Growth Mechanism, Kinetics and Thermodynamics Evaluation of Silver Nanoparticles Prepared by Aqueous Seeds Extract of Ziziphus Spina-Christi

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A B S T R A C T

in the present study, silver nanoparticles, Ag-NPs have been prepared by a Aqueous Seeds Extract of Ziziphus Spina-Christi as reducing agent and a solution of silver nitrate (AgNO$_3$). From poly nuclear growth rate model, the rate of growth was found to be equals 0.0011 nm/min. Different morphologies of silver colloids could be obtained using different temperature. The reduction kinetic of Ag$^+$ was followed the second order model. Also, the synthesis of Ag-NPs was endothermic reaction and spontaneous at medium and high temperature while non spontaneous at low temperature. Gibbs free energy of formation was not constant and was changed with radios of Ag-NPs.

1 Introduction

The Green chemistry method usually uses a reduction strength of the plant extract for conversion the oxidation state of M^{+n} to M^0 in solution (Basalius et al., 2023). The growth of NPs is depended on the growth of its nuclei as the following steps: in initio, and generation of growth species, then, diffusion of the growth species from bulk to the growth surface. The adsorption of the growth species onto the growth surface. Finally, surface growth through irreversible incorporation of growth species onto the solid surface as shown in Figure 1. According the growth theory, the growth of NPs can be determined by the type of growth and initial size of nucleus. Thus, in this research, the growth theory was applied

Figure 1 . Growth of Ag-NPs

This study will allow us not only to understand mechanism of growth of Ag-NPs synthesized but also, to understand the kinetic properties and the thermodynamic properties of Ag-NPs synthesized.

2. Material and methods
2.1. Materials and instrument

Ziziphus Spina-Christi Seeds was collected from Local Market for Cutting, Sebha City, Libya. silver nitrate (chemPUR), UV-Visible spectroscopy (evaluation 3000, ThermoVirsion).

2.2. Preparation of ZSC Seeds Extract and Ag-NPs

ZSCS were washed with distilled water for several times in order to remove the dirt particles and were left on clean paper to dry under room temperature. About 25 g of ZSC seeds powder was taken in a 250 mL beaker containing 70 mL double distilled water and then the mixture was stirred at 400 rpm for 5 h, then filtered through filter paper(Kokila, Ramesh, & Geetha, 2015). Ag-NPs was prepared by adding 1 mM aqueous AgNO₃ solution of 5 ml ZSC seeds extract at different temperature values (25 C⁰, 35 C⁰ and 45 C⁰). Then, the mixture was stirred at 400 rpm and UV-Visible spectrum was measured in each 15 minute until 6 hours in order to indicate the kinetic of formation of Ag-NPs and thermodynamic evaluation.

2.3. Growth mechanism of Ag-NPs

When the growth process controlled by the diffusion of growth species from the bulk solution to the particle surface, the growth rate is given by eq 1.

$$r^2 = k_D t + r_0^2 \tag{1}$$

Where: r is the radius of spherical nucleus, r_o initial size of nucleus equals to the intercept, k_D is constant depended on diffusion coefficient, bulk concentration and surface concentration. For two particles with initial radius difference (δr_o), the radius difference (δr), decreases as time increases or particles grow bigger, according to eq 2.

$$\delta r^2 = \frac{r_o \delta r_o}{(k_D t + r_o^2)^{1/2}} \tag{2}$$

There are two mechanisms of surface growth of Ag-NPs are: mononuclear growth and poly-nuclear growth. In mononuclear growth the growth rate is thus proportional to the surface area as in eq 3.

$$\frac{dr}{dt} = k_m r^2 \tag{3}$$

k_m is a constant, dependent on the concentration of growth species. It can be obtained on a liner equation by integration eq 3 to obtain on eq 4..

$$\frac{1}{r} = \frac{1}{r_o} - k_m t \tag{4}$$

The poly-nuclear growth rate of growth is independent of particle size or time. Hence the growth rate is constant as in eq 5:

$$\frac{dr}{dt} = k_p \tag{5}$$

k_p is a constant dependent on temperature. Integratio form of eq 5 can be write as eq 6 (Cao & Wang, 2011)

$$r = k_p t + r_o \tag{6}$$

In all calculations of size of Ag-NPs synthesized calculated according to Mie scattering theory which can be analyzed of SPR band peak to determine particle size of Ag-NPs using FWAHM of SPR band peak:

$$FWHM = \frac{(\varepsilon_o + 2n^2)c.m\,u_F}{N_C\,e^2.D} \tag{7}$$

Where : ε0, n, m Nc, and D are the frequency independent part of complex form of the dielectric constant, refractive index of water, the velocity of light, mass of electron, electron velocity at the Fermi energy, number of electrons per unit volume, the electron charge and diameter of the particle respectively.

2.4. Kinetic of Ag-NPs

In order to study the reaction kinetic of Ag-NP synthesis, the reference peak intensity of Ag-NPs for the 100% yields must be made, because peak intensity of reference was used to normalize the calculation of the yield (%) synthesized Ag-NPs. The reference of Ag-NPs synthesis for the 100% yields was prepared by adding 0.1g NaBH₄ to the mixture of 5 ml of ZSCS extract and 100 mL of 1 mM AgNO₃ at pH 9.5. The mixture was stirred for 60 min to ensure full reduction of silver cations. The λmax in nm peak intensity of reference was normalized using by the control to calculate the yield (%) as shown in **eq 8**. Then, the remaining Ag⁺ (%) was calculate as shown in **eq 9** and Ag⁺ concentration was calculate according

on initial concentration of AgNO$_3$ as shown in **eq** 10 *(Hu & Hsieh, 2016)*.

$$yields\ \% = (\frac{peak\ intensity\ of\ sample\ at\ \lambda_{max}}{peak\ intensity\ of\ reference}) \times 100 \qquad (8)$$

$$remaining\ Ag^+ = 100\% - yield\ \% \qquad (9)$$

$$[Ag^+] \frac{remaining\ Ag^+(\%)}{100\%} \times [Ag^+]_o \qquad (10)$$

The general rate law expressions are given by:

$$-\frac{d[C]}{dt} = k_n[C]^n \qquad (11)$$

After considering n = 0 as zero order reaction, n = 1 as first order reaction and n = 2 as second order reaction, **equ.11** was integrated and simplified to

$$C_o - C_t = k_o t \qquad (12)$$

$$\ln\frac{C_o}{C_t} = k_1 t \qquad (13)$$

$$\frac{1}{C_t} - \frac{1}{C_o} = k_2 t \qquad (14)$$

2.5. Thermodynamic properties

$(\Delta G_f^0)_{Ag\text{-}NP}$, ΔG, ΔH and ΔS of Ag-NPs can be calculated according eq 15, eq 16 and eq 17, respectively, where δ_{Ag} is the coefficient of surface tension of silver in N/m; M_{Ag} is the atomic weight of silver, 108 g/mol; ρAg is the density of silver, 10.49×10^6 g/m^3; r_{Ag} is the radius of Ag-NPs in nm; T is the temperature in Kelvin (Masoodiyeh, Karimi-Sabet, Khanchi, & Mozdianfard, 2015; Skiba, Pivovarov, Makarova, & Vorobyova, 2018).

$$\Delta G = -RT \ln K_C \qquad (15)$$

$$\ln K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (16)$$

$$\left(\Delta G_f^o\right)_{Ag\text{-}NPs} = \frac{2\delta_{Ag}M_{Ag}}{\rho_{Ag}r_{Ag\text{-}NPs}} \qquad (17)$$

3. Results and discussion

Figure 2 showed that the growth process was controlled by the diffusion of growth species from the bulk solution to the particle surface with r_0 equals 3.44 nm and surface growth rate equals 0.3 nm^2/hr. Figure 3 and Figure 4 were represented the eq 6 and eq 4 of the growth process. These processes were controlled by surface process according to mono nuclear growth rate and poly-nuclear growth rate, respectively. These two models had been studied to investigate the kinetics growth, poly nuclear growth rate was found to be the best model with highest R^2. In the other hand, R^2 of the mono-nuclear growth rate model found that low. Therefore, mono-nuclear growth rate model cannot explain the kinetics of growth of Ag-NPs. From poly nuclear growth rate model could be calculated the rate of growth and its was found to be equals 0.066 nm/hr (Cao & Wang, 2011).

Table 1. Parameters of growth theory of Ag-NPs

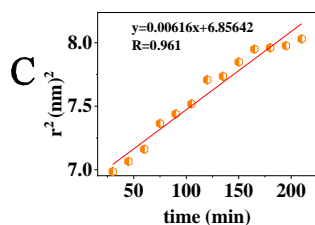| Growth process was controlled by the diffusion of growth species		
Parameters	k_d (nm^2/hour)	r_0 (nm)	R^2
Values	0.3	3.440	0.968
Mono-nuclear growth model of surface growth		
Parameters	k_m (nm/hour)	r_0	R^2
Values	0.0084	2.632	0.959
poly-nuclear growth model of surface growth		
Parameters	k_p (nm/hour)	r_0	R^2
Values	0.066	2.625	0.965

Figure 2. growth process of Ag-NPs was controlled by the diffusion of growth species from the bulk solution to the particle surface
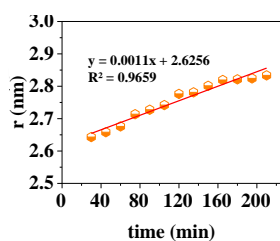

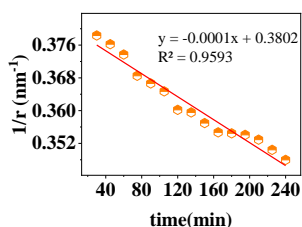**Figure 3.** poly nuclear growth rate of Ag-NPs surface at 218K

Figure 4. mono nuclear growth rate of Ag-NPs surface at 318K.

3.1.   Kinetic study

The kinetic study at different temperature showed that higher temperature and produces smaller particles size and different varieties in shapes. Figure 5 showed the SPR bands of Ag-NPs were prepared with 1 mM aqueous $AgNO_3$ and 5 mL ZSCS extract at 298K, 308K and 318K. Figure 5 (a) and Figure 5 (b) showed that asymmetrical bands of SPR bands and over time, SPR

bands changes to become more symmetrical. This result may be due to non-spherical Ag-NPs was formed, and over time, Ag-NPs changes to become more spherical as showed in Figure 5 (c). The kinetic models for the synthesis of Ag-NPs at different time, t and all kinetic data are listed in Table 2, figure 6 and figure 7 figure 6 illustrate of first and second order models, the second order model was found that the R^2 value was high. Therefore, second order model can explain the kinetics of reduction of silver ions to Ag-NPs found that the reaction in forward direction done by second order mechanism and in first order in backward direction, therefore according the rate constant in forward direction, k_2 and rate constant in backward direction k_1 can be determined the values of, K_c at difference temperature and its value listed in Table **3**(Hu & Hsieh, 2016).
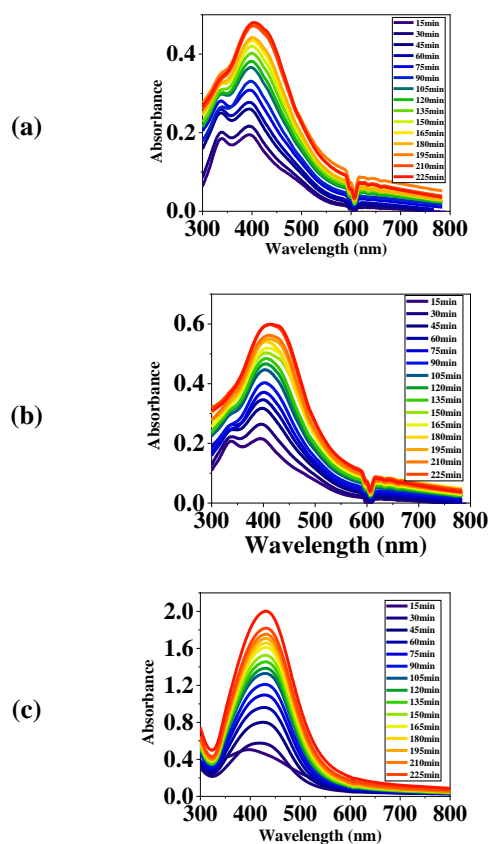

Figure 5. UV–visible spectra of synthesized Ag-NPs at (a) 298K, (b) 308K and (c) 318K
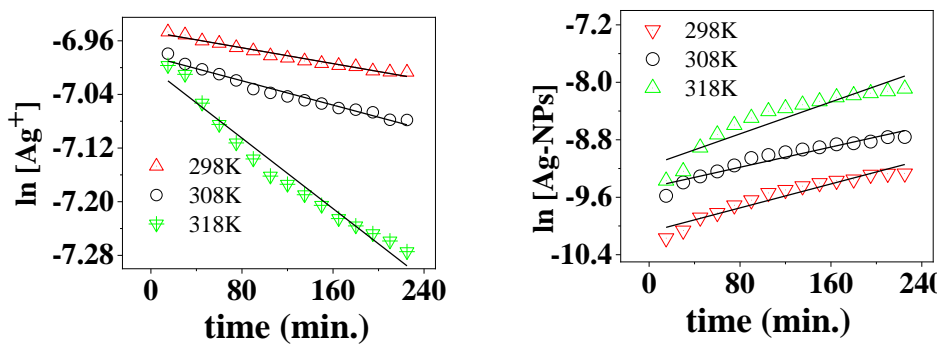
Figure 6. First order model of kinetics of silver ion and Ag-NPs at various temperature
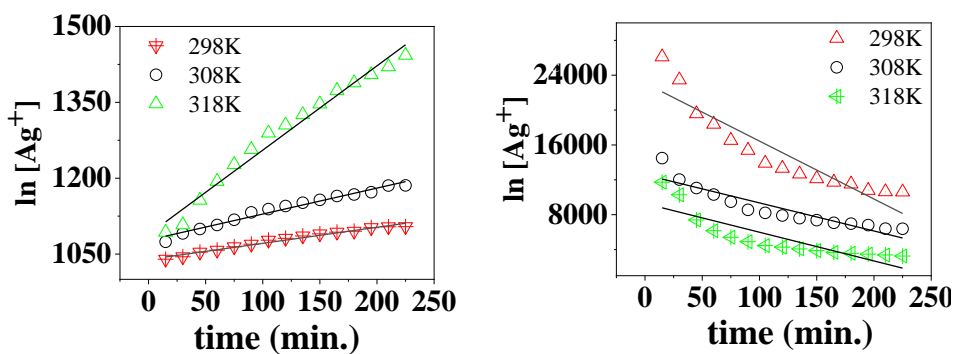

Figure 7. Second order model of kinetics of silver ions and Ag-NPs at various temperature

Table 2. rate constants at various temperatures for different direction of silver ions and Ag-NPs

Ordersparameters	Kinetic of Silver ions			Kinetic of Ag-NPs		
	298K	308K	318K	298K	308K	318K
First order						
k_1	0.00029	0.00045	0.00132	0.004	0.003	0.005
R^2	0.974	0.971	0.971	0.924	0.919	0.862
Second order						
k_2	0.317	0.513	1.699	66.43	32.22	30.60
R^2	0.976	0.975	0.98	0.852	0.848	0.725

Table 3. Kc values of Ag-NPs synthesized at difference temperture

	k_2 in Forward reaction	k_1 in Backward reaction	Equilibrium constant (k_2/k_1)
298K	0.317	0.004	79.25
308K	0.513	0.003	171
318K	1.699	0.005	339.8

1.1. Thermodynamic Study

K_C values at different temperature were greater than 1. Therefore, the reaction is spontaneously in forward direction and non-spontaneously in backward direction. According to **eqs 15**, and **16** and K_C values, ΔG^0, ΔH^0 and ΔS^0 can be determined. ΔG^0 was found negative in all the studied range of temperature, concluding that the Ag-NPs synthesis is spontaneous. In addition, ΔH^0 and ΔS^0 values have positive sign. This findings tell us that the reaction became more spontaneous at high temperatures and opposite at low temperatures *(Masoodiyeh et al., 2015)* $(\Delta G_f^0)_{Ag-NP}$ can be determined according to **eq 16**. It was found that $(\Delta G_f^0)_{Ag-NP}$ in aqueous solutions increases with decreasing size of Ag-NPs Figure 9. This is may be due to the change of the thermodynamic properties with optimum conditions of temperature, particle shape and number of atoms per cluster (Skiba et al., 2018)
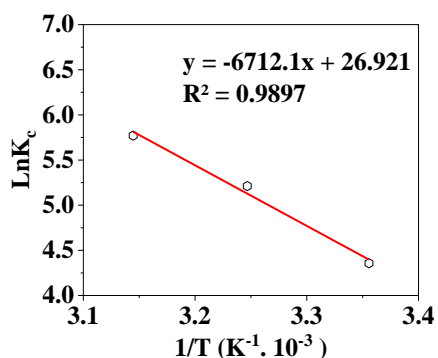

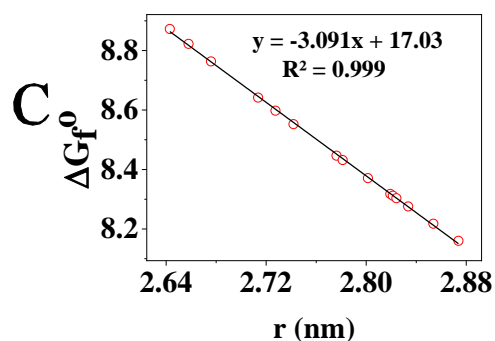**Figure 8**. plot of ln K_C vs 1/T for the Van't Hoff equation

Figure 9. Dependence of the ΔG_f^0 of Ag-NPs on the Ag-NPs radius
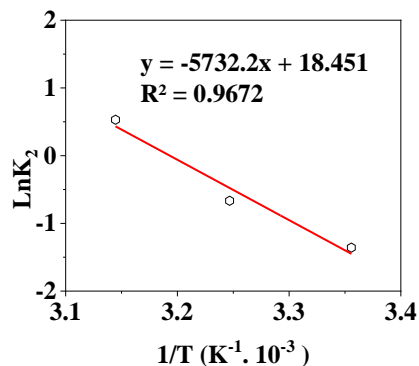

Figure 10. Plots of ln k_2 vs 1/T for the Arrhenius

Table 4. Thermodynamic parameters of Ag-NPs

	Kc	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/k.mol)	Ea (KJ/mol)
298K	79.25	-10.4	55.80	223.82	47.65
308K	171	-12.4			
318K	339.8	-13.8			

4.   Conclusion

Growth of Ag-NPs done by poly-nuclear growth and by diffusion from bulk to surface of cluster. Reduction kinetic of silver ion done by second order model. Thermodynamic studies Synthesis of Ag-NPs was endothermic reaction and spontaneous at medium and law temperature and non-spontaneous at high temperature. Formation free energy of Ag-NPs was not constant and change with radios of Ag-NPs.

5.   References

Basalius, H., Mani, A., Michael, A., Mary, S. M., Lenin, M., Chelliah, P., . . . Islam, M. A. J. A. N. (2023). Green synthesis of nano-silver using Syzygium samarangense flower extract for multifaceted applications in biomedical and photocatalytic degradation of methylene blue. *13*(6), 3735-3747.

Cao, G., & Wang, Y. (2011). *Nanostructures And Nanomaterials: Synthesis, Properties, And Applications (2nd Edition)*: World Scientific Publishing Company.

Hu, S., & Hsieh, Y.-L. J. I. j. o. b. m. (2016). Silver nanoparticle synthesis using lignin as

reducing and capping agents: A kinetic and mechanistic study. *82*, 856-862.

Kokila, T., Ramesh, P., & Geetha, D. J. A. N. (2015). Biosynthesis of silver nanoparticles from Cavendish banana peel extract and its antibacterial and free radical scavenging assay: a novel biological approach. *5*(8), 911-920.

Masoodiyeh, F., Karimi-Sabet, J., Khanchi, A., & Mozdianfard, M. J. P. T. (2015). Zirconia nanoparticle synthesis in sub and supercritical water—particle morphology and chemical equilibria. *269*, 461-469.

Skiba, M., Pivovarov, O., Makarova, A., & Vorobyova, V. J. В.-Е. ж. п. т. (2018). Plasmochemical preparation of silver nanoparticles: thermodynamics and kinetics analysis of the process. (2 (6)), 4-9.