

Green Synthesis of Gold Nanoparticles from Extract of *Origanum majorana* L

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Abstract

The facile synthesis of ultra stable gold nanoparticles (GNPSs) is demonstrated using extract of *Origanum majorana* L. The best parameters for the synthesis of gold nanoparticles were PH and concentration, the absorption increases with increasing PH from 4.3 to 6 and from PH=7 to 9.5 the absorption decreases. The PH of the reaction medium gives AUNPs nanoparticles of different shapes . At low concentration of extract give different nanostructure while at higher concentration the nanoparticles are capped with the extract constituents and only spherical particles exist. The results were verified using UV-VIS spectroscopy, XRD, TEM, FTIR spectra, , the TEM images showed that a mixture of shapes (triangle, spherical and hexagonal).

1 Introduction:

the synthesis of nanogold using *Origanum majorana* L extract as mild reducing agent and capping material. And studying use of water extract of this plant as reducing agent (anti-oxidant) and its ability to convert Au^{3+} to Au^0 nanogold will be investigated.

Origanum majorana L is an aromatic perennial belong to Lamiaceae family, have been heralded for their medicinal and nutritional value for thousands of years. The original home of it, is the south-east of the Mediterranean , it is also grown in Germany and is used as a spice. The *Origanum majorana* L contain many flavonoids, hydroquinone glycosides, caffeic acid derivatives and triterpenes.

Several studies reported that extracts of *Origanum majorana* L had high antioxidant capacity {(Shan et al. 2005)-(Hassain et al. 20)} mostly due to the polyphenolic compounds present in them. A total of 31 polyphenols were identified in *Origanum majorana* in a previous study (Hassain et al. 2010).

The *Origanum majorana* L has carminative, antispasmodic, diaphoretic, and diuretic properties {(Price 1995),(Bruneton et al. 1999)}. It contains up to 3% volatile oil, flavonoid, glycosides, tannins, steroids (e.g., β -sitosterol), triterpenoids (oleanolic acid and ursolic

acid{(Leung et al. 1996),(Vagi et al. 2002)} and phenolic compounds. The phenolic compounds are referred as antioxidative in nature{(Abdel-Aal et al. 2006)-(Zawistowski et al.2003)}.

In this work, we have designed a simple and green synthetic route for the rapid production of gold nanoparticles employing a renewable, biodegradable, non-toxic natural extract from the *Origanum majorana* L. The synthesis was carried out in environmentally, biologically benign aqueous medium at ambient temperature and pressure; without using any form of external energy and chemical reducing and stabilizing agents.

2. Experimental:

2.1 Materials:

The leaf extract was prepared by boiling 2.0g of plant broth for 15 min, filtered with Whatman No 1 filter paper and completed to 100 ml. The prepared extract of *Origanum* 2% that used as reducing agent were stored in the dark at 4 °C to be used within one week. A stock solution of HAuCl_4 was prepared by dissolving 1.0 g $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 100 ml deionized water (2.5×10^{-2} M).

2.2 Instrumentation:

The Uv-vis spectra were recorded at room temperature using a λ -Helios SP Pye-Unicam spectrophotometer with samples in quartz cuvettes. Photoluminescence spectra were recorded on a Perkin Elmer LS 50B luminescence spectrophotometer.

Transmission electron microscopy (TEM) studies were performed using a JEOL-JEM 1200 electron microscope operating at an accelerating voltage of 90 KV. For the TEM measurements, a drop of a solution containing the particles was deposited on a copper grid covered with amorphous carbon. After allowing the film to stand for 2 minutes, the extra solution was removed by means of blotting paper and the grid allowed drying before the measurement. Fourier transform infrared (FTIR) spectra were recorded at room temperature on a Nicolet 6700 FTIR spectrometer. For the FTIR measurements of capped gold nanoparticles, a small amount of gold nanoparticles (0.01g) dried at 60 °C for 4 h was mixed with KBr to form a round disk suitable for FTIR measurements. To obtain the FTIR spectrum of the extract, an appropriate amount of the extract was mixed with KBr.

2.3 Synthesis of gold nanoparticles:

For the synthesis of the gold nanoparticles, a certain volume of the *origanum majorana L* extract (0.1-5) ml of 2% solution was added to the 0.05 ml $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution and the volume was adjusted to 10 ml with de-ionized water. The final concentration of Au^{3+} was 1.25×10^{-4} M. The reduction process of Au^{3+} to Au nanoparticles was followed by the change the color of the solution from yellow to violet to dark pink and green depending on the extract concentration. The effect of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ concentration of the particles formation was studied by adding different $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ concentrations (0.01-0.1) ml of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to 2ml extract 2% solution and the volume was adjusted to 10ml (2.5×10^{-5} - 2.5×10^{-4} M).

The nanoparticles prepared at different pH values, the pH of the solutions (1.3×10^{-4} M AuCl_4^- and 2ml extract in 10ml flask) were adjusted using 0.1N HCl or 0.1N NaOH solutions.

2.4 Effect of pH on the formation and stability of AuNPs using *organum majorana L* extract:

Figure (1) shows the effect of pH on the formation of gold nanoparticles. It can be seen that the absorbance increases with increasing pH from 4.3 to pH 6 with blue shift in the spectra and from pH 7 to 9.5 the absorbance decreased with the spectrum becomes wider. At acidic pH, the particles size is expected to be larger than at the basic pH , as red shift was clearly reported in the SPR spectra (Haiss et al. 2007). This result was confirmed by TEM measurements at pH 4.3 and pH 8.6, Figure (2). The size of the particles at pH 4.3 was larger with formation of hexagonal structures. Furthermore, the particles formed in acidic medium were unstable and precipitated within 12h while the particles prepared at pH 9.5 was stable for one week at least.

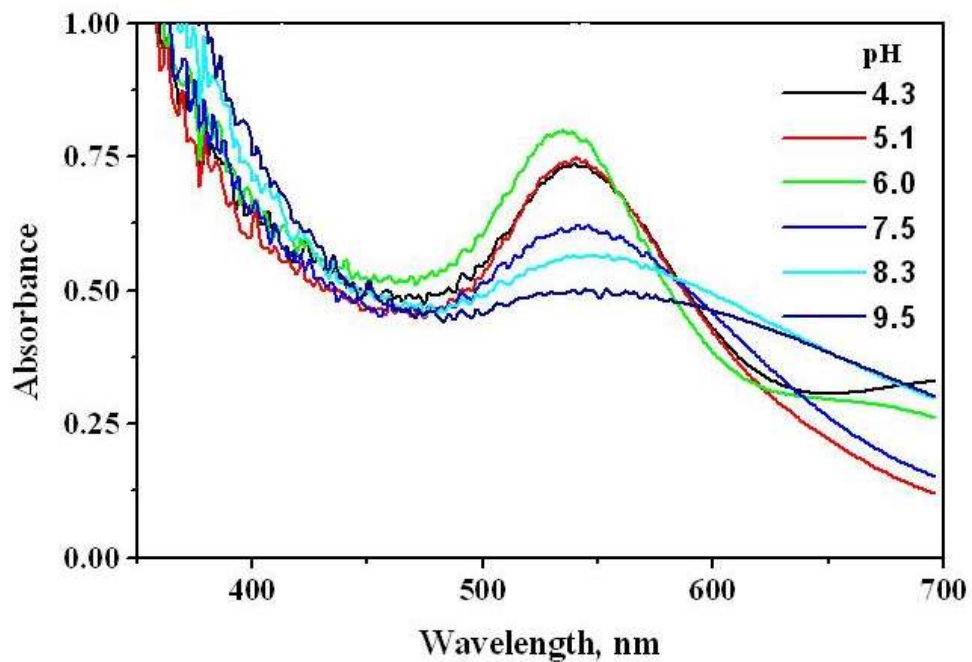


Figure (1): Effect of pH on the formation of AuNPs using origanum majorana L extract.

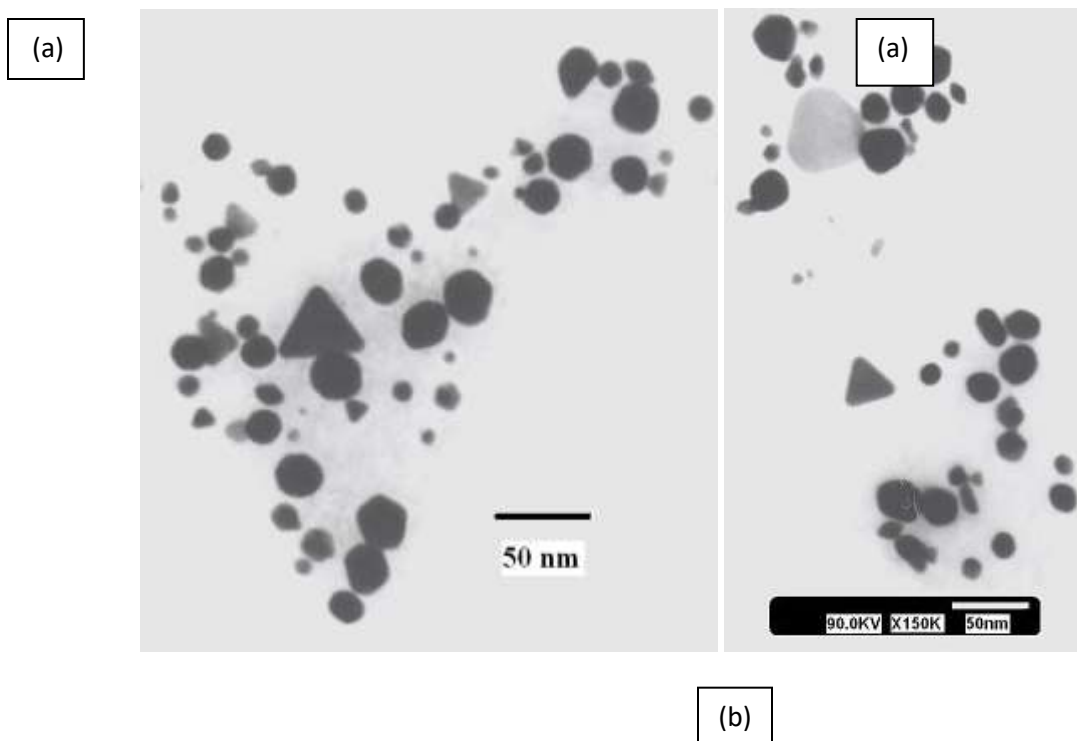




Figure (2): Effect of the pH on the size of the AuNPs (a) pH 4.3, (b) pH 8.6

2.5. Effect of *organum majorana* L concentration:

The Uv-visible spectra of gold nanoparticles formation using constant HAuCl_4 concentration (1.3×10^{-4} M) with different concentrations of extract from 0.1 to 1.6 ml (equivalent to 0.02 to 0.32%) are shown in Figure 3.15. It showed the appearance of strong SPR band absorption peak centered at about 545 nm. Addition of the extract from 0.1 to 0.8 ml leads to increase in the absorption as shown in Figure (3), while addition of the extract from 0.9 to 1.6 ml leads to a slight decrease in the absorption indicating the attainment of the saturation in the bio-reduction of Au^{3+} .

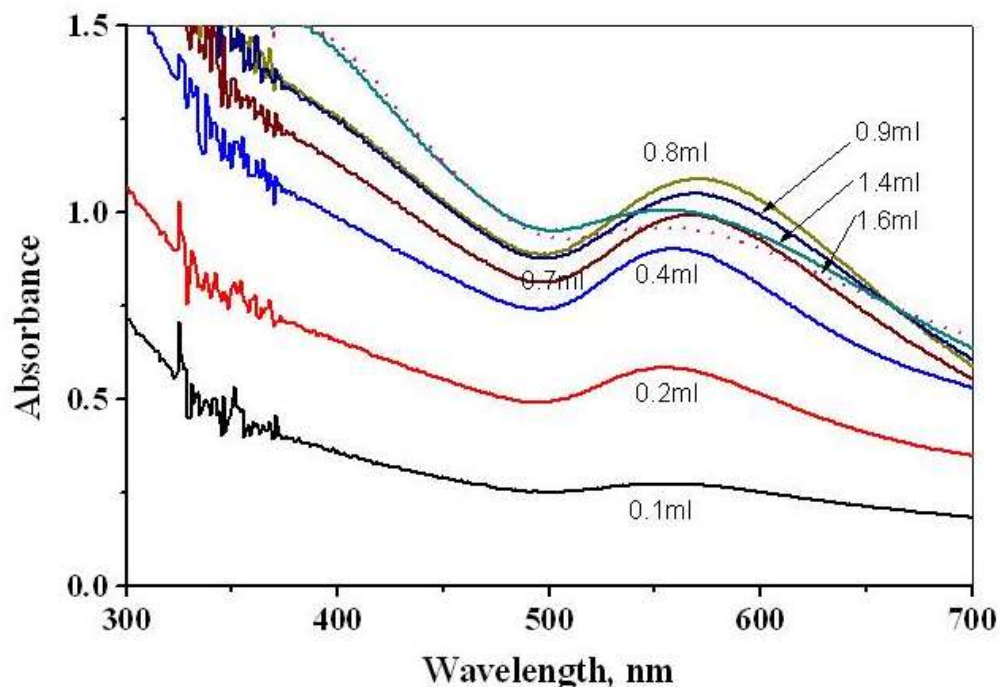
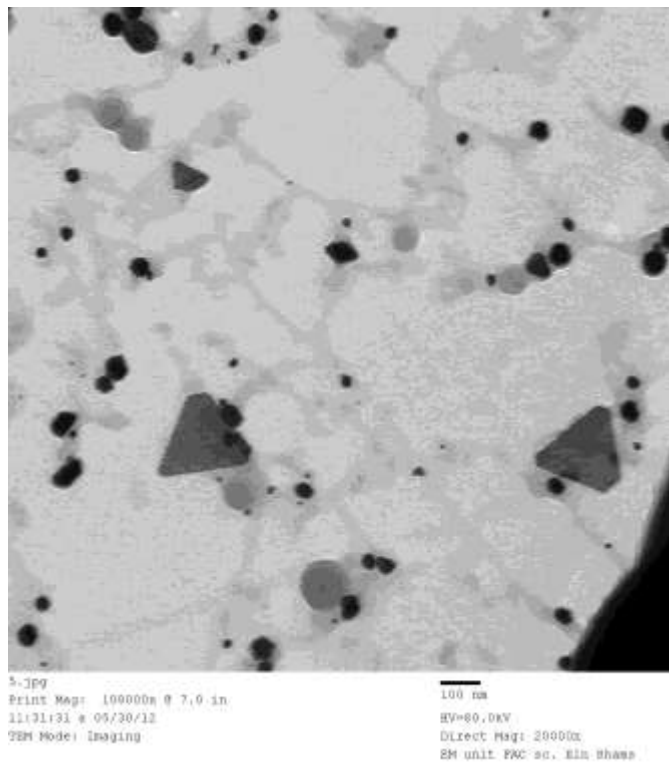


Figure (3): Plasmon resonances of gold nanoparticles reduced by organum majorana L extract

Fig. (4) shows the TEM images of the gold nanoparticles synthesized using different organum majorana L concentrations (A: 0.1%, B: 1%) with 1.25 mM HAuCl₄ at room temperature. As can be seen, a mixture of plate (triangles and pentagons) and spheres was obtained at low concentration while only spherical shapes were obtained at high concentration.

2.6. Effect of Au³⁺ concentration:

Figure (5) shows the effect of increasing the gold ions concentration on the formation of the AuNPs using 2ml extract. With increase in the concentration of the metal ion from 2.5×10^{-6} to 3.05×10^{-5} M, increase in particle size was found as clear from the shift of the maximum wavelength to longer wavelengths



(a)

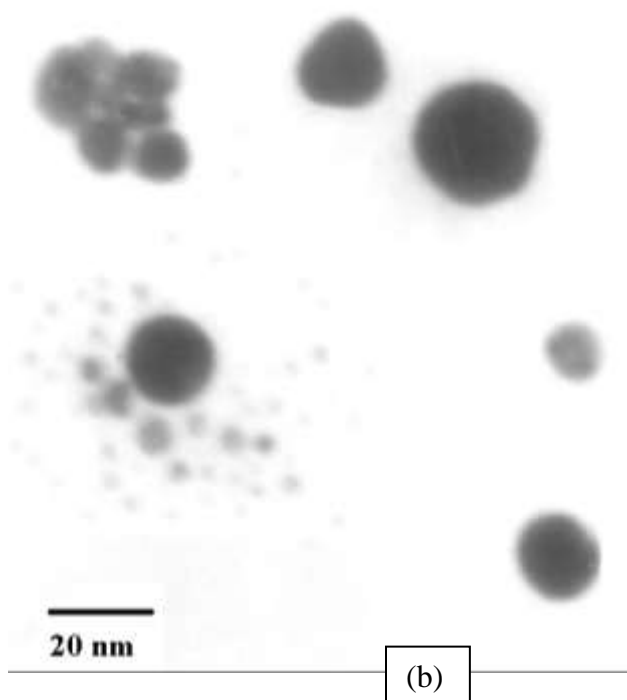


Figure (4): TEM images of the gold nanoparticles synthesized using different organum majorana L concentrations (a: 0.1%; 0.5ml, b: 1%; 5ml) with 1.25 mM HAuCl_4 at room temperature.

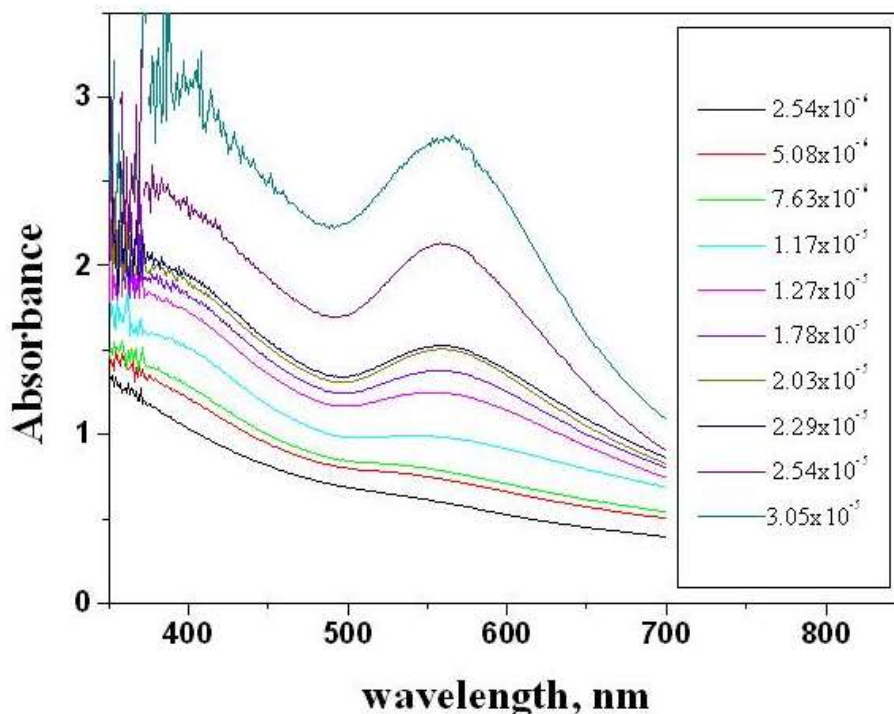


Figure (5): Effect of addition of Au^{3+} to 2ml of the organum majorana L extract.

2.7. XRD of AuNPs produced using organum majorana extract:

The phase of the prepared nanoparticles was investigated by X-ray diffraction technique. The Au NPs synthesized by organum extract showed clear peaks at 38.21 (1 1 1), 44.34 (2 0 0), 64.78 (2 2 0), 77.67 (3 1 1) Fig (6). These peaks coincide well with cubic phases of AuNPs showed in JCPDS No. 03-0921. Thus the XRD pattern proves to be strong evidence in favor of the UV-vis spectra and TEM images for the presence of nanocrystalline Au particles. The broadening of the peaks indirectly represents the smaller size of the nanoparticles (Binupriya, 2010).

2.8. FTIR Spectra:

The FTIR spectra of untreated and treated organum majorana L extract samples containing gold nanoparticles are depicted in Fig. (7). The untreated extract sample show medium or strong absorption bands about at 3313, 2926, 1745, 1654, 1620, 1520, 1390, 1290 and 1110 cm^{-1} . For untreated sample, the absorption bands can be assigned carbonyl peak (C=O stretching) at 1745

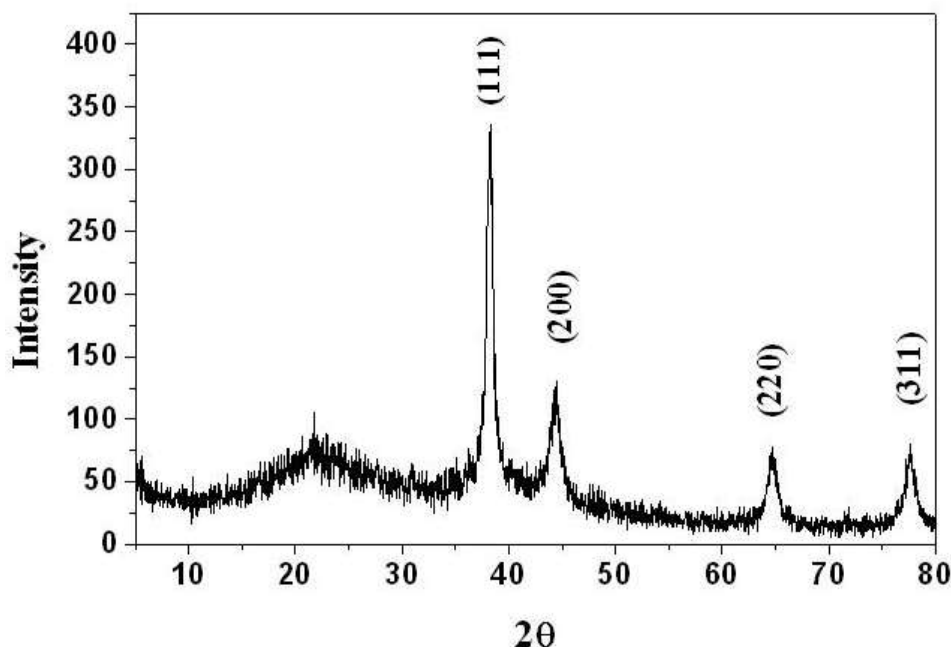


Figure (6): XRD patterns recorded for gold nanoparticles synthesized by treating organum majorana L extract with AuCl_4^- aqueous solutions. The Bragg reflections are indexed on the basis of the fcc gold structure.

cm^{-1} is indicating carboxylate content in plant-based samples, may be from gallic acid and proanthothianidin gallate present in the aqueous organum extract. Bands originating from hydroxy group (from phenolic compounds) at 3313 and 1110cm^{-1} , as well as medium band at 1520cm^{-1} indicating presence of amide/amine groups, as would be expected due to plant-origin of these samples.

Infrared spectra of the gold nanoparticles revealed the medium bands at 1082 , 1380 and strong bands at 1614 and 3413 cm^{-1} (Fig. 7(b)). The band at 1380 cm^{-1} corresponds to C–N stretching vibrations of aromatic amines. The band at 1614 cm^{-1} corresponds to C=O stretching of amide I band and 3413 cm^{-1} corresponds to –NH stretching in amide (II) and 1082 cm^{-1} is characteristic of C–OH stretching of secondary alcohols. The weaker band at 2929 cm^{-1} corresponds to asymmetric stretching of C–H groups. The absorption band corresponding to C=O group at 1745 cm^{-1} in untreated organum is shifted to 1730 cm^{-1} appeared as shoulder. (Shankar et al. 2004a) reported that terpenoids and reducing sugars present in the neem extract were responsible for the stabilization and capping of gold nanoparticles. (Shankar et al. (2004b) demonstrated the synthesis of gold nanoparticles using geranium leaf extract and showed the

oxidation of alcohol groups of terpenoids to carbonyl groups and the presence of amide (III) of proteins during the formation of gold nanoparticles. In the present study, FT-IR spectrum confirmed the presence of aromatic amine, amide (II) groups and secondary alcohols as capping and reducing agents of gold nanoparticles. It was difficult using FT-IR to determine the presence of the antioxidants present in the organum majorana L and their role in the reduction of the gold ions to AuNps.

3.Conclusion:

The high phenolic content of the hot water extract of organum majorana L having strong anti-oxidant properties helped in the reduction of gold cations to Au NPs. The characterization of AuNPs revealed that the morphology of the Au NPs depends on the extract concentration and pH of the used medium. At higher concentration of the extract and basic pH, the pseudo-spherical particles are capped by phytochemicals. This method for AuNP synthesis does not use any toxic reagent and thus has a great potential for the use in biomedical applications and will play an important role in future opto-electronic and biomedical device applications.

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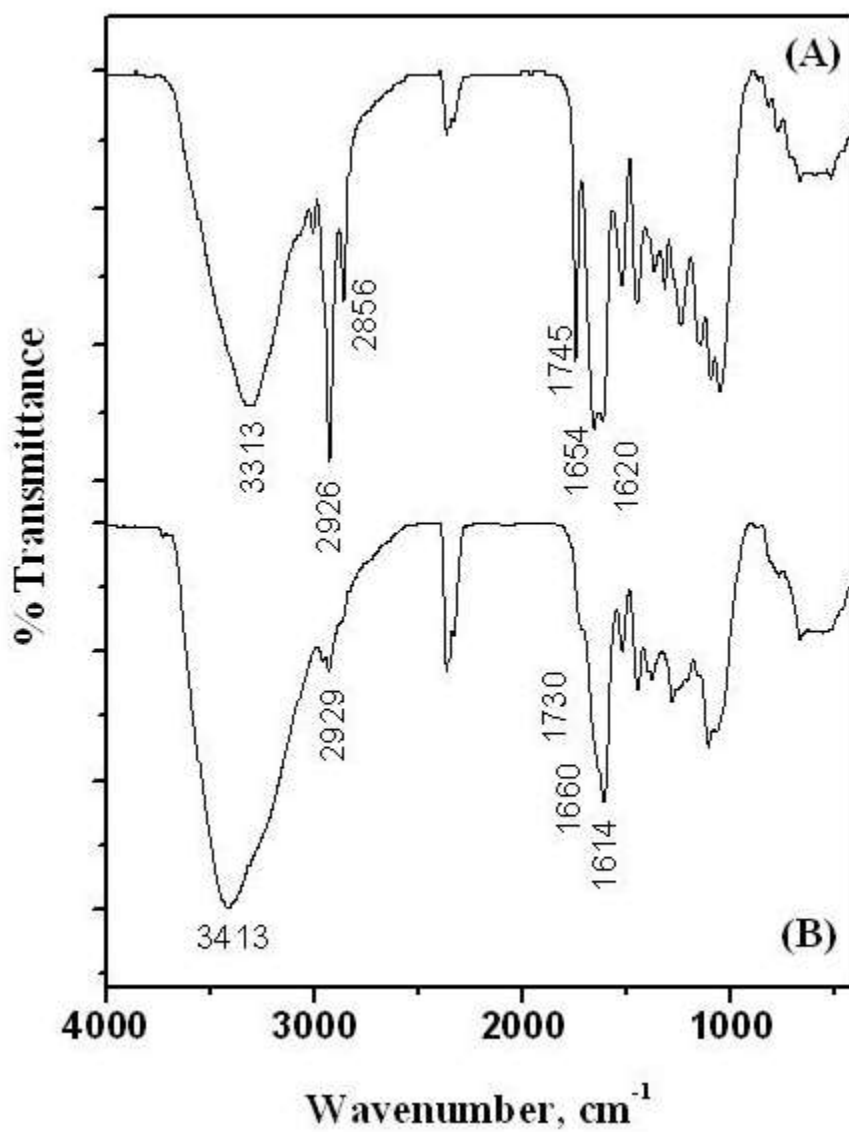


Figure (7): FTIR of organum majorana L (a) and AuNPs (b).

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