Synthesis of ultra-small gold nanoparticles by polyphenol extracted from *Salvia officinalis* and efficiency for catalytic reduction of p-nitrophenol and methylene blue

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**ABSTRACT**

The present research work reports an eco-friendly route for preparing gold nanoparticles (AuNPs) with high catalytic activity using polyphenol extracted from *salvia officinalis*. In both alkaline (pH ∼ 11) and acidic media (pH ∼ 5), the polyphenol induced rapid reduction of the Au (III) salt and lead to the formation of highly monodisperse and spherical small (S) and larger (L) AuNPs, respectively. The average particle size was found to be ∼ 6 nm for S and ∼ 27 nm for L AuNPs, respectively. FT-IR revealed that polyphenol species are capped onto the nanoparticles surface favoring a high aqueous colloidal stability of the AuNPs in a wide pH range. In addition, the produced AuNPs exhibited significant size-dependent degradation rate of p-nitrophenol (p-NP) and methylene blue (MB) to p-aminophenol (p-AP) and leucomethylene blue (LMB), respectively.

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1. Introduction

Growing research efforts are focused on the application of nanotechnology in the field of environmental remediation. Chemical industry is the major source of environmental pollution. The huge organic dyes and nitroaromatic compounds, released in incontrollable way, are among the most hazardous pollutants for our aquatic system (1–3). Nitroaromatic compounds are fundamental chemicals for the manufacture of various products in various applications fields. They are for instance used in the production of pesticides, dyes, pharmaceuticals and explosives (4, 5). Nitrophenol has been identified by the US Environmental Protection Agency (EPA) as one of the priority pollutants due to its danger and toxicity (6). The conventional treatment approaches for the degradation of nitroaromatic compounds from wastewaters are environmentally harmful like microbial degradation, adsorption, photocatalytic degradation and electrochemical treatment degradation (7–12). The nanoparticles of Au, Ag, Pt and Re have attracted much attention as catalysts for the rapid reduction of nitroarenes and dyes in aqueous medium (13, 14). Nevertheless, at the nanoscale the metals are very unstable because of their high surface energy and rapid agglomeration which decreases their catalytic activity (15, 16). Therefore, it is necessary to use a capping agent to prevent the aggregation of the nanoparticles and then stabilize them in the form of colloidal suspension. To overcome the inherent drawbacks, several eco-friendly stabilizing agents, naturally available and with low-cost processing...
were used. Several plant parts such as leaves, flowers, fruits, and seeds have been successfully used for biosynthesizing AuNPs. Moreover, plant extracts, in particular, those derived from plants rich in polyphenols, are good sources of reducing and stabilizing agents (17–21). In this study, we chose the plant *Salvia officinalis* for the synthesis of gold nanoparticles. Indoor work shows that this plant has been widely used in pharmacognosy (22–25). Today German Commission E has accepted the use of *S. officinalis* for a number of medical applications included inflammation and dyspepsia (24). Previous studies have suggested that plant is sources of polyphenol and flavonoids compounds (23–25). The presence polyphenol in ethanolic extract such as salvianolic acid, rosmarinic acid and luteolin glucoside (26, 27), acts as reducing and stabilizers agents for gold salts to produce AuNPs nanoparticles. This work describes a green chemistry method for the synthesis of AuNPs using polyphenol obtained from the *Salvia officinalis* plant without any chemical additive. Two kinds of AuNPs with controlled size were successfully produced in acidic and alkaline aqueous media. The structure, microstructure, optical and surface functionality of the produced AuNPs were studied using UV-visible, and infrared (IR) spectroscopies and transmission electron microscopy (TEM). Finally, the catalytic efficiency of the biosynthesized AuNPs was evaluated by monitoring the degradation of 4-NP and MB.

2. Materials and methods

2.1. Plants materials

The plant *Salvia officinalis* were purchased from the market. Dr. Arbi Guetat, a botanist in the Department of Faculty of Science of Arar, Saudi Arabia, has authenticated the plants as *Salvia officinalis*.

2.2. Extraction of polyphenol

The *Salvia officinalis* was ground and the resulting powder (250 g) was successively extracted with hexane, ethyl acetate and ethanol using the soxhlet apparatus. The extracts were filtered by a Whatman filter. Then, the resulting solutions were evaporated using a rotary evaporator.

2.3. Total phenolic content (TPC)

The quantification of TPC was determined spectrophotometrically, according to the colorimetric method using the Folin–Ciocalteu reagent (28). Briefly, in glass hemolysis tubes a volume 0.2 mL of each of extracts (1.0 mg/mL) and 1.0 mL of 10% Folin–Ciocalteu reagent were reacted in the dark for 6 min before addition of 0.8 mL of 7.5% aqueous solution of Na₂CO₃, and then incubated in dark for 2 h. The absorbance was read at 765 nm. The TPC in extracts was quantified from standard gallic acid curve equation and presented as gallic acid equivalents (mg GAE/g dry extract).

2.4. Synthesis of gold nanoparticles

A controlled experiment was carried out for bio-synthesis of AuNPs in which 5 mL of polyphenol at 8 g L⁻¹ in pH ~11 was added to 25 mL of HAuCl₄ (1 mM) at 25°C. The color of the solution changed rapidly (less than 5 min) from light pale yellow (gold ions) to red-wine indicating the formation of AuNPs. Parallel sets of experiments were also carried out to study the effect of the amount of the polyphenol (2–10 g L⁻¹) and the pH (5 and 11) on the formation and the microstructure of the AuNPs.

2.5. Chemicals

Chlorauric acid (HAuCl₄·3H₂O, 99.99%), sodium hydroxide (NaOH, 99%), 4-nitrophenol (C₆H₅NO₃, 99%), methylene blue (C₁₆H₁₈ClN₃S, 99%) and sodium borohydride (NaBH₄, 99%) were purchased from Sigma-Aldrich. The solvents ethanol (C₂H₅OH, 99%), ethyl acetate (C₄H₇O₂, 99%), n-Hexane (C₆H₁₄, 99%), were purchased from Fisher Scientific UK.

2.6. Characterization techniques

UV-Visible spectroscopy was recorded on double-beam spectrophotometer (Jasco V-670) covering a wavelength range from 190 to 800 nm and equipped with 1 cm wide quartz cells. Fourier transform Infrared spectroscopy (FTIR) on KBr pellets was performed on a Thermo Scientific Nicolet iS5 spectrophotometer. Transmission electron microscopy (TEM) measurement was carried out on JEM-1010 transmission electron microscope operating at 100 kV. Samples were prepared by diluting in methanol a very small volume of AuNPs colloid. The mixture was then sonicated and then one drop was placed onto a carbon coated copper grid and dried. The mean particle size and the size distribution of the produced AuNPs were determined using the Image J analysis software by counting more than 200 particles.

2.7. Catalytic reduction

The reduction of 4-NP to p-AP and BM to LBM by NaBH₄ using the as-produced AuNPs as catalyst was studied as a model reaction (29). To study the reaction, 2.7 mL (2 × 10⁻⁴ M) of 4-NP or BM was mixed with 0.2 mL of reducing
agent NaBH₄ (2 × 10⁻² M). Then, 10 μl of AuNPs with 1 mg/mL were introduced into a quartz cuvette along with the reaction mixture. The reaction time was accounted when a catalyst AuNPs was added into the reaction medium. UV-visible spectra of the samples were recorded against Milli-Q water as a blank in the range of 200–500 nm for p-NP and in the range of 400–700 nm for MB.

3. Results and discussion

3.1. Extraction and quantification of polyphenols

A 250 g of salvia officinal were successively extracted with hexane, ethyl acetate and ethanol using soxhlet apparatus. The ethanolic extract shows the highest value in TPC 486 mg gallic acid/1 g of dry extract (DE), followed by ethyl acetate (87.3 mg GA/1 g DE), and hexane extract (33.83 mg GAE/1 g DE). The richness of the ethanolic extract in polyphenol products allowed us to choose it for the syntheses of gold nanoparticles.

3.2. The microstructure and the optical properties of the produced AuNPs

In order to synthesize stable colloids of almost monodisperse nanoparticles with as small as possible nanosized AuNPs, we studied the effect of two fundamental parameters: the amount of the polyphenols and the pH.

3.2.1. Effect of polyphenol concentration

In an alkaline medium, it was observed that the concentration of polyphenol plays a crucial role in formation of AuNPs from gold salts with controlled microstructure and their colloidal stabilization in aqueous media (30–34). In our experiments, we investigated the effect of the amount of polyphenol at pH ~11. To a fixed amount of HAuCl₄ (25 mL, 1 mM) was added dropwise, under magnetic stirring, 10 mL of polyphenol solution with a concentration varying from 2.0–10 g.L⁻¹. The resulting mixture was then incubated at 25 °C for 30 min. It is observed that for concentrations up to 8 g.L⁻¹, it forms highly stable colloidal suspensions with a color varying from yellow to reddish wine with the increase of polyphenol concentration. Beyond 8 g.L⁻¹, on polyphenol addition, the color change is accompanied by the formation of a reddish precipitate. UV-UV – visible spectra of selected preparations are shown in Figure 1. For all polyphenol concentrations, the spectra exhibited an intense characteristic absorption band at around 520–530 nm arising from surface plasmon resonance (SPR) emission of AuNPs (35). Above 8 g. L⁻¹, the absorption bands become broader, indicating as expected the formation of larger AuNPs resulting in agglomeration (Figure 1).

3.2.2. Effect of pH

The pH of polyphenol plays an important role in the reduction of Au³⁺ into Au metallic nanoparticles (32–34). To study the effect of pH on synthesis of gold nanoparticles, 10 mL of 8 g.L⁻¹ polyphenol solution with a pH ~ 5 (bare polyphenol extract) or a pH of ~ 11 (adjusted by adding 0.1 M NaOH solution) was poured into a gold salt solution (25 mL; 1 mM). In alkaline medium, the color of the colloidal suspension changed from yellow to red wine within 5 min (colloid 5). While in acid medium (pH

Figure 1. The UV – vis spectra of AuNPs colloids obtained with different concentrations of polyphenols. The inset compares selected photos of the prepared colloids.
∼ 5), the color changes very slowly (it took more than 6 h) from yellow to purple (colloids L) (Figure 2).

These faster AuNP synthesis performances at pH ∼11 can be explained by the formation of an intermediate complex between Au$^{3+}$ ions and phenolate and carbonyl groups of polyphenol. Subsequently the phenolate groups are then oxidized to ketones, while the Au$^{3+}$ ions are reduced to gold (Au$^{0}$) (36, 37). In addition the appearance of a sharp SPR band at a relatively wavelength (524 nm) for colloid (S) compared to the colloid (L) (536 nm) (Figure 3), suggest the formation of ultra-small nanoparticles in the alkaline medium. The bathochromic shift of the SPR band from 524 nm towards wavelength at 536 nm, in acidic medium indicating the presence of larger sized nanoparticles (38, 39). Our results also suggest that a pH ∼11 is the most favorable for bio-synthesis of AuNPs using 8 g.L$^{-1}$ of polyphenol. Based on the color changes of the colloids in a basic and acidic solution of polyphenol and UV-vis absorption spectra, the different sizes and shapes of the AuNP formed were profoundly confirmed by the TEM images. The obtained observations are shown in Figure 3 (S) and (L). Clearly, these results suggest that the influence of the pH value of the polyphenol solution on the size and shape of the AuNPs. TEM observations revealed that the AuNP (L) by polyphenol at pH ∼5 was presented various morphologies (hexagonal, cubic, triangular and spherical) with an average size of 26.8 ± 8.6 nm (Figure 3L). When the pH value polyphenol solution was increased to ∼11, mono-dispersed spherical particles with an average size of 5.8 ± 3.5 nm were observed.

**Figure 2.** UV – vis spectra of AuNPs prepared at pH ∼ 5 and ∼ 11. The inset shows the distinctive color of corresponding colloids.

**Figure 3.** TEM image and size distribution histogram of AuNPs (S) and AuNPs (L) prepared at pH ∼11 and ∼ 5, respectively.
The FTIR analysis results revealed several characteristic bands for the AuNPs and polyphenols (Figure 4). The IR spectrum of polyphenols revealed absorption bands for the phenol and hydroxyl groups ($3422 \text{ cm}^{-1}$), carbonyl group of the ester and the carboxylic acid in salvianolic acid and rosemarinic acid ($1701 \text{ cm}^{-1}$), $sp^2$ carbons of the aromatic ring ($1610$ and $1405 \text{ cm}^{-1}$), and stretching vibrations of the C–O bond ($1361$ and $1038 \text{ cm}^{-1}$). The spectrum of the synthesized AuNPs exhibited absorption bands at $3362$, $2922$, $1656$, $1556$, $1280$, and $1038 \text{ cm}^{-1}$.

Figure 4. IR spectrum of dried AuNPs. IR spectrum of polyphenol is also provided for comparison.

Figure 5. UV-Vis spectra showing the degradation of MB by NaBH$_4$ in the presence of (a) AuNPs (S) and (b) AuNPs (L) as catalysts. (c) plot of the first order reaction kinetics for the degradation of MB by NaBH$_4$ in the presence of AuNPs (S) and AuNPs (L).
1378, and 1070 cm\(^{-1}\). As can be noted, these bands are associated to the polyphenol group. By comparing the FTIR spectra of free polyphenol and AuNPs, shifts in the absorption bands of the hydroxyl, carbonyl, and aromatic rings groups were observed. This confirmed that the polyphenol molecules are chemically capped on the surface of the AuNPs.

3.3. Catalysis

In the last years the photocatalytic reduction using nanoparticles is widely used in the removal of organic pollutants like dyes and nitro arenes from wastewater. We have studied the reduction of MB and p-NP by NaBH\(_4\) in the presence of nanocatalyst AuNPs (S) and AuNPs (L) to determine the effect of size on the degradation rates of these pollutants.

3.3.1. Reduction of MB

In the visible range, methylene blue is characterized by two absorption bands exhibiting at 665 and 614 nm (40). When NaBH\(_4\) is added to MB, in the absence of AuNPs as catalyst, the absorbance of MB did not significantly change which indicated a very slow reaction rate. This was explained by the huge difference between the redox potentials of the acceptor and donor restricting the efficient electron transfer (MB (E\(^{\circ}\)(MB/LMB) = −1.33 V) and NaBH\(_4\) (E\(^{\circ}\)(B\(_2\)H\(_6\)/BH\(_4\)\(^{-}\)) = −0.21 V) (41). The catalytic properties of AuNPs were determined by studying the reduction of MB to LMB according to time using UV-Vis spectrometry in the 500–700 nm wavelength range at room temperature (Figure 5(a) and (b)). For this reaction, AuNPs facilitated the transfer of electrons from B\(_2\)H\(_6\)/BH\(_4\)\(^{-}\) (donor electron) to MB/LMB (acceptor electron) (42). Separately adding AuNPs (S) or (L) as nanocatalysts to MB in the presence of NaBH\(_4\) accelerated the reduction rate of MB, and the intensity of the absorption bands at 665 and 612 nm was significantly reduced. The kinetics of the reduction of MB was in good agreement with the pseudo-first order law:

\[
\ln(C_t/C_0) = -k_{app}t
\]

where \(C_t\) represents the concentration of solution at different times, \(k_{app}\) is the apparent rate constant and \(t\) is the reaction time (min). The value of \(k_{app}\) was obtained from the slope of the graph of \(\ln(C_t/C_0)\) vs. time (Figure 5(c)). The rate constants have been determined to be 0.112 and 0.017 \(\text{min}^{-1}\) for catalysts S and L, respectively.
(Figure 5(c)). The highest reduction rate highlighted the superior catalytic efficiency of AuNPs (S) compared to AuNPs (L) due to the reduced size of AuNPs (S) over AuNPs (L). Previous studies showed that in general, the rate of the reduction reaction depends on the size of the NPs because smaller particles promote the adsorption of reagents on their surface (43, 44).

3.3.2. Reduction of p-NP

The reduction of p-NP using NaBH₄ was selected as a model reaction for investigation the catalytic potential of the biosynthesized AuNPs. It is known in aqueous solution p-NP has a maximum absorption band λ_{max} at 318 nm. Immediately after combining NaBH₄ with p-NP, λ_{max} at 318 nm which undergoes a bathochromic shifts near 400 nm, due to the formation of 4-nitropheno-late ions in alkaline medium and the color of solution change light to bright yellow (29). After addition of nanocatalyst AuNPs (S) or AuNPs (L) to p-NP and NaBH₄ mixture the intensity of the band at 400 nm decreases and simultaneously two new bands appear at 280 and 310 nm due to the formation of p-aminophenol via the reduction of p-NP.

Moreover, the bright yellow color of the solution vanished and turns colorless for 5 min for catalyst (S) and 30 min for catalyst (L) (Figure 6). This should be associated with the high catalytic potential of AuNPs (S) with smaller sizes and therefore larger surface when synthesized in a strongly basic medium. Figure 6(c) shows the plot of ln(C_t/C_0) vs time (min) for reduction of p-NA by NaBH₄ in the presence of nanocatalyst AuNPs (S) or AuNPs (L). A good linearity is obtained, (R² = 0.99) in agreement with a pseudo first-order. The calculated of the rate constants k_{app} for reduction reactions was found to be 0.154 for catalyst AuNPs (S) and 0.025 min⁻¹ for AuNPs (L). Results suggest that the rate of reduction was increased with decreased the size of AuNPs. This could be due to the large surface area promoting the adsorption of 4-phenolate ions on the surface of the catalyst, which allows a rapid reduction. These results were reinforced by previous studies on the catalysis capacity of green synthesized of AuNPs, which proves that the catalytic performance depends on the particle size and shape (45, 46).

4. Conclusion

We reported eco-friendly synthesis route of AuNPs using polyphenol isolated from Salvia officinalis. Two sets of AuNPs with an average particle size of ~ 6 nm (S) and ~ 27 nm (L) were produced in polyphenolic solutions of pH ~5 and ~11, respectively. The biosynthesized AuNPs were thoroughly characterized using UV-Vis, IR spectroscopy and TEM. The biosynthesized AuNPs exhibited size dependent catalytic activity; the smallest AuNPs (S) displaying much better catalytic reduction of 4-NP and MB.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Emmanuel, R.; Karuppiah, C.; Chen, S.M.; Palanisamy, S.; Padmavathy, S.; Prakash, P.J. Green Synthesis of Gold Nanoparticles for Trace Level Detection of a Hazardous Pollutant (Nitrobenzene) Causing Methemoglobinaemia. Hazard. Mater. 2014, 279, 117–124.
[2] Zaharia, C.; Suteu, D. Textile Organic Dyes, Characteristics, Polluting Effects and Separation/Elmination Procedures from Industrial Effluents –A Critical Overview. Organic Pollutants Ten Years after the Stockholm Convention Environmental and Analytical Update, 2012, pp 55–86.
[3] Mori, T.; Watanuki, T.; Kashiwaguru, T. Diesel Exhaust Particles Disturb Gene Expression in Mouse Testis. Environ. Toxicol. 2007, 22, 58–63.
[4] Nazeruddin, G.M.; Prasad, N.R.; Prasad, S.R.; Shaikh, Y.J.; Waghmare, S.R.; Adhyapak, P. Coriandrum Sativum Seed Extract Assisted In Situ Green Synthesis of Silver Nanoparticle and its Anti-Microbial Activity. Ind. Crops Prod 2014, 60, 212–216.
[5] Nemanashi, M.; Meijboom, R. Synthesis and Characterization of Cu, Ag and Au Dendrimer-Encapsulated Nanoparticles and Their Application in the Reduction of 4-Nitrophenol to 4-Aminophenol. J. Colloid Interf. Sci 2013, 389, 260–267.
[6] Emmanuel, R.; Karuppiah, C.; Chen, S.M.; Palanisamy, S.; Padmavathy, S.; Prakash, P.J. Green Synthesis of Gold
Gangula, A.; Podila, R.; R, M.; Karanam, L.; Janardhana, C.; Baruwati, B.; Varma, R.S. High Value Products From Waste: Their Sustainable Applications. Curr. Opin. Chem. Eng 2012, 1, 123–128.

[7] Thangamani, K.S.; Andal, N.M.; Kumar, E.R.; Saravanabhavan, M.J. Utilization of Magnetic Nano Cobalt Ferrite Doped Capra Aegagrus Hircus Dung Activated Carbon Composite for the Adsorption of Anionic Dyes. Environ. Chem Eng 2017, 5, 2820–2829.

[8] Tan, B.H.; Teng, T.T.; Omar, A.M. Removal of Dyes and Thangamani, K.S.; Andal, N.M.; Kumar, E.R.; Sayed, M.; Shah, L.A.; Kazem, A.; Shah, N.S.; Nisar, J.; Khan, H.M.; Zhang, P.; Khan, A.R. Efficient Photocatalytic Degradation of Norfloxacin in Aqueous Media by Hydrothermally Synthesized Immobilized TiO2/Ti Films with Exposed {001} Facets. J. Phys. Chem. A 2014, 117, 9916–9931.

[9] Huang, J.; Song, H.; Chen, C.; Yang, Y.; Xu, N.; Ji, X.; Li, C.; You, J.A. Facile Synthesis of N-Doped TiO2 Nanoparticles Caged in MIL-100 (Fe) for Photocatalytic Degradation of Organic Dyes Under Visible Light Irradiation. J. Environ. Chem Eng 2017, 5, 2579–2585.

[10] Torrades, F.; Pérez, M.; Mansilla, H.D.; Peral, J.; Huang, H.; Song, C.; Chen, Y.; Yang, N.; Xu, X.; Ji, C.; Li, J.A. You, Facile Synthesis of N-Doped TiO2 Nanoparticles Experimental Design of Fenton and Photo-Fenton Reactions for the Treatment of Cellulose Bleaching Effluents. Chemosphere 2003, 53, 1211–1220.

[11] Sayed, M.; Khan, J.A.; Shah, L.A.; Shah, N.S.; Khan, H.M.; Rehman, F.; Khan, A.R.; Khan, A.M. Degradation of Quinolone Antibiotic, Norfloxacin, in Aqueous Solution Using Gamma-ray Irradiation. Envion. Sci. Pollut. Res 2016, 23, 13155–13168.

[12] Fu, Y.; Viraraghavan, T. Fungal Decolorization of dye Wastewaters: a Review. Bioresour. Technol 2001, 79, 251–262.

[13] Gangula, A.; Podila, R.; R, M.; Karanam, L.; Janardhana, C.; Rao, A.M. Catalytic Reduction of 4-Nitrophenol Using Biogenic Gold and Silver Nanoparticles Derived From Breynia Rhamnoides. Langmuir 2011, 27, 15268–15274.

[14] Gupta, N.; Singh, H.P.; Sharma, R.K. Single-pot Synthesis: Plant Mediated Gold Nanoparticles Catalyzed Reduction of Methylene Blue in Presence of Stannous Chloride. Colloids Surf. A Physicochem. Eng. Asp 2010, 67, 102–107.

[15] Sau, T.K.; Murphy, C.J. Room Temperature, High-Yield Synthesis of Multiple Shapes of Gold Nanoparticles in Aqueous Solution. J. Am. Chem. Soc 2004, 126, 8648–8649.

[16] Deepika, H.; Jacob, L.; Mallikarjuna, N.N.; Rajender, S.V. Greener Techniques for the Synthesis of Silver Nanoparticles Using Plant Extracts, Enzymes, Bacteria, Biodegradable Polymers, and Microwaves. ACS Sustain. Chem. Eng 2013, 1, 703–712.

[17] Baruwati, B.; Varma, R.S. High Value Products From Waste: Grape Pomace Extract—A Three-in-One Package for the Synthesis of Metal Nanoparticles. Chem.Sus. Chem 2009, 2 (11), 1041–1044.

[18] Nadagouda, M.N.; Varma, R.S. Green Synthesis of Silver and Palladium Nanoparticles at Room Temperature Using Coffee and tea Extract. Green Chem. 2008, 10, 859–862.

[19] Rajender, S.V. Greener Approach and to Nanomaterials Their Sustainable Applications. Curr. Opin. Chem. Eng 2012, 1, 123–128.

[20] Nune, S.K.; Chanda, N.; Shukla, R.; Katti, K.; Kulkarni, R.R.; Thilakavathy, S.; Mekapothula, S.; Kannan, R.; Katti, K.V.J. Green Nanotechnology From tea: Phytochemicals in tea as Building Blocks for Production of Biocompatible Gold Nanoparticles. Mater. Chem 2009, 19, 2912–2920.

[21] Stagos, D.; Portes, N.; Spanou, C.; Mossieros, D.; Allegiannis, N.; Chaita, E.; Panagoulis, C.; Reri, E.; Skaltsounis, L.; Tsatsakis, A.M.; Kouritas, D. Correlation of Total Polyphenolic Content with Antioxidant and Antibacterial Activity of 24 Extracts From Greek Domestic Lamiaceae Species. Food Chem. Toxicol 2012, 50, 4115–4124.

[22] Orhan, I.E.; Senol, F.S.; Erctemin, T.; Kahraman, A.; Celep, F.; Akaydin, G.; Sener, B.; Dogan, M. Assessment of Anticholinesterase and Antioxidant Properties of Selected Sage (Salvia) Species with Their Total Phenol and Flavonoid Contents. Ind. Crop Prod 2013, 41, 21–30.

[23] Ghorbani, A.; Esmaeilizadeh, M. Pharmacological Properties of Salvia Officinalis and its Components. J. Tradit. Complement Med 2017, 7, 433–440.

[24] Ben Farhat, M.; Jordán, M.J.; Chaouech-Hamada, R.; Landoulsi, A.; Sotomayor, J.A. Variations in Essential oil, Phenolic Compounds and Antibacterial Activity of Tunisian Cultivated Salvia Officinalis L. J. Agric. Food Chem 2009, 57, 10349–10356.

[25] Cuvelier, M.E.; Berzet, C.; Richard, H.J. Antioxidant Constituents in Sage (Salvia Officinalis). Agric. Food Chem 1994, 42, 665–669.

[26] Roby, M.H.H.; Sarhan, M.A.; Selim, K.A.H.; Khalel, K.I. Evaluation of Antioxidant Activity, Total Phenols and Phenolic Compounds in Thyme (Thymus Vulgaris L), Sage (Salvia Officinalis L), and Marjoram (Origanum Majorana L.) Extracts. Ind. Crops Prod 2013, 43, 827–831.

[27] Li, H.; Wong, C.; Cheng, K.; Chen, F. Antioxidant Properties in Vitro and Total Phenolic Contents in Methanol Extracts From Medicinal Plants. LWT–Food Sci. Technol 2008, 41, 385–390.

[28] Zeynizadeh, B.; Mohammadzadeh, I.; Shokri, Z.; Hosseini, S.A.J. Synthesis and Characterization of NiFe2O4@Cu Nanoparticles as a Magnetically Recoverable Catalyst for Reduction of Nitroarenes to Arylamines with NaBH4. Colloid Interface Sci 2017, 500, 285–293.

[29] Nagaraj, B.; Krishnamurthy, N.B.; Liny, P.; Divya, T.K.; Dinesh, R. Biosynthesis of Gold Nanoparticles of Ixora Coccinea Flower Extract & Their Antimicrobial Activities. Int. J. Pharm. Biol. Sci 2011, 2, 557–565.

[30] Rastogi, L.; Arunachalam, J. Green Synthesis Route for the Size Controlled Synthesis of Biocompatible Gold Nanoparticles Using Aqueous Extract of Garlic (Allium Sativum). J. Adv. Mater. Lett 2013, 4, 548–555.

[31] Jiahui, K.; Rajender, S.V. Beet Juice Utilization: Expeditious Green Synthesis of Noble Metal Nanoparticles (Ag, Au, Pt, and Pd) Using Microwaves. RSC Adv. 2012, 2, 10283.

[32] Kou, J.; Varma, R.S. Beet Juice-Induced Green Fabrication of Plasmogenic AgCl/Ag Nanoparticles. Chem. Sus. Chem 2012, 5, 2435–2441.

[33] Mallikarjuna, N.N.; Nidhi, I.; Jacob, L.; Changseok, H.; Dionysios, D.D.; Rajender, S.V.; Synthesis of Silver and Gold Nanoparticles Using Antioxidants From Blackberry, Blueberry, Pomegranate and Turmeric Extracts. ACS Sustain. Chem. Eng 2014, 2, 1717–1723.

[34] Vigderman, L.; Zubarev, E.R. High-yield Synthesis of Gold Nanorods with Longitudinal SPR Peak Greater Than
1200 nm Using Hydroquinone as a Reducing Agent. 
*Chem. Mater* **2012**, 25, 1450–1457.

[36] Simard, J.; Briggs, C.; Boal, A.K.; Rotello, V.M. Formation and ph-Controlled Assembly of Amphiphilic Gold Nanoparticles. *Chem. Commun* **2000**, 19, 1943–1944.

[37] Oueslati, M.H.; Ben Tahar, L.; Harrath, A.H. Catalytic, Antioxidant and Anticancer Activities of Gold Nanoparticles Synthesized by Kaempferol Glucoside From Lotus Leguminosae, Arabian Journal of Chemistry. *Ara. J. Chem.* **2018**, in Press. Article in Press. doi:10.1016/j.arabjc.2018.09.003.

[38] Huang, X.; Wu, H.; Liao, X.; Shi, B. One-step, Size-Controlled Synthesis of Gold Nanoparticles at Room Temperature Using Plant Tannin. *Green Chem.* **2010**, 12, 395–399.

[39] Pinto, R.J.B.; Lucas, J.M.F.; Morais, M.P.; Santos, S.A.O.; Silvestre, A.J.D.; Marques, P.A.A.P.; Freire, C.S.R. Demystifying the Morphology and Size Control on the Biosynthesis of Gold Nanoparticles Using Eucalyptus Globulus Bark Extract. *Ind. Crops Prod* **2017**, 105, 83–92.

[40] Lin, J.; Zong, R.; Zhou, M.; Zhu, Y. Photoelectric Catalytic Degradation of Methylene Blue by C₆₀-Modified TiO₂ Nanotube Array. *Appl. Catal. B* **2009**, 89, 425–431.

[41] Cheval, N.; Gindy, N.; Flowkes, C.; Fahmi, A. Polyamide 66 Microspheres Metallised with in Situ Synthesised Gold Nanoparticles for a Catalytic Application. *Nanoscale Res. Lett* **2012**, 7, 182.

[42] Mallick, K.; Witcomb, M.; Scurrell, M. Silver Nanoparticle Catalysed Redox Reaction: an Electron Relay Effect. *Mater Chem. Phys* **2006**, 97, 283–287.

[43] Narayanan, K.B.; Park, H.H.; Han, S.S. Synthesis and Characterization of Biomatrixed Gold Nanoparticles by the Mushroom Flammulina Velutipes and its Heterogeneous Catalytic Potential. *Chemosphere* **2015**, 141, 169–175.

[44] Narayanan, K.B.; Park, H.H. Homogeneous Catalytic Activity of Gold Nanoparticles Synthesized Using Turnip (Brassica Rapa L.) Leaf Extract in the Reductive Degradation of Cationic azo dye. *Korean J. Chem. Eng* **2014**, 2, 1273–1277.

[45] Zhao, P.X.; Feng, X.W.; Huang, D.S.; Yang, G.Y.; Astruc, D. Basic Concepts and Recent Advances in Nitrophenol Reduction by Gold and Other Transition Metal Nanoparticles. *Coor. Chem. Rev* **2015**, 287, 114–136.

[46] Rajan, A.; Vilas, V.; Philip, D.J. Studies on Catalytic, Antioxidant, Antibacterial and Anticancer Activities of Biogenic Gold Nanoparticles. *Mol. Liq* **2015**, 212, 331–339.