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Microwave-assisted green biosynthesis of gold nanoparticles from *Eriobotrya japonica* leaf extract

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Abstract: In this study, as industrial waste, prina was used as an adsorbent substance with its natural and thermally modified form. The prina used in the study was taken as waste material from an olive oil factory in Ayvalık, Turkey. In this study, the removal possibilities of the toxic effect of crystal violet dye found in various industrial wastewaters with prina adsorbent were investigated. By using the pyrolysis method at 600 °C, the biochar form of prina was obtained. Natural and biochar prina and crystal violet (CV) dye have been tried under different adsorption conditions. For this purpose, experiments were carried out at different prina dosages, initial dye concentrations and contact times. The highest removal efficiencies are around 75% in natural prina, while the biochar is around 99% in prina. Also, concentration studies were applied to Langmuir and Freundlich adsorption isotherm models. As a result of the isotherm study, it was seen that the adsorption mechanism was suitable for Freundlich isotherm model. The contact time removal studies were applied to pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models, and adsorption was found to be fit with the pseudo-second-order kinetic model. According to the experiment results, it was observed that the thermal treatment caused a significant increase in the removal efficiency. It was found that it is an efficient adsorbent material that can be used to remove the CV dye from the aqueous solutions.

Keywords: Adsorption; biochar; crystal violet; dye removal; isotherms; kinetics.

1 Introduction

Erioboytrya japonica (Thunb.), known as loquat, is a multipurpose herb. Its leaves have been used as herbal medicine in the treatment of cough thanks to chemical components such as flavonoids, triterpenoid acid and sesquiterpene glycosides . In this study, aimed to the microwave-assisted green synthesis method to obtain gold nanoparticles from *Eriobotrya Japonica* leaves without using toxic chemicals. For this reason, biomolecules and metabolites are *Erioboytrya japonica* (Thunb.) leaves will be used as reducing and capping agents to prevent agglomeration by stabilizing nanoparticles (Zhao et al. 2015). Therefore, it is needed for the improvement of the environment approach to synthesize metal and metal oxide nanomaterials to make use of for the produced of nanoparticles. Plants (Ryaidh et al. 2017), fungi (Molnár et al. 2018), algae (Kathiraven et al. 2015), bacteria (Deljou and Goudarzi 2021) and yeasts (Niknejad et al. 2015) because they ınclude metabolites that own the ability to reduce metallic salts and formulate nanoparticles. Also, these items they act both as a reducing agent and also take part in the stabilization of nanostructures. It has been accomplished with new nanoparticle practices such as antibacterial activity, cancer therapy, antioxidant activity, drug delivery systems, removal of toxic pollutants from wastewater and catalytic activity (Drummer et al. 2021). The biological synthesis route has some advantages such as renewable, minimal energy, sustainable industrialscale manufacturing, operating costs and negligible toxicity in waste.

Plant extracts appear to be excellent biological media because they more stable, reduce metal ions more rapidly (Singh et al. 2016; Hussain et al. 2016; Kharissova et al. 2013). Primary and secondary metabolites of plants are account in order to the reduction of metallic ions in synthesis (Rastogi et al. 2018). Major phytochemicals contain carbohydrates terpenoids, saponins, phenols, proteins and alkaloids that hoped to induce some shape control while the reduction reaction (Ovais et al. 2018). The size and morphology of nanoparticles affect their optical and electrical properties. Therefore, these features are controlled so as to beter improvement in the subject of “green” nanotechnology such as reaction temperature concentration, contact time, pH factors act the properties of green synthesized nanoparticles

(Drummer et al. 2021). Microwave synthesis has been progressively exerted different subjects of materials and chemicals science (Kumar and Sanghi 2012; Tanan and Saengsuwan, 2014) by means of its usually simple, reaction rate and rapid volumetric heating. When determining a method to synthesize NPs, some factors of producing pure NPs are important such as short reaction times, high the efficiency. the shape and morphology of the formed nanostructures can be checked in this procedure (Parveen et al. 2016: El-naggar et al. 2016).

2 Materials and Method

2.1 Materials

Erioboytrya japonica leaves were collected at the Eastern Black Sea region (Trabzon,Turkey). The leaves were air dried on for several days after washed with distilled water. The dried leaves were ground into powder in a grinder to be stored for use. Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4.3H_2O$) were obtained from Sigma Aldrich.

2.2 Preparation of gold nanoparticles

20 g of *Erioboytrya japonic*) leaf powder was shaken in 400 mL distilled water for 90 minutes at 25 ºC before being extracted in a laboratory microwave device (Milestone, Start S Microwave, USA) for 4 minutes at 600 W power. After filtration utilizing Whatman No. 1 filter paper, the filtrate was kept at 4 °C for use in the biosynthesis of AuNP experiments. Various volume of leaf extract (3.4.5 mL) was added to 30 mL of $HAuCl_4.3H_2O$ solution (0.5 mM, 1 mM, 2 mM) to synthesize AuNPs. For the synthesis of AuNPs, optimum reaction parameters were determined by exposing the mixture to a household microwave for 1-60 min. at 90W power. The color change from colorless to pale yellow/purple pink obtained by microwave treatment is evidence of colloidal AgNP formation in solution. Analyzes were carried out in three replicates.

2.3 UV–visible spectroscopy

Biosynthesis of AuNPs can be monitored with UV-vis spectroscopy by reducing the gold ion solution using Erioboytrya japonica leaf extract. The formation of the reduced AuNP colloidal solution was followed using UV-vis spectra. Color changes were watched both visually and by absorbance measurements utilizing a spectrophotometer. Spectra of surface plasmon resonances of AuNPs were registered utilizing a UV-vis spectrophotometer at wavelengths in the range 300-800 nm.

3 Results and Discussion

The color change of the solutions from pale yellow to yellowish brown is a sign of nanoparticle formation (Fig.1).

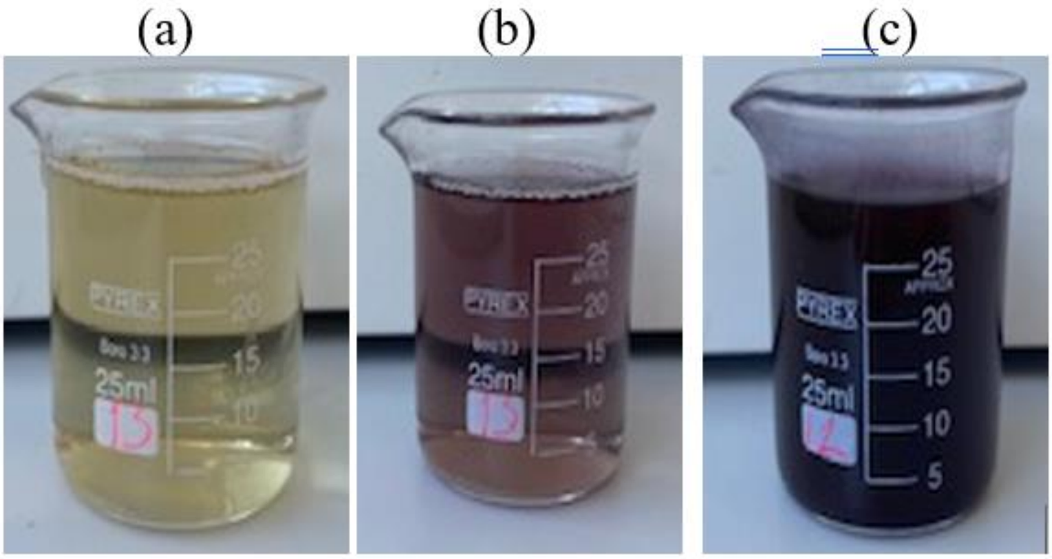

Fig 1. Color change of HAuCl4.3H20 and *Erioboytrya japonica* leaves extract mixture (a) before and (b and c) after microwave treatment.

The UV-visible spectrum of AuNPs is presented in the range 300–800 nm in Fig.(2), Fig.(3), Fig.(4). SPR absorption spectra of silver nanoparticles produced from 0.5 mM, 1 mM, 2 mM $HAuCl_4.3H_2O$ concentration. Spectrophotometric scanning of the mixture of (3,4,5 mL) Erioboytrya japonica leaf extract and (0.5 mM, 1mM, 3 mM) HAuCl4.3H2O solution were performed at different times after microwave treatment. Fig.(2), Fig.(3), Fig.(4) were presented the UV-visible spectrum of AuNPs in the range of 300-800 nm. SPR absorption spectra of silver nanoparticles produced using (0.5 mM, 1 mM, 2 mM) $HAuCl_4.3H_20$ solution are given in below figures.

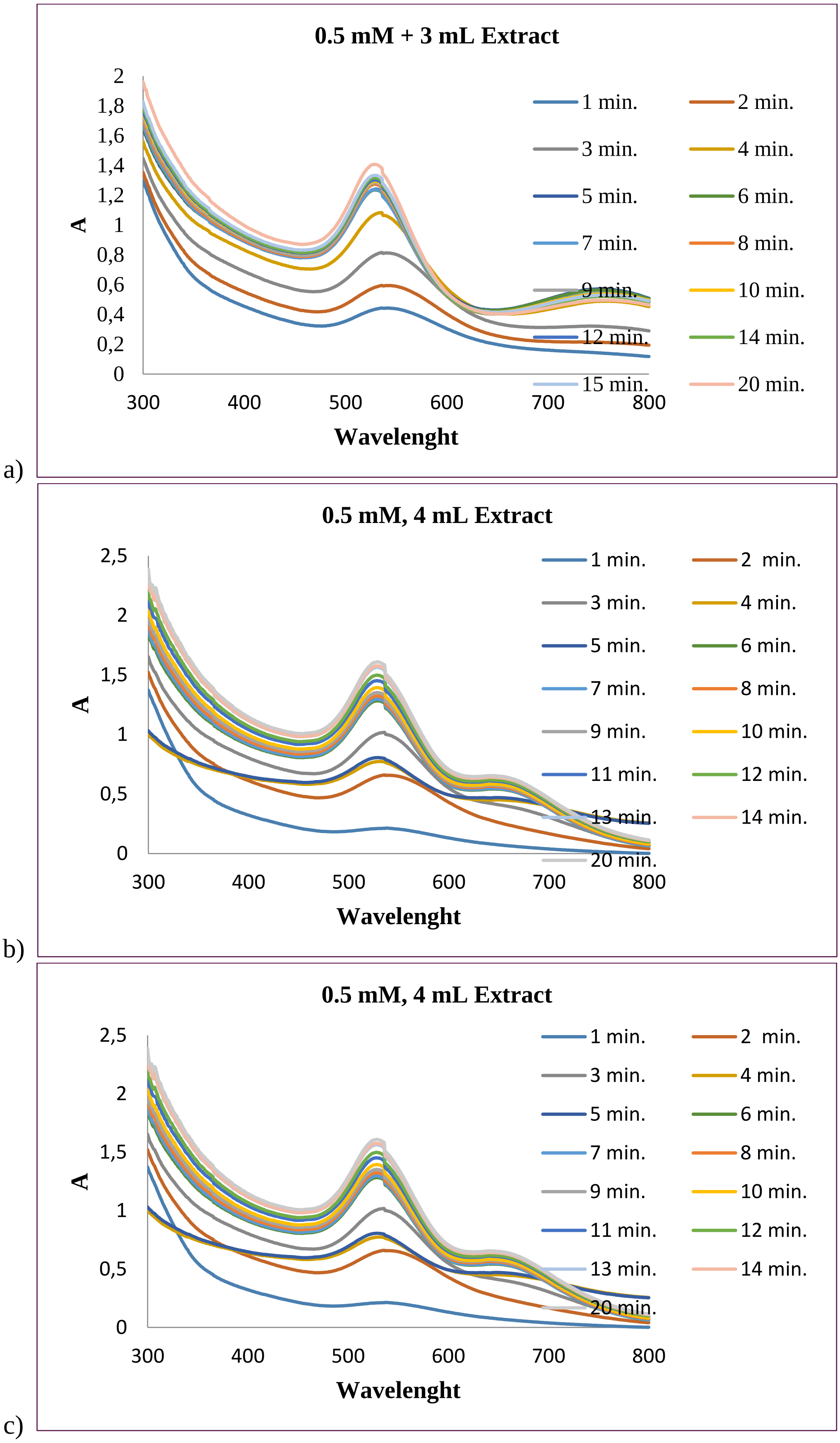

Fig 2. SPR absorption spectra of gold nanoparticles produced from 0.5 mM [a (3 ml), b (4 ml), c (5 ml)] $HAuCl_4.3H_20$ concentration.

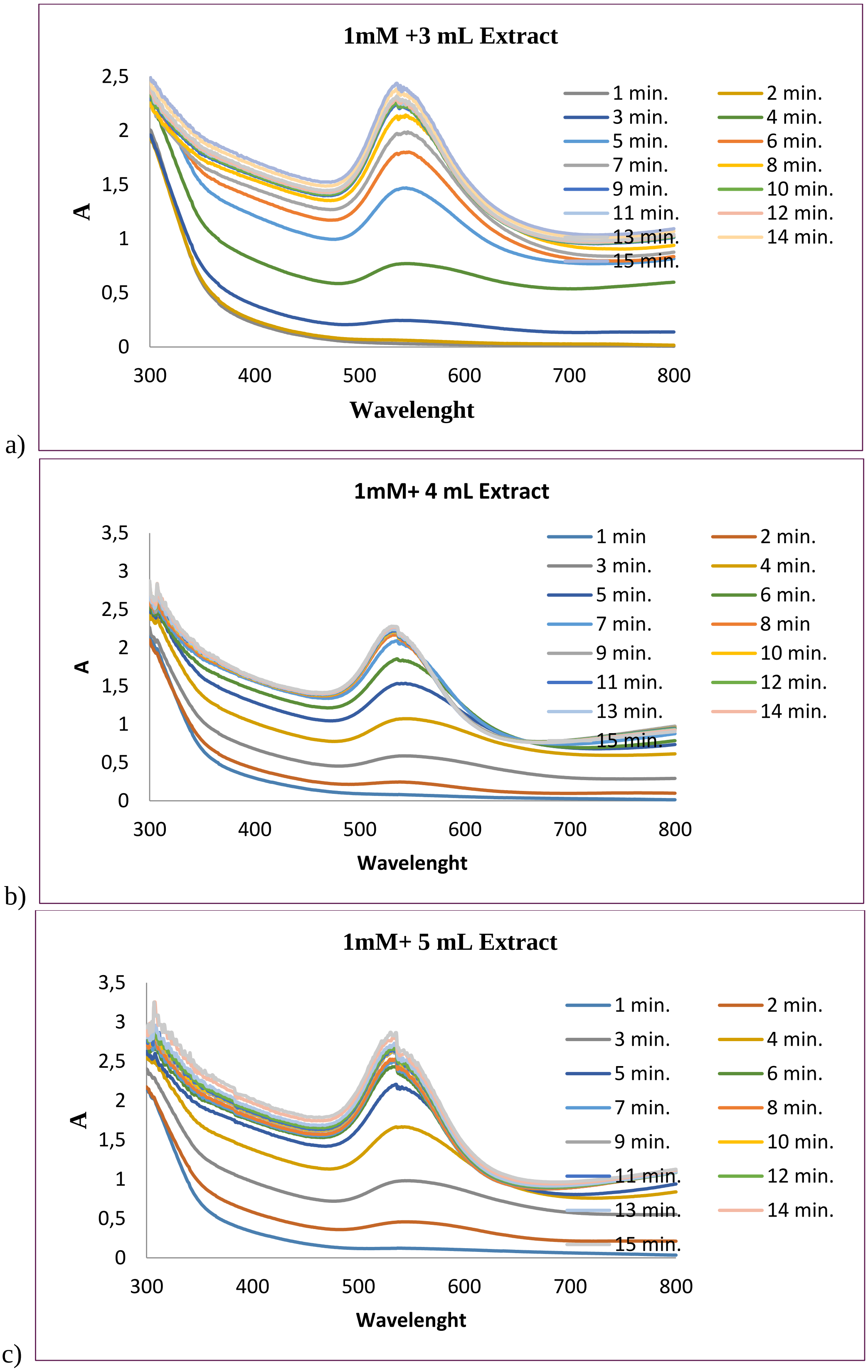

Fig 3. SPR absorption spectra of gold nanoparticles produced from 1 mM [a (3 ml), b (4 ml), c (5 ml)] $HAuCl_4.3H_20$ concentration.

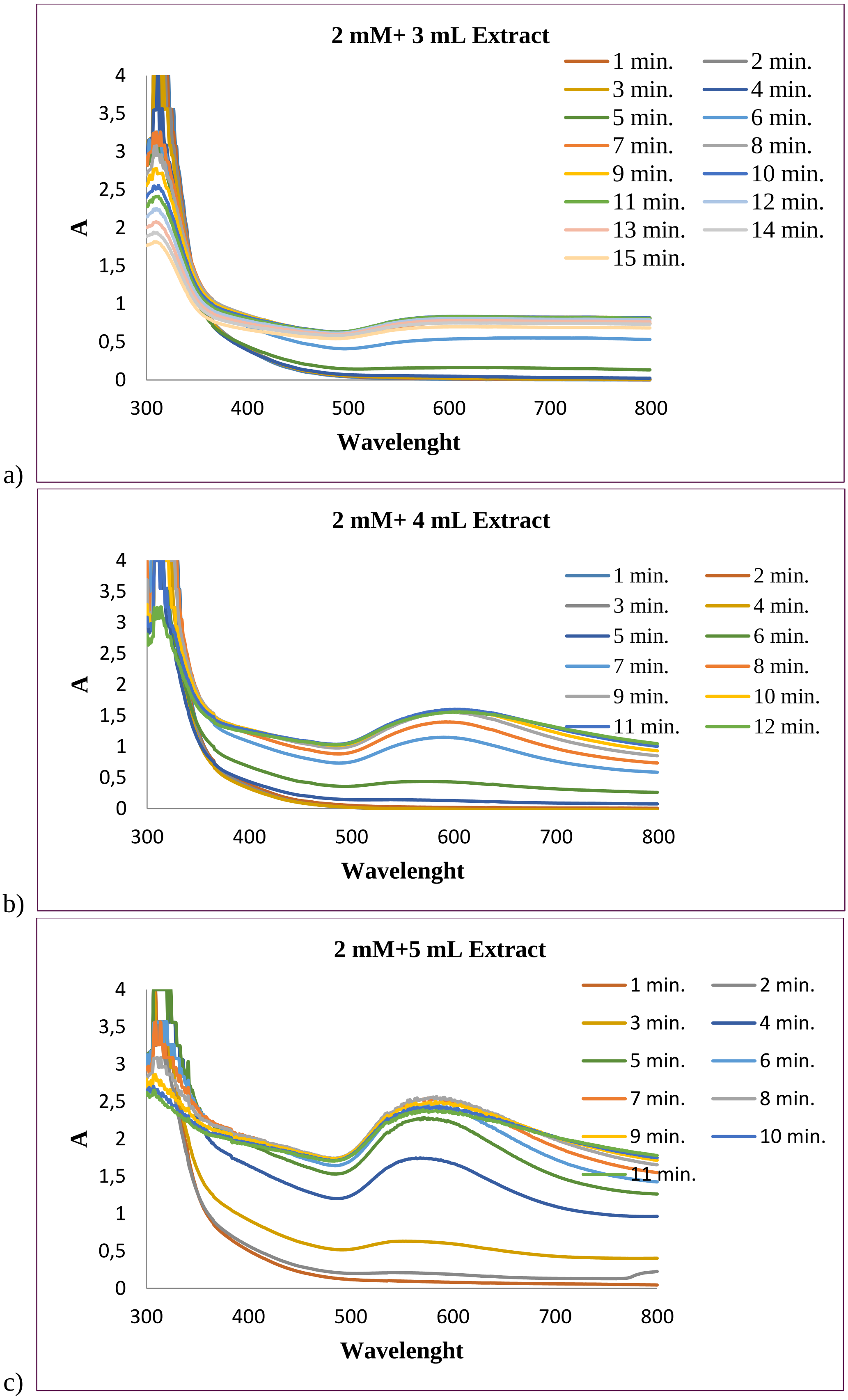

Fig 4. SPR absorption spectra of gold nanoparticles produced from 2 mM [a (3 ml), b (4 ml), c (5 ml)] $HAuCl_4.3H_20$ concentration.

AuNPs were produced as given in Fig.(2), Fig.(3), Fig.(4). By increasing $HAuCl_4.3H_2O$ concentration and keeping other parameters same, obtaining wider resonance bands were showed the formation of larger nanoparticles. SPR absorption spectra was observed 530 and 600 nm region. The specific resonance band was observed after 5 minutes of exposure with 3 mL and 4 mL extracts, while it was observed after 4 minutes with 5 mL of extract. The band reached to maximum height after 7 minutes microwave treatment at 90 W power in Fig (3). The peak intensity and full width at half maximum were affected by the size and degree of agglomeration of particles. Thereby, in all cases the width of the peak can be attributed to the broad particle size distribution (Sökmen et al., 2017).

4 Conclusions

Biomolecules present in extract and microwave treatment facilitates the nanoparticle production are able to reduce gold ions to gold nanoparticles. The color change from light to dark purple color was surveyed throughout the reaction with changing concentration of Erioboytrya japonica leaf extract, which are the SPR of AuNPs in solution. The specific resonance band was observed around 530 - 600 nm region, indicating the formation of AuNPs. It is clear that AuNPs were succesfully produced with 3 mL, 4mL, 5 mL extract and (0.5mM, 1mM) $HAuCI_4.3H_2O$ solution by micowave asisted extraction. Extract concentration has an influence in detecting the size distribution of AuNPs. Produced collaidal solutions were monitored for 40 days. A fast, simple and economical production of AuNP was achieved using *Erioboytrya japonica* leaf extracts, produced stable gold nanoparticles. This study showed green synthesis of AuNPs, as influential bioreduction of Au^{+3} utilizing *Erioboytrya japonica*, treating as reducing and stabilizing agents. Owing to the potential of E. *japonica* to be used as a reducing and stabilizing agents, it can be investigated using in the synthesis of other metal NPs. *Erioboytrya japonica* leaf extract exerted as medicinal values that may help to take adventage from the application in the future AuNPs in medicines.

Conflict of interest disclosure: The author declares no conflicts of interest.

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