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AN UNDEMANDING METHOD OF SYNTHESIS OF GOLD NANOPARTICLES USING *PISONIA GRANDIS* (R. Br.)

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Gold nanoparticles were synthesized using the ethanol extract of leaves of *Pisonia grandis* by four physical techniques. The completion and formation of gold nanoparticles was analyzed by UV- visible spectroscopy. The synthesized gold nanoparticles were characterized by XRD, Scherrer's equation, SEM and FTIR analysis. The concentration, time and method of synthesis play a vital role in the kinetics of gold nanoparticles. The size and shape of nanogold that varied under different conditions explains the uniqueness of the method. The results of the study revealed the formation of gold nanoparticles of size ranging from 20 to 90 nm with 2 mg of extract and 1 mg of gold chloride at room temperature.

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Keywords: *Pisonia grandis*; UV- visible spectroscopy; XRD; SEM; Scherrer's equation; Microwave

1. Introduction

The outstretched growing power of nanotechnology provokes the interdisciplinary field in the betterment of smart materials, therapeutics, alternate energy sources, environmental remuneration and also in several other diverse fields [1]. In modern development of drugs, gold nanoparticles have attracted significant attention in research and sound discovery. Nanogold serves as a resourceful agent in thermo ablation, radiotherapy and drug and gene delivery [2]. In 1970's itself, the "immunogold" exposed applications in biological imaging. The AuNPs-DNA conjugates nanoscaffolds were reported by Mirkin's and Alivisatos' groups in 1996 [3].

Nanoscale particles of gold possess red, blue, or other colors depending upon their nature, size, shape, degree of aggregation and the nature or type of reducing agents used in the study. These visible wide ranges of colors reflect the underlying coherent oscillations of conduction-band electrons (plasmons) upon irradiation with appropriate wavelength of light. The intense absorption and elastic scattering of light were due to this plasmon, which in turn forms the root for many biological sensing and imaging applications of gold nanoparticles [4-6]. Nanogold have found far-reaching applications in life sciences and attracted noteworthy research interests [7].

At present, there is a growing need to develop environmentally benign synthesis of nanoparticles that prevents the use of toxic chemicals to implement green chemistry. The significant aspect of nanotechnology is the development of synthesis of metal nanoparticles is a big confront. The secrets gleaned from nature have led to the development of biomimetic approaches in the growth of advanced nano biomaterials. In many biotechnological applications microorganisms, such as bacteria, fungi and yeast are employed instead of toxic metals. Recently, material scientists have proposed plant extracts as possible eco-friendly nanofactories, for the synthesis of nanoparticles using metals like gold and silver [8].

In this paper, we reported the synthesis of gold nanoparticles using the aqueous solution of ethanol extract of leaves of *Pisonia grandis* and thereby enhancing green nanotechnology.

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2. Materials and Methods

2.1 Preparation of the extract

The leaf ethanol extract (200 mg) of *Pisonia grandis* was weighed and sonicated with 100 ml of water. The soluble portion of the extract was filtered through Whatmann filter paper to get aqueous extract.

2.2 Synthesis of gold nanoparticles

Gold chloride solution (1 ml) was treated with different volumes of plant extract (1 ml, 2 ml, 3 ml, 4 ml and 5 ml) and kept at i) room temperature ii) an elevated temperature (75-80 °C) iii) sonication (Ultrasonics 1.5L (H)) iv) Microwave conditions (Microwave Oven (LG)). A visible transition of colour from yellow to violet indicative of gold nanoparticles formation was noted. The nanogold solutions were centrifuged (Spectrofuge 7M) and characterized to arrive at the size and shape.

2.3 Characterization of gold nanoparticles

The prepared nanogold was characterized by UV-visible spectroscopy, X-ray diffraction analysis, FTIR analysis and scanning electron microscopy.

2.4 UV- visible and FTIR spectroscopy

The formation of nanogold shows visible colour change and was monitored by UV-visible spectroscopy (Double beam spectrophotometer – 2202, SYSTRONICS). The FTIR spectra were recorded in the 4000 to 400 cm^{-1} on a Shimadzu FTIR–8400S spectrophotometer.

2.5 XRD analysis

The X-ray diffractometer analysis (SHIMADZU Lab X XRD-6000) was used to analyze the size and shape of the gold nanoparticles. The crystalline size of the nanoparticle can also be determined using Debye – Scherrer's equation is given below

$$D = k\lambda / \beta \cos \theta$$

D – average crystalline size (nm)
k – dimensionless shape factor (0.9)
λ – X-ray wavelength (1.541 Å)
β – angular / line broadening at FWHM of the XRD peak at the diffraction angle
θ – diffraction angle (degrees)

2.1. Scanning Electron Microscopy

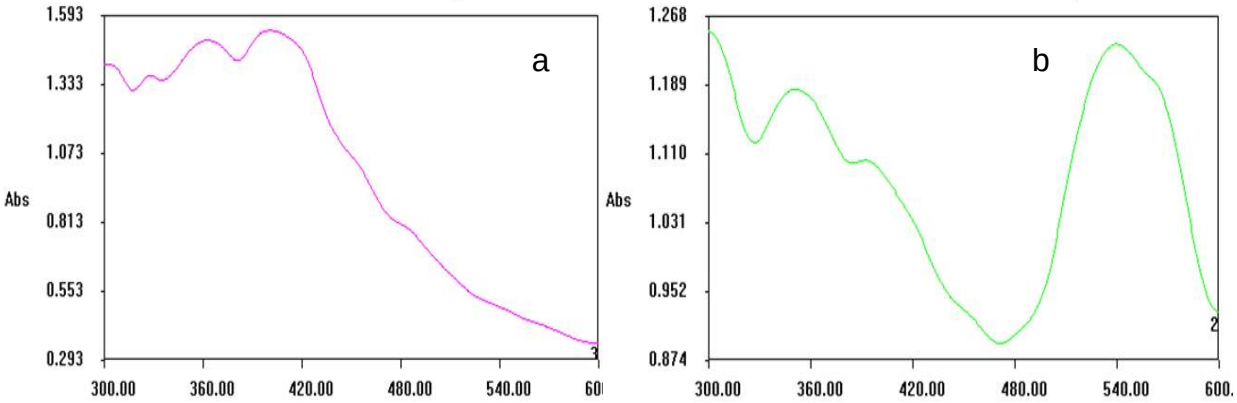
The morphology of the synthesized nanogold was characterized by Scanning electron Microscopy (TESCAN) with Vega TC software for the synthesized AuNP's fabricated on a glass substrate.

3. Results and discussion

Different concentrations of aqueous solution of leaf ethanol extract of *Pisonia grandis* was treated with 1ml of gold chloride solution in the ratio (1:1, 2:1, 3:1, 4:1 and 5:1) at room temperature, elevated temperature (75-80 ºC) and sonication. In Microwave conditions, the 1:1 ratio was optimized by increasing the microwave energy (160, 320, 480, 640 & 800 Watt). In room temperature, the yellow solution changed to violet colour after 60 min indicating the formation of nanogold particles. The formation of gold nanoparticles gets completed in 30 min at higher temperature whereas sonication results within 20 min. In microwave heating gold nanoparticles formed within few seconds.

The UV- visible absorption spectra shows an absorption band at 539 nm which resemble the surface plasmon resonance band (SPR) of gold nanoparticles, whereas this band is absent in aqueous extract of *Pisonia grandis* as shown in figure 1. When the frequency of the electromagnetic field is resonant with the coherent electron motion, a strong absorption band in the visible region around 520 nm in the spectrum is observed for gold nanoparticles, which is called surface plasmon resonance absorption. An electric field interaction results in the polarization of

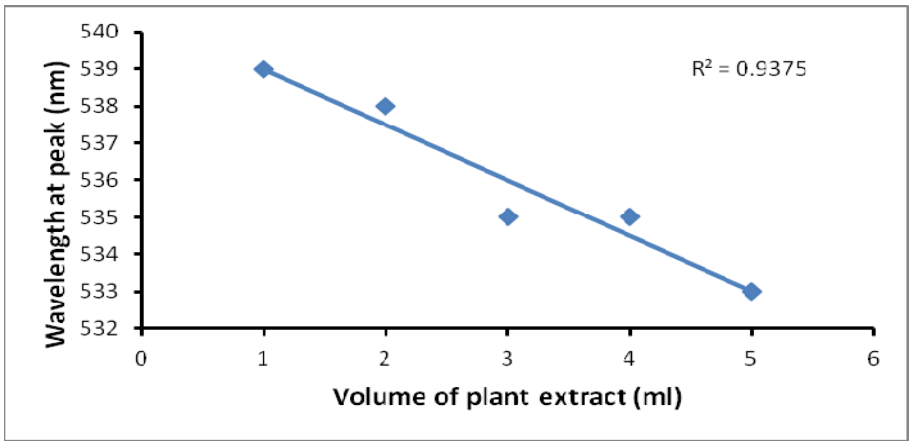
the electrons with respect to the ionic core of a nanoparticle which induce the dipole oscillations of the free electrons, so-called surface plasmon absorption.



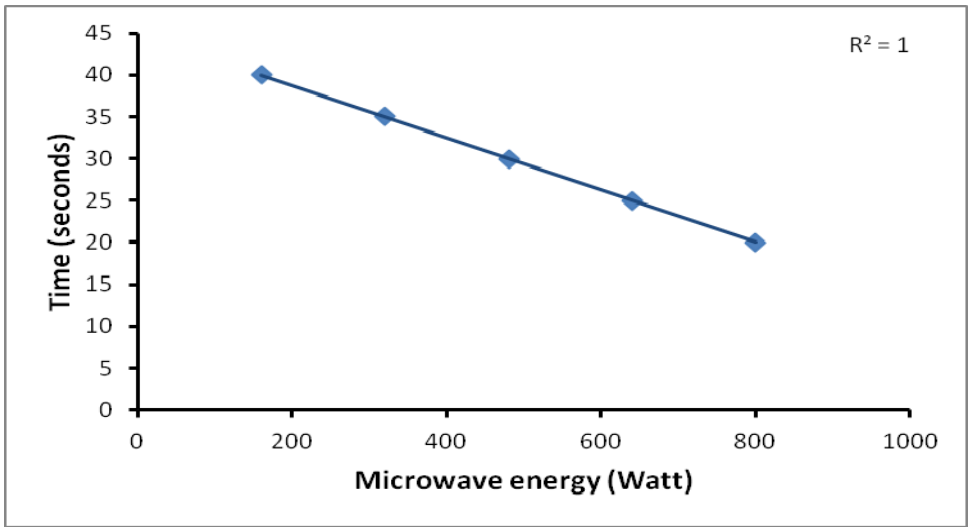
Fig, 1. UV-visible absorption spectra of aqueous solution of leaf ethanol extract of Pisonia grandis (a) and synthesized gold nanoparticles (b)

After the formation of nanogold the solutions were centrifuged. Nanogold was found to form with 1ml of plant extract. On comparing the four completely different conditions for the formation of nanoparticles, two SPR bands were discovered at 520 nm and 564 nm in room and higher temperature conditions. In sonication and Microwave conditions, one SPR band was found at 539 nm and 546 nm respectively. The microwave and sonication assisted synthesis was found to extend the mechanism of the gold nanoparticles. This might flow from to high dispersion in sonication and enhancing product purities by reducing unwanted facet reactions in Microwave condition. These accelerate the reaction rates thereby generating purity in product compared to traditional ways. An analysis of the chemical constituents of *Pisonia grandis* revealed that it is rich in two molecules namely Allantoin and Pinitol [9,10] which might have aided in the formation of gold nanoparticles. The probable method of reduction mechanism of pinitol and allantoin with silver nitrate producing silver nanoparticles is reported [11].

The plot between the volume of plant extract and its wavelength is shown in figure 2. Figure 2 reveals that the wavelength of the synthesized nanogold decreases as the volume of the aqueous solution of leaf ethanol extract of *Pisonia grandis* increases. This may be due to the presence of more reducing phytoconstituents in higher concentration of extract which results in an additional interaction between the surface capping molecules and secondary reduction process obtained through high dispersion in sonication process.



Fig, 2. Plot of λmax values against volume of aqueous solution of Pisonia grandis by sonication method



Fig, 3. Plot of values of microwave energy against time of completion of gold nanoparticles by Microwave method.

The plot between microwave energy and time of completion of gold nanoparticles is shown in figure 3. From this plot, it confirms that the complete formation of nanogold takes place within few seconds as the microwave energy increases. The absorbance at λmax values increases as the time taken for the completion of the reaction decreases is shown in figure 4. This may be due to the polar molecules in the system absorbs extra microwave radiation which fasten the formation of nanogold. The AuNP's will partially agglomerated as the microwave energy increases and shift the λmax value within few seconds.

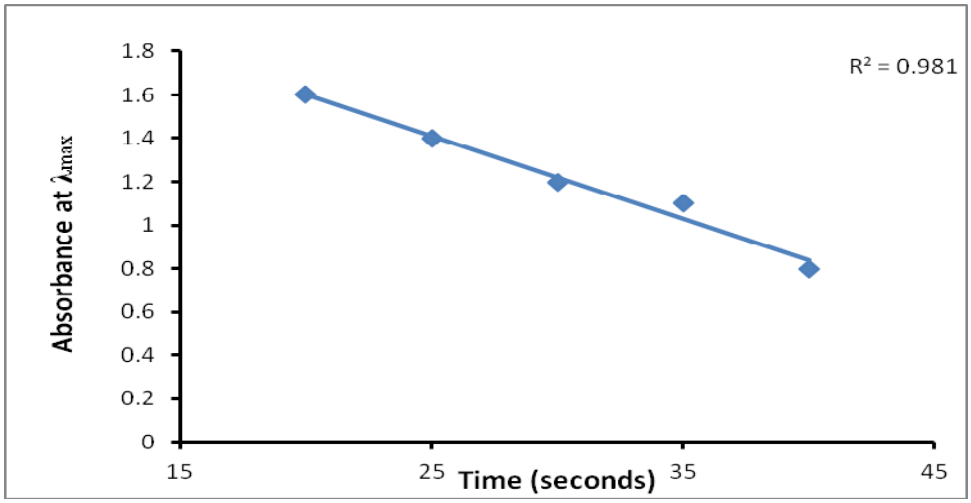


Fig. 4. Plot of time of completion of AuNP's against absorbance for λmax values in Microwave method.

The XRD spectra of the synthesized nanogold using the aqueous solution of leaf ethanol extract of *Pisonia grandis* is shown in figure 5. The XRD patterns showed an intense and sharp peak at 2θ = 38.18º and other peaks at 44.23º, 64.71º, 77.78º which may be indexed to (111), (200), (220), (311) hkl planes respectively (figure 5(a)). The above indexed Bragg's reflection resembles the cubic structures of gold nanoparticles in room temperature condition.

Fig. 5(b) represents the XRD patterns of synthesized nanogold obtained under microwave condition. The Bragg's peaks at (111), (200), (220) and (311) revealed the formation of face centered cubic structure of gold nanoparticles. The particle size of the synthesized nanogold was calculated by Debye – Scherrer's equation is given in table 1. The average particle size of gold

nanoparticles is 22.36 nm and 18.88 nm obtained in room temperature and Microwave method respectively.

Table 1: Determination of crystalline size of AuNP's using Debye-Scherrer's equation

S.No	2θ (degrees)	FWHM (degrees)	t = 0.9l / β. Cosθ (nm)
Room temperature			
1.	38.18	0.1673	50.29
2.	44.23	0.8029	10.69
3.	64.71	0.5353	17.58
4.	77.78	0.9368	10.91
Microwave method			
5.	38.21	0.2342	35.93
6.	44.30	0.6691	12.84
7.	64.59	0.6691	14.07
8.	77.65	0.8029	12.71

The shape and size of synthesized gold nanoparticles were also confirmed by Scanning Electron Microscope analysis. The SEM micrograph shows the formation of spherical gold nanoparticles under room temperature and sonication conditions (figure 6a & 6b). The size of the synthesized nanogold differs in each condition. The particle size of nanogold obtained under room temperature is 60-70 nm whereas in sonication the size is 80-90 nm.

In Microwave condition (Fig. 6(c)), different sizes and shapes of nanogold were observed. The reason is microwave energy can enhance the formation, shape and size of gold nanoparticles during synthesis within few seconds. The nanogold possess spherical, rod and triangular shape of size varied from 90-150 nm. This indicates that the leaf ethanol extract of aqueous solution of *Pisonia grandis* acts as reducing as well as capping agents.

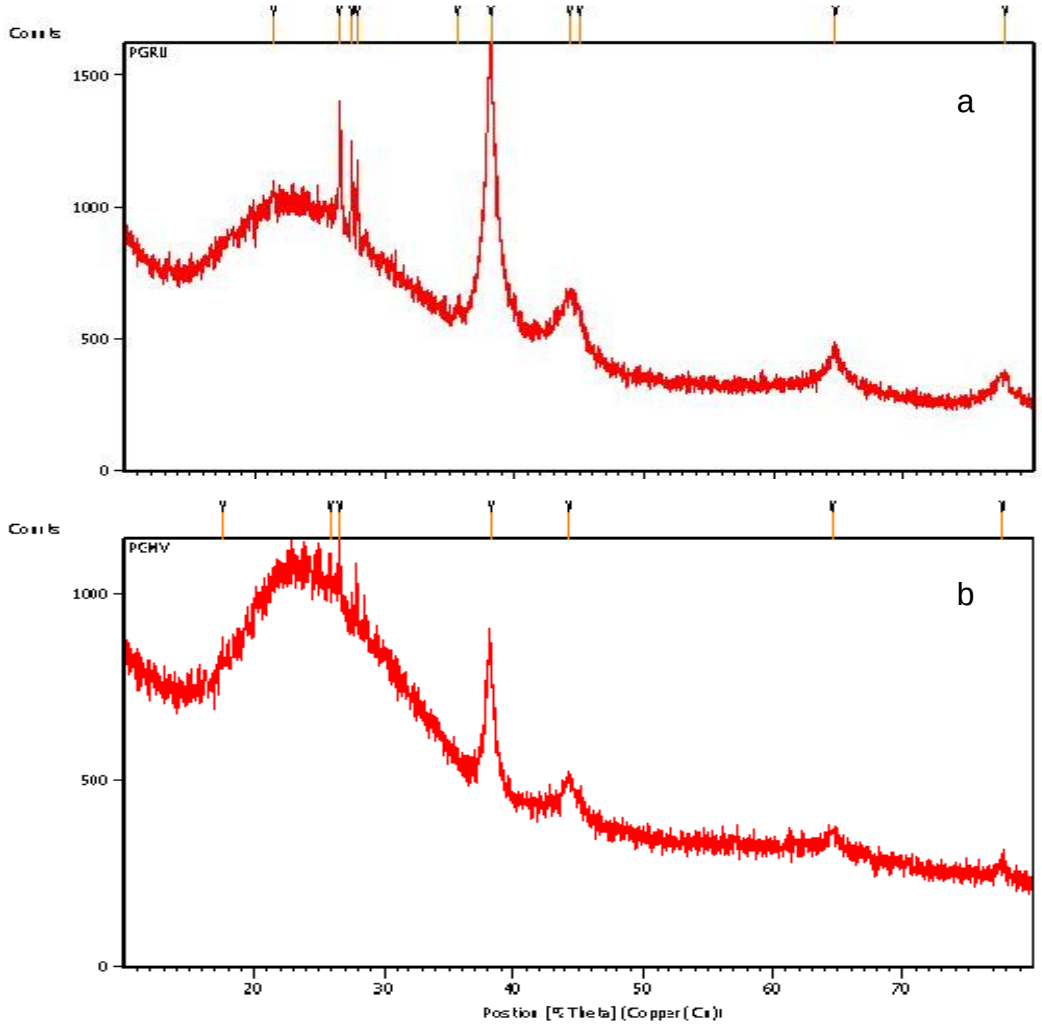


Fig. 5. XRD spectra of gold nanoparticles using Pisonia grandis under room temperature (a) and microwave conditions (b)

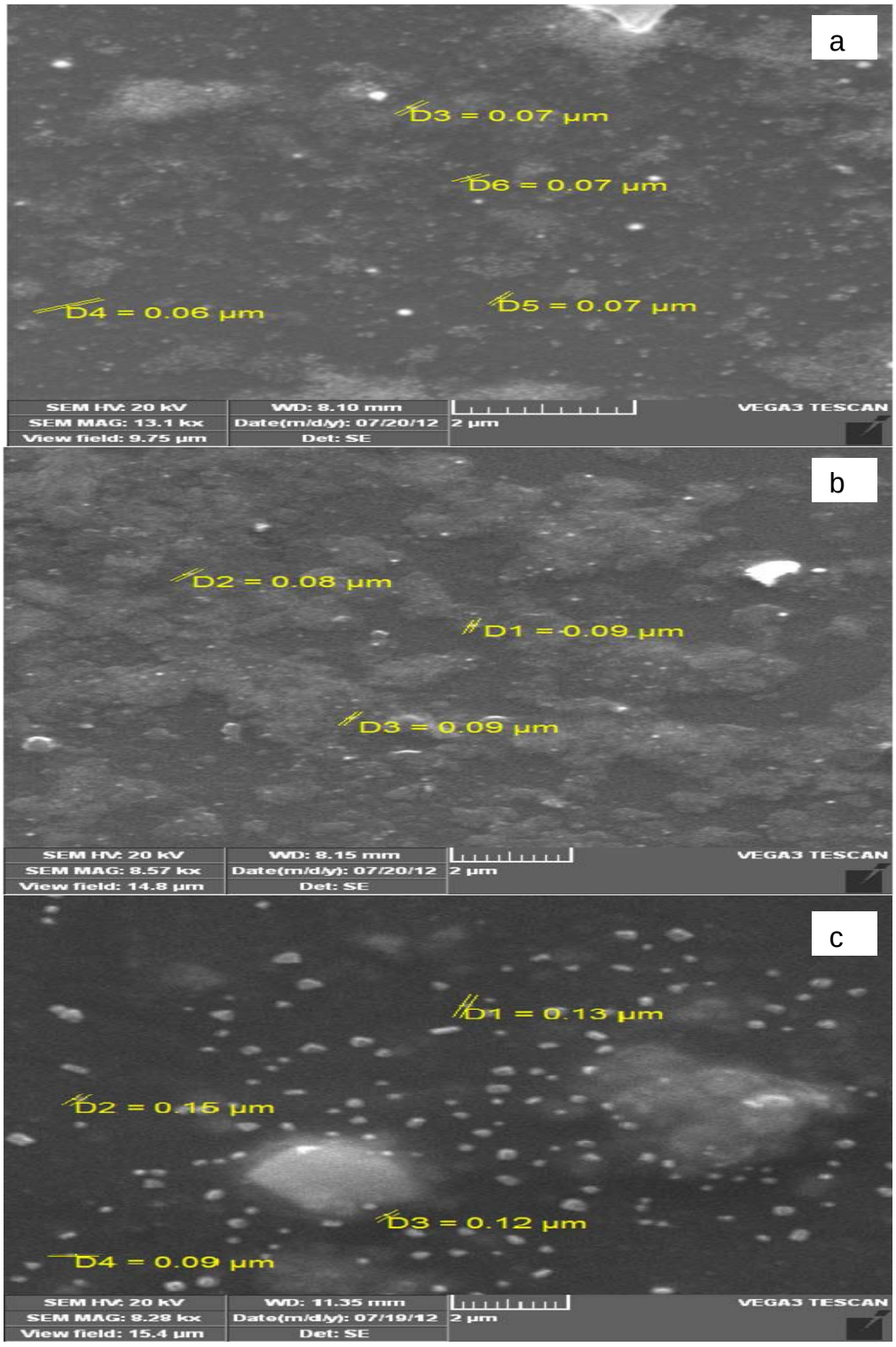


Fig. 6. SEM micrograph of synthesized nanogold obtained from room temperature (a), sonication (b) and Microwave method (c)

The FTIR spectra of aqueous solution of leaf ethanol extract of pisonia grandis and synthesized gold nanoparticles is shown in figure 7 (a&b). The band at 1646 cm^{-1} may be due to the presence of amide bond (fig 7a). The two bands at 2976 cm^{-1} and 3361 cm^{-1} corresponds to the stretching vibrations of the primary and secondary amines respectively (fig 7a). The bands seen at 1044 cm^{-1} and 1383 cm^{-1} were assigned to the C–N stretching frequencies. In fig 7b, the absence

and shift of the aforesaid bands indicates that the metabolites like allantoin and pinitol might have been responsible for the reduction of gold to nanogold.

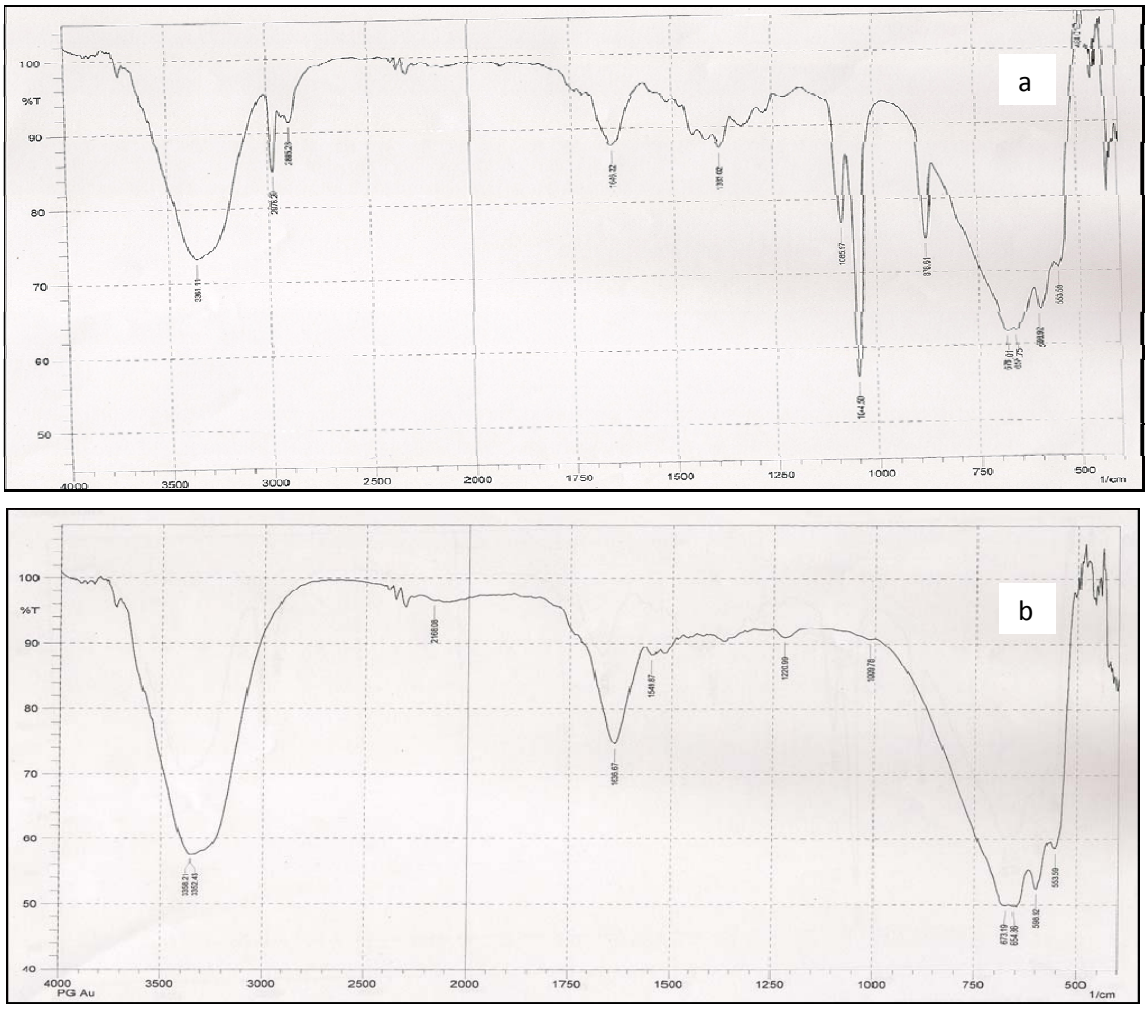


Fig. 7. FTIR spectra of aqueous solution of leaf ethanol extract of Pisonia grandis (a) and synthesized gold nanoparticles (b).

4. Conclusion

The rapid synthesis of nanogold can be achieved in few seconds (20 s) with small quantities (1 ml) of gold chloride solution by Microwave method (800 W) which insists short reaction time with high purity gold nanoparticles synthesis. The kinetics in the synthesis of gold nanoparticles using the aqueous solution of leaf ethanol extract of *Pisonia grandis* depends on the concentration, time and method of synthesis. The phytoconstituents like pinitol and allantoin may be probably be responsible for the reduction of gold to nanogold. The XRD and SEM analysis confirmed the particle size of gold nanoparticles to range between 20 – 150 nm. Thus a simplistic method of synthesis overcomes the traditional chemical production and proves to pave a flourishing pathway towards greener nanotechnology.

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