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# A GREEN BIO-MEDIATED SYNTHESIS OF SILVER NANOPARTICLES FROM THE EXTRACT OF *PEPEROMIA PELLUCIDA* USING MICROWAVE TECHNIQUE AND STUDY OF ITS CATALYTIC ACTIVITY

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**Abstract**

Biological methods are thought to be safer than conventional physicochemical methods for the synthesis of nanomaterials due to their environmentally benign nature. In the present study, silver nanoparticles (AgNPs) were synthesized by microwave irradiation using an aqueous leaf extract of the medicinal plant *peperomia pellucida*. The nanoparticles were also synthesized under ambient conditions without using microwave radiation and the former method was found to be much quicker and efficient than the latter. The silver nanoparticles were characterized by UV-vis., XRD and HR-TEM analysis. UV-vis. spectroscopic studies provided evidences for the formation of nanoparticles. The plant phytochemicals act as stabilizing agent around the AgNPs. XRD and HR-TEM analyses clearly proved the crystalline nature of the nanoparticles. From the TEM images, the nanoparticles were found to be roughly spherical in shape with an average diameter of 23.24 ± 4.28 nm. The nanoparticles showed excellent catalytic activity for the reduction of methyl orange by $NaBH_4$.

**Keywords: Microwave; Silver nanoparticle; Silver nitrate; Methyl orange; Catalysis**

## I. INTRODUCTION

Nanomaterials have brought immense interest these days because of their promising applications in numerous areas of science and technology. Among these, metal nanoparticles are most versatile owing to their properties that depend on their size and morphology which makes them a proper candidate in various applications [1-4]. Several methods are available for nanoparticle synthesis such as chemical [5], photochemical [6], electrochemical [7] and biological methods [8]. Many of these production routes involve the use of toxic chemicals and require harsh reaction conditions. Chemical method of nanoparticle synthesis is still widely used because of its short reaction time. However, in this method, the chemical reagents used as reducing and capping agent are usually toxic and lead to environmental pollution.

With increasing focus on green chemistry, bio mediated synthesis of metal nanoparticles is getting more attention currently because of its simplicity, environment benign nature and cost effectiveness. Plant extracts and several microorganisms such as bacteria, fungi and yeast have been used for the synthesis of nanomaterials [9-11]. Several reports are obtainable on the biological synthesis of nanoparticles using plant extract as both reducing and capping agent [12-16]. Even though, plant mediated biosynthesis can be carried out at ambient conditions, the time required for nanosynthesis is much longer than the chemical methods. Microwave assisted biosynthetic strategy provides a remedy to this problem. The reaction time can be significantly reduced by using microwave irradiation. Microwave-assisted synthesis using plant extracts as both reducing and stabilizing agent is a feasible way for the rapid and simple green synthesis of silver nanoparticles. It has several attractive features such as shorter reaction time, lower energy consumption and better product yield [17]. Microwave irradiation offers rapid and uniform heating of the reaction medium and thus provides uniform nucleation and growth conditions for nanoparticles. Renugadevi and co-workers synthesized silver nanoparticles using leaf extract of *Baliospermum montanum* with the aid of microwave heating [18]. Abboud et al prepared silver nanoparticles by a microwave assisted method using aqueous onion (*Allium cepa*) extract [19].

Peperomia pellucida (L.) is a herb belonging to the family Piperaceae which is commonly known by names such as pepper elder, rat ear and shining bush. The plant is employed as food, flavoring agent and as medicine. The plant is used as medicine for treating various ailments or disorders such as asthma, rheumatism, wound, fever, abdominal issues, kidney infection, hemorrhoid pain, joint pain, hypertension, diarrhea, snake bite and measles. The plant contains phytochemical groups such as alkaloids, flavonoids, saponins, terpenoids, steroids and glycosides. Studies have shown that the plant exhibited several pharmacological activities such as antimicrobial, antioxidant, anti-angiogenic, anti-inflammatory, analgesic, antipyretic, neuropharmacological,

antisickling, anticancer, enzyme inhibitory, antiulcer, hypotensive, immunostimulatory, fracture healing and antidiabetic activities which support the traditional use of the plant [20].

In this work, we report a novel one-pot, microwave assisted method for the synthesis of silver nanoparticles using the leaf extract of *peperomia pellucida* as both reducing and capping agent. This is a simple, green and cost-effective method for the rapid and facile synthesis of silver nanoparticles. The catalytic activity of the silver nanoparticles synthesized by microwave irradiation using *peperomia pellucida* (AgNP- *peperomia*) was examined using the reduction reaction of the azo dye methyl orange by $NaBH_4$.

## II. MATERIALS AND METHODS

### 2.1. Materials

Silver nitrate ($AgNO_3$), methyl orange and sodium borohydride ($NaBH_4$) of analytical grade were purchased from Merck (India) and used as such without further purification. All aqueous solutions were prepared using double distilled water.

### 2.2. Preparation of peperomia pellucida leaf extract

Fresh leaves of *peperomia pellucida* were collected and identified taxonomically. It is washed thoroughly with distilled water and leaves are separated. The leaves are then air dried and 30gm of leaf is weighed using a chemical balance. The sample was taken in a round bottom flask fitted with condenser and boiled for 10 min with 100 mL of double distilled water. It was cooled and filtered through Whatman No. 1 filter paper. The extract thus obtained was stored in a refrigerator for further use.

### 2.3. Synthesis of silver nanoparticles (AgNP- peperomia)

In a typical microwave synthesis, 90 mL of 1 mM silver nitrate solution was taken in a 250 mL beaker. To this, 10 mL *peperomia pellucida* leaf extract was added and stirred well. It was then placed in a domestic microwave oven (Sharp R-219T (W)) operating at a power of 800 W and frequency 2450 MHz. The solution was then subjected to microwave irradiation for 90 sec. The formation of AgNPs was monitored using UV-vis. spectrophotometer by analyzing the reaction mixture after 30, 60 and 90 sec of microwave action. The silver nanoparticle solution was then centrifuged at 10000 rpm for 10 min. The supernatant was decanted and the nanoparticles were redispersed in distilled water. The above process was repeated three times. The purified sample thus obtained was freeze dried to get dry sample.

In order to synthesize AgNP- *peperomia* at room temperature, 10 mL of *peperomia pellucida* extract was added to 90 mL of 1 mM aqueous solution of silver nitrate and allowed to react at room temperature for 4 hours. The reaction mixture was subjected to intermittent UV-vis. analysis at an interval of 60 minutes to examine the formation of AgNP- *peperomia*.

### 2.4. Reduction of methyl orange

The reduction of methyl orange by $NaBH_4$ was used to look into the catalytic efficiency of AgNP- *peperomia*. To track this reaction, 0.5 mL freshly prepared $NaBH_4$ solution (0.06 M) was added to 2 mL of methyl orange solution ($0.1 \times 10^{-3}$ M) taken in a quartz cell. Then 0.5 mL of AgNP- *peperomia* solution was added to start the reaction. The change in the concentration of methyl orange with time was monitored by UV-vis. spectrophotometer. The absorption spectra were recorded at 30 second intervals in the range of 200-600 nm at ambient temperature (26$^o$C).

### 2.5. Characterization

UV-vis. spectral studies were carried out on a Shimadzu UV-2450 spectrophotometer. XRD measurement was made on a PANalytic X'PERT-PRO X-ray spectrometer. High resolution-transmission electron microscopic (HR-TEM) images were obtained using a JEOL JEM-2100 microscope.

## III. Results and Discussion

### 3.1. Synthesis and UV-vis. spectroscopic analysis of silver nanoparticles

UV-vis. Spectrophotometric analysis is used to follow and confirm the formation of silver nanoparticles. The reduction of $Ag^+$ ions into Ag nanoparticles was monitored by recording the absorption spectrum of the reaction mixture with time in the range of 250-700 nm. The UV-vis. spectrum of *peperomia pellucida* extract show a peak in the range of 250 to 700 nm. The formation of AgNP is first evident from the change in colour of the reaction mixture. The addition of *peperomia* extract to silver nitrate solution does not cause any appreciable change in the colour of the solution. The photograph of *peperomia pellucida* plant and that of the reaction mixture before and after microwave irradiation are shown in Figure 1.

(a) (b) (c)

**Figure 1:** Photograph of (a) *peperomia pellucida* plant, (b) reaction mixture containing 1mM $AgNO_3$ and leaf extract before microwave irradiation, and (c) after microwave synthesis

The colour of the reaction mixture gradually changes from colourless to yellowish brown, upon microwave irradiation. The UV-vis. spectrum of the reaction mixture recorded at 30 sec intervals are shown in Figure 2. A peak was observed at about 424 nm after irradiation for 30 sec, the intensity of which increased with increasing reaction time without much change in the wavelength. The microwave synthesis was completed in just 180 sec. The band at 424 nm is due to the surface plasmon resonance (SPR) of silver nanoparticles. The peak is almost symmetrical and there are no peaks in the range of 450-700 nm indicating the absence of silver nanoparticle agglomeration [21]. The SPR band arises due to the collective oscillations of the conduction electrons of nanoparticles in presence of visible light which is highly influenced by shape and size of the nanoparticles [22]. The UV-vis. spectral studies propose that the nanoparticles are uniformly distributed and are more or less spherical in shape. The main attraction of microwave synthesis is that it yields small, uniform sized nanoparticles in much lesser reaction time. The speedy consumption of starting materials reduces the formation of agglomerates in microwave-assisted methods and provides nanoparticles with narrow size distribution.

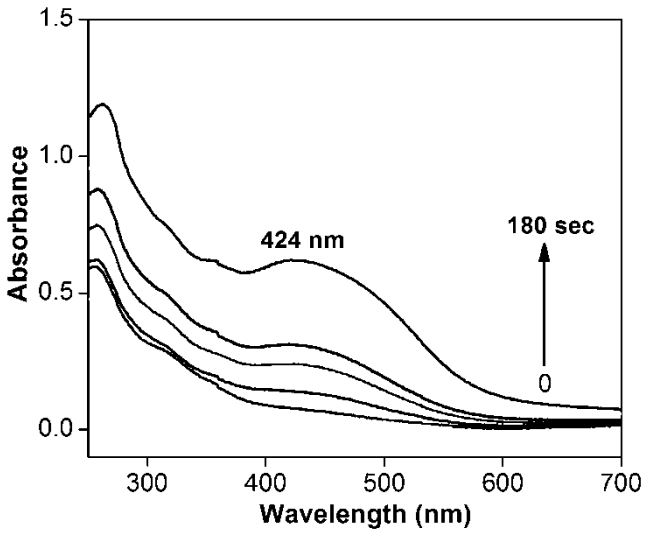


**Figure 2:** UV-vis. absorption spectrum of AgNP- *peperomia pellucida* recorded at different microwave irradiation time

To study the effect of microwave irradiation upon rate of formation of nanoparticle, silver nanoparticles were also synthesized using plant extract at room temperature without microwave irradiation. The UV-vis. spectrum of the reaction medium recorded at 60 min intervals are shown in Figure 3. A peak was observed at 424 nm due to surface plasmon resonance of silver nanoparticles after a reaction time of 1 hour which increased with time till about 240 min of reaction time. This SPR value is higher than that obtained in case of microwave assisted synthesis. It is observed that the SPR band shifts to longer wave length with increasing particle size. Thus, in this synthetic method, microwave assisted synthesis yields relatively small nanoparticles in much less reaction time than room temperature synthesis. This observation is further confirmed by TEM analysis. The reduction of $Ag^+$ ions into Ag and the concomitant formation of stable nanoparticles happened so rapidly within 180 sec in microwave method making this a faster method for nanoparticle synthesis.

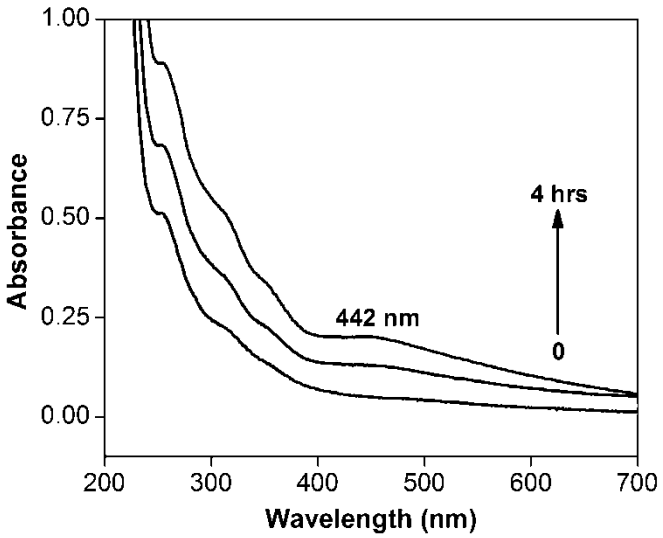


**Figure 3:** UV-vis. spectra of silver nanoparticles at different stages of room temperature synthesis

### 3.3. X-ray diffraction (XRD) analysis

X-ray diffraction studies were conducted to get information about the crystalline nature of silver nanoparticles. Figure 5 shows the X-ray diffraction pattern of AgNP- *peperomia* obtained by microwave method. The XRD image shows four peaks at 2θ values of 38.30º, 44.17º, 64.56º and 77.53º respectively. Comparing this with JCPDS file No. 04-0783, the above peaks can be assigned to (111), (200), (220) and (311) reflections of face centered cubic silver nanoparticles. The X-ray diffraction studies undoubtedly demonstrate that the silver nanoparticles formed in this method are crystalline in nature.

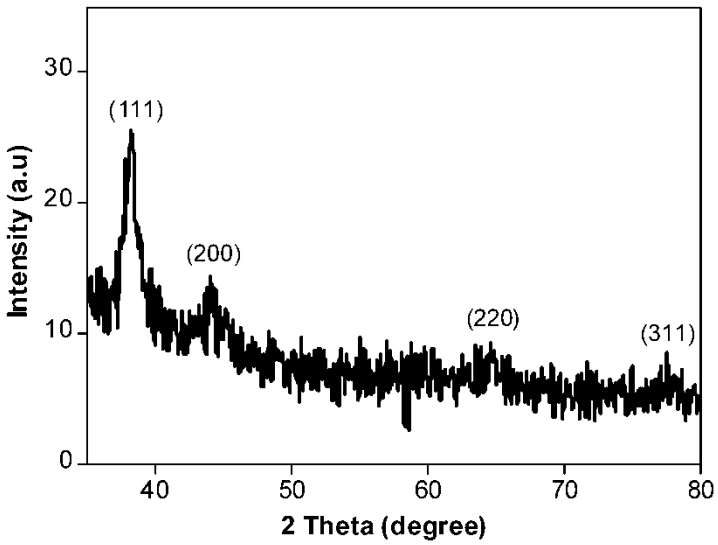


**Figure 5:** XRD pattern of AgNP- *peperomia* synthesized by microwave method

### 3.4. HR-TEM analysis

The size and shape of the synthesized silver nanoparticles were examined using Transmission electron microscopy (TEM) analysis. The TEM images of AgNPs synthesized by microwave method are given in Figure 6. It is clear that the nanoparticles are almost spherical in shape. The particle size distribution histogram drawn after ignoring any tiny particle (Figure 6(b)) shows that the size of the particles comes between 15 to 27 nm and the average particle size is found to be 23.24 ± 4.28 nm. The HR-TEM image (Figure 6(c)) shows clear lattice fringes which indicates that the growth of silver nanoparticles take place preferentially on the (111) plane. The selected area electron diffraction (SAED) pattern (Figure 6(d)) of AgNP- *peperomia* shows circular rings which can be attributed to the face centered cubic structure of silver nanoparticles. The more intense circular ring closer to the centre is due to (111) reflections. The second ring is indexed to the (200) reflections. The third and fourth rings belongs to (220) and (311) reflections respectively. The clear circular rings also suggest that the synthesized silver nanoparticles are polycrystalline in nature.

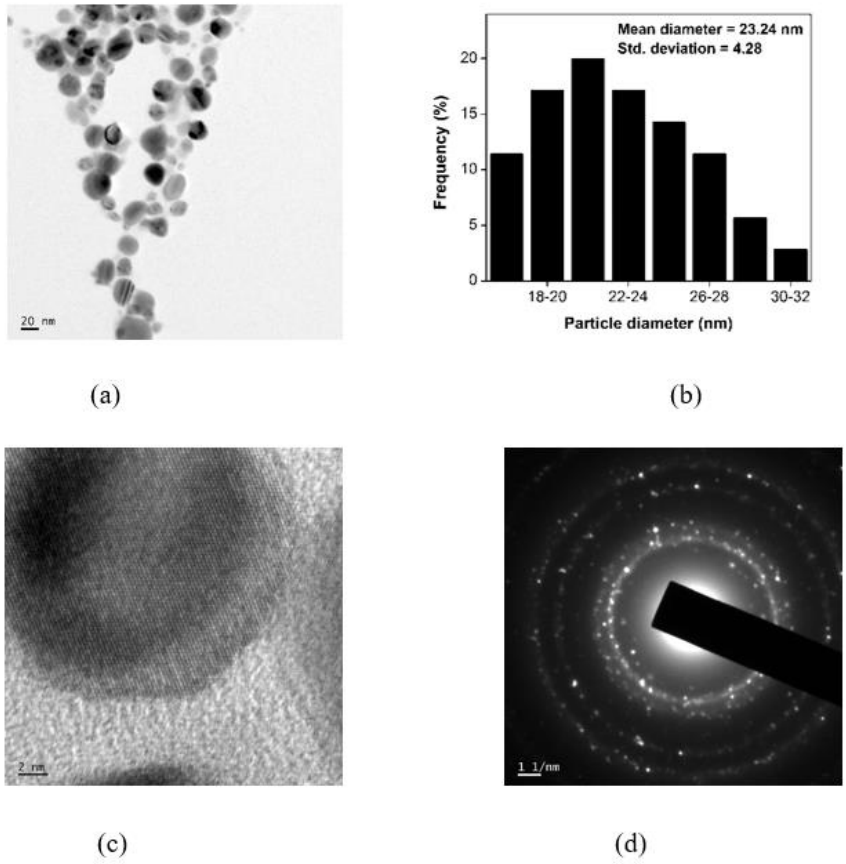


**Figure 6:** The TEM images of AgNP- *peperomia* synthesized by microwave method: (a) image displaying particle distribution, (b) the corresponding particle size distribution histogram, (c) HR-TEM image, and (d) SAED pattern

The TEM images of AgNP- *peperomia* synthesized at room temperature are given in Figure 7. As is evident, the particles obtained in this case are little more aggregated when compared to microwave method. Here, the average size of the nanoparticles is calculated to be 25.60 ± 1.90 nm which is higher than that obtained by microwave method. The results of TEM study are therefore in accordance with UV-vis. spectral study. Thus, in this work, microwave irradiation provides smaller nanoparticles at a faster rate than room temperature synthesis.

### 3.5. Catalytic reduction of methyl orange

The reduction of organic dyes by $NaBH_4$ has often been used for evaluating the catalytic efficiency of metal nanoparticles. A dye is considered to be suitable for catalytic study if it exhibits different colors in the oxidized and reduced forms and also if its absorption maximum does not interfere with the SPR band of metal nanoparticle. Methyl orange is suitable for the catalytic study of silver nanoparticles because its aqueous solution is orange red in colour and upon reduction, it becomes colourless. In addition, the UV-vis spectrum of methyl orange shows strong absorptions in the range of 200-600 nm with $\lambda_{max}$ at 464 nm which is separated from the surface plasmon absorption of silver nanoparticles. The absorption maximum at 464 nm is due to the presence of azo group. The reduction of methyl orange by $NaBH_4$ in the absence of silver nano catalyst is negligibly slow which is evident from the observation that the intensity of the peak remains nearly unchanged for several hours in its absence. On the other hand, a change in peak intensity as well as fading of the colour of methyl orange was observed immediately after the addition of the catalyst indicating the enhancement in reaction rate in presence of the catalyst. The kinetics of this reaction was studied spectrophotometrically by monitoring the absorption peak at 464 nm. The UV-vis. spectra recorded in an interval of one minute during the reduction of methyl orange catalyzed by 0.02 mg/mL AgNP- *peperomia* synthesized by microwave method at 26°C is given in Figure 8.

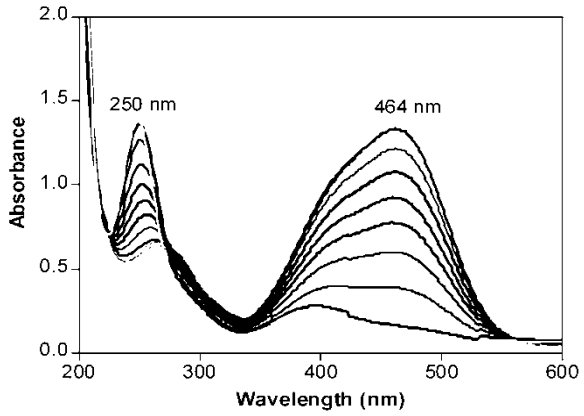


**Figure 8:** UV-vis. absorption spectra for the reduction of methyl orange catalyzed by 0.02 mg/mL AgNP- *peperomia* measured at an interval of 1 min

As is evident from Figure 8, the UV-vis. spectrum of methyl orange has absorptions at 464 nm and 264 nm respectively. The absorbance of the peak at 464 nm was found to decrease with time. At the same time, a new peak appeared at 250 nm whose intensity increased with time. The reaction was completed in 11 min as was evident from almost zero absorption at 464 nm. After completion of the reaction, an absorption band was observed at 396 nm. This is believed to be the SPR band of nano silver. At intermediate stages of the reaction, this weak band is not observed as this peak is covered by the strong absorption band of methyl orange which extends over the range of 350-600 nm. But the SPR band is blue shifted from 417 nm to 396 nm. This is because during the reduction process, the $BH_4^-$ ions relay electrons to the surface of the catalyst resulting in its modification. The main steps involved in this catalytic reaction are: (a) the diffusion and adsorption of the electron donor borohydride ion and the electron acceptor methyl orange on the surface of AgNP catalyst, (b) the electron transfer between them, and (c) the diffusion of reaction products away from the catalyst surface. The capping agents surrounding the nanoparticles help the first step by attracting the reactants closer to the catalyst surface. The nanocatalyst plays the role of a moderator by passing on electrons from the donor to the acceptor. Since the amount of $NaBH_4$ used in this reaction is much higher than that of methyl orange, its concentration remains practically constant during the reaction and hence the reaction may be considered to follow pseudo-first order kinetics. So, the rate equation may be written as $k = 1/t \ln [A_o] / [A]$, where k is pseudo-first order rate constant, $[A_o]$ is the initial concentration of methyl orange and [A] is the concentration at 't' time. Figure 9 shows the plots of ln [A] versus time obtained by using different amounts of AgNP- *peperomia* catalyst. The good linear correlation between the variables reveals that the reaction strictly follows pseudo-first order kinetics. Also, it is evident that the reaction rate increases with increase in the amount of catalyst. A small induction time was observed for all the reactions studied when carried out under air and this was found to decrease with increasing amount of the catalyst

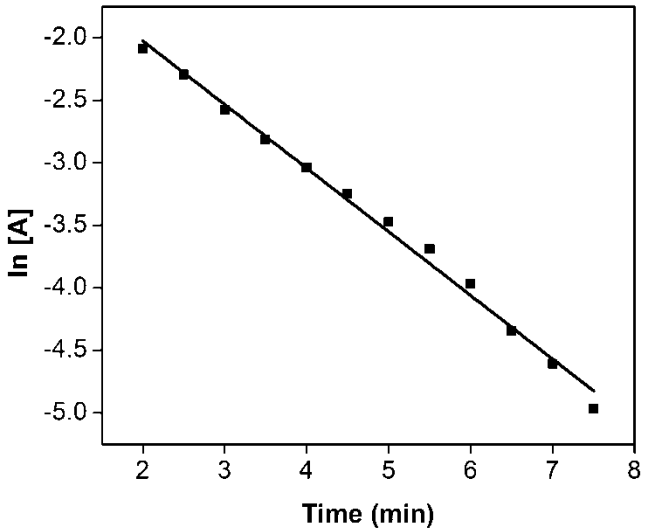


**Figure 9:** Plots of ln [A] versus time for the reduction of methyl orange by $NaBH_4$ using different amount of the catalyst at 26°C

The first order rate constants (k) obtained from the slope of the above linear plots is given in Table 1. It is apparent that the pseudo-first order rate constants increases with increase in amount of the catalyst.

**Table 1**: Catalytic activity of AgNP- *peperomia* for the reduction of methyl orange

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| Amount of AgNP (mg/ml) | Reaction time min) | k ($min^{-1}$) | Correlation coefficient ($R^2$) |
|---|---|---|---|
| 0.01 | 13 | 0.3550 | 0.9976 |
| 0.02 | 11 | 0.3884 | 0.9990 |
| 0.03 | 10 | 0.4229 | 0.9980 |
| 0.04 | 8 | 0.4553 | 0.9943 |

## IV. CONCLUSIONS

In the present study, we have reported a simple, fast, environmentally benign and economic method for the synthesis of silver nanoparticles. Here, silver nanoparticles have been produced by a bio mediated microwave assisted synthetic route using the leaf extract of *peperomia pellucida* as both the reducing and stabilizing agent. They have also been produced at room temperature without the assistance of microwave radiation and it is found that microwave method yields smaller nanoparticles in much lesser reaction time. The formation of silver nanoparticles is confirmed by UV-vis., FTIR, XRD and HR-TEM techniques. The catalytic activity of the synthesized nanoparticles is studied using the reduction reaction of methyl orange by $NaBH_4$. The catalyst exhibits remarkable catalytic activity for this reaction.

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