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Biosynthesis and In-Vitro Study of Gold Nanoparticles Using Mentha and Pelargonium Extracts

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Abstract

By green synthesis method utilization and using two plants, Mentha and Pelargonium plant extracts, gold nanoparticles were synthesized. For medical applications gold nanoparticles performance was observed in PBS media which is as like as human blood. Important features of green synthesized gold nanoparticles were measured using, GC-MS, UV-vis, FESEM, DLS and FT-IR. Main goal of this research was investigating reducing and stabilizing effects of mentioned plants, which was confirmed by GC-MS results. DLS and FESEM results proved nanometric size of green synthesized gold nanoparticles. For describing the performance, might be said that both extracts lead to synthesis of gold nanoparticles which their sizes are identical. Also, the synthesized gold nanoparticles from both plant extracts didn't agglomerated. Result of investigating performance of synthesized gold nanoparticles in PBS media indicates that both extracts will synthesize nanoparticles which will be stable by passing time or increased temperature.

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Keywords: Gold nanopartiles; Green synthesis; Mentha; Pelargonium; PBS media.

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1. Introduction

Metal nanoparticles are some of the most important nano materials which in nano scale, in compare to bulk state, they have new and unique properties, Kumar et al. (2011), Nalawade et al. (2013). These properties depend on the size and shape of the nanoparticles, Giljohann et al. (2010), Kumar et al. (2011). Gold nanoparticles due to having specific chemical, biological, optical properties and adjustable SPR by size, shape and spaces between nanoparticles, Njoki et al. (2007), Saha et al. (2012), are being used in many utilizations like imaging, Murphy et al. (2008), photothermal therapy, Khlebtsov et al. (2006), drug delivery, Ghosh et al. (2008). Different physical and chemical methods for synthesizing pure and well defined nanoparticles have been used, but they're costly expensive, Kumar and Yadav (2009), and even in recent years researches revealed that chemically synthesized gold nanoparticles, due to utilization of some chemical species like sodium citrate ,in production, are toxic, Kimling et al. (2006), Sen et al. (2013). Toxic gold nanoparticles cannot be used in medical applications, Bar et al. (2009). Nanoparticles synthesized using plant extracts and micro organisms are biocompatible and don't have the chemically synthesized nanoparticles issues. Therefore, this method can be a considerable alternative, Aromal and Philip (2012), Philip (2010). Utilizing plant extracts as reducing agents in synthesizing gold nanoparticles due to simplicity, large scale production of gold nanoparticles in nano scale and decreased production time and cost, has been under a great deal of interest, Makarov et al. (2014). Extract of some plants like Diopyros kaki, Magnolia Kobus, Song et al. (2009), Psidium guajava, Raghunandan et al. (2009), Azadirachta indica, Shankar et al. (2004), Ocimum sanctum, Philip and Unni (2011), is being used in synthesizing gold nanoparticles.

In present research, reducing and stabilizing effects of Mentha and Pelargonim extracts in synthesizing gold nanoparticles were investigated. Its ingredients have antibacterial, antifungal and anticancerous properties, Kumar et al. (2011). Pelargonium is a floral plant which is from Geraniaceae Species. It has anti microbial effect and is utilized in production of pesticides, Lis - Balchin et al. (1998).

Mentha and Pelorgonium extracts were obtained and with using GC-MS analysis, their ingredients were identified. By utilization of obtained extracts, gold nanoparticles were finally synthesized and using UV-Vis, FESEM, DLS and FT-IR analyses their main features were measured.The physiological stability of synthesized nanoparticles was investigated in a media as like as human blood which was PBS media.

2. Experimental

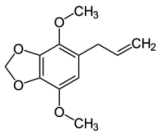
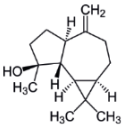
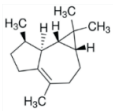
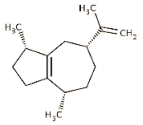
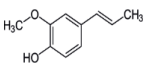
2.1. Materials

Mentha and Pelargonium were acquired from local markets in Tabriz, Iran. At first the plants were washed using deionized water and then chopped to smaller sizes before the extraction process. Chloroauric acid ($HAuCl_4$) was purchased from Merck Company. Aqueous solution of PBS (Sigma–Aldrich) was utilized in the experiments.

2.2. Plant extraction and AuNPs green synthesis

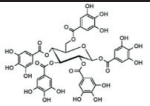
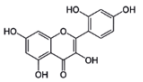
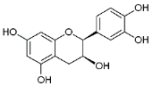
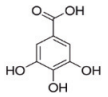
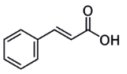
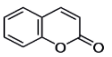
In order to synthesis AuNPs, adequate amount of previously prepared Mentha and Pelargonium plants were boiled for 20 min in 100 mL of deionized water while the mixture was mixed simultaneously. In order to obtain the desirable extract the mixture was filtered. In the next step, the AuNPs were synthesized using prepared extracts. For this aim, plant extracts were added to distinct boiling aqueous solution of $HAuCl_4$ drop wisely which was under stirring. As time passed, the color of solution changed from pale yellow to red, which affirmed the synthesis of AuNPs for each of the extracts.

Table 1. Identified components of *Mentha* extract using GC-MS.

Name , Molecular formula	Structure formula	Retention time (min)	Main fragments
Apiol $C_{12}H_{14}O_4$		27.4	222.23, 208.1, 191,160
Spathulenol $C_{15}H_{24}O$		26.2	220.35, 206,205, 203,126
Ledene $C_{15}H_{24}$		23.2	204.351,189,174,
α-Guaiene $C_{15}H_{24}$		22.6	204.35,174, 162
Isoeugenol $C_{10}H_{12}O_2$		17	164.20, 150, 147,
Menthone $C_{10}H_{18}O$		16	154.25, 140,
Pinene $C_{10}H_{16}$		18.2	136.24

Isoprene: 

Table 2. Identified components of *Pelargonium* extract using GC-MS.

Name , Molecular formula	Structure formula	Retention time (min)	Main fragments
Tannin $C_{76}H_{52}O_{46}$		35	1701.2
Flavonoids		18.2	302, 268, 191.62
		17.1	289, 254.74, 178.87
Sesquiterpenes	3 isoprene[1] units, sesquiterpenes may be linear (acyclic) or contain rings	15.3	204
Phenolic acid $C_9H_{10}O_4$		14.6	182.17, 137, 135
Cinnamic acid $C_9H_8O_2$		12	148.16, 103
Coumarin $C_9H_6O_2$		11.6	146.14, 130
Monoterpenes	2 isoprene units, monoterpenes may be linear (acyclic) or contain rings	10.8	136

2.3. Characterization methods

The components of obtained extracts were identified by GC-MS chromatography (Agilent Technologies, Palo Alto, Canada) analysis. sample preparation has been previously described in, Vahid and Khataee (2013), it is necessary to mention that N,O-bis-(trimetylsilyl) acetamide was added after extraction to produce silylated products which can be detected more conveniently by GC-MS analyzer. The UV-Vis spectrophotometer (Jenway 6705, United Kongdom) was used to determine AuNPs absorption spectra from 400-600 nm. The field emission scanning electron microscopy (FESEM) (Tescan, Mira3 FEG-SEM, Czech Republic) was utilized to observe the morphology of the AuNPs. The Microtrac dynamic light scattering (DLS) instrument (Nanotrac Wave, United states) was applied to reveal the size

distribution of gold nanoparticles. FTIR analysis (Bruker Tensor27, Germany) was used to investigate the functional groups of prepared extracts. Stability of the green synthesized AuNPs was investigated by UV-Vis for as-synthesized AuNPs and in the physiological conditions (PBS, pH 7.4). Also for measuring the Stability of AuNPs in the PBS media, the DLS analysis under a temperature range varying from 25 to 43oC during 12 days under room temperature was initiated.

3. Result and Discussion

3.1. Identification of the extracts

GC-MS analysis was applied to determine the components of extracts by in compare to commercial standards (Tables1 and 2). Isoeugenol and Spathulenol existence in Mentha extract and Flavonoids, Phenolic acid and Tanin in Pelargonium have the reducing effect in synthesizing AuNPs due to having hydroxyl functional groups. Stabilizing effect of Mentha is due to having aromatic rings in Apiol and Isoeugenol. But, the stabilizing effect of Pelargonium is not only due to having aromatic rings in Cinnamic acid, Coumarin, Flavonoids and Phenolic acid but the existence of C=C bonds in monoterpene and Sesquiterpene and carboxylic groups in Cinnamic acid.

3.2. Characterization of the AuNPs

Figure 1 indicates the UV-Vis absorption spectra for the synthesized AuNPs from Mentha and Pelargonium plant extracts. One can notice that the SPR of Synthesized AuNPs using Mentha and Pelargonium plant extracts were located at 537 and 538 nm, respectively. It can be seen that SPRs are in an interval from 510 to 570 nm this confirms the synthesis of gold nanoparticles. Because the obtained SPRs are very close to each other, one can say that synthesized nanoparticles from each plant extract have identical sizes, Link and El-Sayed (1999).

The FESEM images of AuNPs generated by Mentha and Pelargonium were indicated in Fig. 2 for investigation their morphology. It can be understood that particles from Pelargonium extracts are in nano metric scale and only have the spherical shape, but particles from Mentha extracts not only have the spherical shape, but they may be seen as triangular and polygonal shapes. Fig. 3 illustrates the green synthesized AuNPs particle size distributions. It can be noticed that all the particles are in the interval of 10-100 nm, which approves the nano metric size of green synthesized particles. Furthermore, it can be recognize that the average size of synthesized AuNPs by Mentha and Pelargonium plant extract are 34 and 33.80, respectively, proves that the nanoparticles prepared by both extract plants have the same size, which this claim is approved by result of UV-Vis analysis.

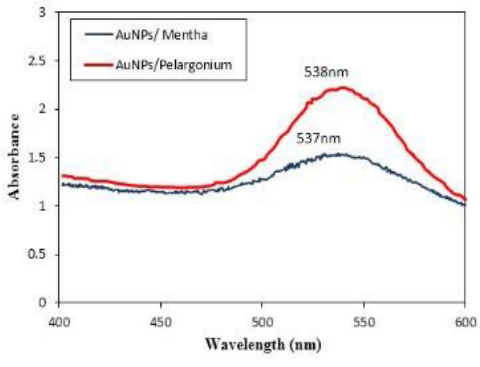


Fig. 1. UV-Visible spectra of green synthesized AuNPs.

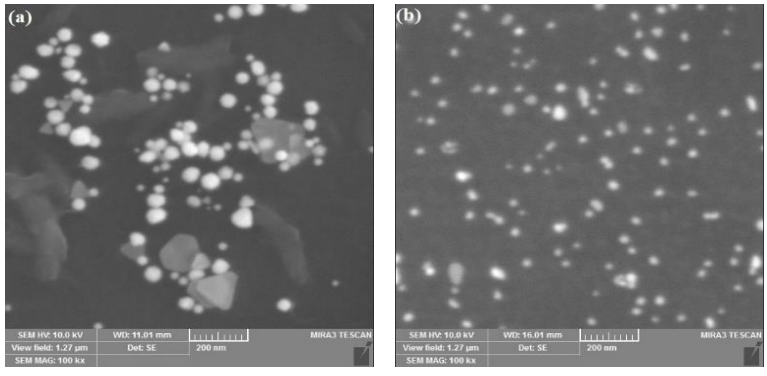


Fig. 2. FESEM images of AuNPs synthesized with (a) Menthe; (b) Pelargonium extracts.

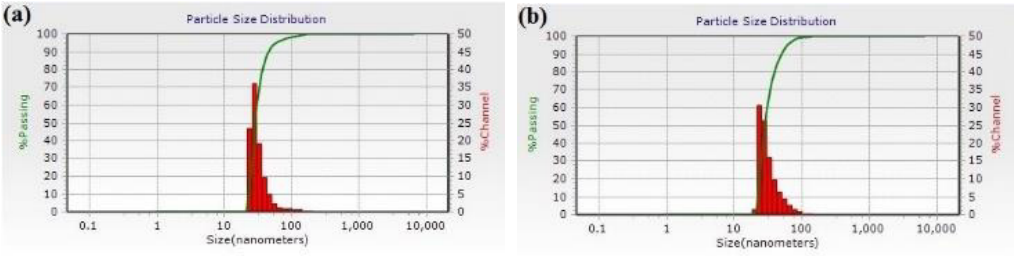


Fig. 3. Particle size distribution of AuNPs synthesized with (a) *Mentha; (b) pelargonium extracts.*

Figure 4 indicates the results of FT-IR analysis for detection of functional groups in the extracts and the AuNPs solutions. The analysis of Pelargonium plant extract shows that the band approximately at 1624 cm^{-1} is related to C=C bonds which confirms the stabilizing effect of the extract. The band approximately at the 3500 cm^{-1} is due to existence of O-H band which proves the reducing property of the Pelargonium extract.

Furthermore results of FT-IR analysis for Mentha extract shows that the bands at 1630 cm^{-1} can be assigned to C=C which proves the stabilizing feature of Mentha. The bands at 1090 cm^{-1} is related to alcoholic C-O bond and the peak.

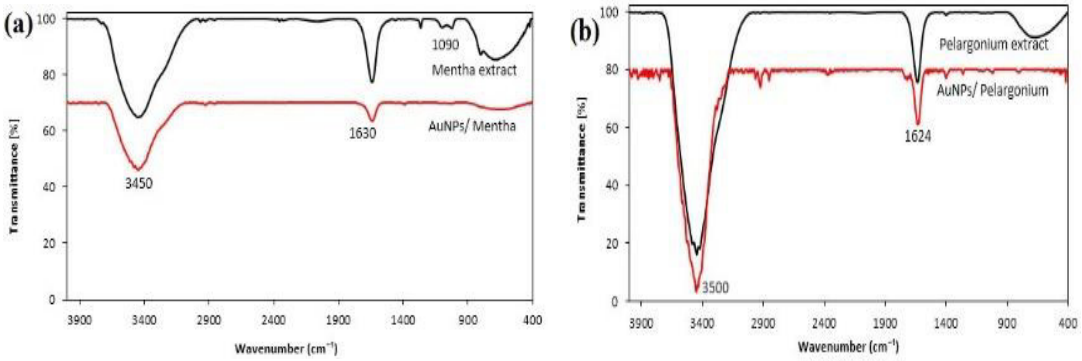


Fig. 4. FTIR spectra of (a) Mentha extract and synthesized AuNPs and (b) Pelargonium extract and synthesized AuNPs.

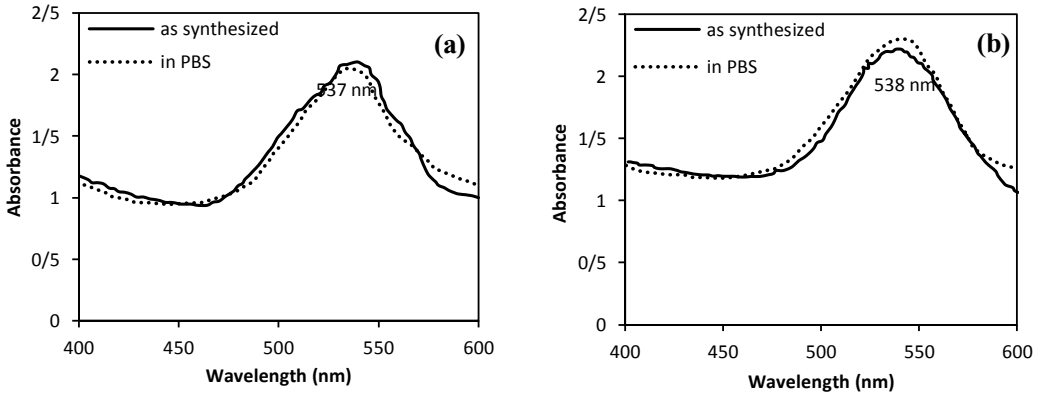


Fig. 5. UV-Vis spectra of AuNPs synthesized with (a) Mentha; (b) Pelargonium extracts under synthetic and physiological (in PBS) conditions.

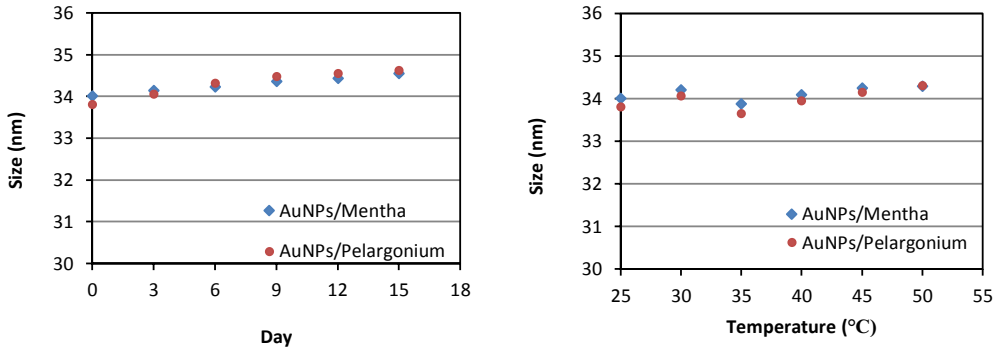


Fig. 6. Average size chenge of AuNPs synthesized with Mentha and pelargonium plant extracts in PBS media as time passes at room temperature.or increased temprature condition.

at 3450 cm^{-1} indicates the O-H bonds existence which approve the reducing property of Mentha extract.

3.3. Stability of the AuNPs, as synthesized and in physiological condition

The SPR of the synthesized AuNPs in the PBS, which is as like as human blood, was compared to the as-synthesized condition (Fig. 5). As can be observed, the SPRs of the green synthesized AuNPs is the same for each of extracts in mentioned conditions. One can say that due to unchanged SPRs, nanoparticles in PBS media are stable and don't agglomerate. At end, DLS analysis was done for investigating the claim about stability of green synthesized AuNPs at time intervals in PBS media. (Fig. 5) and various temperatures (Fig. 6). The average size of the nanoparticles was approximately unchanged while time passed for both plant extracts (Fig. 5) over 15 days at room temperature. Finally, increase in temperature didn't have a considerable effect on average size of green synthesized nanoparticles (Fig. 6).

4. Conclusion

Gold nanoparticles were synthesized using Mentha and Pelargonium extracts. Their components were identified by GC-MS analysis and the results revealed that components like Isoeugeonal and spathulenol in Mentha plant and Flavonoids, Phenolic acids and Tanin in Pelargonium plant due to having hydroxyl functional groups act as reducing agents. Also benzyl rings and carboxyl groups in some of the components in both plant extract, makes them to act as stabilizing agents. UV-Vis analysis revealed that SPRs for synthesized gold nanoparticles by the extract of Mentha and Pelargonium plants was 537 and 538 nm respectively, which they're very close to each other, and this might be the reason why synthesized nanoparticles from both extracts have same sizes and DLS analysis showed same results. The nano metric size of synthesized particles were proven using FESEM imges. Synthesized nanoprticles from Pelargonium plant extract were only seen as spherical shape but, it was concluded that same particles from Mentha extracts might be seen as triangle and polygon shapes. Result of UV-vis analysis proved that synthesized nanoparticles by each of two plants extracts are stable in PBS media. Also as time passes and temperature increases it was observed that obtained average particle size from DLS analysis for synthesized gold nanoparticles by two plant extracts didn't changed considerably and one can conclude that green synthesized gold nanoparticles have perfect stability in PBS environment.

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