

A biomimetic synthesis of stable gold nanoparticles derived from aqueous extract of *Foeniculum vulgare* seeds and evaluation of their catalytic activity

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Abstract A facile biomimetic approach for the synthesis of gold nanoparticles (AuNPs) using aqueous extract of fennel (*Foeniculum vulgare*) seeds have been reported in this article. The seeds of *F. vulgare* are rich in various plant secondary metabolites (phytochemicals) such as polyphenolic acids, flavonoids, and saponins. The phytochemicals of *F. vulgare* seeds play dual role of reducing and stabilizing agents. The formation of gold nanoparticles was evidenced from the appearance of intense purple color at room temperature with λ_{\max} around 550 nm in the UV–Vis absorption spectra. The stable AuNPs were further characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM) analysis. The synthesized nanoparticles were observed to be polydispersed, spherical and ranged from 10 to 30 nm with an average size of 20 ± 2 nm, as obtained from TEM images. The catalytic activity of gold nanoparticles was investigated by studying the reduction of anthropogenic dyes such as methylene blue (MB) and rhodamine B (Rh-B) with sodium borohydride. Results

showed the possible applications of biogenic AuNPs in environment related problems.

Keywords Gold nanoparticles · Biogenic synthesis · Catalytic reduction · Anthropogenic dyes · Fennel seed

Introduction

Several water soluble anthropogenic dyes are extensively utilized in various industrial processes such as cosmetics, textiles, printing, ceramics, pharmaceuticals and food processing (Kant 2012). For example, methylene blue, a thiazine dye, is readily used in textile, data storage and holographic industries (Rajesh et al. 2014). It is also utilized for staining tissues and body fluids during diagnosis and surgeries (American Pharmacists Association 2012). Moreover, it also has applications as anti-malarial agent and chemotherapeutic agent (Schirmer et al. 2003; Mwangi et al. 2016). Similarly, Rhodamine B, a fluorescent staining dye, has applications in the field of flow cytometry (Temmerman and Nickel 2009), fluorescence microscopy and ELISA tracer techniques (Shelley 1969; Forster et al. 2012). Further, it is also utilized as tracer for determination of transport and flow direction of water (Mull 1993; Hardy et al. 2016). All these processes, at various stages, require large quantity of water, and thus produce effluents which are fortified with various hazardous colorants. These waste water discharges with various dye stuffs lead to elevated demand of oxygen chemically as well as biologically (i.e., COD and BOD).

Most of the anthropogenic dyes are carcinogenic and mutagenic and cause high level toxicity to humans, aquatic organisms and whole eco-system. Therefore, the degradation of these dyes is important industrially and

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environmentally. Generally, coagulation, flocculation, adsorption, chemical precipitation and oxidation methods are employed for the removal of dyes. More recently, noble metal nanoparticles because of their enhanced catalytic activity and high stability have gained importance in the area of catalytic degradation of toxic coloring agents, such as dyes and pigments. For instance, the catalytic reduction and degradation of various dye pollutants using metal nanoparticles (MNPs) such as Cu, Ag, Au, Pd and Pt has been reported (Gangula et al. 2011; Sahoo et al. 2014; Kumari et al. 2015; Yang et al. 2015). Various biogenic synthesis routes have been employed in the fabrication of noble MNPs using *Cylindrocladium floridanum* and *Penicillium* fungus (Sadowski et al. 2008; Narayanan et al. 2013), *Vigna radiata* seed extract (Choudhary et al. 2016), *Catharanthus roseus* leaf extract (Kalaiselvi et al. 2015), *Solanum lycopersicum* fruit extract (Umadevi et al. 2013), *Cocos nucifera* coir extract (Roopan et al. 2013), *Artemisia nilagirica* leaf extract (Vijayakumar et al. 2013), etc.

In this report, we have reported the phytochemical preparation of (AuNPs) utilizing aqueous seeds extract of *Foeniculum vulgare* (fennel seeds). Fennel is a flowering herbaceous plant which belongs to the *Apiaceae* family. The *F. vulgare* seeds are native to Southern Europe and popular as most sought-after ingredient in Chinese, Turkey, and Indian cuisines. The seeds of fennel are extensively grown in all over Europe, Middle-East and all over the Mediterranean regions for their distinctive sweet, anise-flavor. Moreover, the seeds of *F. vulgare* have been reported to exhibit antimicrobial (Purkayastha et al. 2012), antioxidant (Roby et al. 2013), antitumor, antiallergic and memory enhancing properties (Badgujar et al. 2014). The major phytochemicals present in the seeds are saponins, tannins, polyphenolic acids and flavonoids (Purkayastha et al. 2012).

The as-synthesized AuNPs were analyzed using various spectroscopic and microscopic techniques such as UV–Vis; TEM, XRD and FT-IR. Further, the AuNPs were employed as nanocatalysts for the borohydride reduction of MB and Rh-B. The catalytic reduction of these carcinogenic dyes was investigated periodically by studying their decline in intensity of absorption using UV–Vis spectroscopy.

Experimental Section

Materials and methods

Hydrogen tetra chloraurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) of reagent grade was obtained from Sigma-Aldrich while methylene blue (MB), rhodamine B (Rh-B) dyes and NaBH_4 for catalytic reduction reactions were purchased from Fisher Scientific, Mumbai. All solutions used in the

synthesis procedure were prepared with double distilled water.

Preparation of fennel seeds extract

Foeniculum vulgare seeds were obtained from the super market of Ludhiana, Punjab, India. The seeds were washed with deionized water three times to remove any dust particles and left overnight to dry. 5 g of dried seeds were refluxed at 80 °C for 30 min in a 250-ml Erlenmeyer flask containing 150 ml of deionized water. After cooling, the aqueous extract was filtered through Whatman no. 1 filter paper and stored in refrigerator for future use.

Biogenic synthesis of gold nanoparticles

For synthesis of AuNPs using fennel seeds, first, 1 mM aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was prepared by dissolving 98.5 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 250 ml of deionized water and then gold solution and aqueous seeds extract in the ratios (7:3, 8:2, and 9:1 v/v) were carefully mixed in three different 250 ml flasks and labeled as FA-3, FA-2 and FA-1 (where the number 3, 2 and 1 corresponds to volume of seeds extract). The flasks containing reaction mixture were stirred magnetically under dark with 700–800 rpm. During the course of reaction, the color of colloidal solution was changed from yellow to purple which indicated the formation of AuNPs.

Characterization of biogenic AuNPs

UV–Vis spectroscopy

The periodical monitoring of AuNPs formation at a regular interval of 15 min was carried out using Shimadzu 2550 UV–Vis spectrophotometer. An intense peak around 540–550 nm in the visible region was observed which corresponds to surface plasmon resonance (SPR) absorption of nanogold. To investigate the stability of the biogenic AuNPs, the λ_{max} value was also recorded after 24 h. For analysis, 0.3 ml of colloidal AuNPs solution was withdrawn and diluted to 3.0 ml, by adding deionized water in a quartz cuvette. The SPR absorption of AuNPs was recorded in the wavelength range between 250 and 800 nm.

FT-IR spectroscopy

The involvement of active molecules of fennel seeds in the reduction and capping of NPs were determined using Perkin Elmer RX-I, FT-IR spectrophotometer. The dried extract and synthesized AuNPs were mixed with KBr and pellets were formed which were subjected to FT-IR

analysis. For KBr pellet formation, 5 mg each of dried extract and AuNPs were separately mixed with 100 mg of KBr and condensed into pellet using hydraulic press.

XRD studies

To investigate the crystalline nature of prepared biogenic AuNPs, analysis through XRD was performed. The AuNPs suspension was washed thrice with double distilled water and collected by repeated centrifugation on a clean glass slide and measurement was made through a PANalytical X'PERT-PRO X-ray diffractometer by employing monochromatic Cu K α radiation (1.5406 Å) running at 45 kV and 40 mA.

TEM analysis

The stable washed AuNPs suspensions were sonicated and diluted with deionized water to get the intensity of absorbance around 0.50 a.u. and a drop of suspensions was taken on 200 mesh carbon coated copper grids (Ted pella, USA) and placed the grids for 2 min, and removed the remaining solution with Whatman paper, and allowed the grids to dry before measurement. After drying, the particles were visualized through Hitachi H-7500 TEM instrument.

Catalytic efficacy of biogenic AuNPs

The catalytic efficacy of synthesized gold nanoparticles was examined for borohydride reduction of two anthropogenic dyes MB and Rh-B as model reaction. Initially, a 20 ml of colloidal solution of AuNPs was centrifuged and washed thrice with double distilled water and twice with ethanol. Afterwards, the gold nanopellet obtained, was dissolved ultrasonically in 20 ml of distilled water to make gold nanoparticles solution free from biomolecules. The degradation of each dye was studied by recording the UV–Vis spectrum for 2 min. The degradation was also studied without AuNPs and NaBH₄ as control reactions.

Results and discussion

The selection of fennel seeds in the present work has proven to be an inexpensive, green and innovative tool for the fabrication of stable gold nanoparticles. Figure 1 shows the brief reaction process for the preparation of AuNPs. The phytoconstituents of fennel seeds, such as polyphenols and flavonoids (such as rosmarinic acid, chlorogenic acid, quercetin and apigenin) exhibiting strong antioxidant properties, (Faudale et al. 2008) provide excess of electrons to the Au³⁺ ions and responsible for reduction to Au⁰ (AuNPs) and subsequently stabilize the AuNPs. Generally,

some organic ligands or ionic surfactants are employed in the preparation of noble metal nanoparticles and are difficult to get rid of them completely from the final products which may block the active sites of catalysts. The major significance of this biomimetic procedure to fabricate the AuNPs using aqueous seeds extract is that the phytochemicals are easily separable and does not allow the formation of layers around the nanoparticles, which makes them effective catalysts. Moreover, it does not involve any external energy input, and the process occurs normally in distilled water at room temperature, making it efficient and green methodology. Further, this seed extract mediated synthesis of AuNPs highlights another advantage of this approach for the preparation of various noble metal–semiconductor nanocomposites materials.

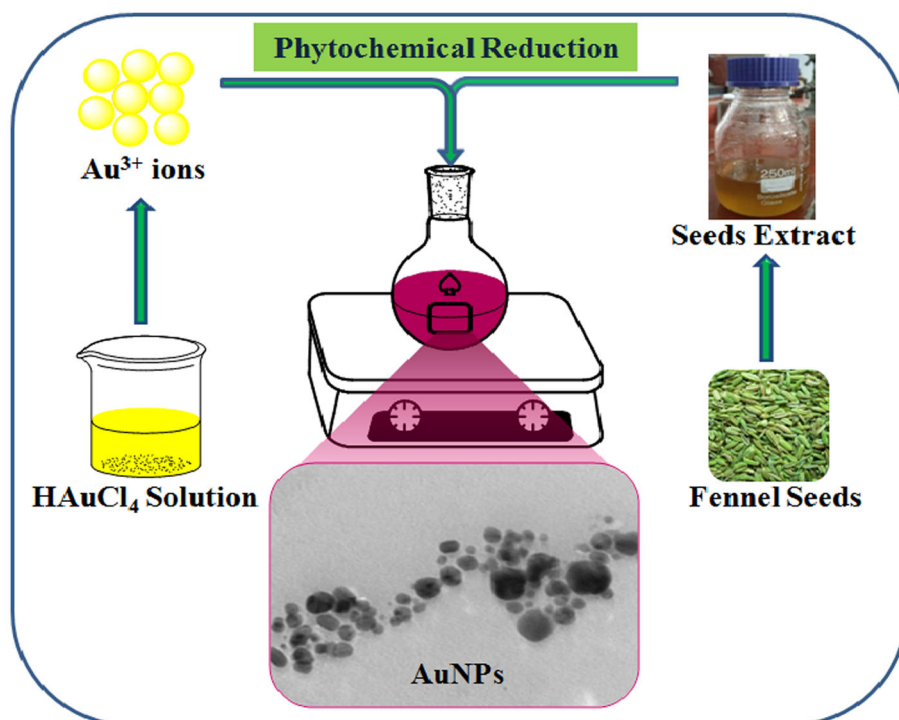
UV–Vis spectroscopy

Figure 2a–c depicts the UV–Vis spectra for FA-1, FA-2 and FA-3. All the three systems showed an optical absorption around 550 nm, which is significant of surface plasmon resonance (SPR) absorption of metallic Au nanoparticles. Further, the effect of time span of reaction between biomolecules of fennel seeds and Au³⁺ ions on the AuNPs synthesis was also investigated and it has been seen that intensity of peak around 550 nm increases with increase in time period. This enhancement in the intensity of SPR can be attributed to increase in number of nanoparticles formation. However, in case of FA-3 sample, where 30 ml aqueous extract was added, reaction reached near completion in 2 h (with no shift in λ_{max} value), which can be attributed to increase in number of phytochemicals involved in reduction process. Figure 2d depicts the UV–Vis spectra of FA-1 (optimized concentration ratio of HAuCl₄.3H₂O: FSE), after 24 h to test the stability of AuNPs. A negligible or slight shift in the intensity of absorption peak was observed, as compared with 2.5 h absorption peak, and no drastic change in intensity of color of solution was observed which indicates that biogenic AuNPs were stable over a period of time.

TEM analysis

The morphologies and sizes of prepared AuNPs were investigated using transmission electron microscopy (TEM) analysis. Figure 3 demonstrates typical TEM images of biosynthesized AuNPs, which depict that the AuNPs were poly dispersed and mostly spherical, while few of the particles were observed to be having irregular shapes. Such variations in morphologies and sizes of biogenic nanoparticles are quite common (Gangula et al. 2011; Choudhary et al. 2016). TEM analysis further revealed that majority of AuNPs had an average size around 18–20 nm. For particle

Fig. 1 Reaction process showing the formation of stable AuNPs by phytochemical reduction of Au^{3+} ions with fennel seeds extract



size distribution, around 120 particles were examined with ImageJ software, and a histogram was plotted (Fig. 3d). From these figures, it has been observed that the average size of particles is approximately 20 ± 2 nm, and the nanoparticles with sizes varying from 10 to 30 nm accounts for around 90% of all particles examined.

X-Ray diffraction analysis

To investigate crystalline structure of the synthesized AuNPs X-ray diffraction study was carried out. The diffraction pattern of the biosynthesized AuNPs (Fig. 4) shows five intense Bragg reflections which are indexed to face-centered cubic (fcc) lattice of gold. A comparison with JCPDS file no. 04-0784 (Lü et al. 2012) confirmed the crystalline structure of AuNPs, as confirmed by the peaks at 2θ values of 38.12° , 44.37° , 64.53° , 77.39° and 81.79° correspond to (111), (200), (220), (311) and (222) planes, respectively. Moreover, the XRD peaks were observed to be broader at their bases, which further confirmed that the formed AuNPs were in nanorange (Ahmad et al. 2010).

FT-IR spectroscopy

The FT-IR spectrum of dried aqueous fennel seeds extract and prepared AuNPs were recorded for investigating the functional groups of phytoconstituents involved in the reduction and capping of the prepared nanoparticles (Fig. 5). The major absorbance band present in the

spectrum of fennel seeds were at 3345.66 , 2928.30 , 2852.83 , 1710.19 , 1619.62 , 1455.85 , 1241.50 , 1167.54 and 1036.23 cm^{-1} . The broad band at 3345.66 cm^{-1} could be assigned to stretching of hydrogen bonded phenolic groups of phytoconstituents. The bands at 2928.30 and 2852.83 cm^{-1} correspond to asymmetric and symmetric stretching vibrations, respectively, of methylene groups. The bands at 1710.19 , 1619.62 and 1455.85 cm^{-1} can be due to carbonyl (C=O), aromatic (C=C) and carboxyl (O=C–O) stretching vibrations, respectively, whereas the sharp band at 1241.50 cm^{-1} corresponds to epoxy (C–O) ring vibrations. The bands at 1167.54 and 1036.23 cm^{-1} were due to the stretching vibrations of C–O group of alkoxy and alcoholic groups, respectively. For AuNPs, the characteristic absorbance bands were observed at 3412.83 , 2923.02 , 1621.13 , 1449.06 , 1366.80 and 1046.03 cm^{-1} , respectively. In comparison with FT-IR spectra of fennel seeds, small shifts in the absorbance bands from 3345.66 to 3412.83 cm^{-1} , 1619.62 to 1621.13 cm^{-1} , 1455.85 to 1449.06 cm^{-1} and 1036.23 to 1046.03 cm^{-1} were observed, which suggest the binding of hydroxyl and carboxylate groups of phytoconstituents with gold nanoparticles.

Mechanism for the formation of AuNPs by phytoconstituents of fennel seeds

To propose the mechanism of redox reaction occurring between the phytoconstituents of fennel seeds and Au^{3+}

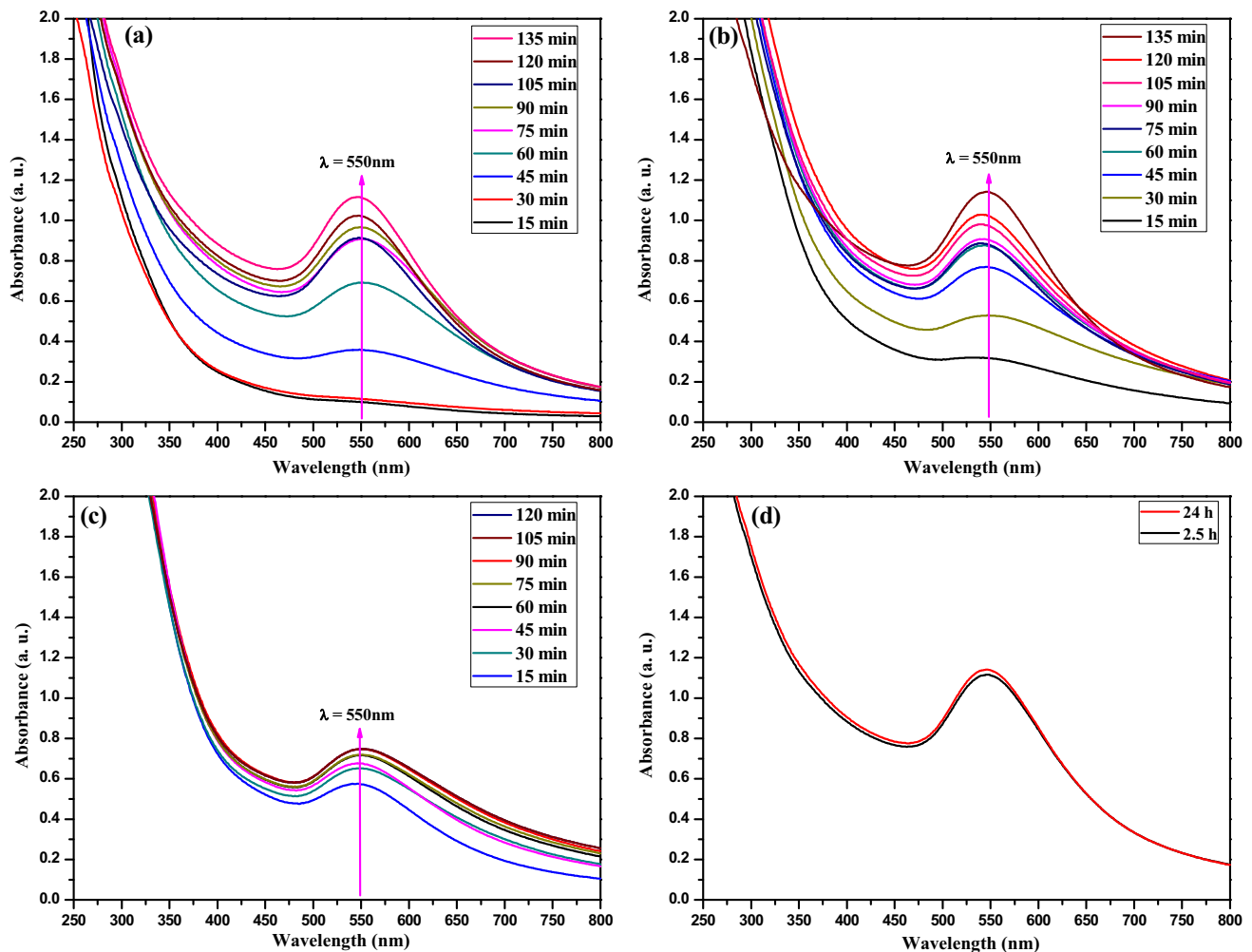


Fig. 2 The UV–Vis spectra of AuNPs synthesized with **a** FA-1 (9:1 v/v), **b** FA-2 (8:2 v/v), **c** FA-3 (7:3 v/v) ratios of gold solution and seeds extract, **d** spectra recorded after 24 h, showing stability of biogenic nanoparticles

ions is very difficult, because every plant material contains diverse range of phytoconstituents with various complex molecular structures. However, an attempt has been made to discuss the process of bio-formation and stabilization of AuNPs. Generally, phytochemicals reduce the metal ions by providing excess of electrons and protect the reduced particles to aggregate by capping them. Therefore, they play a dual role. Figure 6 represents the plausible mechanism for the biogenic formation of AuNPs by active phytochemicals present in the seeds extract. The polyphenolic compounds, such as rosmarinic acid, chlorogenic acid, quercetin, and apigenin (Faudale et al. 2008), containing high density of hydroxyl groups (having common functionalities as shown in mechanism), synergistically reduce the Au^{3+} to Au^0 with concomitant oxidation of the polyphenolic compounds to quinones. Further, collision of these Au^0 nuclei with each other results in the formation of AuNPs, which can be protected from agglomeration by

capping with quinones and other coordinating phytoconstituents present in the seeds extract.

Catalytic activity of AuNPs for reduction of anthropogenic dye pollutants

The catalytic reduction of methylene blue (0.3 ml–250 μM) by NaBH_4 (1.0 ml–10 mM) was carried out using stable colloidal solution of biogenic gold nanoparticles (0.3 ml) as catalyst. Total volume was made 3.0 ml by adding double distilled water. Generally, methylene blue shows absorption maxima around 660 nm and a small shoulder around 610 nm. After adding AuNPs to the solution of methylene blue dye and NaBH_4 , the intense blue color of the solution rapidly disappeared. Within 2 min, complete disappearance of blue color of MB was observed which further reflected in decrease in intensity of MB solution (Fig. 7a). Further, it was found that in the

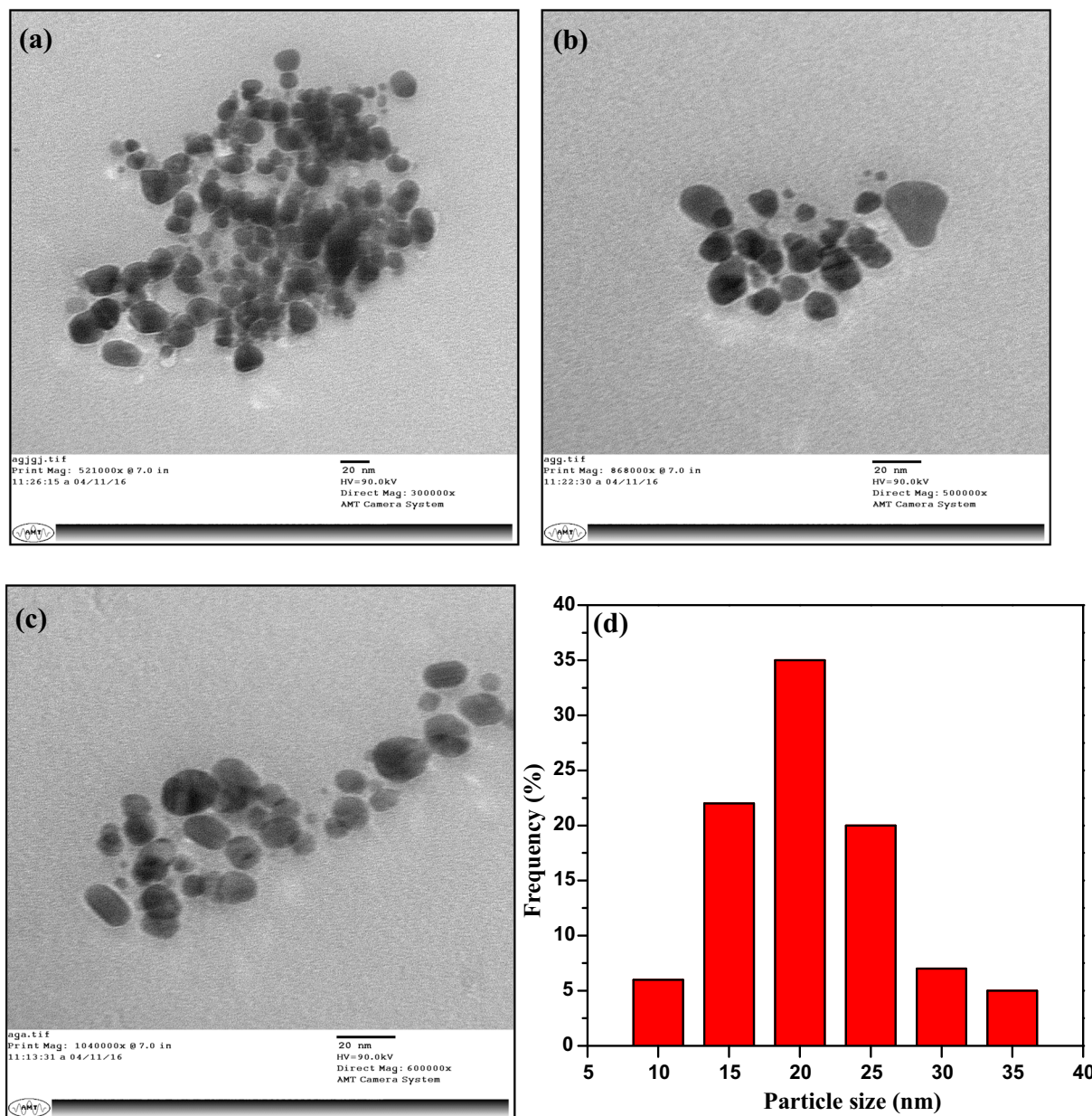


Fig. 3 TEM images (a–c) of AuNPs synthesized with (9:1 v/v) ratio of gold solution and seeds extract and **d** histogram showing the particle size distribution

absence of AuNPs, the degradation of MB did not occur. Similarly, the catalytic efficacy of synthesized gold nanoparticles (0.3 ml) in reduction (degradation) of (0.3 ml–100 μ M) rhodamine B (Rh-B) by NaBH_4 (1.0 ml–10 mM) was also studied at room temperature. The characteristic pink color of Rh-B and the corresponding absorption peak observed at 554 nm was disappeared within 2 min using NaBH_4 and gold nanocatalyst. Moreover, in the absence of gold nanoparticles, NaBH_4 alone was not able to degrade the Rh-B (Fig. 7b). The reduction of anthropogenic dyes using NaBH_4 alone, in the absence of gold nanocatalysts did not occur, due to the kinetic

barrier. Similar results for the degradation of dyes have been reported using palladium nanoparticles (Kora and Rastogi 2016).

This ultra-rapid catalytic activity of biogenic gold nanoparticles towards the degradation of dye pollutants can be explained on the basis of adsorption behavior of dye molecules onto the metal nanoparticles. As discussed earlier that ionic surfactants employed in the preparation of noble metal nanoparticles make insulating layer around them and block the active sites of catalysts, and thereby affect the accessibility of reacting molecules to reach metal particles (Jana et al. 2000). Therefore, a large decrease in

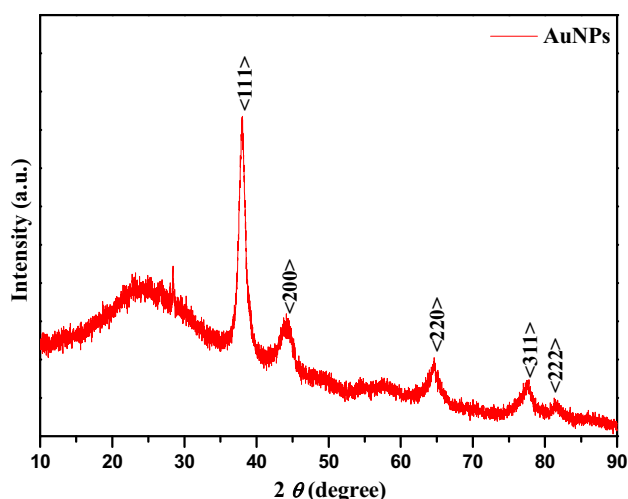


Fig. 4 X-ray diffraction pattern of synthesized AuNPs using fennel seeds extract

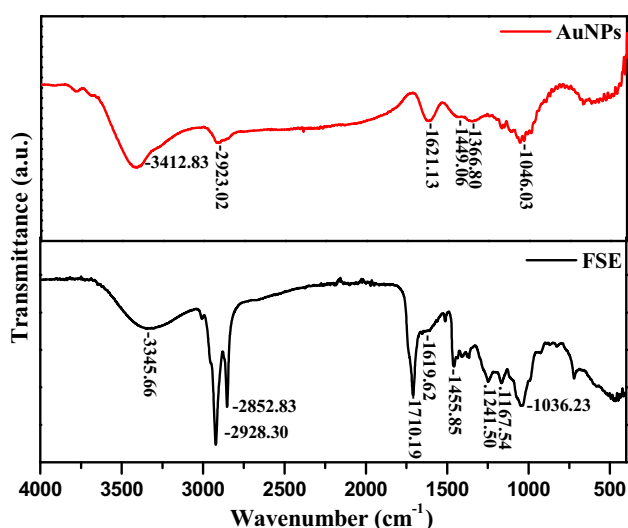
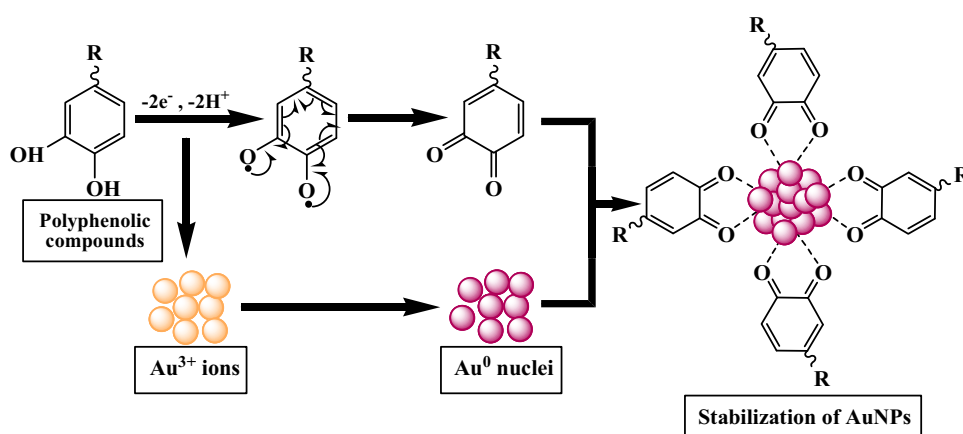
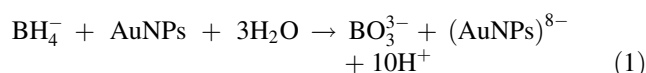


Fig. 5 FT-IR spectra of dried aqueous extract of fennel seeds and stabilized AuNPs

Fig. 6 Plausible mechanism for formation and stabilization of AuNPs by phytoconstituents of fennel seeds



the rate of reaction is observed. However, the biomolecules are easily separable and does not allow the formation of layers around the nanoparticles and make them efficient catalysts. Further, a metal catalyzed reduction/degradation process can be easily discussed by electrochemical mechanism, in which the metal nanoparticles act as electron relay for reductant and oxidant. When the dye molecules and BH_4^- ions are in close proximity, they get adsorbed on the surface of metal particles and electron transfer from BH_4^- ions to dye molecules occurs via AuNPs (Jiang et al. 2005). BH_4^- ions first provide electrons to AuNPs and produce a negatively charged layer around them, as shown by reaction (1).



Therefore, the electron cloud around biogenic gold nanoparticles is easily accessible to the dyes and accordingly no induction period is observed as compared to surfactant stabilized nanoparticles (Fig. 8).

Conclusion

A facile, biomimetic and environment friendly procedure for the preparation of stable gold nanoparticles (AuNPs) was described using aqueous extract of fennel (*Foeniculum vulgare*) seeds. The bioreduction of gold ions to crystalline nanoparticles with an average size of 20 ± 2 nm and subsequent capping was mediated by polyphenolic compounds of fennel seeds. Further, these surfactant free biogenically prepared gold nanoparticles showed an excellent catalytic activity towards the degradation of anthropogenic dye pollutants. Hence, the efficient dye degradation efficacy of biogenic AuNPs can have wide applications in environment remediation of waste water polluted with toxic synthetic dyes and pigments.

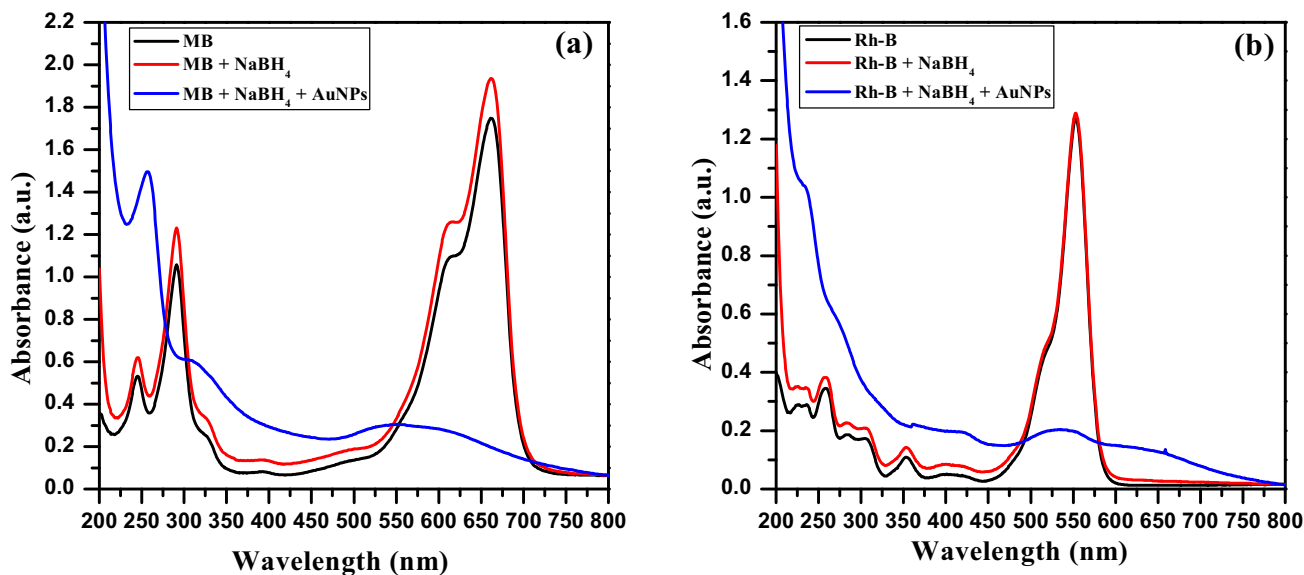


Fig. 7 The UV-Vis spectra of decolorization of dyes by NaBH₄ using AuNPs as catalyst at 2 min. **a** Methylene blue, **b** rhodamine B

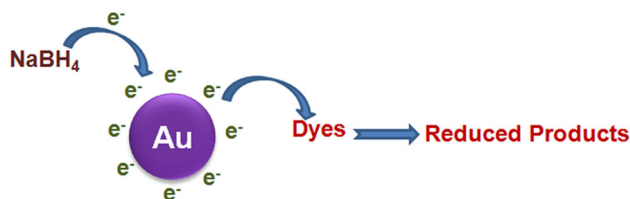


Fig. 8 Proposed mechanism for the catalytic reduction of MB and Rh-B by NaBH₄ in the presence of AuNPs into respective reduced products

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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