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Synthesis of gold nanoparticles using phenolic acids and its application in catalysis

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Abstract

The potentiality of different phenolic compounds, belonging to both hydroxycinamic (caffeic, sinapinic and ferulic acids) and hydroxybenzoic (protocatechuic, syringic and vanillic acids) families to generate different gold nanoparticles (AuNPs) has been investigated. The synthesized AuNPs were characterized by transmission electron microscopy (TEM) andUV-Vis absorption spectroscopy. The influence of different experimental parameters, such as pH, ionic strength, buffer concentration, temperature and presence or absence of a stabilizer agent in AuNP synthesis has been studied. In all cases, the addition of a stabilizer has influence in both the amount of AuNP synthesized and in their size. On the other hand, different UV-vis spectra were obtained depending on the phenolic acid used as reducing agent, which was attributed to the different reducing power and stabilization capacity of the different phenolic acids. Finally, the prepared AuNPs showed good catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol by an excess of $NaBH_4$.

*Keywords:*Gold nanoparticles, phenolic compounds, catalytic activity.

1. Introduction

In the recent years, the synthesis and applications of metal nanoparticles (NPs) have attracted intensive research interest due to their unique physical and chemical properties and for their potential bio-analytical applications. In addition to this, metal NPs are attractive due to their easy synthesis and the feasibility of modification of their size and shape. Numerous applications branch out in various fields of science and technology like catalysis [1], electronics [2] as well as electron microscopy markers [3], in DNA detection [4], etc. Gold NPs (AuNPs), in particular, have received substantial attention with surplus of applications ranging from catalysis [5], single electron tunneling [6], nonlinear optical devices and [7] DNA sequencing [8].

To characterize AuNPs, one of the most convenient techniques is UV-vis extinction spectrophotometry [9], since AuNPs exhibit a unique absorption band derived from collective oscillation of conduction electrons upon interaction with electromagnetic radiation, which is known as localized surface plasmon resonance [10]. This surface plasmon resonance originates an extinction spectrum which depends on the size, shape and aggregation of AuNPs, being very useful to characterize them [11].

The stability, shape, size, colour and morphologies of AuNPs strongly depend on the method of preparation, the experimental conditions used (such as reactant concentration, reducing agent, pH, temperature) and the nature and concentration of stabilizers [12,13]. Different radiation, chemical reduction, photochemical and electrochemical methods and theories have been used for the preparation and characterization of AuNPs [14,15]. Among these methods, chemical reduction is one of the most convenient methods for the synthesis of AuNPs because the synthesis process is simple and the size and shape of the nanostructured metal can be easily controlled. In comparison to other methods, it is much faster, cleaner and more economical. Regarding stabilizers, the use of polymers, ligands, solid matrix and surfactants among others has been suggested [16]. Among the different polymers used in literature, poly(vinylpyrrolidone) (PVP) and poly(vinyl alcohol) have been widely used as stabilizers since both protect NPs by steric stabilization preventing their aggregation [17].

Moreover, due to its optical clarity, their use enables investigation of NP formation [18], being also biologically friendly polymers since they are water soluble and have extremely low cytotoxicity.

Different reducing agents have used for NP synthesis in literature, being the most used ones sodium citrate [19] and sodium borohydride [20]. However, the presence of by-products of these reducing agents may create complications when used in some bio-analytical applications [21]. Then, other reducing agents such as hydrazine [22] or amino acids [10], among others, have been also used.

The antioxidant properties of phenolic acids are widely known. In this work, phenolic acid reducing capacity has been proposed as a “green-alternative” of AuNP generation, due to the gentle reaction conditions which are able to carry out this synthesis. In this case, three of the most representative phenolic acids belonging to hydroxycinnamic and hydroxybenzoic acids have been selected. The selected analytes were caffeic, sinapinic and ferulic acids from the hydroxycinnamic acid family, and protocatechuic, syringic and vanillic acids from the hydroxybenzoic acid family.

Among the different applications of metal NPs, which have been previously described, AuNPscatalyze many important chemical transformations, including oxidation of hydrocarbons, C-C coupling, hydrogenation-dehydrogenation and redox [23].One of the reactions more frequently used as model reaction to check the catalytic activity of AuNPs is the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride [24,25]. This reaction is catalyzed by free or immobilized NPs and proceeds in aqueous solution at ambient temperature. Moreover, it can be easily monitored via UV-vis spectroscopy by the decrease of the strong absorption of 4-nitrophenolate anion at 400 nm, leading directly to the rate constant [26].Different articles have been published by using this model reaction to prove metal NP catalytic activity. Thus, it has been investigated the catalytic activity of silver nanoclusters supported on TiO_2 [24], immobilized gold and platinum NPs in spherical polyelectrolyte brushes [27], full grown and still growing microelectrode silver NPs [28], dispersed silver NPs *in situ* assembled on electrospun silica nanotubes [29] and gold NPs synthesised by reduction with ammonium carbonate in the presence of sodium stearate [30], among others.

In this work, different phenolic acids (caffeic, sinapinic, ferulic, protocatechuic, syringic and vanillic), characterized by different reducing capacities, have been proposed as environmentally benign reducing agents for NP generation of gold. As the optical properties of AuNPs are strongly influenced by the reaction conditions, the influence of different experimental conditions in AuNP synthesis, such as pH, ionic strength, buffer concentration, presence or absence of stabilizer, temperature and metal and reducing agent concentrations were studied. Finally, the catalytic activity of the AuNPs has been studied by using them as catalyst in the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride.

2. Experimental

2.1. Reagents and instruments:

The following analytical grade reagents were used: Gold (III) chloride hydrate ($HAuCl_4 \cdot H_2O$, 99.99%), caffeic acid (≥ 98.0%), protocatechuic acid (≥ 97.0%), sinapinic acid (≥ 99.0%), syringic acid (≥ 95.0 %), ferulic acid (≥ 99.0%), vanillic acid (≥ 97.0%), 4-nitrophenol, sodium borohydride ($NaBH_4$), potassium chloride, ammonium carbonate (≥ 99.0%), polyvinylpyrrolidone (PVP, average MW 10,000) and methanol were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water was obtained with a Milli-Q system (Millipore).

Stock solutions of the gold (0.01M) was prepared in ultrapure water, while phenolic acid solutions (caffeic, sinapinic, ferulic, protocatechuic, syringic and vanillic0.01M) were prepared in methanol. All stock solutions were stored at 4 ºC in amber vials in the dark. Working solutions were prepared daily by proper dilution of the stock solutions.

UV-vis absorption spectra were obtained using an Uvi Light & UVIKON XL/XS, UV-Vis spectrophotometer (SECOMAM) with a 1-cm quartz cell, a flow-cell of 10 mm path length and 18 µL inner volume from Hellma (Jamaica, NY). The flow manifold consisted of a Minipuls-3 peristaltic pump from Gilson (Villiers-le-Bel, France) furnished with pumping tubes and Omnifit PTFE 3-way connectors.

Transmission electron microscopy (TEM) images were obtained using a Jeol (Tokyo, Japan) model JEM-1010 microscope operated at 100 kV. Samples were prepared by placing a drop of work solution on 200-mesh Cu grid coated with an amorphous holey carbon film. Images were obtained using a MegaView III camera and the AnalySIS image data acquisition system.

2.2. Synthesis of AuNPs:

In order to obtain AuNPs, diluted solutions of gold and phenolic acids were prepared in ultrapure water and in an ammonium carbonate buffer at pH 9, respectively, unless specified. Then, both gold and phenolic acid diluted solutions were 1:1 mixed using a FIA system at flow rate 2.5 mL min^{-1} and detected in a flow cell using the “stop-flow method”. For this purpose, metal and phenolic acid solutions were thermally equilibrated in a thermostatic bath, being the reaction vessel in-line pre-equilibrated at the same temperature. Zero time was fixed when both solutions arrive to the reaction vessel.

2.3. Catalytic reduction of 4-nitrophenol:

In a typical process, 23 mL of distilled water were mixed with 1 mL of 4-nitrophenol 5 mM in a 50 mL glass vial. When 1 mL of $NaBH_4$ 0.25 mMwas added, the colour of the solution changed from light yellow to dark yellow immediately, and then the mixture was stirred for 15 min at room temperature. At this stage, the 4-nitrophenol had been converted to 4-nitrophenolate anion. After that, AuNPs were added to the system to give a final AuNP concentration of 10^{-5}M. Then, 2 mL of the reaction solution were quickly taken into a quartz cuvette and successive absorption spectra in the range 250 to 500 nm were recorded at increasing times until de reaction is finished.

3. Results and discussion

As previously stated, the stability, shape, size, colour and morphologies of AuNPs strongly depend on the method of preparation and the experimental conditions used, such as reactant concentration, reducing agent, pH, ionic strength and temperature, as well as the presence or the absence of a stabilizing agent [12,13]. Therefore, the study of the influence of all these parameters is a crucial aspect to be taken into consideration.

Thus, these parameters were optimized for AuNPs synthesis by using a factor by factor method. Three replicates were performed for each experiment by initially mixing 10^{-3}M gold and phenolic acid solutions in a ratio 1:1 in a basic medium (pH 8) provided by an ammonium carbonate buffer at 10 mM and a temperature of 25 ºC.

3.1. Effect of pH.

AuNP synthesis is based in electron transference from the reducing agent (phenolic acid) to the gold (III) ion. As it is a redox reaction, it is essential to fix the pH of the reaction medium in order to control both seeded growth and NP stabilization or aggregation. Thus, and taking into account that a neutral or basic medium is essential to AuNP synthesis, a pH study between 6.5 -10.0 pH range was performed. The phenolic compounds (chemical structures showed in Figure 1)considered as reducing agents in this study are characterized by two or three pKas[31] at similar values: 4.6-4.8 for pKa_1, which corresponded to the dissociation of the carboxylic group; 8.9-9.2 for pKa_2, which corresponded to the dissociation of the hydroxyl group at the *p*-position; and 10.7-11.0 for pKa_3forcaffeic and protocatechuic acids, which corresponded to the dissociation of the*m*-OH group of these acids. Therefore, in the pH range considered in this study (6.5–10.0), the different phenolic compounds studied are, basically, as the first anfolitic specie (molar fraction between 89-94 %, depending on the compound [31]).For all phenolic acids studied, the best results were obtained when a pH = 9 was used, since this pH value provided the largest absorbance value. Thus, a pH = 9 was selected for further studies.

3.2. Effect of ionic strength:

The effect of the ionic strength in NP synthesis was next optimized. For this purpose, the ionic strength of the medium was modified by the addition of different amounts of potassium chloride to the ammonium carbonate buffer solution with an initial ionic strength of 10 mM. Therefore, the ionic strength was ranged between 10 and 50 mM. At the sight of the results obtained, it can be suggested that the ionic strength has a double effect: first, when the ionic strength increased, reaction rate decreased. On the other hand, when the ionic strength increased the intensity of the maximum of absorbance decreased, which indicated that ionic strength control the amount of AuNPs generated. Thus, and taking into account the general interest to hide reducing agent influence as less as possible, the minimal ionic strength was chosen as optimal, which is the ionic strength provided by the10 mMbuffer solution without the addition of any salt.

3.3. Effect of buffer concentration:

Next, the effect of buffer concentration in the synthesis of AuNPwas addressed. For this purpose, different ammonium carbonate buffer concentrations ranged between 5 and 50 mM, at pH 9.0, were tried for the synthesis of AuNPs. As it was observed in the corresponding spectra, buffer concentration has influence in the total amount of NPs generated (different concentrations correspond to different absorbance intensities). Moreover, it has also influence in AuNP size, since for some phenolic acids different buffer concentrations produced differences in the position of the maximum wavelengthof the absorbance spectra. Regarding signal intensity, it can be observed that AuNP formation increased when buffer concentration was increased, but there is a maximum of concentration from which this tendency is inverted, decreasing AuNP formation when buffer concentration was decreased. This tendency could be explained by the influence of two factors: first, the buffer solution needs to be strong enough to keep buffered the solution when the $HAuCl_4$ (acid solution) is mixed with the phenolic acid solution; second, buffer concentration has a strong influence in the ionic strength. This parameter has been widely studied and discussed in the previous paragraph, and it is the reason of the second tendency when the buffer concentration is higher. Thus, the buffer concentration has to be the lowest amount which was able to keep pH constant after mixing the two constituent solutions. Thus, there is not an absolute value for the optimal concentration of buffer solution, but rather it is a relative value proportional to the gold (III) chloride concentration employed in the synthesis. Under the experimental conditions used here, for a 10^{-3} M gold (III) chloride concentration, a buffer concentration of 10 mM was strong enough to keep buffered the pH of the reaction medium. Thus, this concentration was selected for further studies.

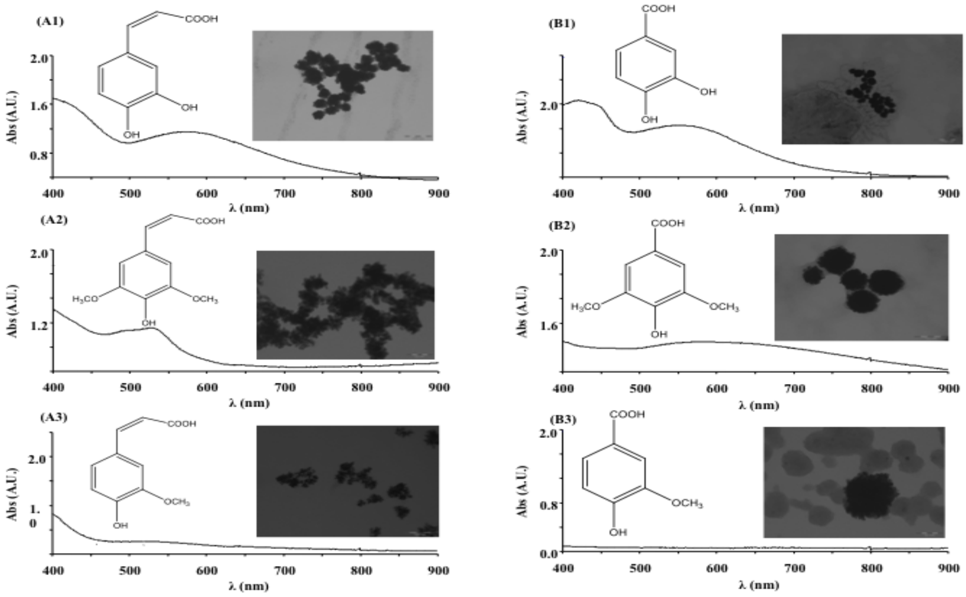

Figure 1. Chemical structures,UV-vis spectra and TEM images obtained at the optimal conditions of AuNPs synthesis by using caffeic (A1), sinapinic (A2), Ferulic (A3), protocatechuic (B1), syringic (B2) and vanillic (B3) acids. Experimental conditions: $AuCl_4^-$ and phenolic acid concentrations, 10^{-3} M; 10 mM ammonium carbonate buffer at pH 9. Spectra were recorded after 5 min at 25 °C.

3.4. Effect of stabilizer (PVP):

It is well known that the presence or the absence of a stabilizer has a strong influence in AuNP synthesis. Among the different stabilizers used, PVP, as a polymeric stabilizer, has been frequently used to protect AuNPs and to improve the quality of particles [32, 33]. Therefore, the influence of the addition of PVP in AuNP synthesis was next addressed. For this purpose, AuNPswere synthesized both in the presence and absence of PVP, which was added to the metal solution in a concentration of 5 g/L. At the sight of the results obtained in the absorbance spectra, it is possible to conclude that the addition of PVP has influence in the amount of AuNP synthesized, since the absorbance intensity is higher in presence than in absence of PVP. In addition to this, it has also influence in the size of AuNPs and in the polydispersity of the generated suspension, since spectra in presence of PVP showed a more defined absorbance maximum at few lower wavelengths.Thus, the fact that PVP effect is not limited to stabilization has been proved. For this reason, all the next studies were carried out in the absence of PVP to do not mask the effect of all the other parameters, especially the effect of the different reducing power of phenolic acids, which will be next discussed.

3.5. Influence of phenolic acids:

In this section, the study of the influence of the reducing agent (phenolic acid) in the growing and stabilization of gold NPs was studied. As it has been previously explained, the phenolic acid selection was based on the different antioxidant capacity of the two families of compounds. This capacity was as follows: caffeic acid >protocatechuic acid >sinapinic acid >syringic acid >ferulic acid >vanillic acid. The AuNP spectra obtained for the six phenolic acids studied under the optimal conditions and their corresponding TEM images are shown in Figure1, respectively.As it can be observed in this Figure, both gold NP spectra and TEM images are different depending on the phenolic acid used as reducing agent. This fact could be due to the different reducing power and stabilization capacity of the different phenolic acids. These two parameters would be related with size and polydispersity of NPs, respectively [11, 19].Thus, sinapinic acid showed a hard sharp maximum at 525 nm, which provided the less polydisperse solution of gold NPs (red colour), with a mean diameter around 50-70 nm [34, 35]. On the other hand, caffeic and protocatechuic acids showed maximum wavelengths in the 600 nm region (wide absorption band, and blue-grey solution colour) related with a diameter higher than 120 nm, which indicated the aggregation of the NPs since any stabilizer agent was added to the solution.Aggregation causes a decrease in the intensity and red shift in the characteristic surface plasmon band (SPB) at 520 nm, displacing this maximum to higher wavelength (600-700 nm) [36]. On the other hand, the SPB is absent with core diameter less than 2 nm, as well as for bulk gold [37]. This could be the explanation for ferulic and vanillic acids, which do not show any sharp band, thus providing the smallest NP size.Therefore, a higher reducing capacity of the phenolic acid employed in the synthesis is related with a higher NP diameter size. It is interesting to compare the behaviour of sinapinic (hydroxycinnamic family) and syringic (hydroxybenzoic family) acids with similar chemical structures and antioxidant capacity. Whereas sinapinicacid rapidly form stable gold NPs, syringic acid forms unstable gold NPs (initial red colour) which turned to aggregated NPs in 4-5 seconds (grey solution). As suggested by Ji et al. [38] for citrate ions, sinapinic acid seems to be a multifunctional compound, acting as both a reducing agent and a stabilizer in the synthesis of gold NPs.

3.6. Relative amount of reducing agent versus metal:

Numerous studies explain the ratio of [reducing agent]/[metal] has an important influence in the nanoparticles formation, as well as in their growth and stabilization. Reduction of $HAuCl_4$ with citrate has been used to obtain particle size in a wide range, from ~10 to 150 nm, by changing the relative amounts of Au precursor to reducing agent. As the concentration ratio of citrate to $HAuCl_4$ increases, the particle size decreases in the first stage and became relatively constant in the second stage [39]. It is important to clarify that in this case citrate acts as both reducing and stabilizing agent. In this work (absence of stabilizing agent), the molar ratio of [phenolic acid]/[Au^{3+}] was adjusted at different relationships and the other experimental parameters were kept constant (25 °C, ammonium carbonate pH 8, 10 mM). UV-Vis spectra were recorded to follow the wavelength of maximum absorbance and the intensity of absorbance.

The different spectra obtained for each [phenolic acid]/[Au^{3+}] ratio provided information about the formation of nanoparticles or the corresponding aggregates. Different effects were observed by increasing the amount of reducing agent. Thus, for caffeic and protocatechuic acid, with the highest reducing capacity, the absorbance is maximum, and almost constant from a ratio of 0,67 to 4 ([phenolic acid]/[Au^{3+}]). The only difference observed is a displacement in maximum wavelength to higher values: from 580 to 630 nm ($\Delta\lambda \cong$ 50 nm) for caffeic acid, and from 590 to 680 nm ($\Delta\lambda \cong$ 90 nm) for protocatechuic acid. As it is well known, the position of the maximum absorption band is strongly dependent on the dimensions of the NPS [40]. In this case, the higher ratio of reducing agent versus gold results in an increase in nanoparticles size, followed by aggregation due to the absence of stabilizer agent. In the case of sinapinic acid, with an intermediate reducing character, the progressive increase of reducing agent proportion results in a proportional increase in the intensity of absorbance, and hence in the amount of nanoparticles generated. In this case, any displacement of the maximum absorption wavelength was found by increasing the [phenolic acid]/[Au^{3+}] ratio from 0,33 to 4. This fact demonstrates the double role of sinapinic acid, as reducing and stabilizer compound in the synthesis of Au-NPs. This observed tendency can be related to the molecular volume. Thus, as the molecular volume increases, the stabilization capability increases: sinapinic acid >caffeic acid >protocatechuic acid. The case of syringic acid is different, with a behaviour closer to ferulic and vanillic acids. A small absorbance maximum at 496 nm was found for 0,33 [phenolic acid]/[Au^{3+}] ratio (a small second band at this wavelength was also found in the case of sinapinic acid, Figure 2). By increasing the amount of syringic acid, a very wide absorption band was obtained (ranged from 550 to 780 nm) with maximum absorbance from 705 nm (0,67 [syringic acid]/[Au^{3+}] ratio) to 610 nm (4 [syringic acid]/[Au^{3+}] ratio). This is an opposite tendency with respect caffeic and protocatechuic acids, demonstrating some stabilization properties of syringic acid, but at very low level than sinapinic acid. The small band at 496 nm for low concentration of syringic acid demonstrates the formation of few amounts of stabilized Au-NPs.

Furthermore, a study of the reaction stoichiometry was carried out, taking into account the [phenolic acid]/[Au^{3+}] ratio from which absorbance intensity of SPB was kept constant. According to the different number of hydroxyl group, two different stoichiometries have been proposed: type A, for phenolic acids containing two hydroxyl groups (caffeic and protocatechuic acids), which are able to give two electrons per molecule; and type B, for these phenolic acids with only one hydroxyl group (sinapinic, syringic, ferulic and vanillic acid), which are able to give only one electron per molecule. Therefore:

Type A: 3***Phenolic acid*** (reduced form) + 2 **Au**$^{3+}$→3 ***Phenolic acid*** (oxidized form) + 2 **Au**^{0}

Type B: 3***Phenolic acid*** (reduced form) + 1 **Au**$^{3+}$ →3 ***Phenolic acid*** (oxidized form) + 1 **Au**^{0}

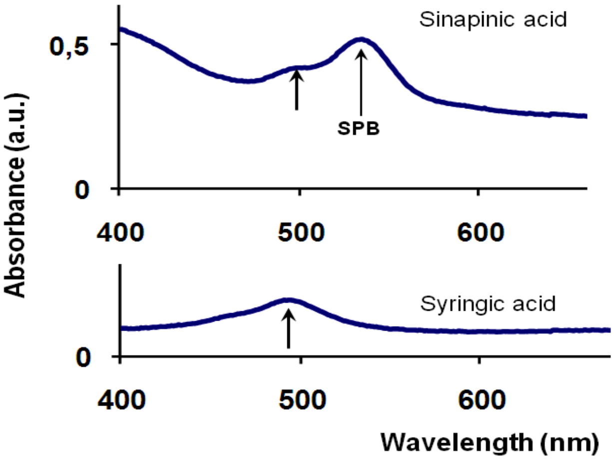

Figure 2. UV-vis spectra obtained for gold NPs synthesis by using sinapinic and syringic acids for a [phenolic acid]/[Au^{3+}] molar ratio of 0.33.

These proposed reactions can explain the reaction stoichiometry, showing how in the case of caffeic acid and protocatechuic acid the stabilization of absorbance versus ratio [phenolic acid]/[Au^{3+}] takes place around a ratio of 1.5; while in the case of sinapinic, syringic, ferulic and vanillic acid, which can donate only one electron, the stabilization would take place around a ratio of 3.

3.7. Application of Au-NPs in catalysis:

In order to evaluate the catalytic activity of the obtained Au NPs, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by $NaBH_4$ was employed as an example of application [41, 42]. The reaction is easily monitored because the presence of both the reactant 4-nitrophenolate anion (λmax = 400 nm) and the product 4-AP (λmax = 300 nm) can be convincingly demonstrated by UV–vis absorption spectroscopy. The UV–vis spectrum of the mixture was studied during the catalytic reduction. In the absence of the Au catalyst, the peak at 400 nm remained unchanged over time, even for a period of several days, suggesting the reduction did not proceed at all. However, when very small quantities of Au NPs were introduced, the absorption peak at 400 nm decreased in intensity and a new peak at 300 nm started to gradually rise in intensity, combined with a fading of the dark yellow color of the 4-nitrophenolate ion in solution. This was due to the reduction of 4-NP to 4-AP.

The reaction was complete within 5, 10, 20, 25, 25 and 50 min by AuNPs reduced with ferulic acid, sinapinic acid, vanillic acid, protocatechuic acid, syringic acid and caffeic acid respectively, at room temperature. Time dependent UV–vis absorption spectra for a typical reduction process are displayed in Figure 3. In this process, Au-NPs acted as a catalyst to transfer the electrons from BH_4^- to 4-NP enabling its reduction. In the current study, the concentration of BH_4^- was so high compared with that of 4-NP that it could be considered to remain constant during the reaction.

Figure 4 shows a plot of ln (*A*) (where *A* is the absorbance at 400 nm) versus time, and a good linear correlation was obtained, characteristic of a pseudo-first-order reaction. The pseudo-first-order reaction rate constants were estimated to be 8.8×10^{-3} s^{-1}, 3.9 x10^{-3} s^{-1}, 2.9 x10^{-3} s^{-1}, 2.1x10^{-3} s^{-1}, 1.9 x10^{-3} s^{-1} and 1.2 x10^{-3} s^{-1} for AuNPs reduced with ferulic acid, sinapinic acid, vanillic acid, protocatechuic acid, syringic acid and caffeic acid, respectively. These results demonstrates that the synthesized Au-NPs have a good catalytic activity for the catalytic reduction of 4-NP. These results demonstrated that the prepared Au-NPs exhibited a dependent reaction property, and the Au-NPs generated with ferulic acid show a higher catalytic activity.

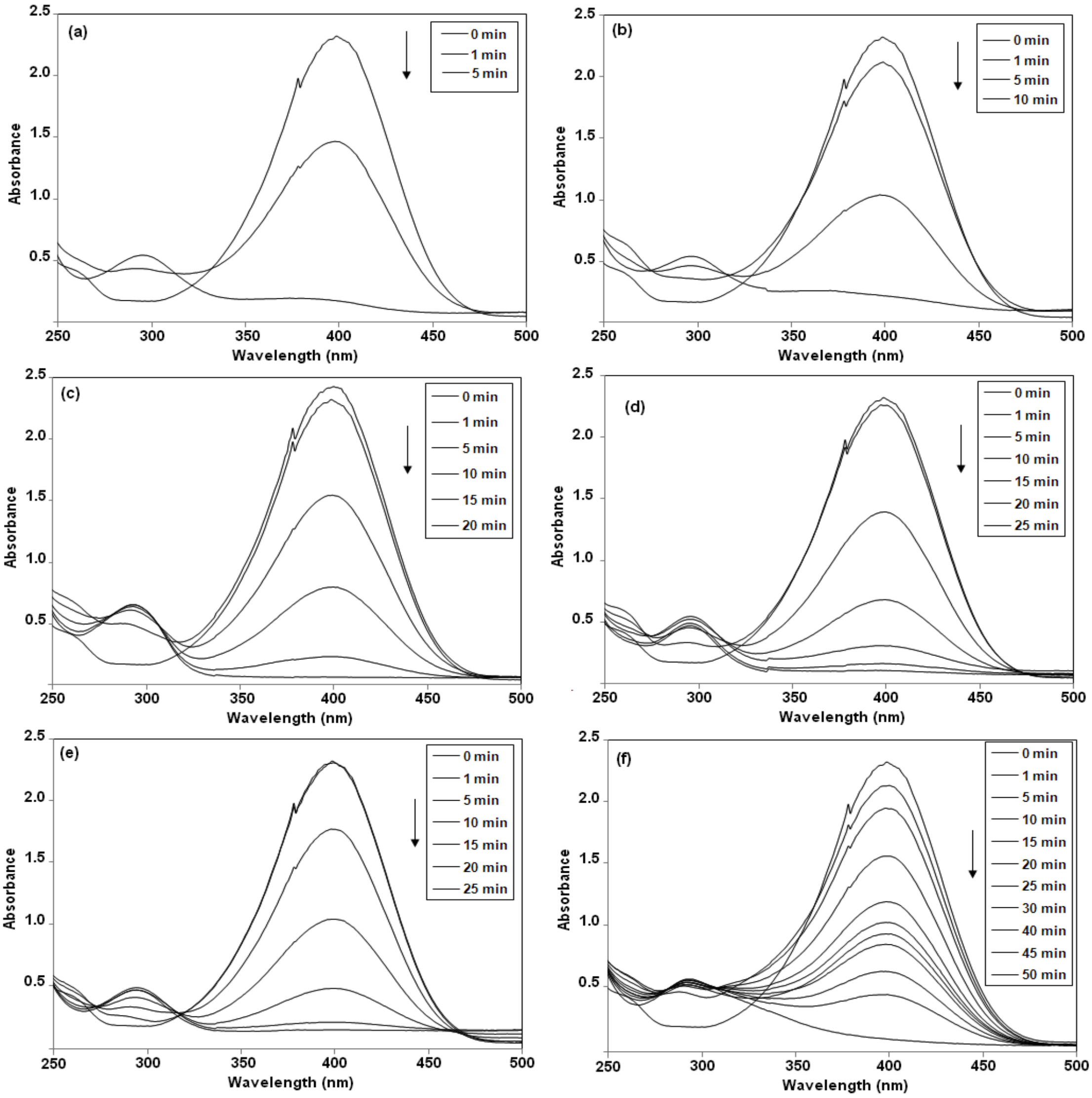

Figure 3. Successive UV–vis absorbance spectra of the reduction of 4-NP by $NaBH_4$ using (A) AuNPs-caffeic acid, (B) AuNPs-sinapinic acid, (C) AuNPs-ferulic acid, (D) AuNPs-protocatechuic acid, (E) AuNPs-syringic acid and (F) AuNPs-vanillic acid as catalysts.

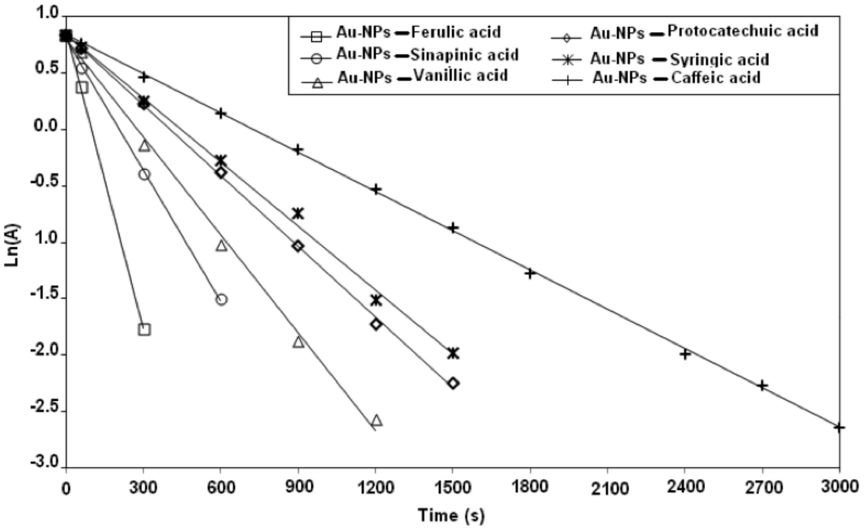

Figure 4. Plots of Ln (A) against time for the catalytic reduction of 4-AP by Au-NPs-phenolic acids. [4-NP] = 2.0×10^{-4}mol/L, [$NaBH_4$] = 0.01 mol/L, and [Au NPs] = 10^{-5}mol/L

Conclusions

In this work, the potentiality of phenolic compounds belonging to bothhydroxycinamic and hydroxybenzoic acid families to generate AuNPs has been evaluated by UV-vis spectroscopy. It has been demonstrated the potentiality of this technique to characterize both size and concentration of AuNPs by SPB maximum wavelength position, being also a good method to real-time monitoring NP growing and stabilization. By using this characterization it has been also possible to demonstrate the importance of experimental conditions such as pH, ionic strength and temperature, which critically affect AuNPs synthesis. On the other hand, it has been possible to establish a direct relationship between the reducing capacity of the phenolic acid used in the synthesis and the size and concentration of AuNPs obtained. Finally, the as-prepared AuNPs showed good catalytic activity in the reduction of 4-NP to 4-AP by using an excess of $NaBH_4$. Considering the high solubility of the synthesized AuNPs in aqueous phase, they may be also a good candidate for biological and other applications in water.

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