

## PREPARATION OF SILVER NANOPARTICLE DISPERSION BY A GREEN SYNTHESIS METHOD

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*This paper deals with a preliminary study on silver nanoparticles obtaining by a green synthesis method, using environmentally friendly polymers and nontoxic chemicals. Alginate, a polysaccharide extracted from brown algae was used both as stabilizing and reducing agent in the synthesis of stable silver nanoparticles well-dispersed in the presence of lignosulfonate. The formation of silver nanoparticles was assessed by monitoring UV-VIS spectra of the silver colloidal suspension at different time intervals. The size and distribution of the nanoparticles were measured by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Optimum reaction conditions were established in terms of reaction time and composition of the colloidal suspension effect on the particle size and zeta potential.*

**Keywords:** silver, nanoparticle, green chemistry, biopolymer

### 1. Introduction

Nanotechnology research on obtaining metal nanoparticles was gaining a tremendous attention in the recent years because of its ability to change drastically the chemical, physical and optical properties of metals. In particular silver nanoparticles received an increasing interest, being among the most commonly utilized nanomaterials due to the known antimicrobial properties, high electrical conductivity, and unique optical properties [1,2]

Silver nanoparticles show good antimicrobial properties due to their large surface area to volume ratio, which provides a better contact with microorganisms. Because several pathogenic bacteria have developed resistance against various antibiotics, silver became recognized again as an effective antimicrobial agent [1]. Silver ions and its compounds are highly toxic to microorganisms exhibiting strong biocidal effects on many species of bacteria but only have a low toxicity toward animal/human cells, high thermal stability and

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low volatility [3,4]. Therefore silver nanoparticles showed their potential to be exploited in various medical applications such as wound dressings for burn treatment, dental materials, coating medicinal devices, textile fabrics, water treatment, sunscreen lotions, nanogels, nanolotions, etc. [1,4]

Various methods to obtain colloidal silver nanoparticles have been developed in the last years by physical, biological and chemical methods, but chemical reduction is the most intensively studied, due to its advantages of yielding nanoparticles without aggregation, high yield and low preparation cost. The chemical reduction method involves the reduction of the silver ion by a chemical reducing agent such as sodium borohydride [5,6], hydrazine [7], formamide [8], formaldehyde [9] in the presence of a stabilizer e.g. sodium citrate [10], polyvinylpyrrolidone [11] or polyvinylalcohol [12], which are able to protect the silver nanoparticles from aggregation. However, most of the reducing agents are considered hazardous/toxic chemicals, thus new approaches have been developed, involving the use of environmentally friendly components [13].

Recent efforts are focused on the development of *green* methods to prepare silver nanoparticles [13-16] aiming to minimize the use of unsafe reactants and maximize the efficiency of synthesis process. Green synthesis of NPs has several advantages over chemical synthesis, such as simplicity, cost effectiveness as well as compatibility for biomedical and pharmaceutical applications. Water is generally used as the environmental friendly solvent, glucose is one of the most widely-used green reducing agent and various polysaccharides [13,14,17,18] have been reported as stabilizing agents for silver nanoparticles. Sometimes polysaccharides are used both as reducing and capping agent [14].

Recent studies reported on the use of sodium alginate as stabilization agent for silver nanoparticles under gamma irradiation [19] and also as both reducing and stabilizing agent at high temperatures [20]. Alginate, a biopolymer extracted from brown algae (*Pheophyceae*) is a polyanionic linear copolymer of 1,4-linked  $\beta$ -D-mannuronate (M) and  $\alpha$ -L-guluronate (G) residues, containing one negatively charged carboxylic ( $\text{COO}^-$ ) group in each M or G unit [21].

This paper presents a preliminary investigation on the synthesis of colloidal silver nanoparticles by a green chemistry process which consists in using sodium alginate and respectively a mixture of alginate and lignosulfonate as stabilizing and reducing agents. The consequences of the colloidal suspension composition on the silver nanoparticles formation, particle size and zeta potential are investigated.

## 2. Experimental

Alginate acid from brown algae sodium salt (ALG) with medium viscosity ( $\geq 2000$  cP, 2%, 25 °C) purchased from Sigma-Aldrich and hardwood ammonium lignosulfonate (LS) from Zarnesti, Romania have been used. Silver nitrate ( $\geq 99\%$ ) was purchased from Sigma-Aldrich. All aqueous solutions were prepared with twice distilled water.

Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Cary 60 UV-VIS spectrometer (Agilent Technologies) scanning from 300 to 700 nm. Samples were run in quartz cuvettes with 10 mm path length. Twice distilled water was used in the reference cell.

The particle size distribution was studied by dynamic light scattering technique (Zetasizer model Nano ZS, Malvern Instruments, UK) with red laser 633 nm (He/Ne), over a measuring range for particle size between 0.6 nm–6  $\mu$ m.

Zeta potential ( $\zeta$ ) measured with the same equipment (Zetasizer model Nano ZS (Malvern Instruments, UK) between -200 to +200 mV, in the size range of 0.6 nm–10  $\mu$ m, was calculated from the electrophoretic mobility ( $\mu$ ) using the Smoluchowski relationship:  $\zeta = \eta \mu / \epsilon$ , with the condition  $k\alpha \gg 1$ , where  $\eta$  is viscosity,  $\epsilon$  is the dielectric constant of the medium and  $k$  and  $\alpha$  are the Debye–Hückel parameter and particle radius, respectively.

TEM investigations were made with a Hitachi High-Tech HT7700 Transmission Electron Microscope, operated in high contrast mode at 100 kV accelerating voltage. Samples were drop casted from diluted solutions on 300 mesh holey carbon coated copper grids (Ted Pella) and vacuum dried.

## 3. Results and discussion

### 3.1. Green synthesis of AgNPs

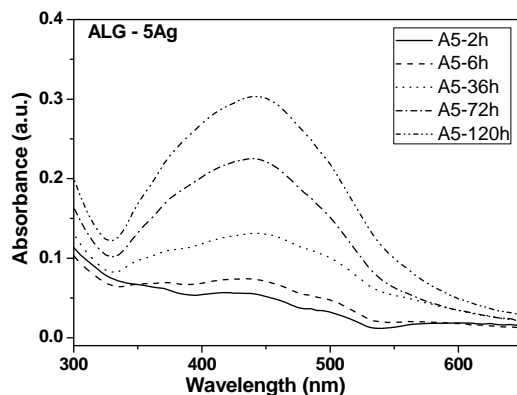
The Ag NPs were synthesized by the reduction of  $\text{Ag}^+$  ions in aqueous solutions of alginate (ALG) and alginate/lignosulfonate mixture (50/50 ALG/LS) at room temperature using  $\text{AgNO}_3$  as silver precursor. In a typical preparation procedure, an aqueous solution of silver nitrate was added dropwise into the aqueous solution of neat ALG and respectively in the 50/50 ALG/LS mixture at room temperature while stirring. Two silver ion concentrations were obtained for each composition, namely 1 wt% (1Ag) and 5 wt% (5Ag). The mixtures were stirred continuously for 5 days. At pre-determined time intervals (2, 6, 36, 72, 120 h), portions of the reaction mixture were taken to measure the surface plasmon resonance (SPR) immediately.

Due to the ability of  $\text{Ag}^+$  ions to interact with negatively charged groups, the presence of both carboxylate groups from alginate and sulfonate groups from lignosulfonate it is assumed to have a favorable effect on silver nanoparticles

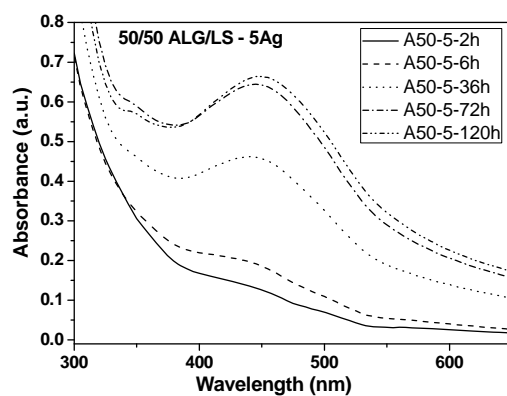
(AgNPs) formation. Such negatively charged groups can prevent agglomeration of nanoparticles by electrostatic repulsion and provide a better stability of the colloidal suspension [22].

### 3.2. Study on Ag NPs formation by UV-VIS spectroscopy

The gradual evolution of the silver nanoparticles was monitored using UV–VIS spectroscopy. This is one of the most important techniques to ascertain the formation of Ag NPs in aqueous solution. The most characteristic evidence of Ag NPs formation is the surface plasmon resonance (SPR) bands which can be observed in the 350–600 nm region [23]. Fig. 1a and b shows the UV–VIS absorption spectra of the Ag NPs dispersions at different reaction time intervals for the two suspension compositions investigated.



(a)

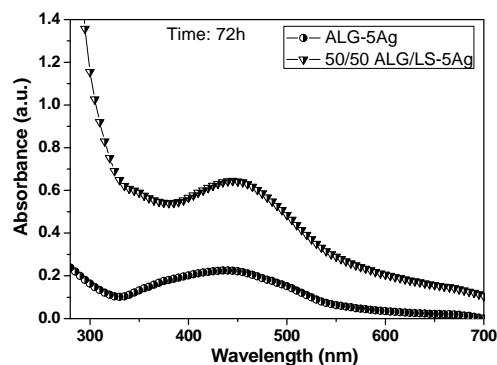


(b)

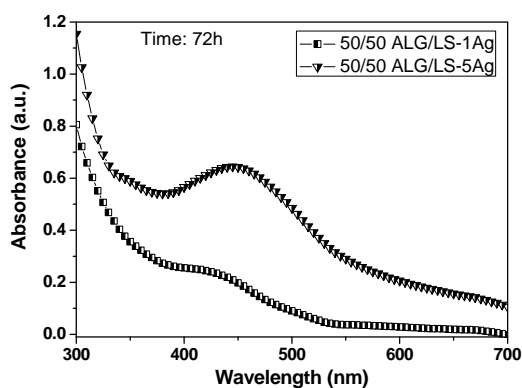
Fig. 1. Effect of the reaction time on the UV–vis spectra of the Ag NPs dispersions obtained in the presence of (a) ALG and (b) 50/50 ALG/LS mixture

The characteristic surface plasmon resonance (SPR) peak recorded at around 440 nm at different reaction times confirmed the formation of Ag NPs. The increase of the peak intensities with the reaction time, from 6 to 120 h indicates the increase in the concentration of the Ag NPs. It can be noticed that 72 h was enough time for Ag NPs formation and stabilization in the presence of the 50/50 ALG/LS mixture since there is not a significant difference between the peak intensities recorded at 72 and 120h. Thus the optimum time for stabilization of the Ag NPs in ALG/LS colloidal suspension was established at 72 h.

In order to study the influence of the LS presence in the composition of the suspension, the reaction was carried out for two  $\text{Ag}^+$  concentrations (1 wt% and 5 wt%) in suspensions with and respectively without LS. The results obtained showed a higher intensity of the SPR peak corresponding to 50/50 ALG/LS suspension compared with neat ALG (Fig. 2a), indicating that a higher yield of silver nanoparticles was produced in the presence of LS at the same reaction time (72 h) as in the suspension containing only ALG.



(a)



(b)

Fig. 2. Comparative UV-VIS spectra of the Ag NPs dispersions: (a) effect of the colloidal suspension composition; (b) effect of  $\text{Ag}^+$  ions concentration

Also a significant increase of the peak intensity was recorded at the higher  $\text{Ag}^+$  concentration (Fig. 2b), as it was expected.

### 3.3. Dynamic light scattering (DLS) measurements

DLS measurements were performed to estimate the size distribution of the Ag NPs. DLS is a non-invasive technique for measuring the size of the nanoparticles in a suspension.

In Fig. 3 the intensity distributions obtained for the two suspension compositions studied (ALG and 50/50 ALG/LS) containing the synthesized Ag NPs are represented.

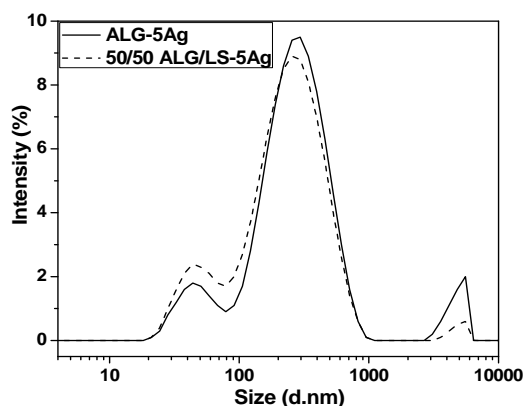


Fig. 3. Size distributions obtained from DLS measurements

The shift of the intensity peak toward lower size in case of LS containing suspension can be attributed to the presence of an increased number of negatively charged groups (carboxylate and sulfonate groups) which are able to increase the electrostatic repulsion in the colloidal suspension and prevent Ag NPs from aggregation, maintaining lower dimensions.

Table 1 shows the Z-average diameter and polydispersity index (PDI) values obtained from dynamic light scattering (DLS) and also the zeta potential. Z-average is the mean hydrodynamic diameter and the PDI is an estimate of the width of the distribution. Zeta potential is an important tool for understanding the state of the nanoparticle surface and predicting its long-term stability. The higher the zeta potential, the stronger the repulsion, and the more stable the system becomes [22]. Nanoparticles with zeta potential values greater than +30 mV or lower than -30 mV typically have high degrees of stability. Dispersions with a

low zeta potential will eventually aggregate due to van der Waals interparticle attraction [24].

Table 1

DLS results			
Sample	Z-Average	PDI	$\zeta$ (mV)
ALG-5Ag	202	0.428	-68
50/50ALG/LS--5Ag	147	0.505	-58.3
50/50ALG/LS---1Ag	177	0.525	-58.1

The average diameter registered by DLS measurements varied from 202 nm in the case of alginate-mediated silver nanoparticles, to 147 nm and 177 nm for those prepared by using 50/50 ALG/LS while PDI values evidence a relatively narrow polydispersity. The values of zeta potential obtained, ranging from -68 mV for alginate-stabilized AgNPs to -58 mV for those stabilized in the 50/50 ALG/LS mixture show the high stability of the system, suggesting that the surface charges prevent the nanoparticles from aggregating through electrostatic repulsion.

DLS results support the UV-VIS data, showing that higher concentrations of Ag NPs with smaller dimensions can be obtained using ALG/LS mixture.

### 3.4. Transmission electron microscopy (TEM) analysis

TEM images acquired evidenced very fine, well-dispersed and randomly distributed Ag NPs of spherical shape with an average diameter of 10 nm (Fig. 4).

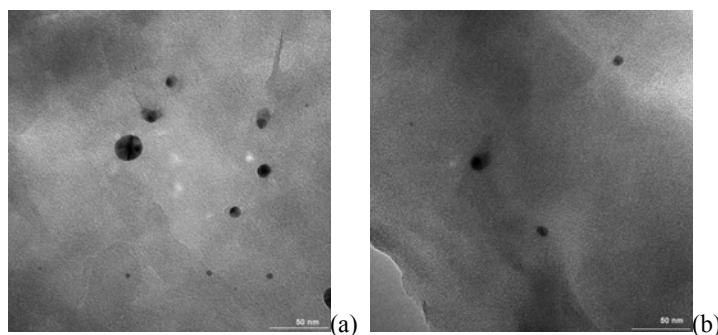


Fig. 4. TEM images of ALG-5Ag (a) and 50/50 ALG/LS-5Ag (b)

The dependence of the nanoparticle size on the composition of the suspension was revealed. Well-dispersed single nanoparticles having slightly decreased dimension in 50/50 ALG/LS are observed, while in ALG the tendency of the Ag NPs to form agglomerates can be noticed, thus a mixture of single particles and aggregates is observed. TEM images evidenced an average size (10 nm) much smaller than the Z-average value (147 nm) obtained from DLS, results

which are in accordance with those found in other similar studies [25,26]. The higher dimensions obtained from DLS compared with TEM can be explained by the predominant contribution of the large particles or aggregates on the light scattering signal and also by the fact that DLS measures the average hydrodynamic diameter of hydrated dispersed nanoparticles under Brownian motion, while TEM requires high vacuum conditions for measuring the size of individual dehydrated particles [27].

#### 4. Conclusions

A green synthesis method was proposed for obtaining silver nanoparticles using silver nitrate as metallic precursor and biodegradable alginate and lignosulfonate as reducing and stabilizing agents. It was shown that by the green chemistry approach used in this study, it was possible to prepare very small silver nanoparticles and to keep a fine dispersion of these nanoparticles.

The Ag NPs formation reaction, monitored by UV-VIS spectroscopy confirmed the obtaining of the Ag NPs and allowed to establish at 72 h the optimum reaction conditions. The effect of composition of the colloidal suspension on the particle size and zeta potential studied by DLS and TEM evidenced the high stability of the colloidal suspensions and presence of randomly distributed Ag NPs of spherical shape with an average diameter of 10 nm.

Alginate and lignosulfonate are non-toxic and biocompatible compounds that make the prepared colloidal suspension promising for applications in the medical or packaging fields.

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