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## ORIGINAL ARTICLE

# Phyto-crystallization of silver and gold by *Erigeron annuus* (L.) Pers flower extract and catalytic potential of synthesized and commercial nano silver immobilized on sodium alginate hydrogel



Palanivel Velmurugan <sup>a,1</sup>, Min Cho <sup>a,1</sup>, Sang-Myung Lee <sup>a</sup>, Jung-Hee Park <sup>a</sup>,  
Kui-Jae Lee <sup>a</sup>, Hyun Myung <sup>b</sup>, Byung-Taek Oh <sup>a,\*</sup>

<sup>a</sup> Division of Biotechnology, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan, Jeonbuk 570-752, South Korea

<sup>b</sup> Department of Ecology Landscape Architecture-Design, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan 570-752, South Korea

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## KEYWORDS

*E. annuus* flower extract;  
Silver;  
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Catalytic activity

**Abstract** A green, eco-friendly approach for the synthesis of silver and gold nanoparticles (AgNPs and AuNPs) using *Erigeron annuus* (L.) pers flower extract as both the reducing and capping agent is reported for the first time. Optimal nanoparticle production was achieved by adjusting various parameters including pH, extract concentration, metal ion concentration, and time. Initial verification of AgNP and AuNP production was done by visual observation and measuring surface plasmon spectra at 434 and 537 nm, respectively. The synthesized AgNPs and AuNPs were characterized by high resolution-transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), energy dispersive spectrophotometry (EDS), Fourier transform infrared spectroscopy (FTIR) and zeta potential. The catalytic potential of *E. annuus* flower extract, silver ions, synthesized AgNPs, commercial grade AgNPs, and a mixture of flower extract and AgNPs immobilized on sodium alginate hydrogel beads (Na/Al HB) was analyzed. The ability of these immobilized materials to degrade methylene blue was investigated. Commercial grade AgNPs immobilized with Na/Al HB 1.5 g/20 mL were observed to have good catalytic activity followed by a mixture of syn-

\* Corresponding author. Tel.: +82 63 850 0838; fax: +82 63 850 0834.

E-mail address: [btoh@jbnu.ac.kr](mailto:btoh@jbnu.ac.kr) (B.-T. Oh).

<sup>1</sup> These authors contributed equally to this work.

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thesized AgNPs immobilized with Na/Al HB and *E. annuus* flower extract immobilized with Na/Al HB at 1.5 g/20 mL.

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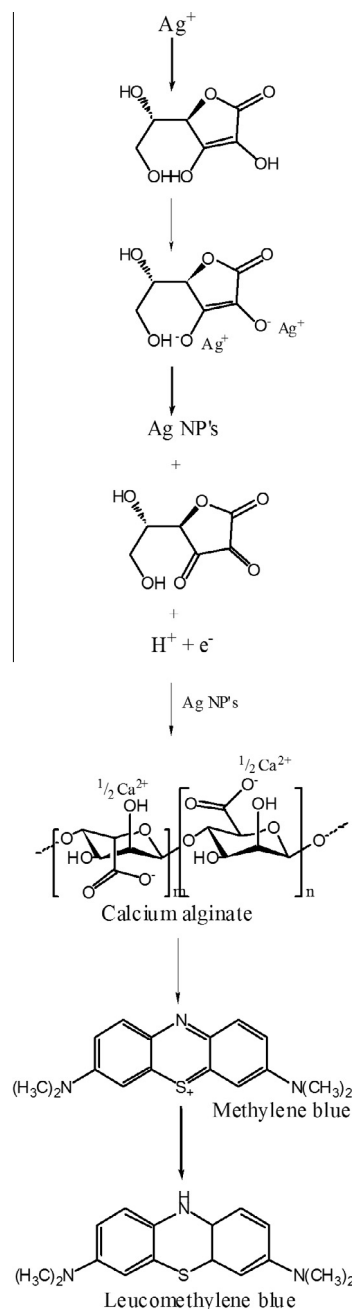
## 1. Introduction

Green nanotechnology is gaining more attention due to its eco-friendly and economical approach to nanoparticle synthesis. In recent years, researchers have been attracted by metal nanoparticles due to their unique optical, electrical, and biological properties, which make them central to numerous applications such as in catalysis, bio-sensing, imaging, drug delivery, and optical spectroscopy including surface-enhanced Raman scattering (SERS) [1]. Several chemical, electrochemical, photochemical, photophysical, and physical methods are employed for the synthesis and stabilization of different metal nanoparticles. However, these methods have been found to show certain toxicological effects in the medical research field [2]; also, some reagents are both hazardous and expensive. To overcome these limitations, we fabricated AgNPs and AuNPs in an eco-friendly and safe process by an easily obtainable flower extract. Several earlier studies reported that a safer mode of metal nanoparticle synthesis has been achieved by different microbes and by their biomolecules [3,4]. Recently, AgNP and AuNP synthesis using several flowers extracts as reducing and capping agents has been reported including *Mirabilis jalapa* [5], *Nyctanthes arbortristis* [6], *Ixora coccinea* [7], *Achillea wilhelmsii* [8], *Calotropis Procera* [9], *Carthamus tinctorius* [10], *Gnidia glauca* [11], *Lonicera japonica* [12], *Cassia Auriculata* [13], *Ipomoea indica* [14], and *Saraca indica* [15]. Among the various metal nanoparticles, silver nanoparticles have the greatest potential for applications in various industries and have unique catalytic, optical, and electrical properties [16].

In this manuscript, we report for the first time the synthesis of silver and gold nanoparticles by the reduction of metal silver and gold ions using *E. annuus* flower extract. The genus *E. annuus* belonging to the family Asteraceae (tribe Astereae), and involving about 150 species occurs in the northern hemisphere, mainly in North America. *E. Annuus* is an annual plant and reaches a height of up to 150 cm. It possesses erect, branched stems that end with inflorescences. The central disk florets are numerous, very small, and yellow; they are surrounded by 50–120 white ray florets. Both kinds of florets can be self-fertile. They often settle in places like roadsides and wastelands. *E. annuus* has been used in Chinese folk medicine for the treatment of indigestion, enteritis, epidemic hepatitis and hematuria. Constituents of the aerial part of *E. annuus* include  $\gamma$ -pyranone derivatives, flavonoids, phenolic acids and their derivatives, sesquiterpenoids, and cyclopentenone derivatives [17].

The main focus of this study is to reduce ionic silver and gold to gold and silver nanoparticles, respectively, using eco-friendly, non-toxic, cost effective and easily available biomaterial *E. annuus* flower extract. We investigated the effects of reaction parameters, such as pH, metal ion concentration, time of reaction and percentage of extract on the formation of silver and gold nanoparticles. We also studied the reduction of meth-

ylene blue dye catalyzed by (i) immobilization of *E. annuus* flower extract with synthesized AgNPs, (ii) *E. annuus* flower extract, (iii) silver ions, (iv) commercial AgNPs, and (v) control alginate beads (Scheme 1). Methylene blue is a thiazine dye used in many industrial applications like aqua culture,



**Scheme 1** Possible mechanism of Ag NP formation and dye removal [15,23].

anti-malarial drugs, chemotherapeutics and medicine [15]. To support the experimental results and to gain insights into the molecular mechanism of the reactions at the atomic level for the reduction of silver into nano silver using green materials, a computational study of the reactions between the reductant and the metal ions is needed.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Flower material

The *E. annuus* flowers were collected from the side of the road near Chonbuk National University, Iksan, South Korea, and were washed thoroughly with copious amounts of reverse osmosis (RO) and nanopure water (conductivity = 18  $\mu\Omega/\text{m}$ , TOC < 3 ppb, Barnstead, Waltham, Massachusetts, USA). Such flowers (100 g) were separated using scissors and were added to 250 mL nanopure water and were crushed using a juicer. The extract was filtered through a Whatman Filter paper and stored at 4 °C for further experiments.

#### 2.1.2. Chemicals

Silver nitrate ( $\text{AgNO}_3$ ) (99.9%), sodium alginate, and calcium chloride were acquired from DaeJung Chemicals, South Korea. Gold (III) chloride ( $\text{HAuCl}_4$ ) (99.9%), silver nanopowder (99.5%, < 100 nm) and methylene blue were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were used as supplied. Nanopure purified water was used throughout this investigation.

### 2.2. Synthesis, production optimization of silver and gold nanoparticles

For all experiments, the sources of silver and gold were silver nitrate ( $\text{AgNO}_3$ ) and gold (III) chloride ( $\text{HAuCl}_4$ ), respectively, in nanopure water. A typical reaction mixture contained 5 mL of the extract in 45 mL of  $\text{AgNO}_3$  and  $\text{HAuCl}_4$  solutions (1 mM each). To optimize production for AgNPs and AuNPs, syntheses were conducted for various pH values (4, 5, 6, 7, 8, 9, and 10), various extract concentrations (1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9% and 10%), various metal silver and gold concentrations (0.25, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mM), and various times (15, 30, 45, 60, 95, 110, 125, 140, 175 and 190 min). Stability of the synthesized nanoparticles was checked by exposing the samples to ambient conditions for several months. The absorbance of the sample was measured at 436 and 531 nm for Ag and AuNPs, respectively. Bulk production was achieved using the optimal parameters obtained. The reaction mixtures were filtered through 0.22  $\mu\text{m}$  Steritop Millipore filters and were centrifuged at 12,000 rpm for 15 min for AgNP and AuNP isolation. The resulting pellets were redispersed in nanopure water to eliminate any uncoordinated molecules. The process of centrifugation and redispersion in nanopure water was repeated several times to ensure better separation of free entities from the metal NPs. The obtained NPs were stored by freeze-drying to obtain a powder. All experiments were carried out in triplicate and representative data are presented here.

### 2.3. Characterization of silver and gold particles

The optical absorption spectra of the AgNPs and AuNPs were observed using a UV-1800 UV-vis spectrophotometer (Shimadzu, Japan). Morphology and size of AgNPs and AuNPs were evaluated using a HR-TEM model (JEOL-2010, Japan). The elemental composition of the AgNPs was confirmed by scanning electron micrograph-energy dispersive spectroscopy (SEM-EDS; JEOL-64000, Japan). FT-IR spectra of Ag and Au NPs were obtained with a Perkin-Elmer FTIR spectrophotometer (Norwalk, USA) in the diffuse reflectance mode at a resolution of 4 particles  $\text{cm}^{-1}$  in KBr pellets. X-ray powder diffraction was used to determine the crystalline nature of the samples (Philips, X'PERT-MRD). Scanning was done in the region of  $2\theta$  from 10° to 80° at 0.04°/min with a time constant of 2 s. Electrokinetic measurements (zeta potential) of AgNPs and AuNPs were evaluated at different pH values, ranging from 5 to 10 for Ag and pH 3–10 for Au using a Zetasizer (Malvern).

### 2.4. Immobilization of different materials on Na/Alg HB

Immobilization of Na-Alg beads-AgNPs, flower extract, silver ions, commercial grade AgNPs and Na-Alg (control) was performed according to the literature [18,19] with minor modifications. In brief, 1 mL of 1 mM AgNPs, 5 mL flower extract, 0.05 mg commercial grade AgNPs with 10 min ultra-sonication treatment (Elma S 30 H Elmasonic sonicator, Germany) and 1 mM silver ions were added to a sodium alginate solution at 40 °C and were mixed properly using a magnetic stirrer (Misung Scientific Co., Ltd, South Korea) to obtain a final concentration of alginate of 1%. Each mixture was prepared in an individual beaker. The mixture was added using a 5 mL syringe with approximately the same quantity of drops in each 0.1 M solution of  $\text{CaCl}_2$  under continuous magnetic stirring to form beads having a diameter of approximately 2 mm. Dark brown, translucent beads indicate flower extract mediated synthesized AgNPs, a light pink color indicates silver ions, light yellow indicates flower extract, light black indicates commercial grade AgNPs, and pure white is indicative of Na-Alg (control). The presence of divalent  $\text{Ca}^{2+}$  ions caused gelation to form different material-embedded beads of a spherical nature, having a diameter of  $\sim 3$  mm. The beads were kept immersed in a  $\text{CaCl}_2$  solution for further cross-linking to achieve additional stability. After 24 h of cross-linking, the beads were filtered and washed several times with copious amounts of nanopure water until the washing was  $\text{Cl}^-$  free. Finally, the beads were stored in nanopure water for further use.

### 2.5. Catalytic study

To study the catalytic activity of *E. annuus* flower extract six reactions were carried out in a 50 mL capacity conical tube including those with synthesized AgNPs, silver ions, commercial AgNPs, extract + AgNPs, and control sodium alginate hydrogel beads. Absorbance values were monitored using a UV-vis spectrophotometer after 30 min of reaction in a scanning range of 200–700 nm. A series of reactions were carried

out with 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 g of immobilized Na-Alg beads with (i) AgNPs, (ii) flower extract, (iii) commercial grade AgNPs, (iv) silver ions, (v) the control, and (vi) (i) + (ii) at a 1:1 ratio. These components were added with 20 mL of methylene blue ( $1 \times 10^{-4}$  M) and were shaken in an orbital shaker at 250 rpm. The reaction was monitored after 30 min. Values of absorption maxima ( $\lambda_{\max}$ ) were compared with those of methylene blue [20–24].

### 3. Results and discussion

#### 3.1. UV-visible spectrophotometry

In green synthesis, it is believed that the plant extracts act as reducing and stabilizing agents for the production of metal nanoparticles. The reaction media (metal ions + *E. annuus* flowers extract) was transformed from light yellow to striking colors, brown with a yellow shade for Ag (Supplementary Fig. 1a & inset) and a red wine color for Au (Supplementary Fig. 1b & inset) at room temperature. This change is due to the excitation of surface plasmon vibrations in the formed nanoparticles. The distinct color changes thereby provide visual evidence for nanoparticle formation.

In the present study, *E. annuus* flower extract serves as a reducing and capping agent during the synthesis of AgNPs and AuNPs. UV-vis absorption spectrometry was carried out to identify the formation of silver and gold nanostructures. A sharp band of AgNPs was observed at 434 nm (Supplementary Fig. 1a). The intensity of the absorption band increases with increasing time. AgNPs  $\lambda_{\max}$  values were reported to be in the visible range of 400–500 nm. Supplementary Fig. 1b shows the characteristic surface plasmon resonance absorption band at 537 nm (AuNPs), the same absorption band was earlier observed in silver NPs production from *Solanum torvum* [20], *Swietenia mahogani* JACQ leaves [25], *Cannonball* leaves [26], and in gold NP production from *Momordica charantia* fruit peel extract [27], common aromatic plants [28], and red tomato aqueous extract [29].

#### 3.2. Optimization of production parameters

To obtain maximum nanoparticle production, we studied various process parameters like pH, metal precursor concentration, reaction time, and substrate concentration. All the reactions were carried out at room temperature.

#### 3.3. Effect of pH on production and stability of NPs

The stability of the AgNPs and AuNPs synthesized using *E. annuus* flower extract was estimated using zeta potentiometer measurements at various pH values and their corresponding SPR measurements from pH 5 to 10 AgNPs and AuNPs pH 3 to 10 (Supplementary Fig. 2a–c & inset). The size and shape of the NPs are correlated with the spectral responses of individual NPs [30,31]. From Supplementary Fig. 2a and b, a high absorbance peak was observed at pH 8 for AuNPs and pH 7 for AgNPs. The broader absorbance at lower pH (3–5) might be due to the varying size and shape of the nanoparticles. Synthesized NPs are stable in a wide range of pH as there is less variation in the zeta potential (Supplementary Fig. 2c), which

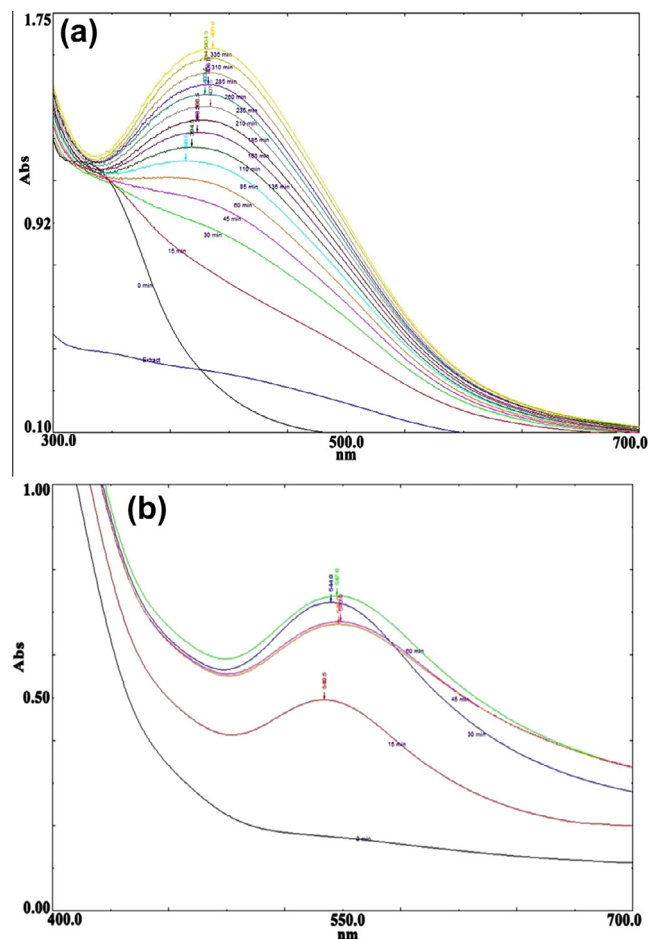
can be observed from SPR. At high pH, the value of the zeta potential has only slight variation for AgNPs and AuNPs (Supplementary Fig. 2c), which was observed for UV-vis spectra as well [31]. These data provide evidence that the AgNPs and AuNPs are stable over a wide range of pH.

#### 3.4. Effect of flower extract on NP production

The flower extract concentration was varied (1%, 2%, 3%, 4%, 5%, 6%, 7%, 8% and 9%) in silver nitrate and gold (III) chloride solutions used to produce AgNPs and AuNPs. Based on Supplementary Fig. 2d, 2e and the inset, color changes were observed from light yellow to brown with a yellow shade for AgNPs and light yellow to ruby red for AuNPs with an increasing percentage of *E. annuus* flower extract. Notably, 4% is the minimum flower extract content effective in generating AgNPs (Supplementary Fig. 2d). For AuNPs, 3% is the minimum concentration effective for the generation of AuNPs (Supplementary Fig. 2e).

#### 3.5. Effect of metal ion concentrations on NPs synthesis

To study the various metal ion concentrations for the synthesis of AgNPs and AuNPs, the  $\text{Ag}^+$  and  $\text{Au}^+$  ion concentration was varied from 0.01 to 4 mM. Increases in the production



**Figure 1** UV-visible absorption spectra for the production of (a) AgNPs, (b) AuNPs at various time intervals.

of AgNPs and AuNPs were found for higher metal ion concentrations (Supplementary Fig. 2f, g and the inset). The absorbance and peak sharpness increase at 1.5 mM silver ion concentration for AgNPs, and at 2.0 mM for gold ions in AuNPs synthesis. Increased metal ion concentration will also increase nanoparticle size [31,32]. The synthesis of AgNPs and AuNPs was slowest at the lowest metal ion concentration, and hence absorbance was also weaker.

### 3.6. Effect of time on NP synthesis

To evaluate the effect of time on AgNP synthesis, absorbance scanning was performed using UV–vis spectroscopy from 0 to 335 min. In the case of AuNP synthesis, the contact time was from 0 to 85 min. It was noted that, with increasing contact time, the peaks become sharper (Fig. 1a and b). Formation of NPs started within 15 min and increased up to 3 h for AgNPs (Fig. 1a) and 1 h for AuNPs (Fig. 1b). For longer times, the peaks become stable for both types of nanoparticles.

### 3.7. Characterization of Ag, Au, nanoparticles

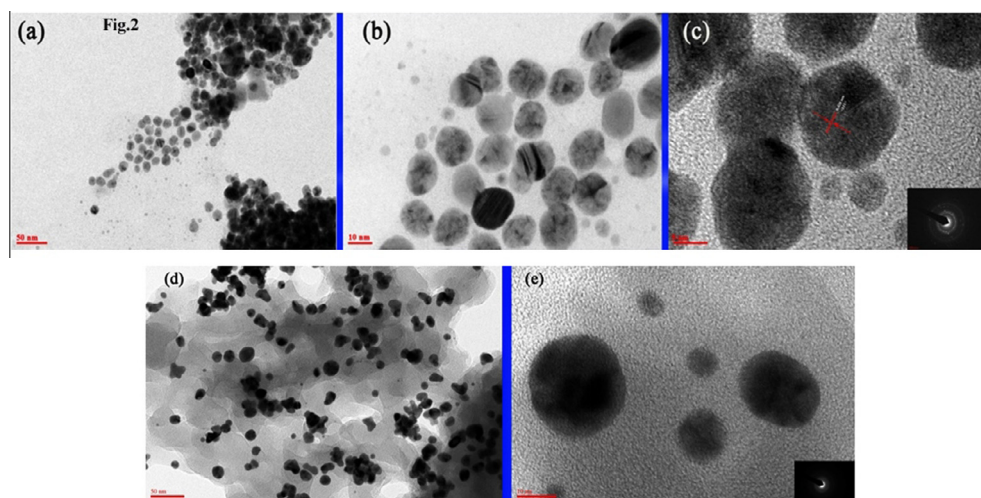
#### 3.7.1. SEM-EDS and HR-TEM study

SEM-EDS analysis showed the presence of elemental silver and gold, which indicated the reduction of silver and gold ions

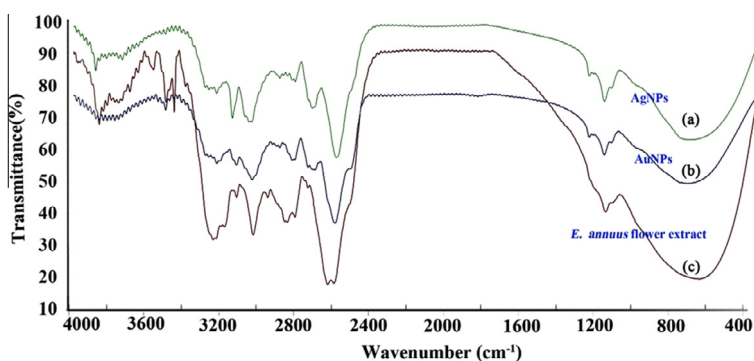
to elemental silver and gold (Supplementary Fig. 3a and b). TEM images of AgNPs and AuNPs of optimized production parameters of silver and gold ions were taken, and it was noted that the approximate size of the particles was found to vary from 15 to 60 nm and 20 to 100 nm for AgNPs and AuNPs, respectively (Fig. 2a–e). The HR-TEM image (insert Fig. 2c) with fringes having a spacing of 0.428 nm reveals the preferential growth direction of the AgNPs along the (111) plane. The SAED pattern (Fig. 2c, e & insert) with bright circular fringes shows the highly crystalline nature of the obtained AgNPs and AuNPs [33].

#### 3.7.2. FTIR spectra studies

The possible phytoconstituents responsible for the reduction and the stabilization of synthesized metallic nanoparticles can be achieved by FTIR studies, which can help in further functionalization with other molecules for various applications [32]. Fig. 3a–c, show the FTIR spectra of AgNPs, AuNPs and flower extract. The silver nanoparticles show prominent bands at  $3200\text{ cm}^{-1}$ ,  $3100\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $2620\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$ ,  $1100\text{ cm}^{-1}$ ,  $622\text{ cm}^{-1}$ , while gold nanoparticles show peaks at  $3100\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $2620\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$ ,  $1100\text{ cm}^{-1}$ , and  $620\text{ cm}^{-1}$ . Peaks associated with the extract appear at  $3300\text{ cm}^{-1}$ ,  $3100\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $2620\text{ cm}^{-1}$ ,  $1100\text{ cm}^{-1}$ , and  $600\text{ cm}^{-1}$ . The bands at  $1300\text{ cm}^{-1}$ ,  $1100\text{ cm}^{-1}$ , and



**Figure 2** HR-TEM and inserted SAED images of synthesized (a–c) AgNPs and (d, e) AuNPs under different magnifications.



**Figure 3** FT-IR spectra of aqueous synthesized (a) AgNPs, (b) AuNPs and (c) *E. annuus* flower extract.

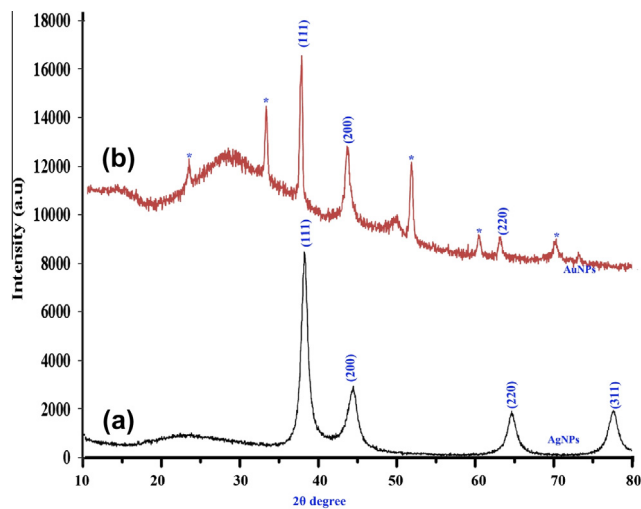
622  $\text{cm}^{-1}$  in the spectra of silver nanoparticles, gold nanoparticles and extract correspond to  $\text{C}\equiv\text{C}$  groups or aromatic rings or  $\text{C}=\text{O}$  stretching [15] in carboxyl groups (amide I & II band) of proteins. The strong, broad peak at 2620–3300  $\text{cm}^{-1}$  is characteristic of the  $\text{N}-\text{H}$  stretching vibration. Also, the hydroxyl peak at 3420 and 3500  $\text{cm}^{-1}$  decreases in the presence of nanoparticles, which indicates that  $\text{Ag}^+$  and  $\text{Au}^+$  ions reacted with the hydroxyl groups of the flavanoid and polyphenol, and the hydroxyl groups are oxidized to carbonyl groups [23]. The sharp bands at 2850 and 3100  $\text{cm}^{-1}$  arise from  $\text{C}-\text{H}$  stretching modes. In particular, the 1300  $\text{cm}^{-1}$  band arises most probably from the  $\text{C}-\text{O}$  group of polyols such as hydroxyl flavones.

### 3.7.3. X-ray diffraction studies

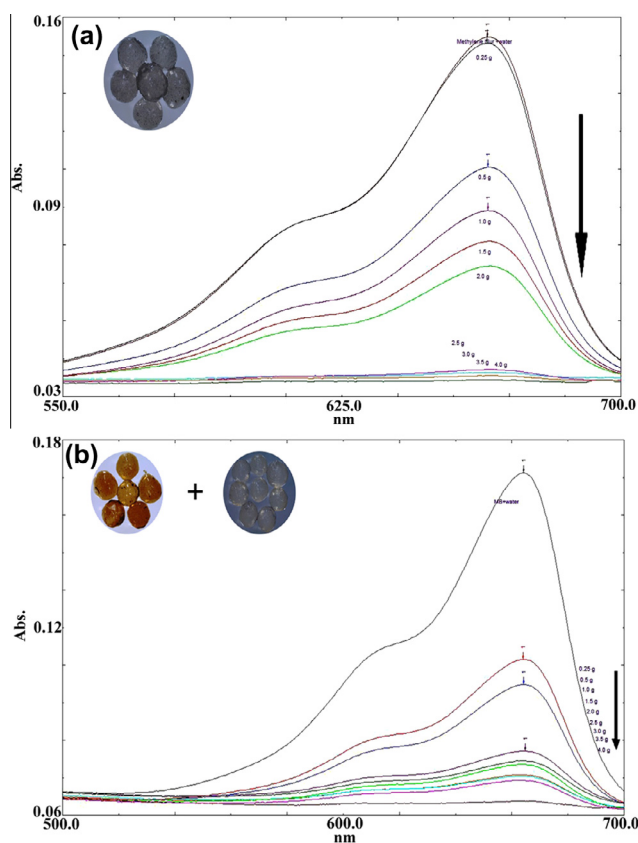
The XRD pattern recorded for AgNPs and AuNPs shows a few intense peaks in the whole spectrum of  $2\theta$  values ranging from 20 to 80 (Fig. 4a and b). The AgNPs show diffraction peaks characteristic of a metallic face-centered cubic silver phase (PDF-2 4-0738) at 39.1°, 44.2°, 64.9°, and 78.0°, in  $2\theta$ . No diffraction peaks corresponding to potential silver oxides ( $\text{Ag}_2\text{O}$  or  $\text{Ag}_2\text{O}$ ) were noted [32]. The AuNP samples show similar characteristic peaks of metallic gold, and a few unidentified peaks were also observed. The standard XRD patterns for Ag and Au are similar [Joint Committee on Powder Diffraction Standards (JCPDS) file no: 04-0783 for Ag and 01-1174 for Au]. The XRD patterns clearly show that the obtained AgNPs and AuNPs are crystalline in nature.

### 3.7.4. Catalytic activity

The aim of the present work was to remove methylene blue by Na/Al HB immobilized with *E. annuus* flower extract, silver ions, synthesized AgNPs, commercial grade AgNPs and a blend of flower extract and AgNPs, as presented in Fig. 5a and b and Supplementary Fig. 4 a–c. Several earlier reports [15,22–24,33] showed that the catalytic activity of obtained AgNPs and their composites had greater catalytic activity for methylene blue reduction and removal. Pure methylene blue has a  $\lambda_{\text{max}}$  value of 664 nm. However, in our study, the commercial grade AgNP Na/Al HB (1.5 g) Fig. 5a, showed greater



**Figure 4** XRD pattern of synthesized (a) AgNPs and (b) AuNPs.



**Figure 5** UV-visible spectra of methylene blue reduction and inset sodium alginate beads: (a) commercial grade AgNP embedded Na/Al HB, (b) bead mixture of synthesized AgNPs and flower extract.

catalytic activity followed by a blend of flower extract and AgNP Na/Al HB (1:1(1.5 g)), Fig. 5b. After 30 min, the absorbance gradually decreased and shifted to a higher wavelength. This reveals that commercial grade AgNP Na/Al HB acts as an electron transfer mediator between the Na/Al HB and methylene blue by acting as a redox catalyst, demonstrating the electron relay effect [22]. Using NPs separately may result in reduced activity due to particle aggregation. Using NPs with Na/Al HB may improve dye removal. Specifically, a system containing dye, phytoextract and AgNP Na/Al HB showed a marked decrease in the absorbance of methylene blue and an increase in SPR peaks of AgNPs (Fig. 5b) after a 30 min time interval. To confirm Na/Al HB has removal capacity, the control beads were studied separately. No remarkable results were obtained for the *E. annuus* flower extract, silver ion, synthesized AgNP grafted Na/Al HB sample, as shown in Supplementary Fig. 4 a–c.

## 4. Conclusion

A green synthetic method using flower extracts has shown great potential in AgNP and AuNP preparation by making use of *E. annuus* flower extract. No chemical or physical patterns were required in this method, and it has the advantage of being eco-friendly with a readily available substrate source (road side weeds). The phytoconstituents present in the *E.*

*annuus* flower extract act as reducing and capping agents for the preparation of AgNPs and AuNPs, as is evident from FT-IR and EDS studies. *E. annuus* flower extract was prepared and successfully used for the synthesis of Ag and AuNPs in the size range of 20–50 nm as was evident from HR-TEM. The synthesized AgNPs and AuNPs were found to have a crystalline nature with a face-centered cubic geometry, as studied by XRD. The mixture of synthesized AgNPs and *E. annuus* flower extract embedded Na/Al HB acts through the electron relay effect to catalyze degradation of methylene blue with an activity comparable to that of commercial grade AgNPs. Based on this work, silver nanoparticles may have multiple industrial applications like pollution removal, water purification and medicinal applications.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jscs.2014.09.004>.

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