Affordable and environmentally friendly method for the synthesis of a green silver nanophotocatalyst based on *Mespilus germanica*

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Abstract

Leaves of *Mespilus germanica* have been utilized as a green and inexpensive reducing and stabilizing agent to synthesize silver nanoparticles without using any capping agent or harsh and toxic solvents. In this protocol a silver nanophotocatalyst was synthesized by a green method via immobilization of Ag NPs on the surface of *Mespilus germanica* seed as a green photocatalyst. The biosynthesized nanophotocatalyst was characterized by ultraviolet–visible, Fourier-transform infrared, X-ray diffraction, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, and transmission electron microscopy. The photocatalytic activity of the synthesized silver nanocatalyst was investigated by using it for the degradation of methylene blue under sunlight. The results showed good photocatalytic activity without any agglomeration. In addition, the silver nanophotocatalyst can be recycled and reused several times in the same reaction without significant loss of activity.

Graphic abstract

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1 Introduction

Pollution is currently one of the biggest concerns of societies. It has a real effect not only on environment but also on people's lives [1]. There have been many efforts to eliminate or at least minimize the environmental impact of chemical processes and use of photocatalysts is one of the cleanest and cost-effective methods [2]. A photocatalyst could be activated in an aqueous solution and in the presence of sunlight and is normally not very sensitive to temperature [3–7].

Metal nanoparticles have been used widely in chemistry as well as in optics and electronics. They can be tuned to photo-degradation of organic dyes [8–13]. The reduced size of metal nanoparticles results in a high surface to volume ratio which can enhance the reactant-catalyst interaction [14–16]. Silver nanoparticles (Ag NPs) are capable of absorbing visible light through electronic transitions between the bands and are prominent as active photocatalysts in the sunlight frequency range [17–19]. They have high optical and thermal performance due to their surface plasmon resonance properties [20]. There are many reports in the literature on the application of Ag NPs as a photocatalyst [21–25] and they have been widely used in different industries because of their low toxicity and antibacterial properties [26, 27]. Ag NPs have been used extensively in electronic industries to enhance electrical conductivity [28] or for printable electronics [29]. However, using Ag NPs as a photocatalyst in the pure form is limited because of agglomeration and recombination of electron-hole pairs. These issues can be resolved by using substrates with good dispersion ability to stabilize and immobilize nanoparticles [30].

Applications of green methodologies for the preparation of silver nanoparticles have more merit than conventional physical and chemical methods. One of the methods of this approach is use of plant extracts as a natural and inexpensive resource for the synthesis of various nanoparticles with suitable shapes and sizes [31–37]. These extracts play an important role in the stabilizing, reducing, and capping of nanoparticles [38–45]. Therefore, attempts to synthesize these nanoparticles with green technology and using plant extracts are becoming more popular.

Mespilus germanica belongs to the Rosaceae flower family [46] and grows in various weather conditions and in many locations such as North Anatolia, Southeastern Europe and Iran [47]. Different parts of this plant such as its fruit, flower and leaves have been widely used in traditional medicine to treat diarrhea, bloating and gastric acid,

intestinal swelling, and oral ulcers [48, 49]. The *Mespilus germanica* fruit seed contains ascorbic acid (AA) and a high total phenolic content which is responsible for its antioxidant activity [46]. These functional groups could be used as active sites to immobilize silver nanoparticles (Ag NPs). Overall, leaf extract of *Mespilus germanica* could be considered a natural source of antioxidants, phenolic acids, flavonoids, fatty acids and tannins [50, 51].

In continuation of our work on the green preparation of nanomaterials [Rashidi, 2019 #50], herein we report the use of *Mespilus germanica* leaf extract for biosynthesis of Ag NPs. The *Mespilus germanica* leaf extract was used as a reducing and capping agent to synthesis Ag NPs without using any toxic and additive substances. Ag NPs were immobilized on the *Mespilus germanica* seed as a green and inexpensive support for the preparation of nanophotocatalysts. The synthesized nanophotocatalyst was used for photodegradation of methylene blue under sunlight. The obtained results showed that the synthesized nanophotocatalyst has a high photocatalytic activity, and can be recycled and reused without significant decrease in its activity.

2 Experimental

2.1 Instruments and reagents

Silver nitrates (AgNO_3), methylene blue (MB) and solvents were purchased from Merck and Aldrich chemical companies and used without further purification, *Mespilus germanica* was obtained from Shiraz area, (City of Shiraz, Province of Fars, Iran). Products were identified by comparing their physical and spectral data with those of known compounds. The synthesized nanophotocatalyst was characterized by Infrared Spectroscopy (FT-IR Bruker, Germany, RT-DLATGS detector). The X-ray Diffraction (XRD) patterns were examined on a model X'PertPro diffractometer (Panalytical, Almelo, and the Netherlands) using Cu K α radiation. Ultraviolet-visible Spectroscopy (UV-Vis) was performed in the range of 200–900 nm on a Cary 50 single detector double beam in time spectrophotometer (Varian, Australia). The morphologies and sizes of the prepared samples were characterized by A LEO 912AB Transmission Electron Microscopy [49] with an accelerating voltage of 100 kV, Free Emission Scanning Electron Microscopy (FESEM-TESCAN-MIRA3) and Energy Dispersive X-ray Spectroscopy (EDX, FESEM-TESCAN MIRA3).

2.2 Preparation of *Mespilus germanica* leaf extract (MGLE)

The leaves of *Mespilus germanica* were washed with distilled water, and then completely dried and powdered. The phytochemicals were extracted using a Soxhlet extractor. The extract solution has been prepared by adding deionized water (175 mL) and ethanol (175 mL) into a 500 mL flask and the dried *Mespilus germanica* leaf powder (10 g) was placed in Soxhlet cartridge. The solution was heated to 100 °C for 24 h and then solvents were removed using a rotary evaporator. The extract was dried at room temperature and stored in a refrigerator.

2.3 Biosynthesis of Ag NPs using MGLE

2 mL of MGLE (3.5% w/v) was stirred into an aqueous solution of AgNO₃ (10 mg AgNO₃ in 10 mL water) at 60 °C. The biosynthesized Ag NPs completely formed in about 10 min by reduction of the silver ions (Ag⁺) to Ag NPs and the color of the solution gradually changed from brown to dark indicating the formation of the Ag NPs. The resulting solution was analyzed by UV–Vis spectrophotometry. The precipitated Ag NPs was centrifuged at 3500 rpm for 15 min. The precipitate was subsequently washed with water and ethanol to remove uncoordinated phytochemicals and the black powder silver nanoparticle was dried overnight at room temperature.

2.4 Green synthesis of Ag NPs/*Mespilus germanica* seed nanophotocatalyst (Ag NPs/MGS NPC)

The silver photonanocatalyst has been prepared according to our recently reported method [51]. The *Mespilus germanica* seeds were washed with distilled water, dried, formed into a powder and dried overnight at room temperature. In order to prepare the Ag NPs/*Mespilus germanica* seed, 0.1 g of *Mespilus germanica* seed powder was mixed in water and then aqueous solution of AgNO₃ (10 mg AgNO₃ in 10 mL water) was added to the mixture and stirred at 60 °C for 12 h. Then 2 mL of the MGLE (3.5% w/v) was added to the above suspension at 60 °C. After the reaction was completed and the Ag NPs formed, the color of mixture turned dark. Finally, the suspension of the Ag NPs/*Mespilus germanica* seed was centrifuged at 3500 rpm for 15 min. The prepared sediment was washed three times with deionized water and one time with ethanol and then dried overnight at room temperature.

2.5 Photodegradation of methylene blue by Ag NPs/*Mespilus germanica* seed nanophotocatalyst (Ag NPs/MGS NPC)

To evaluate the efficiency of the synthesized nanophotocatalyst, in a typical experiment, to 25 mL of an aqueous solution of methylene blue (MB, 5 ppm) 7 mg nanophotocatalyst (Ag NPs/MGS NPC), was added. Then the reaction container was placed in the dark for 30 min to achieve an adsorption/desorption equilibrium between Ag NPs/MGS NPC and dyes before irradiation. Then, this suspension was stirred under sunlight (10 AM). The UV–Vis spectrophotometer was used to investigate the progress of MB photodegradation at certain time intervals. After the completion of the reaction, the catalyst was separated from the reaction mixture by brief centrifugation and washed with distilled water and ethanol and dried for the next run. The recycled catalyst was used 6 times without significant change in its activity, which confirms the stability and recyclability of the catalyst. The effects of factors such as pH, temperature, light source and amount of nanophotocatalyst on the degradation of MB were also investigated and the percentage of degradation was measured according to the following equation

$$\text{Degradation \%} = \frac{A_0 - A}{A_0} \times 100$$

In the above equation A_0 is the initial absorption of MB before irradiation and A is the absorption of MB after irradiation at selected time intervals.

3 Result and discussion

Environmentally friendly syntheses of nanoparticles have been of interest in the past decade. Herein, we utilized a safe method for the synthesis of Ag NPs by using *Mespilus germanica* leaf extract (MGLE) as an inexpensive reducing and stabilizing agent. The synthesized NPs were immobilized on *Mespilus germanica* seed (MGS). The seed of this fruit is considered waste but here we succeed in using the *Mespilus germanica* seed as a support for Ag NPs as a new nanophotocatalyst (Scheme 1).

Scheme 1 Image of Ag NPs/*Mespilus germanica* seed nanophotocatalyst synthesis steps

Fig. 1 UV-Vis spectra of MGLE

Fig. 2 UV-Vis spectra of biosynthesized Ag NPs

Fig. 3 FT-IR of MGLE (a) and biosynthesized Ag NPs (b)

Fig. 4 FT-IR of MGS and Ag NPs/MGS NPC

3.1 Characterization of MGLE and biosynthesized Ag NPs

3.1.1 UV-Vis of MGLE and biosynthesized of Ag NPs

The UV-Vis spectra of MGLE and Ag NPs are shown in Figs. 1 and 2 respectively. The absorptions in the 200–300 nm range are related to the presence of poly-phenolic compounds and conjugated aromatic systems containing benzoyl rings [52–54]. It is clear that after the

Fig. 5 XRD pattern of MGS (a) and Ag NPs/MGS NPC (b)

addition of MGLE to Ag^{1+} solution, the Ag NPs are formed (Fig. 2). This can be confirmed by the appearance of a peak in the 420–430 nm range. The stability of synthesized Ag NPs was studied using its UV-Vis spectrum after 30 days. The resulting UV-spectrum was similar to Fig. 2, which indicates good stability of Ag NPs as no significant changes in the shape and position of the absorption band were observed.

3.1.2 FT-IR of MGLE and biosynthesized Ag NPs

The FT-IR spectra of MGLE and biosynthesized Ag NPs are presented in Fig. 3, which shows only slight difference in the shape and location of absorption bands. As shown in Fig. 3a, the broad band at 3405 cm^{-1} relates to OH groups in compounds such as alcohols, phenols and carboxylic acids in the MGLE. Also absorption bands at 2927, 1681, 1618, 1518 and 1405, 1282, 1045, 889, 818, 766 and 610 cm^{-1} are related to C–H stretching, C=O stretching, C=C stretching of aromatic ring, C–O stretching of ether groups, C–H bending of hydrocarbons and O–H bending of hydroxyl groups, respectively. Figure 3b displays feature due to several functional groups after formation of the desired Ag NPs by using MGLE. The presence of almost the same absorptions in the IR spectrum of Ag NPs as in MGLE indicates the existence of Ag NPs on the surface of MGLE.

Fig. 6 FE-SEM of Ag NPs/MGS NPC

3.2 Characterization of MGS and Ag NPs/MGS NPC

3.2.1 FT-IR of MGS and Ag NPs/MGS NPC

IR spectroscopy was used to clarify the functional groups on the surface of the nanocatalyst. The FT-IR spectra of MGS and Ag NPs/MGS NPC were taken and shown in Fig. 4. As previously mentioned, the main component of *Mespilus germanica* seed is ascorbic acid. Therefore, the typical functional groups for this compound are expected to be observed in FT-IR spectra.

The IR spectrum which was shown in Fig. 4a indicates that the O–H, C–H, C=O, C=C, C–O, C–H, O–H functional groups appeared at 3425, 2925, 1653, 1521 and 1436, 1155, 1080, 1019, 859, 763, 576 and 525 cm^{-1} respectively. Some of these functional groups play an important role in immobilization of Ag NPs on the surface of MGS. These absorptions are all shifted towards lower frequencies, which indicates a strong bond between the Ag NPs and MGS. In comparison with *Mespilus germanica* seeds, the FT-IR analysis of Ag NPs/MGS NPC confirms that there were no changes in the functional

Fig. 7 EDS of Ag NPs/MGS NPC **Fig. 8** TEM of Ag NPs/MGS NPC

groups after the immobilization of Ag NPs on the *Mespi-lus germanica* seeds.

3.2.2 XRD of MGS and Ag NPs/MGS NPC

In order to detect the phase of the samples and nanophotocatalyst components, the XRD patterns of MGS and Ag NPs/MGS NPC were obtained and are shown in Fig. 5. As shown in Fig. 5a, there are three clear signals at 2θ of 16° , 22° and 34° which suggests the presence of ascorbic acid

as the main component in MGS. This is consistent with the previous reports [55]. As shown in Fig. 5b, in addition to the peaks related to MGS, there are also peaks of silver nanoparticles. Figure 5b clearly shows peaks at 38.2° , 44° , 64° and 78° which corresponded to the crystal reflections of the (111), (200), (220) and (311) planes of Ag NPs, respectively. The results are consistent with the JCPDS card (87-0717) for Ag NPs [56]. Furthermore, the size of Ag NPs was calculated using the XRD results. The estimated

Table 1 The influence of time on the photodegradation of MB dyes in the presence of 7.0 mg of MGS and Ag NPs/MGS NPC

Irradiation time (min) sunlight	Percentage degradation (%)	
	MGS (7.0 mg)	Ag NPs/MGS NPC (7.0 mg)
0	—	0
5	—	77
10	—	83
15	—	88
20	—	90
25	—	92
30	—	93
35	—	97
35	—	97

Reaction condition: pH = 10, MB concentration = 5 ppm

Fig. 9 The effect of pH on photodegradation of MB using Ag NPs/MGS NPC

average size of Ag NPs is 21 nm using the Debye–Scherer's equation. The results are consistent with TEM analysis.

3.2.3 FE-SEM of Ag NPs/MGS NPC

To evaluate the morphology of the prepared nanophotocatalyst, an analysis of the FE-SEM was performed and is shown in Fig. 6. The FE-SEM images of Ag NPs/MGS NPC indicate that the Ag NPs have spread over the porous surface MGS support and form smaller particles. The Ag NPs appear as bright points in Fig. 6. It should be noted that the greater porosity in the structure of support increases the surface to volume ratio, which prevents the aggregation of nanoparticles and also increases photocatalytic activity.

Fig. 10 The effect of the amount of Ag NPs/MGS NPC on the photodegradation of MB **Fig. 11** The effect of light on the photodegradation of MB

3.2.4 EDS of Ag NPs/MGS NPC

EDS analysis was used to study the elemental composition of the Ag NPs/MGS NPC. The results are presented in Fig. 7. As shown in the Fig. 7, there are C, N, O and Ag elements in the nanophotocatalyst Ag NPs/MGS NPC. The presence of Ag in the nanophotocatalyst structure confirms the synthesis of Ag NPs on the MGS and these results are consistent with the above findings.

3.2.5 TEM of Ag NPs/MGS NPC

To illustrate the shape and size of the Ag NPs/MGS NPC, the TEM analysis was done and their images are exhibited in Fig. 8. These images show that MGS has porosity and the silver pseudo spherical nanoparticles with an average size of 10 to 30 nm are dispersed on the surface without any agglomeration. The Ag NPs are seen as dark dots on the MGS.

3.2.6 The photocatalytic activity of Ag NPs/MGS NPC

The photocatalytic activity of Ag NPs/MGS NPC was studied by analysis of the degradation of methylene blue under sunlight in the presence of 7.0 mg of the Ag NPs/MGS NPC. The reaction progressed in the presence of the nanophotocatalyst with 97% degradation in 35 min. Meanwhile, in the presence of 7.0 mg of MGS support alone, no progress was observed. The results are presented in Table 1. Further, the effects of environmental factors on the photocatalytic activity were investigated.

3.2.7 The effect of pH on photodegradation of MB

Previous studies indicate that pH is the main factor in the photocatalytic degradation of dyes [57, 58]. Therefore, the effect of pH (range 2–12) on the degradation of MB in the presence of 7.0 mg of photocatalyst was evaluated under sunlight for 10 min. The pH of the solution was adjusted by adding 1 M HCl and/or NaOH. The results are shown in Fig. 9. These results reveal that by increasing the pH from

2 to 10, the degradation of MB increases from 65 to 97%. However, by increasing the pH from 10 to 12, the degradation percentage of MB decreased to 88%. Based on the results, it can be assumed that pH affects the properties of the nanophotocatalyst surface and the number of its active sites. Also, by increasing the pH, the number of hydroxide ions in solution increases which can lead to generation of a higher radical concentration. Higher radical concentration will accelerate the dye degradation process. But at a pH higher than 10, high concentration of hydroxide ion may lead to degradation and change in the catalyst surface, and the photodegradation progress of the dye is reduced. Therefore pH 10 was chosen as the optimum pH.

3.2.8 The effect of Ag NPs/MGS NPC amount on photodegradation of MB

In order to determine the importance of the amount of nanophotocatalyst on the rate of dye photodegradation, the degradation of MB aqueous solution (constant concentration of 5 ppm) was tested with different amounts of Ag NPs/MGS NPC (5.0–9.0 mg) at pH 10 under sunlight for times up to 35 min. According to the results shown in Fig. 10, with an increase in the amount of photocatalyst from 5.0 to 7.0 mg, the degradation rate also increased from 57 to 97%. The reason for this phenomenon is that the amount of catalyst effects the amount of light absorption [59]. By increasing the amount of photocatalyst from 7.0 to 9.0 mg, the dye degradation rate was reduced. Although we haven't investigate this effect any further, it may be due to the darkness of the solution and light scattering rather than light adsorption [60]. Therefore, the optimal amount of photocatalyst was 7.0 mg.

Fig. 12 The effect of temperature on photodegradation of MB (in the absence sunlight)

Fig. 13 The proposed mechanism for photodegradation of MB

Table 2 Comparing the results of this work with other methods published in the literature for the degradation of MB

Entry	Photocatalyst	Light source	Time	Degradation (%)	References
1	Ag NPs	Solar light	60 min	1.1	[65]
2	Ag NPs	Visible light	12 h	46	[66]
3	Ag NPs	UV light	4 h	28	[67]
4	Ag-ZrO ₂	Blue light	60 min	48	[21]
5	Ag-SiO ₂	Blue light	60 min	50	[21]
6	Ag-zeolite Y	Blue light	60 min	68	[21]
7	Ag/ZnO nanoflower	Visible light	2 h	40	[68]
8	Ag-TiO ₂	Visible light	150 min	50	[69]
9	NiO-ZnO-Ag nanocomposite	UV light	90 min	94	[70]
10	Ag NPs/MGS NPC	Sunlight	35 min	97	This work

Fig. 14 Recycling of Ag NPs/MGS NPC on degradation of MB under similar conditions

3.2.9 The effect of source light and temperature on photodegradation of MB

The above-mentioned degradation reaction was repeated in the presence and absence of sunlight in order to investigate the effect of light on photocatalytic activity. As shown in Fig. 11, the degradation percentage of MB in the absence of sunlight was 42% within 100 min but it was 97% in the presence of sunlight at ambient temperature within 35 min (Fig. 10). These results indicate the importance of sunlight as the source of photons. The reason for this observation can be attributed to an increase in radical creation which facilitates the process of photodegradation of the dyes [61]. Subsequently, the degradation reaction was carried out under the same conditions at 60° C, but no significant change was observed in the progression of the reaction (Fig. 12). Therefore, sunlight was considered as a free, endless and safe source of photons for the photodegradation process of MB.

3.3 Photocatalytic mechanism

Herein, we propose a possible mechanism for the degradation of MB based on photoelectron-hole pairs. When the Ag NPs that are immobilized on the surface of *Mespilus germanica* seeds absorb sunlight, the surface electrons get excited and are transferred to a higher energy state. This is based on the Surface Plasmon Resonance (SPR) effect and the interband transition of the 4d electrons to the 5sp band. Those electrons interact with water-soluble oxygen molecules to form superoxide anion radicals ($O_2^{\cdot-}$) which degrade the MB molecules. On the other hand, the resulting holes in the valence band of silver react with water in a redox reaction to form hydroxyl radicals ($OH^{\cdot}$). Finally, the radical species ($O_2^{\cdot-}$ and $OH^{\cdot}$) will attack the MB molecules that are adsorbed onto the surface of catalyst and degrade the dye. In addition, methylene blue dye degradation by electron-hole pairs is also possible. Generally, the resulting electron-hole pair migrates onto the surface of the catalyst and will photodegrade the MB dye molecules [62–64]. The proposed mechanism is shown in Fig. 13.

Table 2 shows the comparison of the results of this protocol with the other reported method. The prepared nanophotocatalyst has shown excellent photocatalytic activity in the degradation of MB with the lowest time compared to the previously reported methods.

3.4 Photocatalyst recyclability and reusability

Recyclability and reusability are the two main factors for each nanophotocatalyst, especially for commercial and industrial applications. The silver nanophotocatalyst was separated by centrifugation after each reaction, washed

with distilled water and ethanol, and then dried. They were used in the degradation reaction of MB under the same reaction conditions six times. The results are reported in the Fig. 14. As can be seen, the recycled nanophotocatalyst shows similar catalytic efficiency after several uses.

4 Conclusion

In this report, we have presented an inexpensive and green method for the synthesis of Ag NPs using *Mespilus germanica* leaf extract. Subsequently, the nanophotocatalyst was synthesized through immobilization of Ag NPs on the surface of *Mespilus germanica* seeds. The prepared nanophotocatalyst has shown excellent photocatalytic activity in the degradation of MB with the least amount of photocatalyst (7.0 mg) under sunlight as a safe energy source. The catalyst can be used at least 6 times without significant decrease in its activity.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding authors state that there is no conflict of interest.

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