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Biostabilised icosahedral gold nanoparticles: synthesis, cyclic voltammetric studies and catalytic activity towards 4-nitrophenol reduction

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ABSTRACT

A green and cost-effective biosynthetic approach for the preparation of icosahedral gold nanoparticles (AuNPs) using an aqueous leaf extract of *Polygonum minus* as reducing and stabilising factor is described. The reduction of Au^{3+} ions to elemental Au rapidly occurred and is completed within 20 minutes at room temperature. The size of the nanoparticles is highly sensitive to the $AuCl_4^-$/leaf extract concentration ratio and pH. Transmission electron microscopy and X-ray diffraction data indicated that the nanoparticles were in a crystalline shape (face-centred cubic), mostly icosahedral and nearly monodispersed with an average size of 23 nm. Cyclic voltammetric studies suggested that flavonoids, such as quercetin and myricetin present in the leaf extract had a tendency to donate electrons to Au^{3+} ions and the formation of elemental Au was possible due to the transfer of electrons from these flavonoids to Au^{3+} ions. Infrared absorption of the AuNPs and the leaf extract revealed that the oxidised (quinone) form of quercetin and myricetin were presumably the main stabilising agents in the formation of stable nanoparticles. The present biosynthesis of AuNPs was simple, rapid, cost-effective and environmentally friendly. The newly prepared biostabilised icosahedral AuNPs show good catalytic activity in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).

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1. Introduction

In recent years, noble metal nanoparticles have received considerable attention owing to their unique properties which are promising in diverse fields with a variety of technological applications. For example, gold nanoparticles (AuNPs) are one of the common nanometals used in biomedical science,[1] catalysis,[2] sensor,[3,4] etc. The inherent physical and chemical properties of AuNPs lead to their indispensable applications which can simply be tuned by tailoring the size and shape of nanoparticles. The particle size- and shape-controlling processes in synthesising metal nanoparticles play an important role in manufacturing advanced materials on a large scale and therefore, well-controlled synthesis of nanoparticles is necessary to unambiguously correlate the structural properties of them with their catalytic properties.[5]

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Of these two parameters, shape is often not feasible enough to be tailored deliberately. As a result, there is a growing demand to develop feasible, cost-effective and environmentally safe procedures and conditions that favour the formation of shape-controlled metal nanoparticles. Basically, parameters, such as concentration of metal ions, pH, incubation time, nature of reducing and stabilising (surfactants) agents, seeds and etc., are the main factors affecting the nucleation and growth conditions and eventually the shape and geometry of formed AuNPs.[6]

Vast numbers of chemical, physical and biological strategies have been employed to synthesise AuNPs of different shapes.[7] Among these approaches, biological processes are preferred for environmental and economic concerns.[8] Physical and chemical methods require expensive high technology, high temperature, high pressure, toxic environment and are neither suitable for mass production nor energy-efficient. On the other hand, biosynthesis of AuNPs is environmentally safe, more affordable and suitable for mass production as well as allowing tight control over the particle size distribution in many ways. In recent years, the biosynthetic methods employing plant extract are gaining attention due to its simplicity and environmental friendly.[9] Moreover, the AuNPs produced by plants are more stable and the rate of synthesis is high.[10]

Polygonum minus, from the family *Polygonaceae*, is locally known in Malaysia as 'kesum'. It is a local medicinal plant commonly consumed raw as a salad for preventive health care. The plant leaves are aromatic and is popularly utilised as an ingredient in Malaysian foods. *P. minus* has been reported to have the highest total phenolic content and greatest ability in the reducing process among several herbs in Malaysia.[11–13] *P. minus* contains flavonoids, such as quercetin and myricetin that are well-known to have high antioxidant activities.[14] In order to better describe the bioinspired synthesis of AuNPs, evaluation of the synthesis process with various plants is still important. In this study, we explore the possible application of aqueous extract of *P. minus* leaves in the simple and environmentally safe synthesis of AuNPs and discuss the chemical components responsible for the reduction of Au^{3+} ions to elemental Au and stabilising agents in more details.

Bulk Au has been regarded as an uninteresting metal from the viewpoint of catalysis. However, the catalytic properties of Au are revealed when the size is reduced to a few nanometers and surprisingly it exhibits high catalytic activity towards many chemical reactions.[15] The catalytic activity of biosynthesised AuNPs has been commonly evaluated in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).[16–19] 4-NP is a common industrial waste and environmental hazard with long degradation time. It is widely used in the preparation of pesticides, explosives and pharmaceutical industries. This compound poses significant health risks due to its carcinogenic activities.[20] Thus, the removal of this compound is important for public health and can help to restore impacted environments. On the other hand, 4-AP is an important intermediate for the production of pharmaceuticals substances, photographic materials and rubber materials.[21] Since the reduction of the nitro group into an amine is an important process, in this study, we focus on the application of biosynthesised AuNPs for the reduction of 4-NP to 4-AP with the presence of excess hydrazine hydrate as reductant.

2. Experimental

2.1. Materials

Tetrachloroauric(III) acid trihydrate $HAuCl_4.3H_2O$ (99.5%) were obtained from Merck. Fresh leaves of *P. minus* were purchased from a local market in Johor, Malaysia.

2.2. Preparation of leaf extract

P. minus leaves were washed several times with deionised water to remove dust and dried at room temperature for one week. Then, finely powdered leaves (2 g) were added to 100 mL deionised water in an Erlenmeyer flask. The extraction was carried out on a magnetic heater stirrer at 100 °C for

15 minutes. The mixture was then filtered to remove any residual biomass from it. Finally, the filtrate was kept in a sealed amber glass bottle and stored at 5 °C for further experiments and was used as the leaf extract in preparation of AuNPs.

2.3. Biosynthesis of AuNPs

The leaf extract in different volumes (1, 2, 3, 4 and 5 mL) was diluted to 10 mL with deionised water and added to an aqueous solution of $HAuCl_4$ (10 mL; 1 mM) at room temperature and pH = 5 (initial pH of the leaf extract). Colour change occurred from pale yellow to ruby red after ~1 minute, indicating the formation of AuNPs. Then, the pH of the extract was adjusted to 9 with 0.2 M NaOH. The investigation on the effect of pH was carried out at 1 mM volume of $HAuCl_4$ and 2 mL extract volume. All reactions were performed at room temperature.

2.4. Characterisation of the biosynthesised AuNPs

The formation of AuNPs was followed by UV−visible spectroscopy (Shimadzu spectrophotometer) in the range of 400−800 nm. One mL of AuNPs colloids was diluted to 3 mL in the UV−visible experiments. After washing several times with deionised water to remove the free entities by re-dispersing them in deionised water and centrifuging at 13,000 rpm for 15 minutes, AuNPs colloids were dried in vacuum desiccators and subjected to X-ray diffraction (XRD) experiment. The crystalline structure of AuNPs was determined by XRD (Bruker D8 Advance) with CuKα radiation (λ = 1.5406 Å) in the 2θ range of 20°−90° operating at 40 kV and 30 mA. The Fourier transform infrared spectroscopy (FTIR) analysis of AuNPs was carried out by Shimadzu 8300 spectrometer in the range 400−4000 cm^{-1}. The same sample preparation for the XRD analysis was used for the FTIR analysis. The morphology and the average particle size of AuNPs were determined by transmission electron microscopy (TEM) (JEOL JEM-2100, 200kV). The presence of elemental gold was determined by using energy dispersive X-ray spectroscopy (EDX) coupled with FESEM (JEOL-JED 2300). All electrochemical measurements were performed using EA163 potentiostat. A conventional three electrode cell configuration was used for the voltammetric measurements. The working electrode was a glassy carbon electrode and a silver/silver chloride (Ag/AgCl) as a reference electrode on platinum wire as the auxiliary electrode was employed. All potentials are quoted relative to this reference electrode.

2.5. Catalytic activities of the biosynthesised AuNPs in the reduction of 4-NP

Two mL of 4-NP (0.1×10^{-3} M) was mixed with a freshly prepared aqueous solution of 2 mL of hydrazine hydrate (0.3×10^{-3} M) under continuous stirring at room temperature. Then, 1 mg of the AuNPs powder was added into the above reaction mixture. A UV−visible absorption spectrum of the reaction mixture was recorded with time to monitor the change in absorption intensity of the reaction mixture in the scanning range of 200−500 nm. The same procedure was repeated using 2 mg of the AuNPs powder.

3. Results and discussion

3.1. UV−visible absorption study

First, the step-by-step progress of the formation of AuNPs was monitored by using time-dependent UV−visible absorption spectra (Figure 1). As seen in Figure 1(a), the spectrum corresponding to the initial stage of formation (~2 minutes) showed one intense absorbance band at λ = 535 nm (surface plasmon resonance band of gold nanoparticles; SPR) [22] whose intensity later increased in consistence with the time of reaction. The colour of the reaction mixture changed immediately

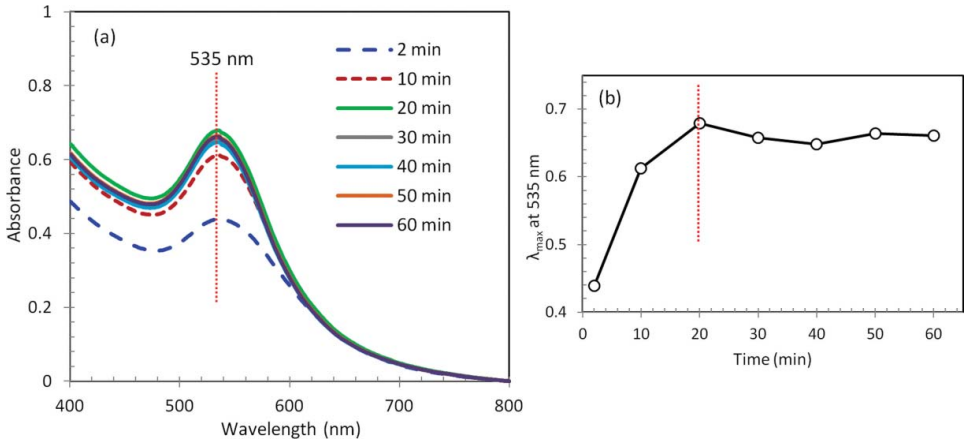

Figure 1. (a) UV−visible spectra of reaction mixture for different time intervals. (b) Time-dependent change in the absorbance of solution containing $HAuCl_4$ and leaf extract of *Polygonum minus* at 535 nm.

from pale yellow (the colour of the initial aqueous solution of Au^{3+}) to ruby red. To investigate the kinetics of the formation of AuNPs, the changes in the absorbance of band at $\lambda = 535$ nm with respect to time were recorded (Figure 1(b)) and it was observed that the reduction process reached saturation within 20 minutes of the reaction, and after that only slight variation could be noted in the intensity of the bands. Thus, the present procedure introduces a biosynthesis route to AuNPs by using only aqueous extracts of *P. minus* leaves as both the reducing and stabilising agents without any foreign chemical, surfactant and extra control.

Only a few studies have reported the formation of AuNPs by using leaf extract as reducing agent in less than 30 minutes. Khalil et al.,[23] Noruzi et al.[24] and Kesarla et al.[25] have reported the formation of AuNPs in 20 minutes, 10 minutes and less than 10 seconds, respectively. As a result, the biosynthesis reaction rate in this research is comparable with the traditional chemical approaches, such as the Turkevich method.[26]

In order to offer new mechanistic insights into AuNPs shape evolution, it would be informative to investigate whether the *P. minus* leaf extract to Au^{3+} ions concentration ratio influences the size and shape of AuNPs. In order to evaluate this, bioreduction process of Au^{3+} ions was studied in the presence of different volumes (concentration) of leaf extract and the results are shown in Figure 2. It

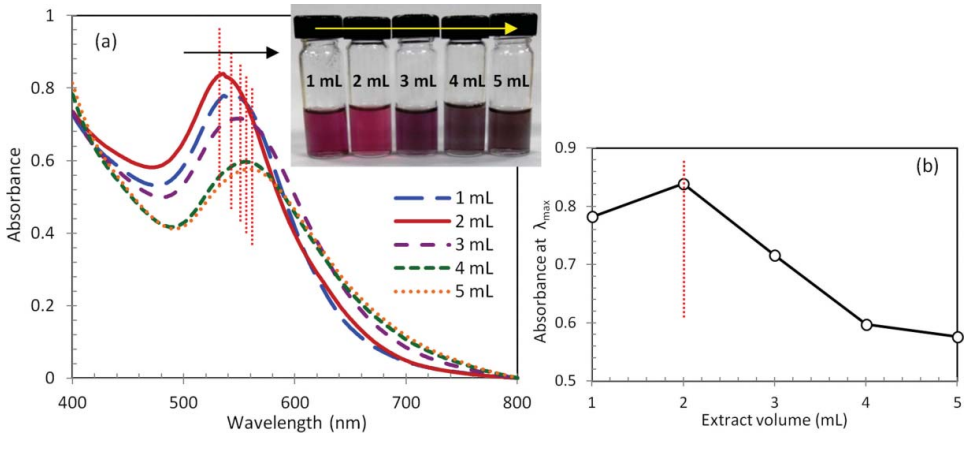

Figure 2. (a) UV−visible spectra and optical images of reaction mixture with different volumes of the extract and (b) a plot of maximum absorbance versus extract volume.

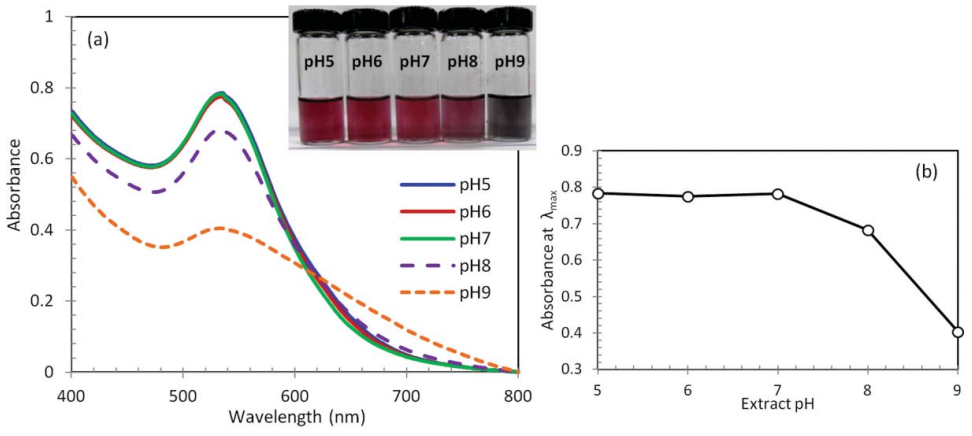

Figure 3. (a) UV−visible spectra and optical images of reaction mixtures at different pH values of the extract and (b) a plot of maximum absorbance versus extract pH.

is already reported that the position of the SPR band in the UV−visible spectra of AuNPs is highly sensitive to particle size, shape, local refractive index and its interaction with the medium.[27] From the spectra in Figure 2, it is clear that when the volume of *P. minus* leaf extract was increased from 1 to 2 mL, the SPR band was sharper and its intensity got higher (Figure 2(a)), suggesting an increase in the reaction rate and therefore, the formation of the smaller and monodispersed AuNPs.[28] When the reaction rate increased, most of the Au^{3+} ions are consumed in the formation of nuclei and consequently give smaller particle sizes and this implies that the precursors (extract/Au^{3+}) ratio is a critical parameter affecting the nucleation and growth processes of AuNPs formation. However, when the extract volume was increased from 2 to 5 mL (Figure 2(b)), the SPR band broadened and shifted towards the longer wavelength region from 535 to 559 nm which implies an increase in particle size and a characteristic of polydispersed AuNPs. Too many reducing agents may cause the secondary reduction process on the surface of the preformed nuclei which leads to the formation of larger AuNPs. These observations are consistent with other previous reports.[24,29] In addition, when the extract volume was increased from 2 to 5 mL, the colour of AuNPs colloidal formed became darker as shown in Figure 2. Thus, these results revealed that the particle size and distribution of the synthesised AuNPs depended strongly on *P. minus* leaf extract to Au^{3+} ions concentration ratio.

The UV−visible spectra of AuNPs at different pH from 5 to 9 are given in Figure 3. As seen, there was no significant difference between the intensity of the SPR bands in the pH range from pH 5 to 7, probably indicating that the particle sizes were of similar size. As the pH increased from 7 to 9, the SPR band became broader and decreased in intensity and the colour of AuNPs turned to dark blue as shown in Figure 3(a) suggesting the existence of larger particle and a polydispersed distribution of AuNPs. This might partially be due to the reaction of sodium hydroxide and the acidic phenolic groups on flavonoids in the extract. One can suppose that the deprotonation of phenolic groups may prevent stabilising functional groups from protecting the AuNPs against aggregation, causing the average particle size to become larger as suggested earlier by Noruzi et al.[24] Thus, the results showed that the particle size and distribution of the synthesised AuNPs also depended strongly on the extract pH.

3.2. TEM and EDX analyses

TEM has been used to identify the size, shape and morphology of the synthesised AuNPs. The typical TEM images obtained for AuNPs using 2 mL extract volume at pH 5 are shown in Figure 4. From the images, it is clear that the morphology of AuNPs is almost icosahedral. This is in good

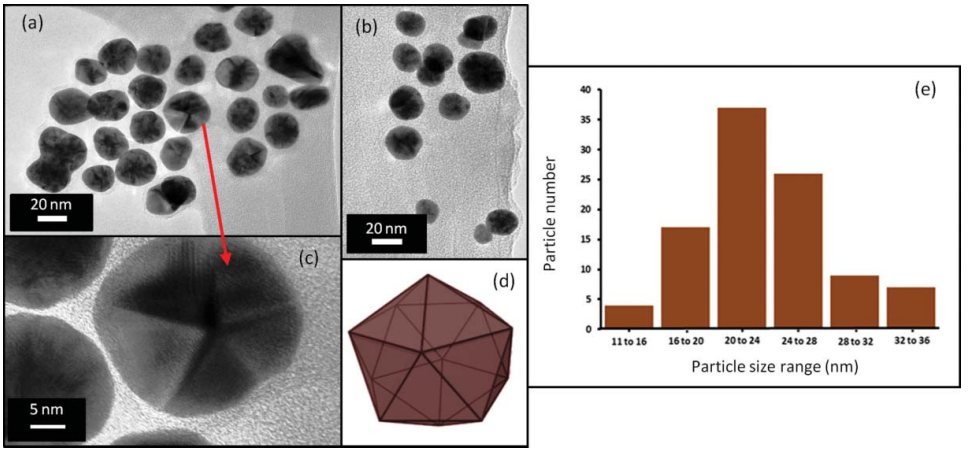

Figure 4. (a–c) TEM images of AuNPs (2 mL extract volume, pH 5) at different magnification, (d) Model of icosahedral particle and (e) Particle size distribution histogram.

agreement with the previous studies which reported that icosahedral particles are composed of face-centred cubic (fcc) tetrahedral subunits joined along twin boundaries and sharing axes of five-fold symmetry.[30,31] To the best of our knowledge, only few papers have reported the simple and green shape-controlled formation of icosahedral AuNPs from plant mediated biosynthesis. The icosahedral nanoparticle had been observed through the reaction of Au(III) solution with *Medicago sativa* (alfalfa) [32,33] and *Triticum aestivum* (wheat).[34] Figure 4(e) showed the size distribution histogram of the synthesised AuNPs. This histogram was prepared by manual analysis of 100 particles using Image J software. The particle size distribution is in the range of 11–36 nm, with an average particle size of 23 nm. Also, the EDX inspection (Figure 5) of the synthesised AuNPs showed strong signals for gold atoms along with signals from carbon and oxygen atoms. The appearance of the carbon and oxygen signals in the EDX spectrum could have arisen from the organic moieties adsorbed on the surface of the AuNPs, thus suggesting the biomolecules from the

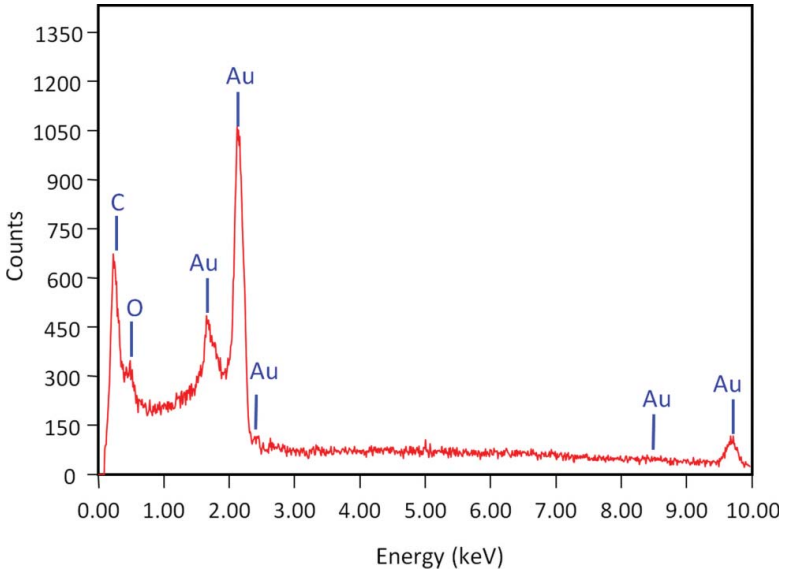

Figure 5. EDX spectrum of AuNPs.

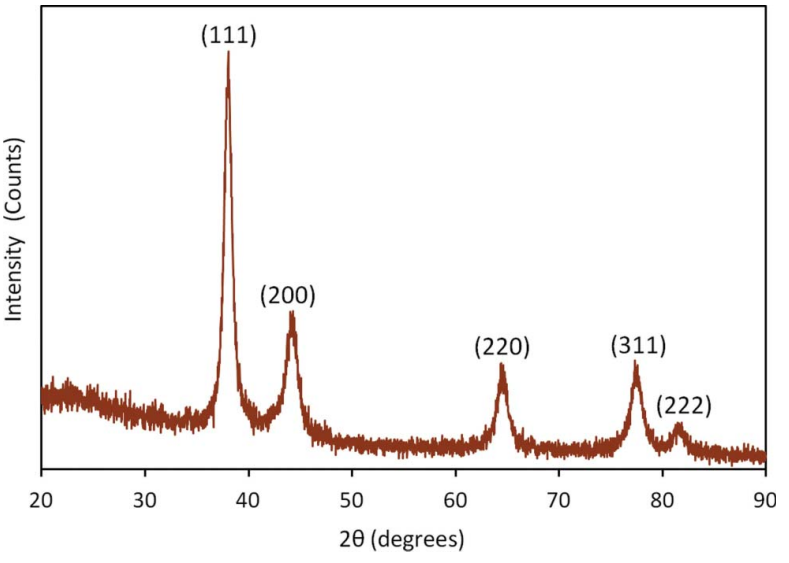

Figure 6. XRD pattern of AuNPs.

leaf extract had acted as reducing and stabilising agents in the formation of AuNPs. This result was similar to that previously observed by other researchers.[35,36]

3.3. XRD analysis

The XRD pattern (Figure 6) showed that the AuNPs are crystalline in nature. Reflection peaks appeared at 38.07°, 44.21°, 64.41°, 79.38° and 81.52°, which correspond to (111), (200), (220), (311) and (222) planes of the fcc structure.[24,37] All the peaks were broad which indicated the formation of AuNPs [29] and the peak corresponding to the (111) plane is more intense than the other planes suggesting that it is the predominant orientation.[38]

3.4. FTIR analysis

The FTIR analysis was carried out to identify the possible functional groups of biomolecules present in the *P. minus* leaf which are responsible for the reduction of Au^{3+} to elemental gold and stabilising of the formed AuNPs. FTIR spectra of the *P. minus* leaf powder and the synthesised AuNPs using 2 mL of *P. minus* extract at pH 5 are shown in Figure 7. The FTIR spectrum of leaf powder (Figure 7(a)) showed characteristic bands for O−H stretching vibrations at 3425 cm^{-1} (polyols), asymmetric stretching vibrations of C−H at 2925 cm^{-1}, stretching vibrations of C=O at 1638 cm^{-1} (unsaturated carbonyl group) and stretching vibrations of C−O at 1071 cm^{-1} (polyols).[19,36] The presence of phenolic compounds like flavanoids (quercetin and myricetin) has been reported in the *P. minus* leaf aqueous extract.[14]

Meanwhile, the FTIR spectrum for the synthesised AuNPs (Figure 7(b)) showed the appearance of similar peaks as observed in the FTIR spectrum of the *P. minus* leaf powder. The decrease in intensity of the O−H stretching band at 3427 cm^{-1} is probably due to the oxidation of catechol moiety of flavanoids (quercetin and myricetin) to their corresponding quinone forms. This is further supported by the appearance of a new stretching band for C=O at 1653 cm^{-1}, consistent with the results reported by Dauthal and Mukhopadhyay [36] and Ghoreishi et al.[39] This observation probably suggests the involvement of the flavanoids of the *P. minus* leaf extract in the bioreduction process of Au^{3+} to Au(0) and stabilising the AuNPs. This preliminary assumption was further investigated and proved by using cyclic voltammetry studies in the next section.

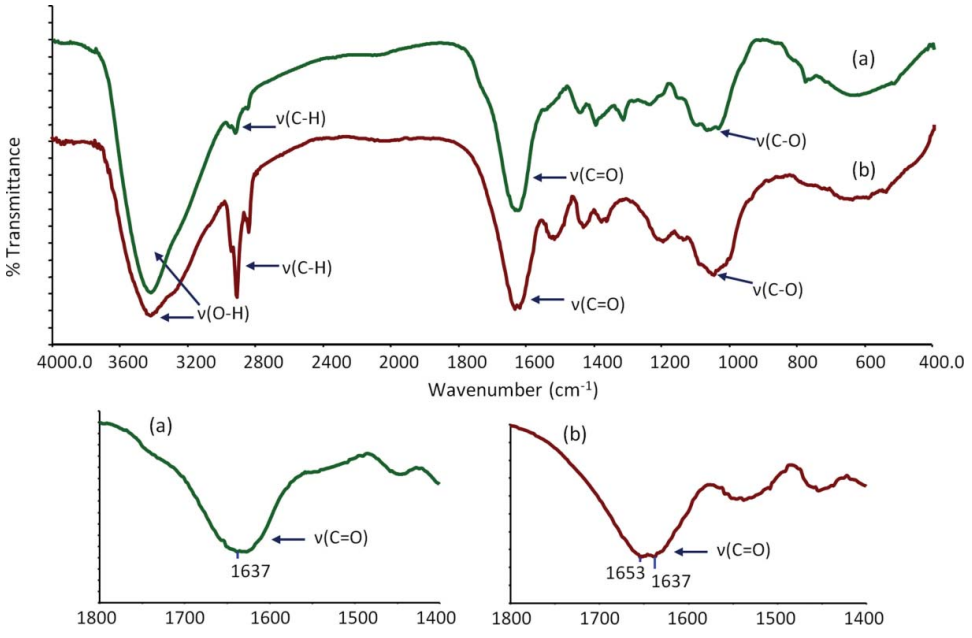

Figure 7. FTIR spectra of (a) *Polygonum minus* leaf powder and (b) as-synthesised AuNPs.

3.5. Cyclic voltammetry studies of the leaf extract and the as-synthesised AuNPs

The proposed mechanism for the reduction of Au^{3+} ions to AuNPs by virtue of the oxidation of catechol form (A) of quercetin and myricetin (found in leaf extract) to their corresponding quinone form (B), and the possible ways for AuNPs stabilisation by responsible biomolecules are schematically depicted in Figure 8. The cyclic voltammograms of aqueous extract of *P. minus* leaf and the leaf extract stabilised AuNPs colloid were obtained in an aqueous 0.2 M sodium acetate solution on a glassy carbon electrode at room temperature are shown in Figure 9. This study was basically probed to provide more evidences of the biological reduction of gold ions to AuNPs, as well as confirming the stabilising role of the biomolecules of leaf extract. The mechanism of electrochemical oxidation of flavonoids, particularly quercetin, using cyclic voltammetry has been reported by several researchers.[40,41] In general, the oxidation of the catechol moiety occurs first at low positive potential, at about +0.15 V, which is a two electrons and two protons reversible reaction, leading to the formation of the corresponding *ortho*-quinone. Figure 9(a) showed the cyclic voltammogram of an aqueous extract of *P. minus* leaf and as seen, an intense peak at + 0.12 V was observed, which was presumably related to the oxidation of the form A of quercetin and myricetin to their corresponding form B. In contrast, cyclic voltammogram of the leaf extract stabilised AuNPs colloid (Figure 9(b)) showed the peak possibly for the back-reduction of form B to form A at −0.6 V and no considerable oxidation peak was observed in this case. These results clearly implied that the oxidised forms of two flavonoids are predominantly attached to the surface of AuNPs and as a result, among various possible suggestions, combination of AuNPs+B (Figure 8) is the proper composition of the AuNPs stabilised with biomolecules.

3.6. Stability of the leaf extract

The UV−visible spectra of AuNPs colloids prepared using a freshly prepared leaf extract and the leaf extract after being kept for 50 days are shown in Figure 10. As can be seen, there was no significant difference between the intensity of the SPR band for both reaction mixtures. This signified that

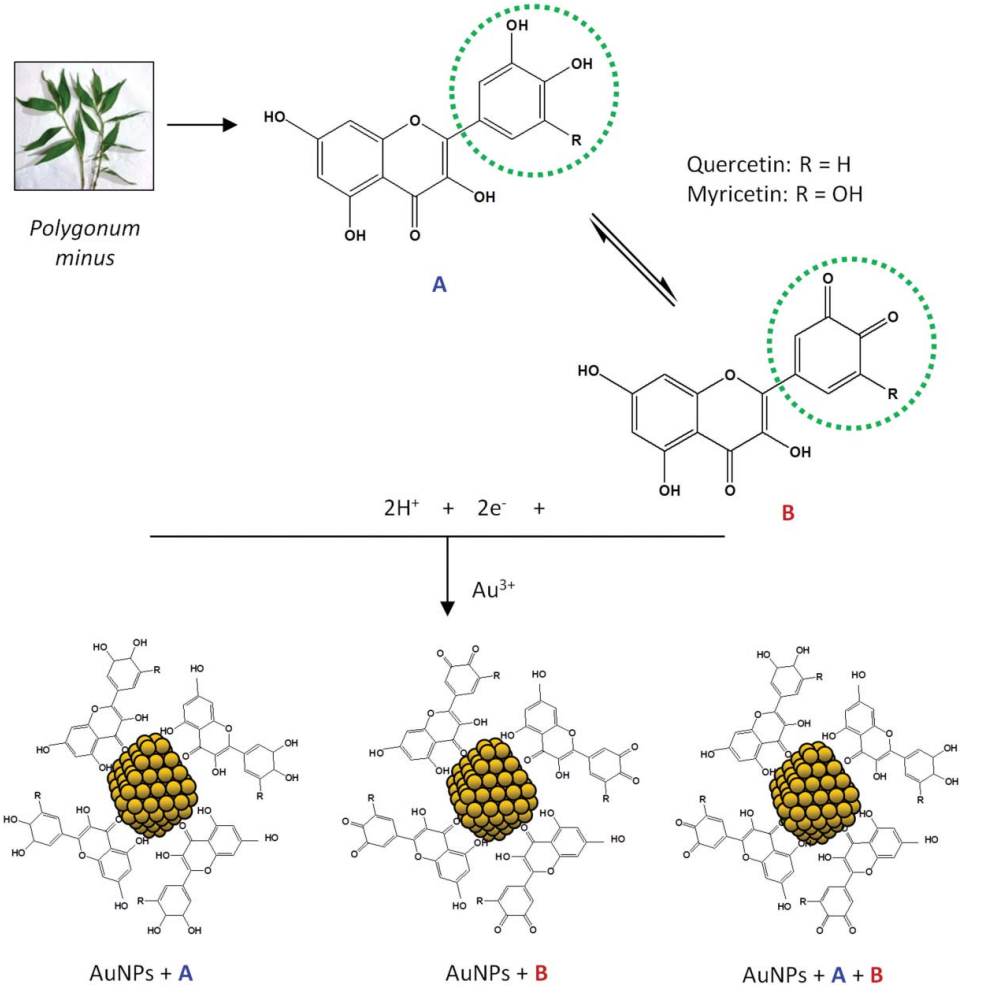

Figure 8. Proposed mechanism for the formation and stabilisation of AuNPs with the help of possible structures of flavonoids of leaf extract.

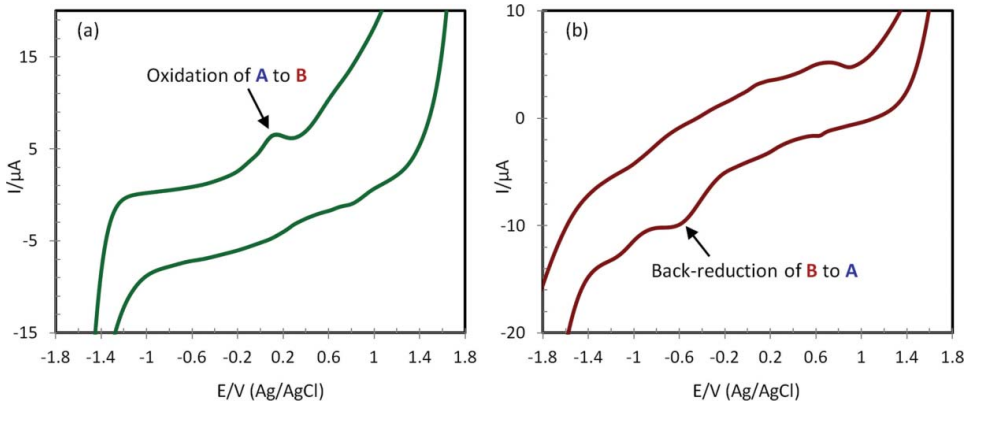

Figure 9. Cyclic voltammograms of (a) aqueous extract of *Polygonum minus* leaf and (b) leaf extract stabilised AuNPs; scan rate: 100 mVs^{-1}.

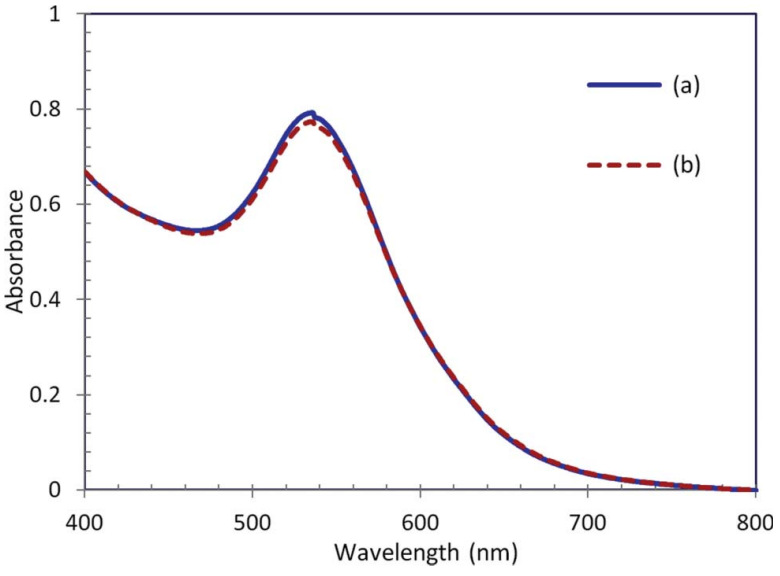

Figure 10. UV−visible spectra of AuNPs colloids prepared using (a) fresh leaf extract and (b) leaf extract after being kept for 50 days

the *P. minus* aqueous leaf extract maintained its stability as reducing and stabilising agent for 50 days when stored at 5 °C in a sealed amber glass bottle.

3.7. Catalytic reduction of 4-NP

The catalytic activity of biosynthesised AuNPs studied for the reduction of 4-NP in the presence of excess hydrazine hydrate is presented in Figure 11. The UV−visible spectra of aqueous solution of 4-NP showed an absorption maxima at 318 nm (Figure 11(a)). After the addition of hydrazine hydrate, a red shift was observed with absorption maxima at 401 nm which is due to the formation of 4-nitrophenolate ions. But with the addition of AuNPs catalyst, fading of the dark yellow colour of 4-nitrophenolate ions was observed. Figure 11(c) and 11(d) showed the decrease in absorbance for the 4-nitrophenolate ions peak at 401 nm along with a gradual increase of a new peak at 316 nm which indicates the formation of 4-AP.[36] In the absence of AuNPs catalyst (Figure 11(b)), the peak at 401 nm showed only slight decrease in intensity after 70 minutes of reaction time, thus suggesting that no significant reduction has occurred without the presence of catalyst.

The catalytic reaction was carried out in excess of hydrazine hydrate concentration as compared to 4-NP. Therefore, the concentration of hydrazine hydrate is considered as constant and the reaction rate (K_a) of the reduction only dependent on 4-NP concentration. Hence, the rate was assumed to follow the first-order kinetics and was calculated by using the following kinetic equation:

$$-K_a t = \ln(C_t/C_0) = \ln(A_t/A_0),$$

where C_t and A_t are the concentration and absorption of 4-NP at time t while C_0 and A_0 are the concentration and absorption of 4-NP at the start of the reaction.[19] The rate constant (K_a) was studied by using different amount of the AuNPs powder and calculated from the slop of the plot of ln (A_t /A_0) versus the reaction time (t) as displayed in Figure 12. The rate constant of reaction that using 2 mg AuNPs is 0.0007 s^{-1}, which is higher than those using 1 mg AuNPs (0.0002 s^{-1}). Hence, the rate of reaction was increased with increasing of the AuNPs amount as the surface area of the active site of Au catalyst increased. This trend of the rate constant is in agreement with previously reported by Tamuly et al.[42]

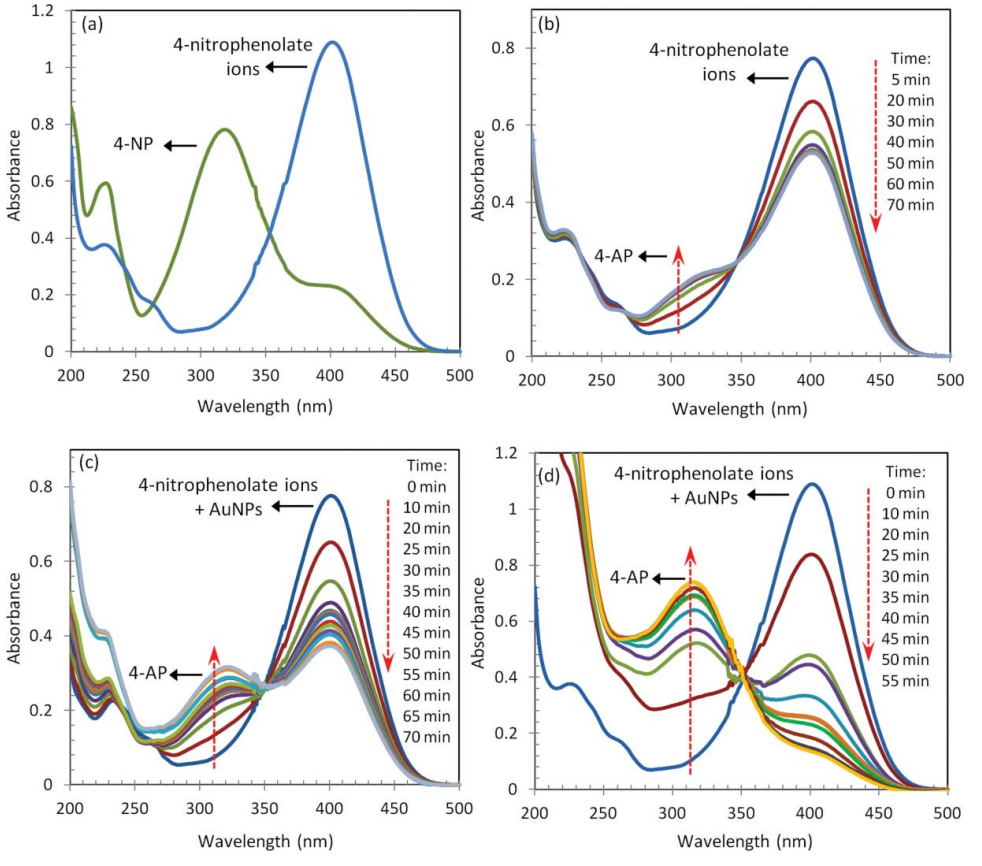

Figure 11. (a) UV−visible spectra of 4-NP before and after addition of hydrazine hydrate. (b) UV−visible spectra of 4-nitrophenolate ions devoid of AuNPs. Time-dependent UV−visible spectra for the reduction of 4-NP with (c) 1 mg and (d) 2 mg AuNPs catalyst.

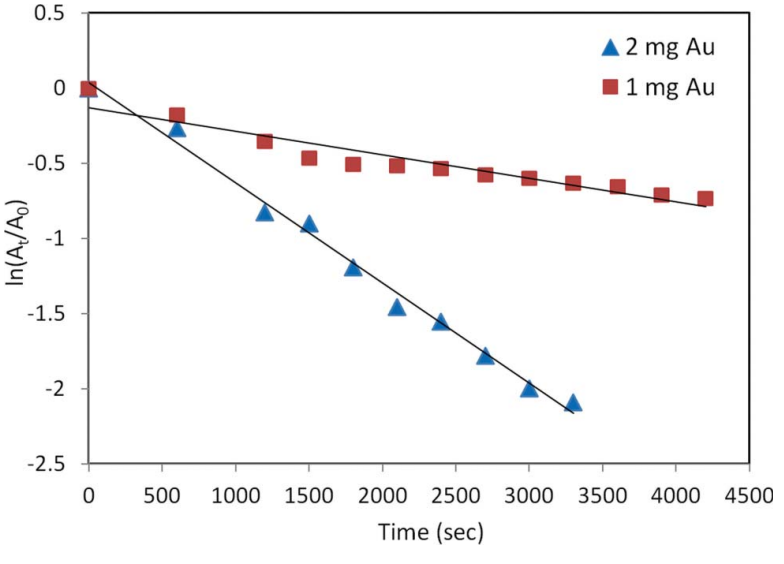

Figure 12. Plot of $\ln(A_t/A_0)$ versus time (t) for the reduction of 4-NP by using biosynthesised AuNPs as catalyst.

4. Conclusions

An environmentally safe approach for the synthesis of AuNPs using an aqueous leaf extract of *P. minus* was explored in this study, which is simple, time saving and eco-friendly. This biosynthesis require only 20 minutes, giving AuNPs with the average particle size of 23 nm. The size of particles depends strongly on the extract volume and pH. Biosynthesised AuNPs in this study are mostly icosahedral and crystalline in nature. FTIR and cyclic voltammetry analyses confirmed that the biomolecules (flavonoids) present in the leaf extract plays an important role as reducing and stabilising agents. The biosynthesised AuNPs show strong catalytic activity in the reduction of 4-NP to 4-AP. The rate constant of the catalytic reaction was increased with increasing of AuNPs amount.

Disclosure statement

No potential conflict of interest was reported by the authors.

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