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CONTROL AND STABILIZATION OF SILVER NANOPARTICLES SIZE USING POLYVINYLPYRROLIDONE AT ROOM TEMPERATURE

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The main objective of this study was carry out synthesis of silver nanoparticles (AgNPs) stable at room temperature with controlled morphology and size. To achieve our aim, chemical reduction method was used. In the experimental design, it studied effect of concentration of silver nitrate, hydrazine and Poly(N-vinylpyrrolidone)(PVP), as well as reaction temperature on the synthesis of AgNPs. Prepared AgNPs were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and UV-VIS spectroscopy. AgNPs size was evaluated using DinamicLigth Scattering (DLS) and its stability with Zeta Potential analysis using ZetasizerNano ZS. The results obtained in this study shown the preparation of AgNPs with spherical morphology and 10 nm size, stable at room temperature for further applications. The optimal reaction was in aqueous medium at low temperature, 25 mM AgNO3 and 100-125 mg of PVP.

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Keywords: Silver nanoparticles, Stable nanoparticles, Poly(N-vinylpyrrolidone), Chemical reduction

1. Introduction

In recent years there has been increasing interest for studies with nanostructures whose applications are innumerable from the electronics, chemical, pharmaceutical, medical and food packaging, among other [1, 2, 3, 4, 5]. In this context,the studies silver nanoparticles are important because it found in commonly consumed products[6], as metal exhibits distinctive properties such as good conductivity, chemical stability and catalytic activity [7], moreover, it has relevance in the field of medicine for their antimicrobial effects including bacteria, viruses and fungi [8, 9, 10]; it has been shown that the antibacterial activity of silver is increased with decreased particle size, and decreases when there is formation of nanoparticle aggregates [11]. Moreover, it is known that the degree of absorption of a nanoparticle in biological systems (example, gastro-intestinal tract) depends on factors such as size, surface charge, hydrophobicity, and the presence or absence of surface ligands that interacting with receptors, in general, the absorption is increased with a reduction in size of the nanoparticle [12]. The size and shape of silver nanoparticles plays an important role in their biological effects that might have on living organisms, for example, the subcutaneous administration of silver nanoparticles (50-100 nm) in rats induces translocation of nanoparticles in a variety of organs as kidney, liver, spleen, lung and vascular endothelial cells of

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the blood-brain barrier in which were detected small amounts of nanoparticles [13]; in contrast, when was administrated nanoparticles with a size of 2 nm were detected larger aggregates in liver, kidney and cardiac tissue [14].

The physical and chemical properties of nanoparticles depend on the reaction conditions used during synthesis. Silver nanoparticles can be synthetized and stabilized by chemical [15], physical [16] and biological methods [17]. The chemical reduction is the most common method for the synthesis of nanoparticles [18]. Silver nanoparticles are synthetized by reduction of metal salts like silver nitrate in a suitable medium using reducing agent such as citrate or polymers like PVP (Polyvinylpyrrolidone), PVA (Polyvinyl alcohol) and PMVE (Poly (methilvynilether)), however, the polymers are the stabilizers and protective agents most employed in nanoparticles synthesis [15].

Currently, nanomaterials are a novel field of study with great potential in applications. The utility of the nanoparticles depends mainly on its physical and chemical properties,representing a challenge find controlled synthesis methodsto obtain nanoparticles with specific characteristics. The importance of a controlled synthesis method will allow a major development in areas as the nanomedicine, in this case in future works could study the physiological effects of silver nanoparticles on the mammalians to finding new therapeutic alternatives for treatment of diseases. In this work, we reported a controlled synthesis for silver nanoparticles using chemical reduction method. The main objective was carry out synthesis of silver nanoparticles stable at room temperature with controlled morphology and size.

2. Experimental part

2.1 Methods

Different techniques were usedto characterization of silver nanoparticles. The nanoparticles structures were obtained using a Scanning Electron Microscopy (SEM) JSM-74001F and Transmission Electron Microscopy (TEM)Philips CM-200. The samples were prepared by forming a thin layer, by depositing a drop of silver nanoparticles fluid on silice holderletting the water evaporate completely.The distributionof silver nanoparticlessize was analyzed by Dynamic Light Scattering (DLS), and its stability with Zeta Potential analysis using ZetasizerNano ZS (Malvern Instruments UK). The absorption spectra UV-VIS were carried out on a Perkin Elmer Lambda 19 UV/Vis/NIR spectrophotometer in the wavelength range of 200-600 nm. The spectra were measurement at room temperature using 1 cm quartz cuvette.

2.2 Materials

Silver nitrate ($AgNO_3$, M. W. 169.87 gr/mol, 99.99%), poly(N-vinylpyrrolidone (PVP, M. W. 40000 gr/mol) and hydrazine (N_2H_4 to 50-60%, M. W. 32.05 gr/mol, density 1.029 gr/ml) were used as precursor, stabilizer and reducing agent, respectively, and were obtained from Sigma Aldrich. Deionized water was used.

2.3 Samples preparation and stability

The reaction conditions modified to obtain the nanoparticles with the best features were the concentrations of reactants, temperature and reaction time.Initially, silver nanoparticles were obtained by dissolving 300 mg of PVP in 8 ml ofsilver nitrate (25 mM). This solution was diluted with 14 ml of deionized water, and after 5 min, was added one drop of 4 ml of hydrazine (70 mM). All these steps were performed at room temperature under continuous stirring on a magnetic stir plate to ensure homogeneity.Subsequently the nanoparticles in suspension were centrifuged at 13500 rpm for 60 minutes, separating the sediment and re-suspended in deionized water. This procedure was conducted two times to reduce the amount of waste produced by the reaction.

The procedure to study the size and the stabilization of the nanoparticles was as follows: Firstly, was varied the concentration of silver nitrate (5-50mM) maintaining constant the amount of PVP (300mg) and hydrazine concentration (4ml, 70 mM); second, hydrazine concentration was varied. Subsequently, reaction temperature was varied to 6 ± 2°C. Then, the amount of PVP (50-600mg) was varied and the reaction temperature was cooled or heating (6 and 25°C), keeping constant the concentration of silver nitrate (25 mM) and hydrazine (4 ml, 70 mM). Finally,adjusted

the value of hydrazine concentration (1ml,70 mM), for different PVP amount (100-200mg) with 25 mg of silver nitrate and temperature of 6 ± 2°C.

2.3.1. $AgNO_3$ concentration study

The effect of $AgNO_3$ concentration in the reaction is shown in Table 1.

Table 1.Study of the effect of silver nitrate concentration variation on the formation of nanoparticles. It shows the initial conditions of the reaction.

Synthesis	$A_gNO_3$concentration (mM)	PVP (mg)	N_2H_4 concentration and volume
s-1	2.5	300	70 mM, 4 ml
s-2	5	300	70 mM, 4 ml
s-3	10	300	70 mM, 4 ml
initial	25	300	70 mM, 4 ml
s-4	50	300	70 mM, 4 ml

2.3.2. N_2H_4 concentration effect

The study of the concentration of N_2H_4 reducing agent is shown in Table 2.The time to add the reducing agent is decreased from 5 to 2 minutes.

Table 2.Study of the effect of reducing agent concentration on the formation of nanoparticles.

Synthesis	$A_gNO_3$concentration (mM)	PVP (mg)	N_2H_4 concentration and volume
s-5	2.5	300	50 mM, 4 ml
s-6	5	300	50 mM, 4 ml
s-7	10	300	50 mM, 4 ml
s-8	25	300	50 mM, 4 ml
s-9	50	300	50 mM, 4 ml

2.3.3. Change in hydrazine concentration and reaction temperature

Table 3 shows the effect of change in reaction temperature and the N_2H_4 concentration; as well as the variation of the concentration $AgNO_3$ in the AgNPs size.

Table 3.Effect ofreaction temperature on the formation of nanoparticles for values shown in table 1.

Synthesis	Ag NO_3concentration (mM)	PVP (mg)	N_2H_4concentration and volume	reaction temperature
s-10	2.5	300	70 mM, 4 ml	6 ± 2 º C
s-11	5	300	70 mM, 4 ml	6 ± 2 º C
s-12	10	300	70 mM, 4 ml	6 ± 2 º C
s-13	25	300	70 mM, 4 ml	6 ± 2 º C
s-14	50	300	70 mM, 4 ml	6 ± 2 º C

2.3.4. PVP quantity and reaction temperature study

ThePVP quantity and reaction temperature studied in the reaction is show in Table 4.

Table 4.Study of the effect of PVP amount and reaction temperature on the formation and stabilization of silver nanoparticlessize.

Synthesis	**$AgNO_3$concentration**(mM)	**PVP (mg)**	**N_2H_4 concentration and volume**	**reactiontemperature**
s-15	25	50	70 mM, 4 ml	6 ± 2 º C
s-16	25	100	70 mM, 4 ml	6 ± 2 º C
s-17	25	150	70 mM, 4 ml	6 ± 2 º C
s-18	25	200	70 mM, 4 ml	6 ± 2 º C
s-19	25	250	70 mM, 4 ml	6 ± 2 º C
s-20	25	300	70 mM, 4 ml	6 ± 2 º C
s-21	25	600	70 mM, 4 ml	6 ± 2 º C
s-22	25	50	70 mM, 4 ml	25 º C
s-23	25	100	70 mM, 4 ml	25 º C
s-24	25	150	70 mM, 4 ml	25 º C
s-25	25	200	70 mM, 4 ml	25 º C
s-26	25	250	70 mM, 4 ml	25 º C
s-27	25	300	70 mM, 4 ml	25 º C
s-28	25	600	70 mM, 4 ml	25 º C

2.3.5. Optimal conditions for the reaction

The optimal reaction conditions to stabilize nanoparticles size at room temperature, are shown in table 5.

Table 5.Optimal experimental conditions of the reaction for the formation and stabilization of silver nanoparticlessize.

Synthesis	**$AgNO_3$concentration (mM)**	**PVP (mg)**	**N_2H_4concentrationand volume**	**reactiontemperature**
s-29	25	100	70 mM, 1 ml	6 ± 2 º C
s-30	25	125	70 mM, 1 ml	6 ± 2 º C
s-31	25	150	70 mM,1 ml	6 ± 2 º C
s-32	25	175	70 mM, 1ml	6 ± 2 º C
s-33	25	200	70 mM, 1 ml	6 ± 2 º C

3. Results and discussion

3.1 AgNPs Formation

UV-Vis spectroscopy was used for the study of formation and growth of AgNPs. Fig. 1 shows the UV-Vis absorbance spectrum for optimal solution (see Table 5) with different PVP quantities. All spectra shows a strong peak associated with surface plasmon resonancecentered in 400 nm. This suggests that silver nanoparticles are the main product.This data is agreed to literature, a previous study reported the plasmon resonance peak near 400 nm with silver nanoparticles of 12 ± 2 nm [19], while others works have reported a maximum peak between 405-418 nm with silver nanoparticles size of 9-30 nm [8, 20].

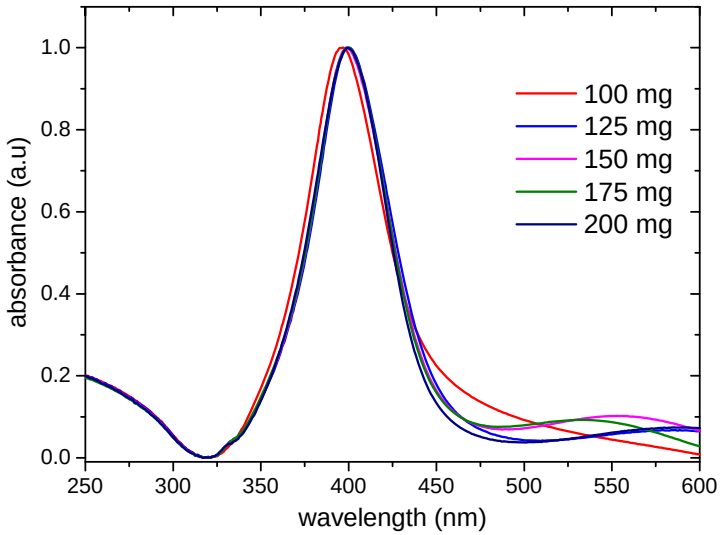

Fig. 1. UV-Vis absorbance spectra for optimal solution with different PVP quantities.

3.2 Structural properties of Ag NPs

The morphology of AgNPs was obtained by SEM. Figure 2 shows the micrography and histogram of the sample that contains 100 mg and 200 mg PVP quantities for initial and optimal conditions of reaction. Fig. 2 a) confirms the presence of nanoparticles with a size less than 20 nm, as well as the presence of nanoparticles of greater size, but in minimum quantities. The histogram shows that particle diameter is 16 ± 2 nm, with a full width at half height of the peak (FWHM) of 6 nm.This tells us that we have a suspension of nanoparticles monodisperse. Fig. 2b) shows the electron micrograph and histogram of the sample that contains 200 mg of PVP.In the micrograph is observed spheroidal nanoparticles with a size of about 20 nm. The histogram indicates the presence of nanoparticles with a size of 18 ± 5 nm, with a full width at half height of the peak (FWMH) of 13 nm.Therefore we also have a systemthat only monodisperse with a variation in particle size higher. Fig. 2c) shows in the same way the micrography and histogram of the initial summary, from which it began to make changes. This contains a concentration of 25 mM silver nitrate, 300 mg of PVP and 4 ml of hydrazine 70 mM. In the micrograph shows that the size and shape of nanoparticles are very different,while particles with sizes of 30, 40, 60, 80 and higher than 100 nm, beside to that presents different forms of particle like prisms, hexagons and bars. The histogram shows the presence of nanoparticles with a size of 34 ± 15 nm, with a full width at half height of the peak of 36 nm. Therefore, it is clear that in this synthesis of nanoparticles is obtained a polydisperse suspension and varied morphology.

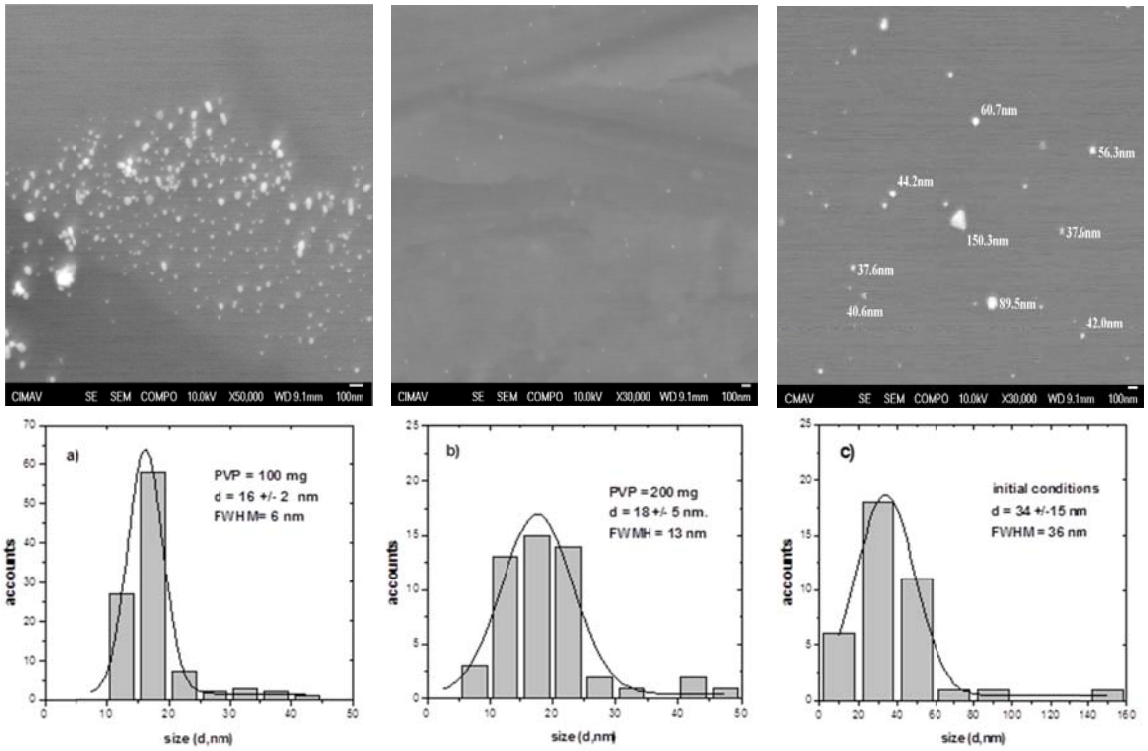

Fig. 2. Images SEM and DLS analysis with different amounts of PVP: a) 100 mg, b) 200 mg and c) initial conditions.

3.3 PVP effect on silver nanoparticles

The Fig. 3 shows the DLS analysis of AgNPs size with a different of PVP quantity and reaction temperature. The Fig. 3 a) shows the concentration by volume (percent) of AgNPs with the increasing the quantity of PVP. The AgNPs average size was 12 nm in PVP range of 100 - 300 mg and very low percent, nanoparticles of 15 nm.Likewise, a small percentage of nanoparticleswere produced for 50 mg (40 nm and 345 nm) to 600 mg (50 nm and 176 nm) of PVP.We observe that NPs size depends of the PVP quantity in the system. Fig. 3 b) shows the effect of variation in reaction temperature (6 ± 2 °C)in the silver NPs size. The effect of changing the reaction temperature was very varied; however,we note thatAgNPs production in percent is similar between of 100-250 mg PVP quantities. Outside this PVPrange it is not achieved stabilization of the Ag NPs, which gives evidence of the lack of homogeneity of the samples. Therefore, this suggests that between 100-250mg of PVP, stabilization of the AgNPssizein high percentage is achieved.

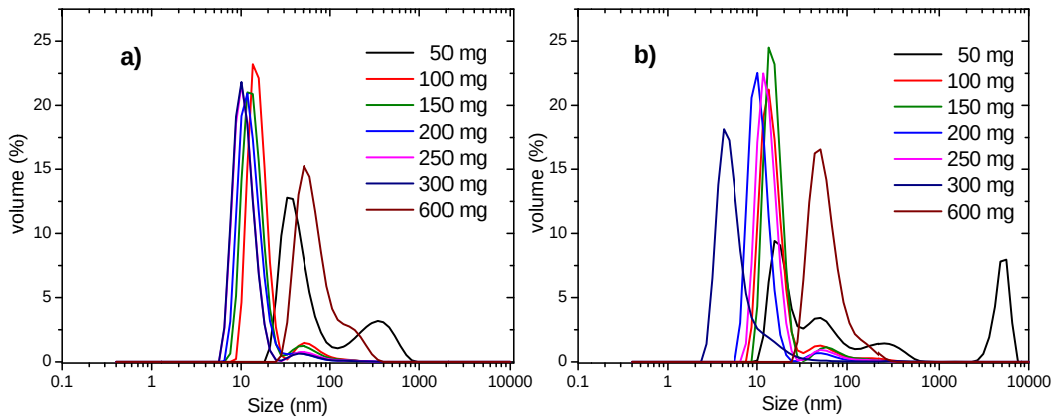

Fig. 3.DLS curves of size ofAgNPs (percent): a) varying the quantity of PVP and b) the reaction temperature. Other parameters were remaining constant.

3.4 Silver nitrate study

The Fig. 4 shows DLS analysis of AgNPs size with different $AgNO_3$ concentrations and low reaction temperature (see Table 1 and 3). The Fig. 4 a) shows the concentration by volume (percent) of AgNPs with increasing $AgNO_3$ concentration. The AgNPs average size was 12 nm in $AgNO_3$ concentration range of 10-25 mM and very low percent, nanoparticles of 50 nm and 45 nm. However, high percentage nanoparticle of high size was produced for 2.5 mM (198 nm), 5 mM (65 nm) and 50 mM (48 nm) of $AgNO_3$ concentration. Theeffect of variation of $AgNO_3$ concentration and low reaction temperature (6 ± 2°C) is shown in Fig. 4 b). We observe that AgNPs production in percent is similar for 10, 25 and 50 mM (20 nm, 4 nm and 3.5 nm respectively). For small $AgNO_3$ concentrations the production of NPs is of the bigger size.The above results suggest that with concentration of 25 mMsilver nitrate is achieved the stabilization of size of nanoparticles, producing in high percentage.

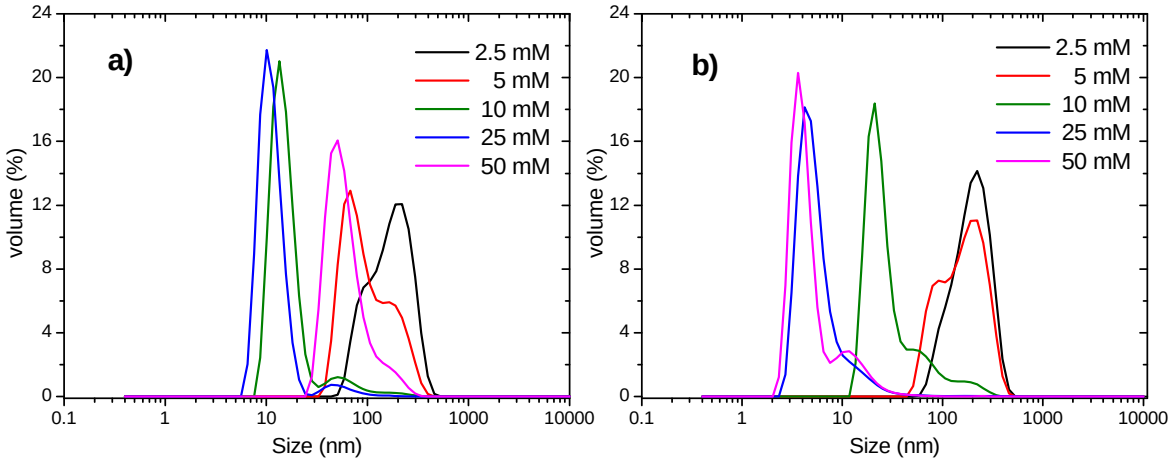

Fig. 4. DLS curves of sizeof AgNPs (percent):a)varying the A_gNO_3 concentrationand b) reaction temperature.Other parameters were kept constant.

3.5 Optimal conditions for the reaction

The Fig. 5 shows DLS analysis of AgNPs stabilization and size in optimal reaction experimental conditions (see Table 5). The Fig. 5 a) shows DLS intensity analysis where there appear two bands well defined for all reactions. The most intense bands are located in 98 and 84 nm, while bands of less intensity are located in 14, 12 and 13 nm. The Fig. 5 b) shows DLS volume analysis for all reactions, where two well-defined bands appear about in the same position. The most intense band is located 10 nm, while bands of much less intensity appear in 43, 40, 46, 35 and 43 nm respectively. The above results suggest that optimal conditions for stabilization and production of AgNPs are those shown in table 5. The Z-potential analysis confirms the above results. Fig. 6 shows Z-Potential analysis for all reactions of table 5. We observe that stabilization of AgNPs size is greater in the synthesis containing 100, 125 and 200 mg of PVP, and all reactions produce negative AgNPs. However, fig. 6 b) shows the reaction more stable because it has a Z-potential value -20.1 mV. The above results suggest that to stabilize the size of the AgNPs, it is necessary that the reactions contain among 100-125 mgof PVP, confirming the DLS analysis.

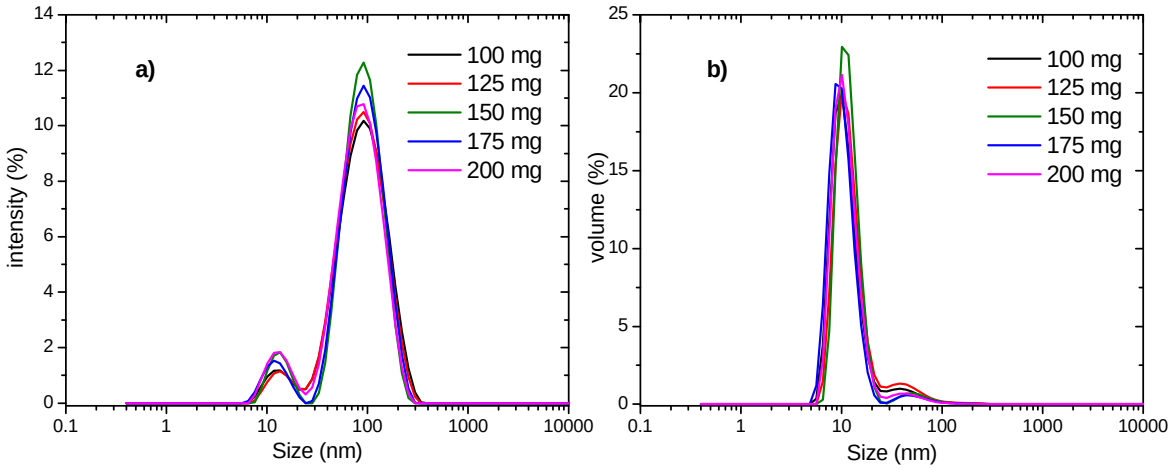

Fig. 5. Intensity and volume DLS curves of AgNPssize, varying the amount of PVP and volume of reducing agent. Other parameters were kept constant.

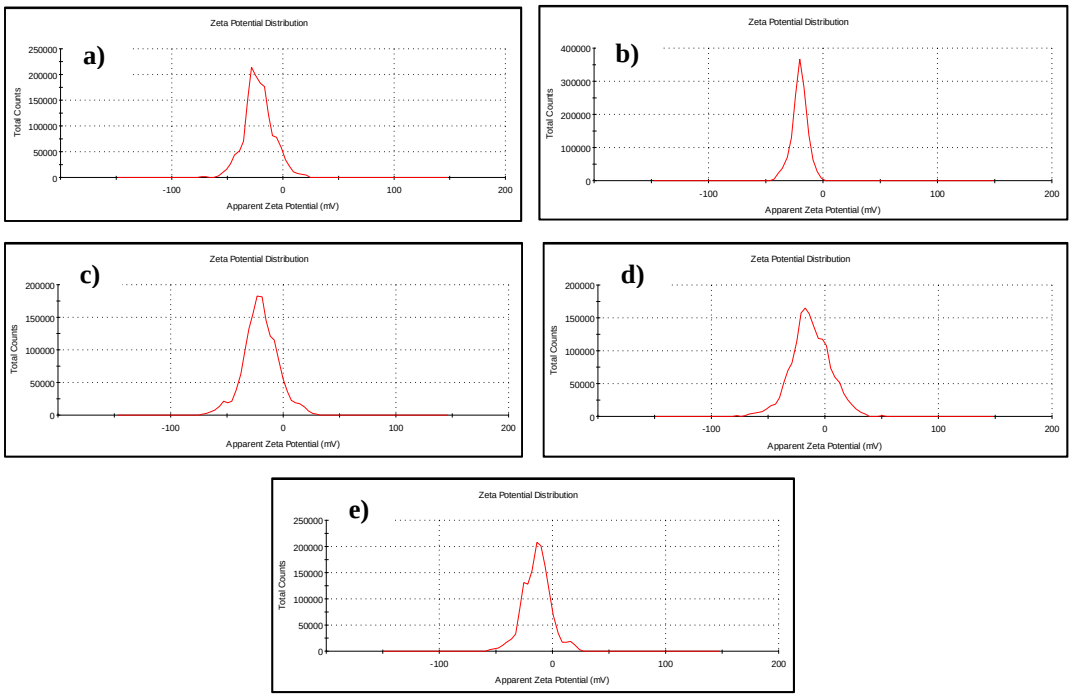

Fig. 6. Z-Potential analysis for all reaction conditions of the table 5 with a PVP quantity of: a) 100 mg, b) 125 mg, c) 150 mg, d) 175 mg and e) 200 mg.

4. Conclusions

We performed a systematic experimental study of the influence of different reaction parameters on the silver nanoparticles synthesis. The $AgNO_3$ concentration, PVP quantities, hydrazine concentration and volume, and reaction temperature were studied and results obtained in this investigation shown the optimal values of the different parameters for the synthesis of silver nanoparticles stable at room temperature.With the optimal parameters reported in this work, silver nanoparticles of a size of 10 nm were synthesized and remained stable for months at room temperature.

References

[1] S. Pothukuchi, Y. Li, C. P. J. Wong, App. Polym. Sci. **93**, 1531 (2004).
[2] M. P. Andrews, G. A. Ozin, J. Phys. Chem. **90**, 2929 (1986).
[3] S. Dhar, E.M. Reddy, A. Shiras, V. Pokharkar, B.L.V. Prasad, Chem. Eur. J. **14**, 10244 (2008).
[4] P. Sanpui, A. Chattopadhyay, S.S. Ghosh, ACS Appl. Mater. Interfaces. **3**, 218 (2011).
[5] T.V. Duncan, J. Colloid Interface Sci. **363**, 1 (2011).
[6] S.F. Hansen, E.S. Michelson, A. Kamper, P. Borling, F. Stuer-Lauridsen, A. Baun, Ecotoxicol. **17**, 438 (2008).
[7] S.Sarkar, A. D. Jana, S. K. Samanta, G. Mostafa, Polyhedron. 26, 4419 (2007).
[8] M.G. Guzmán, J. Dille, S. Godet, Int. J. Chem. Biol. Eng. 2, 104, (2009).
[9] Y. Mori, T. Ono, Y. Miyahira, V.Q. Nguyen, T. Matsui, M. Ishihara. Nanoscale Res. Lett. **8**, 93 (2013).
[10] K.J. Kim, W.S. Sung, S.K. Moon, J.S. Choi, J.G. Kim, D.G. Lee, J. Microbiol. Biotechnol. **18**, 1482 (2008).
[11] C.N. Lok , C.M. Ho, R. Chen , Q.Y. He, W.Y. Yu, H. Sun , P.K. Tam, J.F. Chiu, C.M. Che , J. Biol. Inorg. Chem. **12**, 527 (2007).
[12] A.T. Florence, Drug. Disc. Today. Technol. **2**, 175 (2005).
[13] J. Tang, L. Xiong, S. Wang, J. Wang, L. Liu, J. Li, J. F. Yuan, T. Xi, Nanoscience Nanotechnol. **9**, 4924 (2009).
[14] L. Garza-Ocañas, D.A. Ferrer, J. Burt, L.A. Diaz-Torres, M. Ramirez-Cabrera, V. Tamez-Rodriguez, R. Luján-Rangel , D. Romanovicz , M. Jose-Yacaman, Metallomics. **2**, 204 (2010).
[15] D. Malina, A. Sobczak-Kupiec, Z. Wzorek, Z. Kowalski, Dig. J. Nanomater. Bios. **7**, 1527 (2012).
[16] Y. Zhou, S. H. Yu, X. P. Cui, C. Y. Wang, and Z. Y. Chen, Chem. Mater. **11**, 545 (1999).
[17] K. Kalimuthu, R.S. Babu, D. Venkataraman, M. Bilal, S. Gurunathan, Colloid. Surface. B. **65**, 150 (2008).
[18] C.I. Contescu, K. Putyera, Dekker encyclopedia of nanoscience and nanotechnology, vol. I-VI. ISBN 13 978-0-8493-9639-7. (2009).
[19] S.D. Solomon, M. Bahadory, A.V. Jeyarajasingam, S.A. Rutkowsky, C. Boritz, J. Chem. Edu. **84**, 322 (2007).
[20] E. Saion , E. Gharibshahi, K. Naghavi. Int. J. Mol. Sci. **14**, 7880 (2013).