Influence of Temperature on the Growth of Silver Nanoparticles Synthesized Using *Salvia officinalis* Aqueous Extract

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In this paper the silver nanoparticles (AgNPs) are synthesized by bottom-up approach using Salvia officinalis aqueous extract as reducing agent, and under such circumstances, the ultraviolet-visible (UV-Vis) spectroscopy is used to evaluate the evolution of the synthesis process, scannings in the wavelength range of 230 nm to 750 nm. The presence, position and shape of the absorption maximum in the region of 400-430 nm were monitored, and associated with AgNPs formation . Interactions of organic substrate with the generated silver nanoparticles were put into evidence by using infrared spectroscopy. The experiments were conducted at four temperatures and five different volumetric ratios of AgNPs precursors, the plant extract and silver nitrate 10 mM aqueous solutions. Conclusions on the synthesis parameters effect on process evolution were drawn. It was found that the temperature and the initial ratio of synthesis precursors influence the growth process and characteristics of the obtained AgNPs. Infrared spectra confirmed the interactions between the organic substrate and the formed AgNPs, as well as with nitrate ions present in the synthesis mixture. Thus, the position and the shape of the recorded peaks in the ranges 1500 - 1600 cm^{-1}, 800 - 900 cm^{-1} and around 3400 cm^{-1} showed significant changes during the nanoparticles synthesis.

Keywords: silver nanoparticles green synthesis, Salvia officinalis, ultraviolet-visible and infrared spectroscopy

Surface plasmon resonance (SPR) is the resonant oscillation of conduction band electrons at the interface of different electric permitivity mediums. The resonance conditions are attained when incident photons frequency is the same with the natural frequency of conduction band electrons from the interface [1, 2]. Consequently, SPR is fundamental for many analytical applications, because it correlates qualitatively and quantitatively the effect of analyte adsorption on the nanoparticles surface [3]. The result consists in changing the shape and size distribution, which could affect the plasmonic properties highlighted by changes the absorption spectra [4, 5].

Silver nanoparticles show a particular interest due to their sensitive response of UV-Vis spectra assigned to the size and the shape of aggregated particles present in solution. These properties make AgNPs useful for designing of miniaturized biosensors and lab-on-a-chip sensors [6, 7].

Many applications of the biosensors nanoparticles-based need a sensing unit with a reduced toxicity, and for this reason, the use of biosynthesized nanoparticles has the advantage of low toxicity [8, 9].

The present study describes the synthesis of silver nanoparticles from aqueous solution of silver nitrate as a rapid eco-friendly technique using aqueous extract of *Salvia officinalis*, and the plasmonic response was evaluated by UV-Vis spectroscopy.

Sage (*Salvia officinalis*) is a perennial, evergreen shrub, with woody stems, grayish leaves, and blue to purplish flowers. It has a long history of medicinal and culinary use. For a long time ago, sage species have been used in traditional medicine to relief pain, protecting the body against oxidative stress, free radical damages, angiogenesis, inflammation, bacterial and virus infection, etc. [10]. Several studies demonstrated that the aqueous extract of *Salvia officinalis* contain multiple organic species with reductive capacity that makes it a good candidate for the synthesis of the AgNPs [11-13]. Design of sensing systems based on AgNPs as efficient tools for alimentary or medicinal use, help people to know how to avoid the toxic chemicals and achieving of biological compatibility as serious conditionalities [14, 26].

The AgNPs synthesis occurs by three stages process: (i) reduction of ionic silver; (ii) growth of AgNPs and (iii) the stabilization of formed nanoparticles. In the third stage, the shell, that stabilizes the generated nanoparticles, consists of chemical species bound to the silver surface in order to maintain the size of particles at the nano dimension, with autocatalytic growth dynamics process [15]. In general, the nanoparticle synthesis is considered successful if the growth of stable particles led to specific sizes / shapes as well as size / shape distributions. Also, the mechanism for AgNPs formation and the working parameters could be deliberately adjusted to obtain adequately nanoparticle systems [16]. The biosynthesis of AgNPs is influenced by temperature, *p*H of the reaction medium, reductive agents, stabilizing agents, reaction time and the amount of silver added to the mixture [18].

The AgNPs formation is detectable by colour change of plant extracts and confirmed through UV-Vis spectroscopy as a result of plasmonic properties of silver nanoparticles. The absorption maximum position and the shape of absorption band from UV-Vis spectra is related to size, shape and structure of nanoparticles [8]. Also, interactions

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of the organic substrate (plant extract) with the generated silver nanoparticles were followed by the infrared spectroscopy. [11,15,19].

The present study proposes an experimental setup built to evaluate the influence of temperature on the AgNPs synthesis for different precursors ratios (silver nitrate 10 mM solutions and *Salvia officinalis* aqueous extract. Complementarity with other reported data have been described, mainly considering the AgNPs sensing response perspective [19,20].

Experimental part

Silver nitrate powder of analytical grade, (Merck Millipore) was used to prepare a stock solution of silver nitrate 0.1 mol.L^{-1} was prepared. For all the synthesis procedures, a 10 mM silver nitrate was used, freshly prepared before the experiments. Redistilled water (conductivity below 0.10μS·cm^{-1} at 25°C) was used for all the experiments.

As plant extract was used a mixture of dried *Salvia officinalis* stems, leaves and blossoms, purchased from a local certified medicinal plants supplier (Plafar S.A.).

A water bath Selecta Precisterm was used for temperature experiments, with a thermostating stability of ±1 °C. The centrifuge operations were performed using the Hettich Rotofix 46H system with glass vials, at a speed of 1000 rpm. The *p*H of the solutions was measured with a WTW InoLAB Multi 9430 meter, equipped with an IDS SenTix 980 pH-sensor.

For the UV-Vis spectroscopy measurements were performed with the double beam system Thermo Evolution 260 Bio, scannings were performed at 1 nm intervals, for the wavelengths range of 230-750 nm, and quartz cuvettes with light path of 1 cm were used as sample support.

Salvia officinalis extraction procedure

The plant extracts were prepared by classic maceration at room temperature (72 h/ no light exposure). The ratio of dried plant to redistilled water was of 10 g to 150 mL. After the extraction time, the mixture was centrifuged for 5 minutes at 1000 rpm, at room temperature (25°C). The supernatant (extract stock solution) was collected and stored at 4°C for the synthesis experiments. One single stock solution of *Salvia officinalis* aqueous extract was used in all experiments.

Silver nanoparticles synthesis

The colloidal silver nanoparticles were prepared by mixing 10 mM silver nitrate solutions and aqueous *Salvia officinalis* extracts from stock solution, in different volumetric ratios. The following volumetric ratios of plant extract (stock solution) to silver nitrate (solution 10 mM) were studied: 1:5, 1:2, 1:1, 2:1 and 5:1 (v/v). Comparation samples with 0 % plant extract, and 0 % $AgNO_3$ respectively were prepared. Triplicate samples of synthesis mixture were prepared, with a total volume of 50 mL. Reagents were added as follows: first dilution water was added, then plant extract, and in the end $AgNO_3$ solution were added.

During the experiment, the synthesis mixtures were maintained in dark, thermostated at the test temperature for three hours, except the short period of UV-Vis spectra recording. Test temperatures of present study were: 25 , 40 , 55 , 70 °C. After the first three hours of reaction time at studied temperatures, samples were allowed to cool down, then left in dark, at room temperature, for 8 days. During this period, UV-Vis spectra were recorded at different time intervals, as shown in the data included in next sections.

UV-Vis measurements

UV-VIS spectra were recorded using Thermo - Evolution 260 BIO spectrophotometer in the range 230 nm to 750 nm, at 1 nm intervals, using 1 cm quartz cuvettes. Redistilled water was used as blank solution. AgNPs characteristic absorption bands, with maxima in the wavelength range of 400 - 430 nm, were monitorized during data acquisition. The measurements at different temperatures and different volumetric ratios of the precursors in the synthesis mixtures have been performed. The UV-Vis spectra were also collected for solutions prepared in the same manner as the synthesis mixtures, but having either 100 % silver nitrate 10 mM and 0 % *Salvia officinalis* extract or the vice-versa.

The relative areas were calculated for recorded spectra, as the area under the absorption band of the synthesis mixtures, after subtracting the signals corresponding to precursors solutions. Calculations were made for the wavelengths range of 350 to 600 nm, selected as the area of UV-VIS spectra comprising AgNPs plasmonic properties modifications [3]. The values of relative area were considered an indicator of the presence of the silver nanoparticles formed during the studied process, giving a plasmonic response.

Infrared spectroscopy

The infrared spectra of dried sage extract and of the synthetized colloidal silver nanoparticles samples were recorded on a Bruker Vertex 80 infrared spectrometer. The scanning of each sample was performed in the wavenumbers range of 4000 cm^{-1} to 400 cm^{-1}. The dried samples were obtained by maintaining corresponding solutions at 30 °C for 24 h in glass Petri dishes. A known amount of sample was placed in the stainless steel vial of a laboratory ball mill together with dried KBr, in a gravimetric proportion of 0.24 %, then grounded and mixed for 60 s. The KBr pellets were then prepared in a lab hydraulic press.

Results and discussions

The process parameters as pH, temperature, content of sage extract, concentration of ionic solution, reaction time etc, affect the reduction reaction of metallic ion, the growth of nanoparticles and their stabilizing stage. The shape of absorption band has a maximum in the region 350 - 600 nm, considered to cumulate the plasmonic properties of all the AgNPs present in solution [3].

As may be observed in figure 1, the individual precursors solutions show slight absorption phenomena in this wavelength range (specifically - plant extract solution has

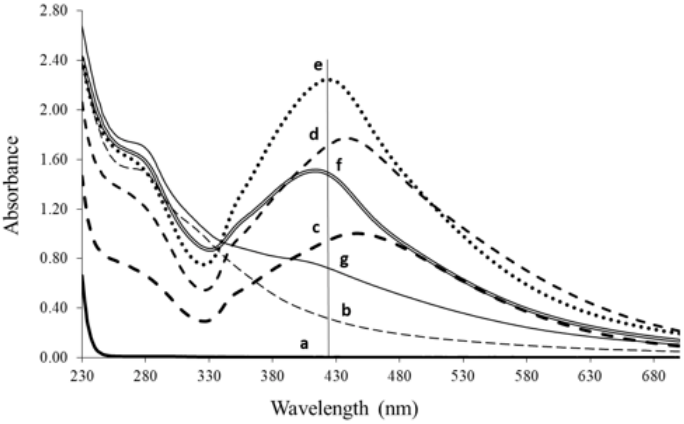

Fig. 1. Recorded UV-Vis spectra (25°C) for synthesis solutions at 8 days from precursors mixing, for: a) 0 % plant extract, b) 0 % $AgNO_3$ 10 mM, and initial (v/v) ratios extract : $AgNO_3$ 10 mM of: c) 1:5, d) 1:2, e) 1:1, f) 2:1, g) 5:1.

a higher absorption than silver nitrate one), with no maxima. For all the synthesis solutions, two absorption bands were recorded, with different intensities, and at different wavelengths values for different synthesis solution compositions. Thus, the expected characteristic peaks corresponding to AgNPs formation [3, 4], were found in the range 400-440 nm, for all the studied compositions. When equal volumes of AgNPs and aqueous *Salvia officinalis* extract were mixed in the synthesis solution (1:1 precursor's initial mixing ratio), the UV-Vis spectra show the highest absorbance value, and the peak positioned at 425 nm [22]. For higher silver ions content in the synthesis initial mixture, a batochromic shift was observed. As demonstrated in previous studies [21] this red shifts may correlate with formation of larger nanoparticles. If the plant extract was added in higher volumes than 10 mM silver nitrate solution, the UV-Vis spectra showed smaller absorption maximum, and their corresponding wavelength were blueshifted compared with the 1:1 (v:v) precursors ratio. This finding was considered an indication for particles with smaller size. Another observation from figure 1 is the shoulder observed around 350 nm, more visible when the added silver nitrate solution exceeds the volume of *Salvia officinalis* extract. This finding could indicate the formation of larger AgNPs with thinner shell [23].

Figure 2 shows the time variation of relative areas, calculated as previously described, for a monitoring period of 8 days. The inset shows data for measurements peformed after the first three hours reaction time, and up to 8 days from precursors mixing. Relative areas vs. time plots have been preferred to plots of the maximum absorption vs. time, because the recorded absorption bands had different characteristics (maximum intensity, bandwidth, shape) when different initial ratios sage extracts: silver nitrate were used for AgNPs synthesis. According to calculation approach, the relative areas correlate with the amount of nanoparticles formed in the synthesis solution up to a certain time. Under these considerations, figure 2 shows slow and continuous nanoparticles formation during the monitored 8 days, for samples where the initial volumetric ratio between silver nitrate and plant extract is higher than 1. Higher values of relative areas were obtained for studied synthesis mixtures where initial ratios (v:v) sage extract : silver nitrate 10 mM of 1:1 or higher. On the other hand, the time evolution of relative areas calculated from UV-Vis spectra shows a rapid growth of AgNPs in the first three hours from the mixing moment of reactants. The main line of figure 2 indicates that AgNPs formation process occurred with different reaction speeds in the first 30 min, for different initial ratios (v:v) of plant extract : silver nitrate. Thus, the relative areas at this reaction time were different for different initial compositions of synthesis mixture, the highest values were recorded for 1:1 reactants ratio. Also, for all the studied mixtures, a slight plateau is reached after 150 min reaction time. The inset figure 2, show data collected during process observation for longer periods (days). Increases of relative areas were found for synthesis mixtures where the initial volumetric ratios plant extract : silver nitrate were 1:5, 1:2 and 1:1. When the initial mixtures contained higher quantities of plant extract (2:1 and 5:1, v:v), small modifications of the relative areas in time were recorded.

Figure 3 shows variation of relative areas calculated as described above with silver nitrate percentage, for different reaction times, at 25°C. Also, figure 3 reveals that, when the synthesis mixture has initial low silver nitrate content, the plasmonic response is weak, meaning that reduced amounts of AgNPs are formed. Slight increase in the plasmonic response was recorded when the content of silver nitrate exceeds the plant extract content (percentages higher than 50 %), and a higher relative area values were calculated. The initial precursors mixing ratio of 1:1 (v:v) may be considered optimal for the biosynthesis of AgNPs using Salvia officinalis extract at room temperature.

The reaction temperature could play an important role in particle size and shape distribution, especially for silver nanoparticles [20]. The experimental findings from our setup is considered an input information in optimizing the biosynthetic processes studied. Figure 4 shows variation of calculated relative areas vs. time, in the first three hours of the AgNPs synthesis, at different working temperatures and different compositions of the synthesis mixture. The graphs plotted in figure 4 show a general behavior: for most of studied samples, higher relative areas at higher temperatures experiments were obtained; this may be associated with the fact that higher amounts of AgNPs were obtained when temperature increases. On the other hand, the temperature influences the speed of AgNPs formation, correlated with the slope of relative area vs. time graphical representation, fig 4 a)-d). Increasing the temperature a higher speed is observed by the slope of the graphs. An exception was encountered for the mixture silver nitrate / sage extract with initial ratio of 5:1 (v/v), where experiments showed that temperature does not influence. According to fig. 4 b), the most significant influence of temperature is exhibited on the mixture having initial ratio plant extract : $AgNO_3$ of 1:2 (v:v). Thus, an increase of relative area calculated for this ratio may be observed at

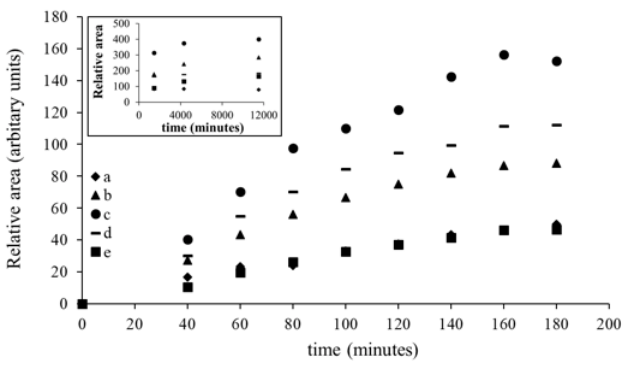

Fig. 2. Evolution of calculated relative areas in time, within 8 days from silver nanoparticles synthesis precursor mixing with initial (v/v) ratios extract : $AgNO_3$ 10 mM of: a) 1:5, b) 5:1, c) 2:1, d) 1:1, e) 1:2 (Inset: Data for synthesis time higher than 3 h)

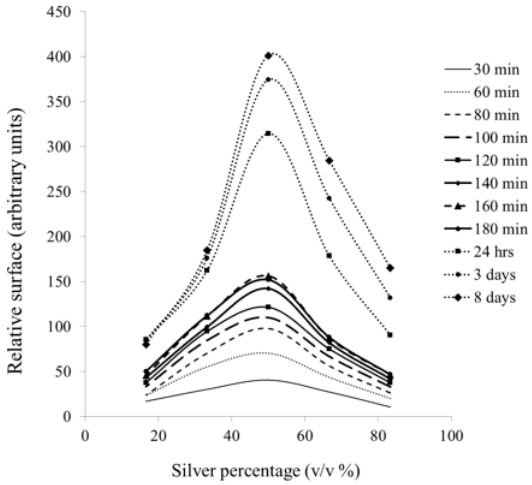

Fig. 3. Relative areas at different reaction times, versus $AgNO_3$ percentage in the initial mixture, for a synthesis process conducted at 25 °C

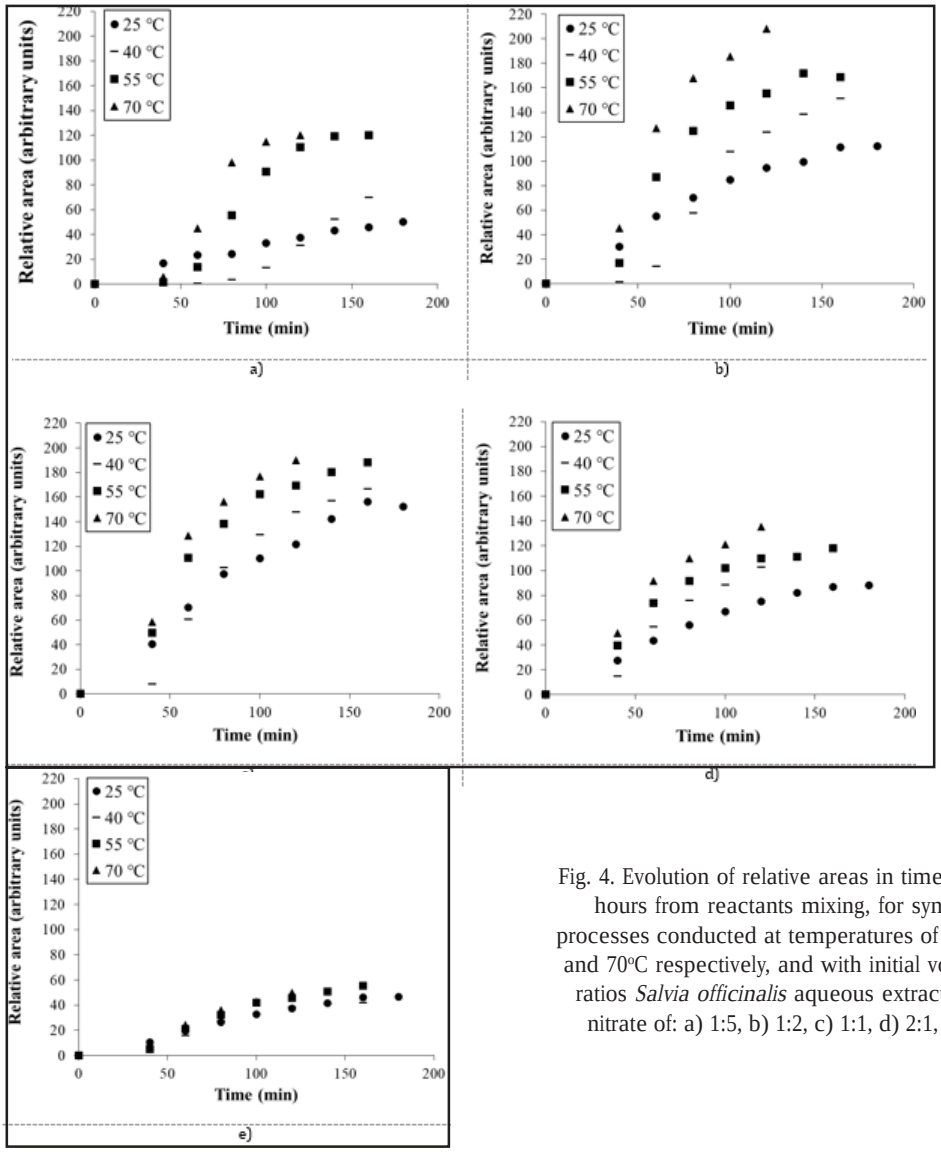

Fig. 4. Evolution of relative areas in time, within 3 hours from reactants mixing, for synthesis processes conducted at temperatures of 25, 40, 55 and 70ºC respectively, and with initial volumetric ratios *Salvia officinalis* aqueous extract : silver nitrate of: a) 1:5, b) 1:2, c) 1:1, d) 2:1, e) 5:1.

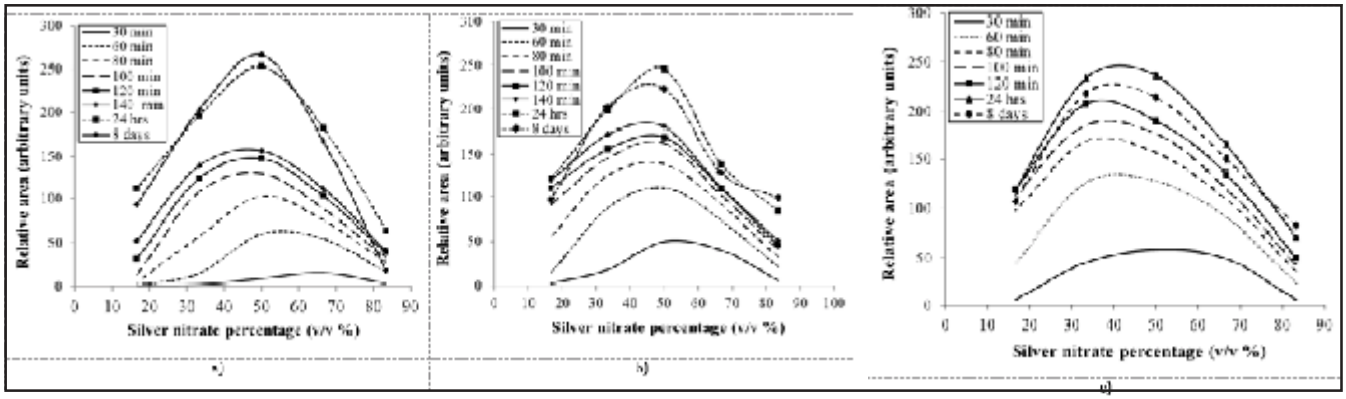

Fig. 5. Relative areas at different reaction times, *versus* $AgNO_3$ percentage in the initial mixture, for a synthesis process conducted at a) 40ºC, b) 55 ºC and c) 70 ºC

all studied temperatures, and consequently an increased quantity of nanoparticles is assumed in these situations.

In figure 5, relative area values at different reaction times were plotted versus silver nitrate percentage, for synthesis processes realized at 40, 55 and 70 ºC respectively. It may be observed that, in the first three synthesis hours, at both 40 and 55ºC, the optimum volumetric ratio silver nitrate to sage extract in the initial mixture is 1:1, the maximal values of calculated relative area being obtained at this ratio. However, when the synthesis temperature arises at 70 ºC, the maximum of the relative area versus silver nitrate percentage shifts towards smaller values of initial silver content in synthesis mixture. This may be associated with aggregation of silver in the synthesized nanoparticles [5,6,25].

The information presented in figure 6, obtained from the infrared spectroscopy were used to provide information on the nature of interactions of organic substrate with the formed silver nanoparticles. It was considered that shifts of some peaks recorded in the infrared spectrum after formation of metallic nanoparticles, may be generated by the interactions of some functional groups of the organic species from synthesis mixtures with the metallic surface, at the interface [24, 27]. Thus, by comparing the infrared

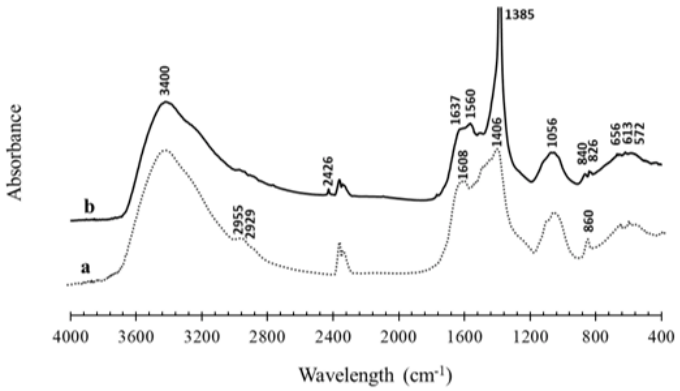

Fig. 6. Infrared spectra of: a) *Salvia officinalis* extract, and b) mixture *Salvia officinalis* extract : silver nitrate (1:1, v/v)

spectrum of individual plant extract with the one of a synthesis mixture, several changes may be observed. Specifically, appearance of absorption peaks at 2426 cm^{-1}, 1560 cm^{-1}, 1385 cm^{-1}, 840 cm^{-1} and widening of the absorption band at 3400 cm^{-1} are caused by the nitrate ion introduced in the reaction environment together with the monovalent silver ions. Notable modifications were observed in the range 1500 -1600 cm^{-1}, and 800- 900 cm^{-1}, where the maximum from 1608 cm^{-1} in the a) spectrum was shifted to 1637 cm^{-1} and a new peak appears at 1560 cm^{-1}, and two peaks appear at 826 cm^{-1} and 840 cm^{-1} in b) spectrum instead of one peak at 860 cm^{-1} in a) spectrum. These findings could indicate interactions of organic substrate with the metallic interface, forming a protective layer around the metallic nanoparticles.

Conclusions

UV-Visible spectroscopy was used as analytical tool for monitoring AgNPs formation and growth. Correlations between size and shape of synthetized AgNPs with peak positions in the wavelengths range of 400 - 440 nm were highlighted. When characteristics of AgNPs change, recorded spectra show shifts in recorded absorption band. These shifts also correlate with precursors (plant extract and silver nitrate 10 mM) initial mixing ratios. For the 1:1 initial volumetric ratio of precursors, the maximum absorption band was found at 425 nm.

By the use of relative areas calculated for recorded spectra in the range 350 -600 nm, and their time evolution, considerations on the nanoparticles growth were possible. The growth of silver nanoparticles was found to be rapid process in the first 3 h from precursors mixing, different reaction speeds were observed for different initial compositions of synthesis mixtures. Significant differences were recorded in the first 30 min of the reaction time, while after 150 min a stabilization plateau is reached, also small modifications after 8 days were observed, for all the studied compositions of the initial synthesis mixtures.

Temperature influences the growth process of silver nanoparticles, a general behavior was observed for studied samples. Thus, temperature increase generally leads to higher formation speeds for different initial volumetric ratios of precursors, with 1:2 (v/v silver nitrate to plant extract) ratio showing the most significant influence, while an exception was observed, for the same v/v ratio of 5:1, where temperature apparently does not influence.

Interactions of the organic substrate and formed silver nanoparticles, as well as with nitrate ions from the reaction environment, were confirmed by the changes in the IR spectra. Thus, comparison of the infrared spectra recorded for mixture *Salvia officinalis* extract : silver nitrate (1:1, v/v) with spectra recorded for individual plant extract showed shifts and changes of IR absorption bands in the wavenumber range 1500 - 1600 cm^{-1} and 800-900 cm^{-1}, as well as widening of the absorption band at 3400 cm^{-1} indicating possible interactions of organic substrate with the metallic interface.

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