yellow to ruby red within 15 min confirms the reduction of HAuCl_4 .

Characterization of gold nanoparticles: The UV-visible absorption spectra of as-prepared gold nanoparticles was recorded using UV-Vis-NIR Spectrophotometer Cary 5000 having a spectral range of 175-3300 nm. The morphology of AuNPs was studied using JEM 2100 Transmission Electron Microscope. Fourier transform infrared (FTIR) studies was recorded in the spectral range of 4000-400 cm^{-1} by instrument Thermo Nicolet, Avatar 370. The stability and size of synthesized AuNPs was determined by Zetasizer Nano S90 (Malvern) instruments.

Photocatalytic degradation of methylene blue dye: The catalytic activity of AuNPs was carried out for the reduction of methylene blue in the presence of sodium borohydride using Heber Visible Annular Type Photoreactor. This photoreactor comprises of a borosilicate immersion well, tungsten halogen lamp with an inlet and outlet to cool the lamp. It consists of an aerator for effective mixing of the micro-samples in the sample tubes and a provision for a safety hood to be placed at the top once the reaction tubes are set. A 2 mL of prepared NaBH_4 (0.2 M) was mixed with 50 mL aqueous solution of methylene blue (10 mg L^{-1}) followed by the addition of 1 mL of as-synthesized gold nanoparticles and stirred continuously for a time period of 2 min. The complete reaction was carried out at room temperature ($32 \pm 1^\circ\text{C}$). About 4 mL of the reaction mixture was withdrawn and the absorbance spectrum was measured in regular intervals of time to check the effect of as-synthesized AuNPs for the decolouration of methylene blue dye.

RESULTS AND DISCUSSION

UV-visible analysis: Formation of gold nanoparticles in aqueous colloidal solution was confirmed by UV-visible spectroscopy (Fig. 1). Initially, the surface plasmon resonance (SPR) band was observed around 536 nm in 1 h, which gets red shifted and appeared around 538 nm after a time interval of 10 h. The symmetric SPR peak indicates the production of spherical nanoparticles whose nature is highly dependent on

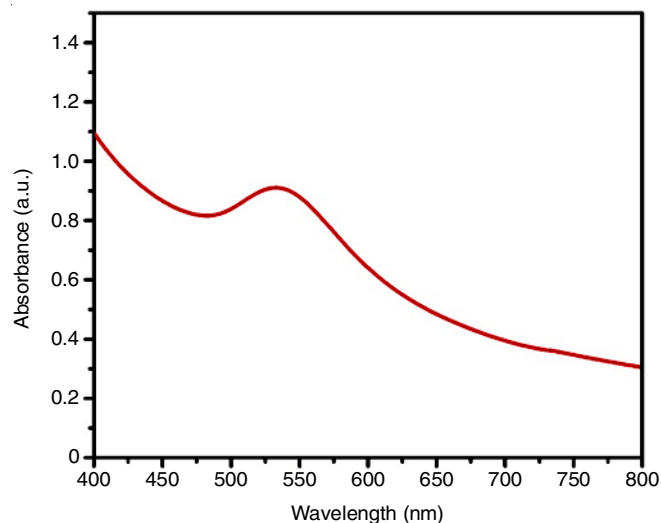


Fig. 1. UV-visible spectra of gold nanoparticles

the pH value as well as the reaction time of medium [13,14]. The rate of formation of AuNPs is lower in acidic pH than in basic pH. A visual colour change from pale yellow to ruby red is achieved at a neutral value of pH 7 and is due to the ionization of polyphenols such as quercetin, cyanidin, ellagic acid and pelargonidin present in the fruit extract [15].

FT-IR analysis: Fourier transform infrared studies were carried out to identify the nature of biomolecules accountable for the reduction and effective stabilization of gold nanoparticles synthesized with *Fragaria ananassa* fruit extract. An absorption peak at 1636.34 cm^{-1} is assigned to the amide I bond of proteins (Fig. 2), which arises due to the carbonyl stretching in proteins [16]. The strong absorption peak at 3452.97 cm^{-1} is characteristic of O-H stretching of alcohols, flavonoids and ascorbic acid present in the fruit extract [17]. The weaker band at 2071.59 cm^{-1} corresponds to the asymmetric stretching of C-H groups, while the IR band at 541.25 cm^{-1} can be attributed to C-Br stretching vibrations indicating the presence of 4-bromo-1-naphthalenammine compounds [18]. The FTIR spectrum supports the presence of polyphenols, anthocyanins and amide functional groups responsible for the synthesis of gold nanoparticles.

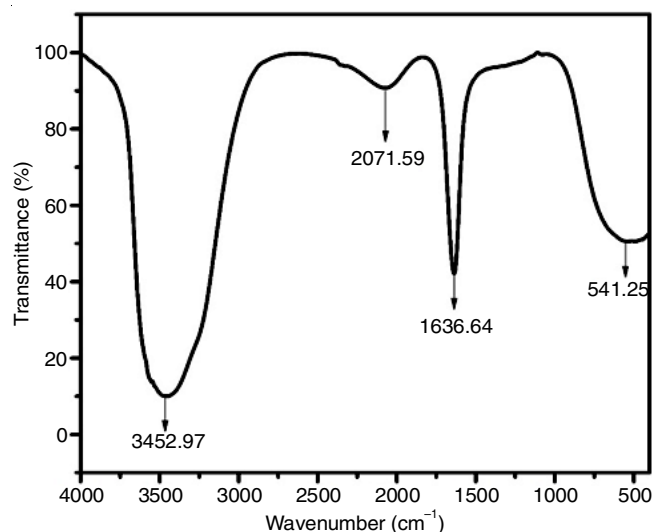


Fig. 2. FTIR spectrum of gold nanoparticles synthesized from *Fragaria ananassa* (Strawberry) fruit extract

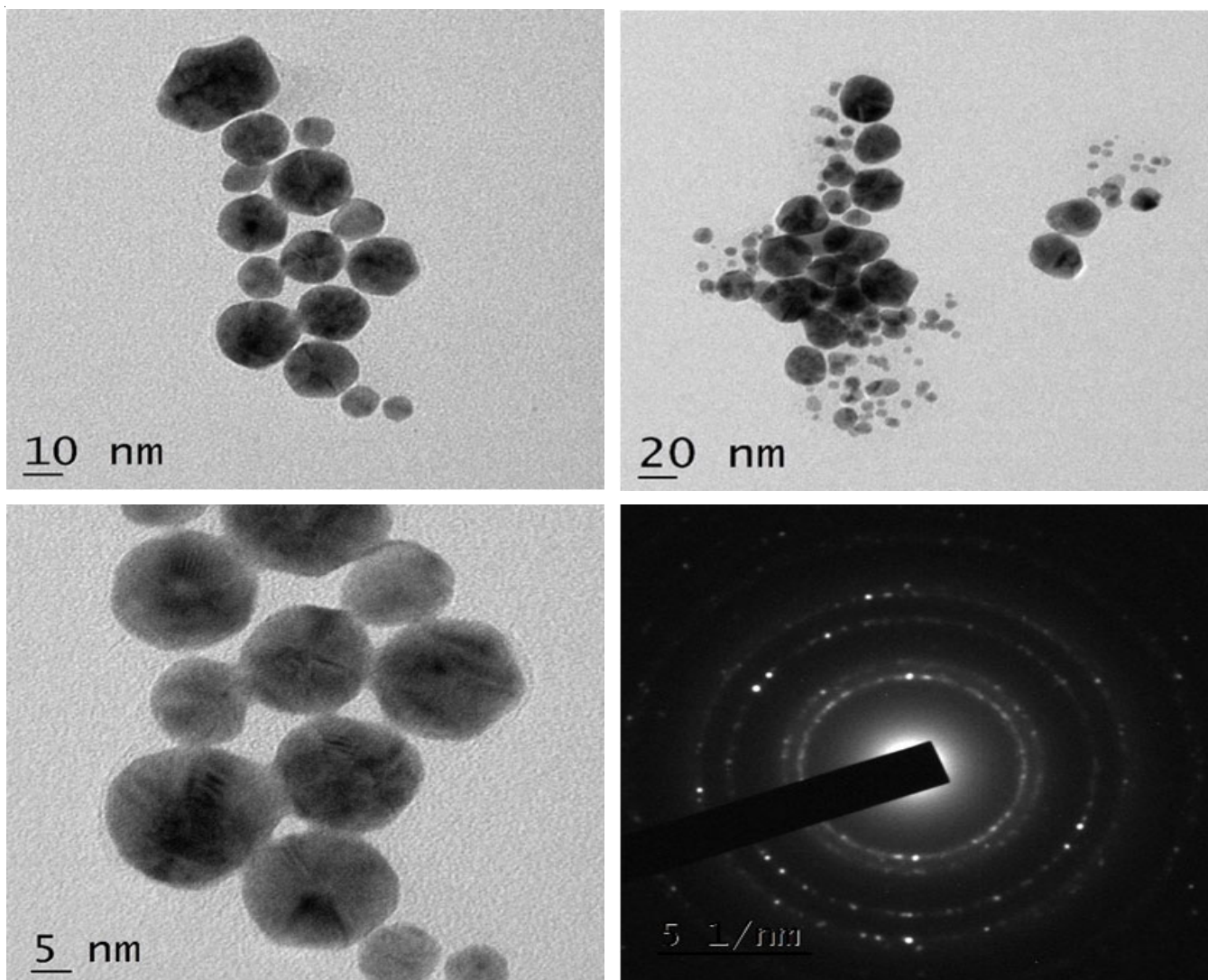


Fig. 3. HRTEM images of as-synthesized gold nanoparticles and SAED pattern

HRTEM analysis: The HRTEM images of as-prepared gold nanoparticles are shown in Fig. 3. The images showed abundance of circular particles, which are evenly distributed in the reaction medium and exhibited no visible agglomeration. The particle sizes are in the range of 10 to 40 nm and most of the AuNPs are separated by a fairly similar interparticle distance. From the images, the particle size and monodispersity of AuNPs is in good agreement with UV-visible spectroscopic studies. The selected area electron diffraction (SAED) pattern showed bright circular fringes confirming a good crystalline nature of the synthesized AuNPs.

Particle size and stability of nanoparticles: The particle size and stability of AuNPs was further investigated by the dynamic light scattering (DLS) and zeta potential (ZP) measurements. Since the DLS method calculates the thickness of bio-molecules, which are capped on the synthesized gold nanoparticles surface [19,20], the average particle size is found to be 48.04 nm with a PDI index of 0.438. Smaller particle sizes in the range of 10-20 nm is also evident in Fig. 4 and is in agreement with the HRTEM measurements.

The stability of biosynthesized AuNPs was evaluated by zeta potential studies. It was noted that synthesized AuNPs

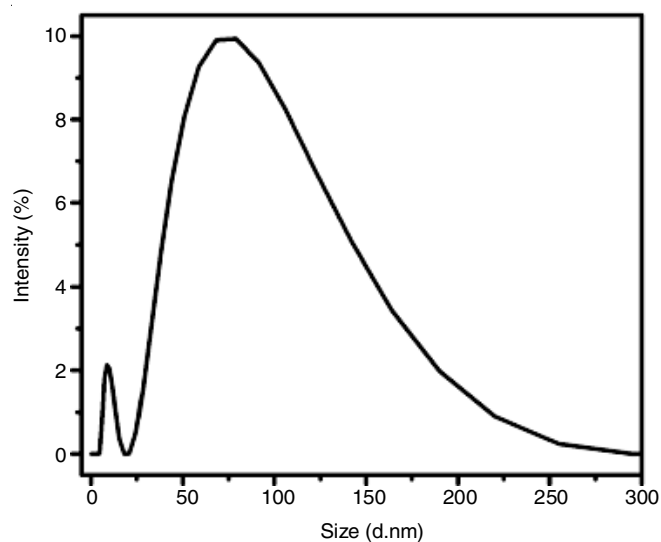


Fig. 4. Dynamic light scattering determining the size of AuNPs

are more stable when the pH range is at 7 with the zeta potential and zeta deviation values to be -10.9 mV and 7.85 mV, respectively as shown in Fig. 5. The zeta potential of AuNPs was

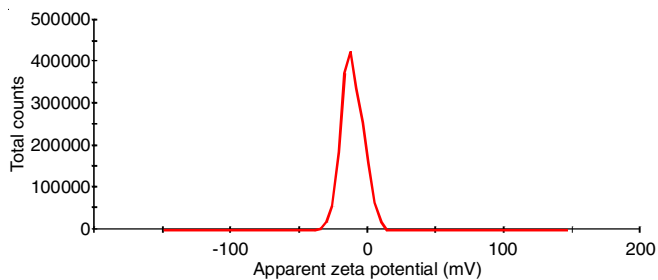


Fig. 5. Zeta potential analysis to determine the AuNPs stability

evaluated with water as the dispersant and the system was maintained at 25 °C and a count rate of 181.0 bcps. The negative value of zeta potential can be attributed to the electrostatic repulsion between the particles and hence maintaining the high stability property of AuNPs [21]. The results obtained by UV-visible, DLS and ZP studies remain unchanged in value even after a period of 2 months.

Catalytic activity: The size dependent catalytic activity of as-synthesized AuNPs was investigated for the degradation of methylene blue. The UV-visible spectrum of methylene blue shows absorbance peak at 664 and 614 nm and displays a dark blue colour [22]. Two conditions were observed *i.e.* no significant change in the concentration of dye with only the presence of AuNPs after a time interval of 45 min and also NaBH_4 cannot degrade methylene blue on its own in absence of a nanocatalyst. When the three components are mixed together, AuNPs play an active role in the shifting of electrons from donor BH_4^- ion to the acceptor methylene blue. The electron relay process occurs due to the adsorption of BH_4^- ion on the surface of AuNPs and hence causing degradation of dye. Due to this reaction, dark blue colour of methylene blue solution gradually decreases in intensity with an increase in the reaction time and eventually becomes colourless. This proves that NaBH_4 acts as a reducing agent and AuNPs act as a good catalyst for the reaction to occur. The complete reaction takes a time span of 10 min with a calculated percentage degradation value of 93.3 % (Fig. 6). The reduction method follows the pseudo-first order reaction [23], $\ln C_0/C = kt$, where C and C_0 corres-

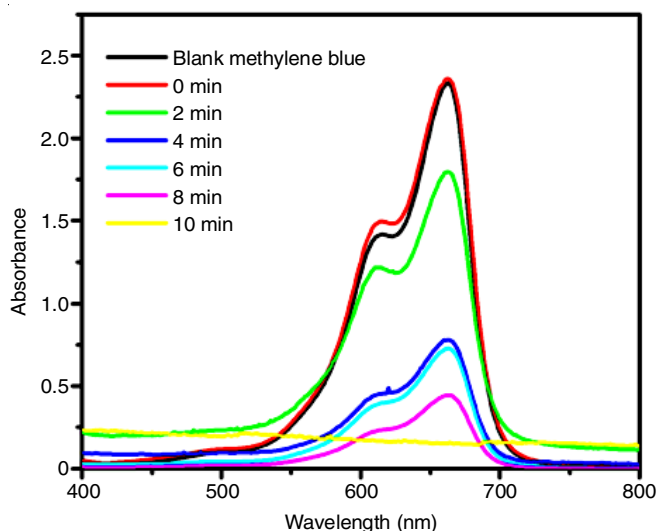


Fig. 6. UV-visible absorption spectra indicating reduction of methylene blue in a time interval of 10 min

ponds to the concentration of solutions at various time intervals, t is the rate of reaction and k corresponds to the rate constant of the reaction [24]. The graph shown in Fig. 7 indicates y value of $0.2736x$ and R^2 as 0.9292.

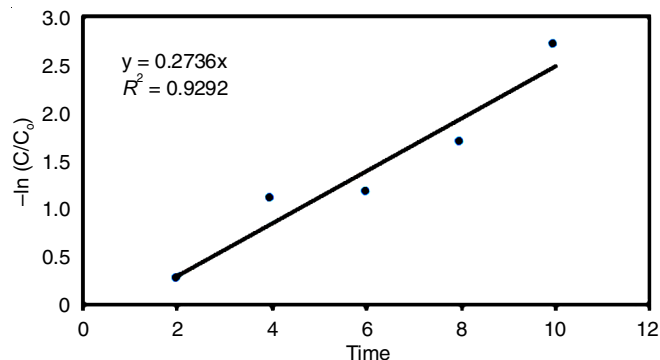


Fig. 7. A plot of $-\ln(C/C_0)$ versus time

Moreover, major phytochemicals of fruit extract remain unaltered owing to room temperature conditions, there is an enhanced surface plasmon resonance effect as a function of uniform size distribution of AuNPs. Hence in the catalytic study, there is a remarkable influence of increased content of polyphenols resulting in an efficient binding between *Fragaria ananassa* fruit extract and gold nanoparticles for the production of stable AuNPs with a high negative zeta potential value. These AuNPs have a higher specific surface area and can facilitate an effective electron transfer between the acceptor and donor molecules which increases their catalytic performance due the adsorption of the reactants on its surface. The presence of functional groups in the fruit extract have a strong ability to reduce the metallic ions at room temperature and can be proposed to exhibit a good photodegradation activity using an environmental friendly green synthesis procedure.

An increase in temperature can cause a pronounced reduction in the total composition of phenolic compounds, tannic acid and flavanoids, thereby affecting the stability and antioxidative properties of the plant extracts [25]. There is a correlation between the percentage of polyphenols determining the morphology of as-synthesized nanoparticles.

The suitability of the present work is further compared with the several reported works, where gold nanoparticles was successfully used for the degradation of methylene blue (Table-1). It is found that AuNPs synthesized from *Fragaria ananassa* fruit extract is almost similar with other reported works regarding the degradation of methylene blue dye.

Conclusion

Stable gold nanoparticles were successfully synthesized through a facile and cost-effective green route using the fruit extract of *Fragaria ananassa*. The bioconstituents such as anthocyanins, flavanols, polyphenols, tannic acid, gallic acid present in the fruit extract play a vital role in the stability and capping of gold nanoparticles. The UV-Vis, TEM and DLS studies confirm a similar particle size and the zeta potential studies indicate a high stability of as-synthesized nanoparticles. The monodisperse characteristic of AuNPs play a significant role in the degradation of methylene blue dye in a short time span and hence can find applications in industries dealing with treatment of wastewaters.

TABLE-1
COMPARISON OF THE GOLD NANOPARTICLES
EFFECTIVE FOR THE DEGRADATION OF METHYLENE
BLUE DYE AS REPORTED IN PREVIOUS WORKS

Material	Time of degradation (min)	Particle size (nm)	Ref.
Ayurvedic Kashyam	20	15-50	[26]
<i>Punica granatum</i>	15	18	[27]
<i>Costus pictus</i>	105	37.2	[28]
<i>Sesbania grandiflora</i>	51	7-34	[29]
<i>Sterculia acuminata</i>	12	9-38	[30]
<i>Pogostemon benghalensis</i>	8	10-50	[31]
<i>Flammulina velutipes</i>	23	20	[32]
<i>Brassica rapa</i>	18	16-46	[21]
<i>Fragaria ananassa</i>	10	10-30	Present work

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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