CHEMICAL ENGINEERING TRANSACTIONS
VOL. 81, 2020
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš

ISBN 978-88-95608-79-2; **ISSN** 2283-9216
DOI: 10.3303/CET2081233

Green Synthesis of Gold Nanoparticles Using Kiwifruit Juice

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The use of kiwifruit juice as a source of metal-reducing and stabilizing agents for the production of gold nanoparticles (AuNPs) was investigated. The reaction was carried out in batch by mixing appropriate amounts of kiwifruit juice and gold(III) chloride solution. The formation of AuNPs was monitored by measuring the intensity of the surface plasmon resonance (SPR) band of gold. The effects of temperature (20–60 °C), pH (8–12) and gold-to-polyphenol ratio (GPR) were investigated. Characterisation of AuNPs by XRD, DLS and zeta-potential measurements showed that they were highly crystalline, with an average hydrodynamic diameter of about 50 nm and a zeta-potential ranging between –29.2 and –21.7 mV. Under the best reaction conditions (60 °C, pH 9, GPR = 5 mol Au^{3+}/mol GAE), AuNPs with an average size of about 30 nm were produced. The results obtained suggest that kiwifruit juice is a suitable medium for the production of small-sized and stable AuNPs.

1. Introduction

In the last few decades, gold nanoparticles (AuNPs) have been extensively studied due to their unique optical, chemical and thermal properties that make them suitable for a variety of applications in medicine, biotechnology and material science (Bai et al., 2020). As for other metal nanoparticles, the behaviour of AuNPs is dependent on their size, shape and surface chemistry. For example, highly efficient chemical and biological sensing devices were obtaine by using AuNPs of controlled size and shape (Alex and Tiwari, 2015). The size and surface charge of AuNPs were shown to affect their intestinal absorption and accumulation in target organs after oral administration (Schleh et al., 2012).

The most common approach for the production of AuNPs is chemical synthesis (Daruich De Souza et al., 2019). This strategy is based on the reaction of a metal salt, typically gold chloride, with a reducing compound, such as sodium borohydride or sodium citrate (Zhao et al., 2013). Reducing agents supply electrons to gold ions and convert them into zero-valent metallic gold. Stabilizing agents, such as trisodium citrate, sulfur ligands (especially thiolates), polymers and surfactants are then used to inhibit the aggregation of the nanoparticles.

The above methods are often expensive and involve the use of chemicals that may be toxic, limiting their application in biology and medicine. The production process can have a significant impact on the environment. For these reasons, in recent years growing efforts have been made to develop green and environmentally sustainable processes for the synthesis of AuNPs (Nadeem et al., 2017). The investigated strategies include the intracellular synthesis of nanoparticles by microorganisms (bacteria, fungi and microalgae) or plants or the use of plant extracts (Bhattarai et al., 2108). The latter is considered as the most attractive due to its simplicity, economic viability and environmental sustainability (Noruzi, 2015).

As a further step to the development of completely green and sustainable techniques, the use of extracts from agro-industrial wastes has been explored (Zuorro et al., 2019). Kanchi et al. (2018) showed that AuNPs of different shapes (spherical, triangular and hexagonal) can be obtained using aqueous extracts of a de-oiled jatropha waste. In another study, AuNPs were synthesized using a grape waste consisting of grape skins, seeds and stalks (Krishnaswamy et al., 2014). In a very recent study by Reddy et al. (2020), AuNPs were produced using a ginger waste extract under microwave irradiation.

Although the above results support the exploitation of agro-idustrial wastes for the green synthesis of AuNPs, the relatively few studies on this topic make it difficult to draw definitive conclusions. Little is known about the effects of the type of waste and the extraction conditions on the characteristics of the resulting nanoparticles (Baiocco et al., 2016).

Paper Received: 03/07/2020; Revised: 11/07/2020; Accepted: 13/07/2020
Please cite this article as: Zuorro A., Iannone A., Lavecchia R., Natali S., 2020, Green Synthesis of Gold Nanoparticles Using Kiwifruit Juice, Chemical Engineering Transactions, 81, 1393-1398 DOI:10.3303/CET2081233

In this paper we investigate the use of kiwifruit juice as a source of reducing and stabilizing agents for the production of AuNPs. According to FAO statistics (FAO, 2020), Italy is the second leading producer of kiwifruit in the world, preceded by China and followed by New Zealand. From this activity, significant amounts of low-quality or damaged fruits are produced. As a result, there is a potentially large availability of kiwifruit juice, which increases during periods of overproduction. The main objectives of this study were to evaluate the effects of temperature, pH and reactant ratio on the characteristics of the AuNPs produced using the fruit juice and a metallic gold precursor. The results obtained indicate that kiwifruit juice is a promising starting material for the green synthesis of small-sized and stable AgNPs.

2. Experimental

2.1 Chemicals and plant material

Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), potassium persulfate, hydrochloric acid (37 wt%), DPPH (2,2-diphenyl-1-picrylhydrazyl) and the Folin-Ciocalteu reagent were purchased from Sigma-Aldrich Co. (St. Louis, Mo, USA). Ethanol, sodium hydroxide, sodium carbonate, sodium acetate trihydrate and ferric chloride hexahydrate were obtained from Carlo Erba (Milano, Italy). ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) and TPTZ (2,4,6-Tri(2-pyridyl)-s-triazine) were from Alfa Aesar Haverhill (Massachussets, USA). All chemicals were of analytical grade and used without further purification. Demineralized water was used for the preparation of aqueous solutions.
Fresh kiwifruits were purchased from a local market. The fruits were peeled with a knife and cut into small pieces, which were poured into a food processing centrifuge (Moulinex, Italy). The resulting kiwifruit juice was stored at 4 °C and used within a few days.

2.2 Analytical methods

Total phenolics were determined by the Folin-Ciocalteu method following the procedure described elsewhere (Zuorro and Lavecchia, 2013). The results were expressed as gallic acid equivalents (GAE) using a calibration curve obtained with gallic acid standards.
The antioxidant activity was determined by the DPPH, ABTS and FRAP (Ferric Reducing Antioxidant Power) methods, according to the procedures reported by Maietta et al. (2017). The results were expressed as Trolox equivalents (TE) using a calibration curve obtained with Trolox standards.
Dynamic light scattering (DLS) and zeta-potential measurents were made on a Litesizer™ 500 (Anton Paar, Graz, Austria).
An X'Pert PRO diffractometer (Philips, Eindhoven, The Netherlands) was used for XRD measurements. The instrument was operated at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5406 Å). The 2θ angle was varied from 20 ° to 80 °. The step size was 0.04 ° and the counting time was 20 s per step.

2.3 Synthesis of AuNPs

AuNPs were synthesized by mixing appropriate amounts of gold(III) chloride solution with kiwifruit juice. The reaction was carried out in screw-capped glass vials thermostated at the selected temperature and magnetically stirred at 350 rpm. At the desired time, an aliquot of the reaction mixture was taken and assayed. The formation of AuNPs was monitored spectrophotometrically (UV-2700, Shimadzu, Japan) by measuring the intensity of the surface plasmon resonance (SPR) band of gold at 500–550 nm.
All experiments were made at least in duplicate. The reaction temperature was varied between 20 and 50 °C, the pH between 8 and 12, and the gold-to-polyphenol ratio (GPR) between 1 and 9 mol/mol. GPR was defined as the ratio of Au^{3+} concentration to the total polyphenol concentration expressed as GAE.

3. Results and discussion

3.1 Characterization of kiwifruit juice

The total phenolic content of kiwifruit juice was 634 ± 12 mg GAE/L. Its antioxidant activity, determined by the DPPH, ABTS and FRAP methods and expressed as Trolox equivalents, is shown in Figure 1. As can be seen, the antioxidant activity values were dependent on the assay employed (with DPPH < ABTS < FRAP). This is commonly observed when methods involving different radical species or based on different reaction mechanisms are used (Wootton-Beard et al., 2011).

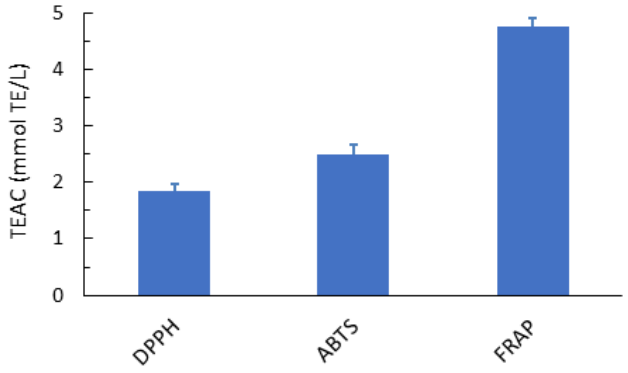

Figure 1: Trolox equivalent antioxidant capacity (TEAC) of kiwifruit juice determined by the DPPH, ABTS and FRAP methods

3.2 Production of AuNPs

Typical UV-Vis spectra of the solution containing gold chloride and kiwifruit jouice at different reaction times and fixed temperature, pH and GPR are displayed in Figure 2. The formation of AuNPs is clearly attested by the appearance of a strong SPR band at around 520 nm. Tthe reaction was accompanied by a progressive colour change of the solution, from pale yellow to deep red. The intensity of the SPR band increased with time up to about 5 h, when the reaction was complete. This increase is a reflection of the increase in the number of synthesized AuNPs during the reaction.

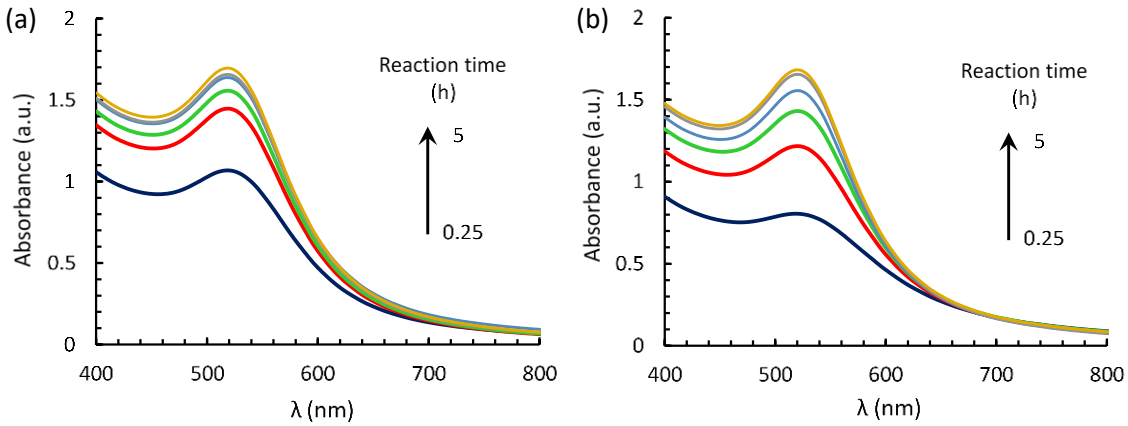

Figure 2: Formation of AuNPs as revealed by absorption spectra. Reaction conditions: (a) T = 30 °C, pH = 12, GPR = 5 mol/mol; (b) T = 50 °C, pH = 9, GPR = 5 mol/mol

The influence of GPR on the production of AuNPs was preliminarily investigated by setting it at 1, 5 and 9 mol/mol and by changing the temperature and pH within their corresponding ranges. As revealed by spectrophotometric measurements, the intensity of SPR band increased with GPR values (Figure 3), suggesting that this factor has a positive effect on the amount of synthesized AuNPs. Increasing GPR also caused a decrease in the size of AuNPs (data not shown). However, the average size of the synthesized nanoparticles at GPR = 5 mol/mol was not much different from that at GPR = 9 mol/mol, whereas their stability, as indicated by the zeta potential values, was higher. For this reason, all subsequent experiments were performed at GPR = 5 mol/mol.

Changes in the reaction conditions caused a variation in the spectral features of the SPR band. In particular, an increase in pH from 8 to 12 produced an increase in its intensity and a slight blue-shift. The observed changes were also affected by the temperature (Figure 4).

The hydrodynamic diameter (HD) and zeta-potential (ζ) values of the synthesized AuNPs are reported in Tables 1 and 2. HDs ranged from 31.4 to 88.3 nm (average: 54.9 nm), whereas zeta potential varied between −29.2 and −21.7 mV (average: –26.1 mV). AuNPs with the smallest size (31.4 nm) were obtained at 60 °C and pH 9, whereas the most stable (ζ = −29.2 mV) were produced at 20 °C and pH 9. It should be pointed out that ζ values varied only marginally under the investigated conditions and were always negative.

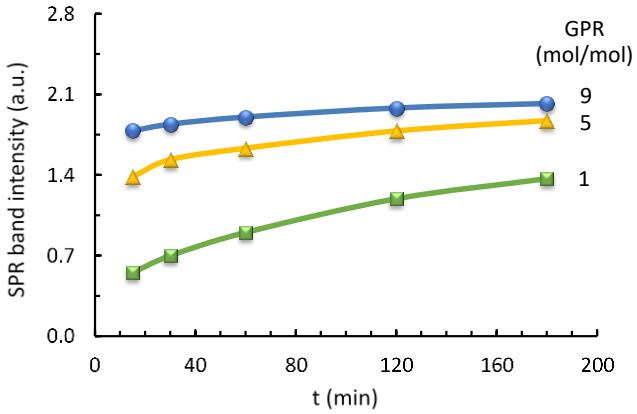

Figure 3: Effect of gold-to-polyphenol ratio (GPR) on the intensity of the SPR band (T = 40 °C, pH = 12)

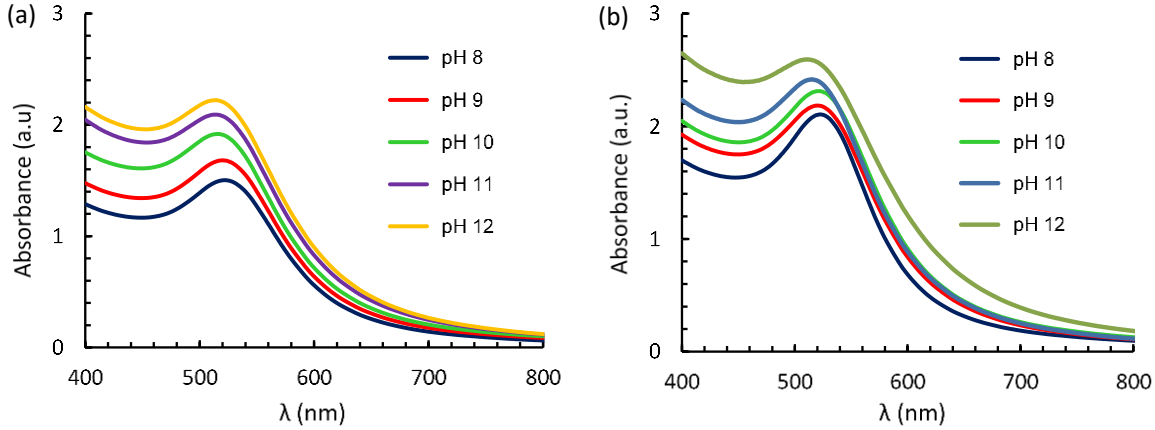

Figure 4: Effect of pH on the absorption spectra of AuNPs at T = 50 °C (a) and T = 60 °C (b). Other reaction conditions: reaction time = 5 h, GPR = 5 mol/mol

Table 1: Effect of temperature and pH on the hydrodynamic diameter (nm) of the synthesized AuNPs (other reaction conditions: reaction time = 5 h, GPR = 5 mol/mol)

pH	20 °C	30 °C	40 °C	50 °C	60 °C
8	55.7 ± 1.4	79.8 ± 1.8	64.1 ± 0.8	78.6 ± 1.5	88.3 ± 1.7
9	39.2 ± 1.1	61.1 ± 0.9	38.3 ± 0.5	65.7 ± 1.1	31.4 ± 1.0
10	43.5 ± 0.8	64.8 ± 1.2	51.5 ± 1.2	67.9 ± 0.9	58.8 ± 0.7
11	36.2 ± 1.0	62.4 ± 0.9	37.3 ± 0.6	67.9 ± 0.6	45.9 ± 1.2
12	37.2 ± 1.2	54.5 ± 0.6	45.0 ± 1.3	58.8 ± 1.0	39.4 ± 1.1

Table 2: Effect of temperature and pH on the zeta potential (mV) of the synthesized AuNPs (other reaction conditions: reaction time = 5 h, GPR = 5 mol/mol)

pH	20 °C	30 °C	40 °C	50 °C	60 °C
8	–26.7 ± 0.4	–25.6 ± 1.1	–22.6 ± 0.9	–27.8 ± 0.5	–25.1 ± 1.0
9	–29.2 ± 0.5	–26.7 ± 0.9	–28.6 ± 1.2	–25.1 ± 0.6	–26.3 ± 0.9
10	–27.2 ± 0.6	–25.8 ± 0.3	–25.4 ± 0.4	–24.9 ± 0.8	–21.7 ± 0.6
11	–24.0 ± 0.8	–26.0 ± 1.2	–27.3 ± 0.8	–26.5 ± 1.1	–25.2 ± 0.5
12	–28.3 ± 1.2	–27.1 ± 0.7	–26.6 ± 0.7	–28.1 ± 1.0	–25.8 ± 0.8

As indicated by XRD patterns, the synthesized nanoparticles exhibited high crystallinity (Figure 5). Four major peaks were detected at 38.2 °, 44.3 °, 64.5 ° and 77.3 °, which correspond to the planes (111), (200), (220) and

(311) of the fcc structure of gold. The peak at 38.2 ° was the most intense, suggesting that the preferred orientation was along the (111) crystal plane.

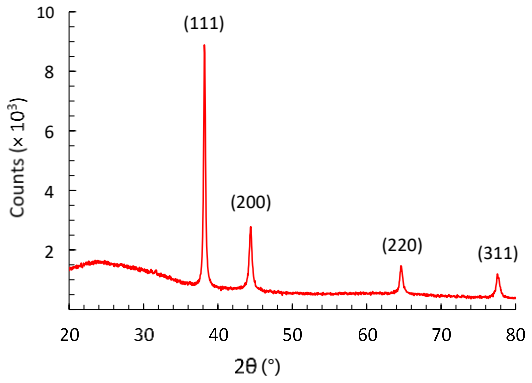

Figure 5: XRD pattern of AuNPs with the four main peaks of metallic gold

The formation and growth of AuNPs can be described by the following reactions:

$$Au^{3+} + 3\ e^- \rightarrow Au^0 \quad (1)$$

$$n\ Au^0 \rightarrow (Au^0)_n \quad (2)$$

according to which the reduction of gold ions to metallic gold (Reaction 1) is followed by the aggregation of metal nuclei to form primary gold nanoparticles (Reaction 2). As a result of aggregation, the nanoparticles grow until reaching their final size. In chemical synthesis methods, size control is accomplished by using coating agents acting through different mechanisms, such as electrostatic repulsion and steric hindrance (Kang et al., 2019). Since the reaction medium used in this study consisted only of kiwifruit juice and the gold salt solution, it follows that some juice components, most likely the phenolic compounds, are responsible for the formation of AuNPs (Gao et al., 2014).

Most of the current knowledge on the mechanisms of nanoparticle formation in the presence of phenolic compounds comes from studies on phenolic acids (Liu et al., 2018). It is generally agreed that the hydroxyl groups of phenolic acids are involved in the reduction of metal ions, while the carboxyl groups act as stabilizing agents (Bhutto et al., 2018). For example, in the case of gallic acid (GA), the following electron-transfer reaction has been proposed:

$$GA \rightarrow GAQ + 2\ e^- + 2\ H^+ \quad (3)$$

where GA is oxidized to its quinone form (GAQ) with the production of hydrogen ions and electrons, which allow the reduction of metallic ions to the zero-valent metal. The carboxyl moiety can interact with the nanoparticle surface, leading to the formation of a coating layer around the nanoparticle that can be further stabilized by hydrogen bonds that are formed between the surface-capped molecules (Yoosaf et al., 2007). As is evident from reactions (3) and (1), the pH of the reaction medium can affect the oxidation of phenolic compounds and the nucleation of nanoparticles, as well as their interactions with the surface of nanoparticles, which control the formation and the strength of the capping layer. The balance of these contributions will finally determine the overall effect of pH on the characteristics of the synthesized nanoparticles will result.

Similar considerations can be made for the temperature (Baghizadeh et al., 2015), which can affect the kinetics of nanoparticle formation and growth as well as the build-up of the coating layer (Mashwani et al., 2015).

4. Conclusions

The results of this study indicate that kiwifruit juice can be effectively used as a source of reducing and stabilizing agents for the synthesis of small-sized and stable AuNPs. However, as all plant materials, its composition may change with fruit variety and developmental stage. More research is needed to evaluate the extent to which these changes may affect the characteristics of the resulting nanoparticles. The possibility of controlling the size and stability of AuNPs by proper selection of the reaction conditions is another important issue to be investigated in the future.

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