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Synthesis of nano-silver by spinning disc reaction method

Hoang Van Duc*, Tran Ngoc Ha, Nguyen Thi Thuc Phuong, Nguyen Thanh Chung

Institute of Technology for Radioactive and Rare Elements (ITRRE)
Vietnam Atomic Energy Institute (VINATOM)
Email: hoangvanduc11@gmail.com

Abstract: This work has investigated preparation of silver nano-particles using spinning disc reactor. The effects of technological factors and experimental conditions such as: concentrations of $AgNO_3$, glucose, PVP K30 (polyvinylpyrrolidone), spinning speed... on quality of nano-silver particles have been studied. With experimental conditions: rotation speed of 2000 rpm, weight rate of m_{PVP}:m_{AgNO3} = 1, $AgNO_3$ concentration of 0.01 M, glucose concentration of 0.02 M, silver particles of about 12 nm were obtained and the nano-silver solution were stable for more than 42 days.

Key words: *spinning disc reactor, silver nano-particles.*

I. INTRODUCTION

In the past decade, many researchers around the world have focused on synthesis, structural analyses and characterization of nano-size materials. In the recent years, industrial requirements of using nano-materials have been growing up sharply that forced researchers to investigate and develop nano-material preparation methods with low cost and high capacity.

Based on recently published documentary, nano-silver prevents many kinds of bacterial from development, destruction of cell membrane of about 650 kinds of dangerous single-celled bacterial, especially Staphylococcus aureus ($Gram^+$) and Escherichia coli ($Gram^-$). The impact of nano-silver on baterium is not similar to that of anti-biotic medicine. While anti-biotic medicine affects on baterium in a long time, nano-silver destroys baterium in a very short time [1].

Nowaday, nano-silver product has many potential applications in many daily fields such as aquaculture, breeding, farming fields and daily demands....However, applications of nano-silver are still limited due to high cost of the product.

Recently, investigation of general nano-sized materials, specially nano-Ag has been paid much attention in Vietnam. Some initial results has been obtained, especially in applications of nano-product. However, reported investigations almost use costly resources and are based on conventional methods, so the product price is high, that limited wide applications of nano-silver [2].

In this work, spinning disc reaction method has been used to prepare nano-silver, in which reactions take place on the surface of spinning disc, not only causing significantly improved micro-mixing effection, but also intensifying mass-transfering rate and shortening reaction time [3, 4].

II. EXPERIMENTAL SECTION

A. Materials:

Materials and precursors were used in this work include $AgNO_3$, NaOH, PVP,

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HPMC, glucose, D-glucose… All the chemicals used were analytical grade.

B. Equipment*:*

The parameters of spinning disc reactor (SDR): The main part of the SDR is a stainless-steel disc, 20 cm in diameter, driven by a variable-speed motor. The spinning disc is enclosed in a cylindrical chamber of 30 cm in diameter and 10 cm in width. Maximum rotation speed of spinning disc is 3000 rpm.

A schematic diagram of the spinning disc reactor for preparation of nano-silver was shown in Figure 1, in which tank A contained aqueous solution of $AgNO_3$ and protecting agent (PVP, PVA, PEG…), tank B contained aqueous solution of alkali (NaOH, NH_4OH, Na_2CO_3…) and reducing agent (glucose, starch, HCHO, $NaBH_4$…..)

The reaction between Ag cations and glucose in NaOH solution is as follows:

$$2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag^0 + C_6H_{11}O_7^- + 3H^+ \quad (1)$$

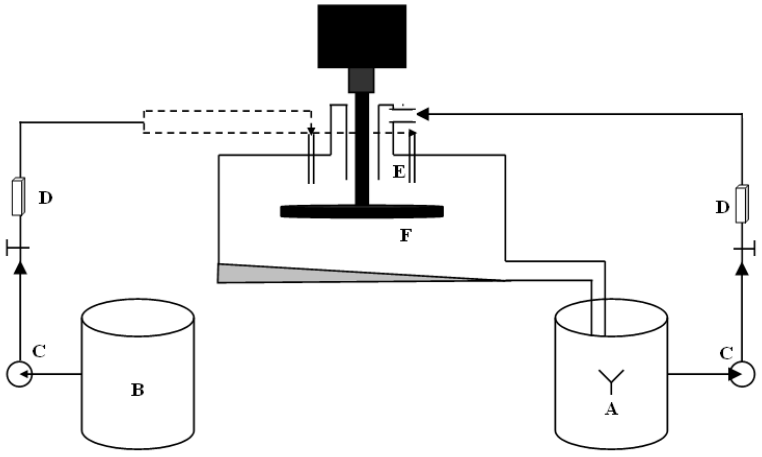


Fig.1. Experimental setup for preparation nano-silver using spinning disc reactor.
A. Solution of $AgNO_3$ and protecting agent; B : Solution of NaOH and reducing agent;
C : Pump; D : Flowmeter ; E : Liquid distributor; F : Spinning disc.

At first, tank A contained $AgNO_3$ and protecting agent solutions, tank B contained NaOH and reducing agent solutions with certain rates. The solutions in tank A and tank B were pumped by pump C at a specific flow ratio onto the center of the spinning disc with a rotation speed ranging from 0 to 3000 rpm. The liquid was accelerated due to centrifugal force, causing it to spread over the disc surface and forming a thin film where the reducing reaction took place. After that, the slurry of reaction products was shooted out to wall of spinning disc F and then flowed into tank A to mix with $AgNO_3$ solution. After the solution in tank B was exhausted, solution in tank A was continuously pumped for a certain time. The recycle operation was adopted to give a high yield because the retention time on the spinning disc was too short.

III. RESULTS AND DISCUSSION

A. Effect of protecting agent PVP concentration on nano-silver particle size.

The experimental shown in Fig. 1 indicated that while increasing PVP concentration, nano-Ag particle size decreased. In details, nano-Ag particle size decreased

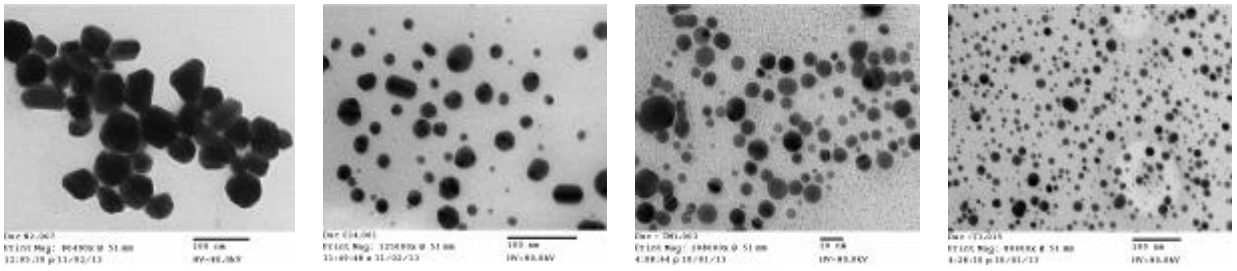
from 55.26 nm to 14.40 nm while increasing m_{PVP}/m_{AgNO3} weight rate from 0.25 to 2.

Fig. 2(1) has shown TEM image of nano-silver with weight rate of m_{PVP}/m_{AgNO3} = 0.25, indicating that nano-Ag particles aggregated, causing mean particle size was about 55.26 nm.

The experimental result shown in Table 1 indicated that mean particle size changed insignificantly with m_{PVP}/m_{AgNO3} = 1 and m_{PVP}/m_{AgNO3} = 2. TEM images shown in fig 2(3) and fig 2(4) indicated that particle size distribution was quite large.

Table I. Effect of PVP concentration on nano-Ag particle size

Sample	1	2	3	4
m_{PVP}/m_{AgNO3}	0,25	0,5	1	2
Particle size (nm)	55,26	22,10	15,15	14,40



1 2 **3** **4**

Fig.2: TEM images of nano-Ag solution.

(Flow rate L_A = 800ml/m; L_B = 200 ml/m; [$AgNO_3$] = 0,01 M; [glucose] = 0,01 M; [NaOH] = 0,05 M; Rotation speed of disc = 1500 rpm).

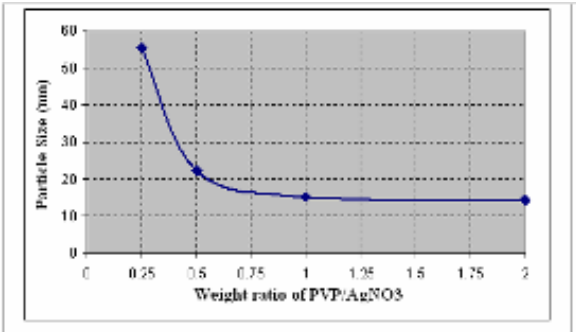


Figure 3: Correlation of nano-Ag particle size and weight ratio of PVP/$AgNO_3$.

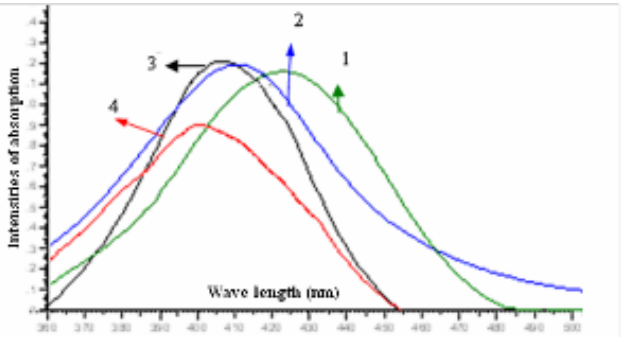


Figure 4: UV-vis absorption spectrum of nano-Ag samples (1, 2, 3, 4)

UV-vis absorption spectrum of samples 1, 2, 3, 4 shown in fig. 4 indicated that wave length and intensities of the maximum peaks as bellows:

- Sample (1): wave length of absorption peak: 425 nm - absorption value (ABS): 1.178
- Sample (2): wave length of absorption peak: 410 nm - absorption value (ABS): 1.185
- Sample (3): wave length of absorption peak: 403 nm - absorption value (ABS): 1.193

• Sample (4): wave length of absorption peak: 400 nm - absorption value (ABS): 0.825

The position of peak on UV-vis absorption belongs a range of 400 - 425 nm corresponding with typical tawny color of nano-silver solution. In general, the position of peaks on UV-vis absorption spectrum changed insignificantly, moving slowly to the left from samples 1, 2, 3 to sample 4, respectively, meaning that particle size decreased gradually. The absorption intensities (ABS) of maximum absorption peaks of samples 1, 2 and 3 changed negligibly in a range of 1.178 - 1.193 ABS. UV-vis spectrum of sample 4 (Fig. 4) showed that while increasing PVP concentration, maximum absorption value decreased to 0.825 ABS. This can be explained by steric effect of PVP structure and high viscosity of solution that reduced micro-mixing ability and prevented reducing reaction transforming Ag^+ into Ag^0.

Based on experimental data, in order to improve micro-mixing effect and boost reaction productivity, the weight rate of $m_{PVP}:m_{AgNO3}$ = 1 has been selected as optimal rate for later experiments.

B. Effect of glucose concentration on quality of nano-silver particle.

The concentration of precursors such as glucose, $AgNO_3$ has influenced on quality factors of nano-Ag product such as particle size, particle size distribution, morphology, incoherence, specific surface area, stability…. and equipment productivity. In this section, the effect of glucose concentration on nano-silver quality has been investigated.

Table II: Effect of glucose concentration on nano-silver particle size

Glucose concentration (M)	3	5	6	7	8
	0,01	0,02	0,03	0,04	0,05
Nano-silver particle size (nm)	15,15	16,03	19,45	25,96	-

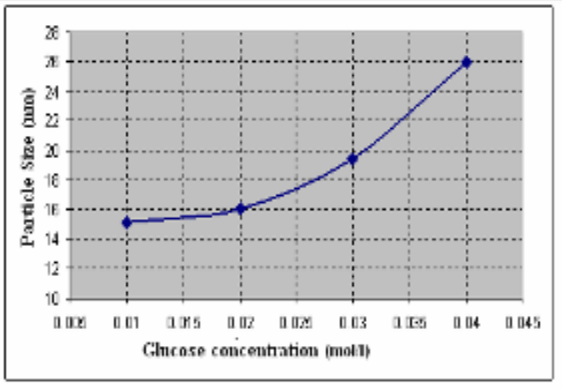


Fig. 5: Correlation of nano-Ag particle size and Glucose concentration.

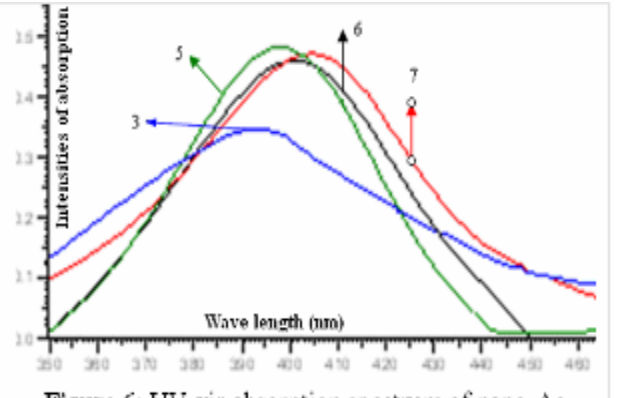


Figure 6: UV-vis absorption spectrum of nano-Ag samples (3, 5, 6, 7).

The results shown in Table II and Fig. 5 indicated that effect of glucose reducing agent on nano-Ag particle size and particle size distribution. When increasing reducing agent concentration from 0.01 to 0.04 M, nano-Ag size increased from 15.15 to 25.96 nm. When glucose concentration continued to increase to 0.05 M, TEM image in Fig. 3.10 showed that nano-Ag particles aggregated so it was impossible to determine the mean size.

This can be explained that when increasing glucose concentration, the reaction took place very quickly, making many crystal nucleation at the same time. These crystal nucleation have big surface energy and then they aggregated together making silver particles with larger size, leading to the mean size of silver product increased correlatively.

TEM images in Fig. 7(5) indicated that with glucose concentration = 0.02M, obtained nano-silver particle size was quite uniform and the mean particle size was about 16.03 nm.

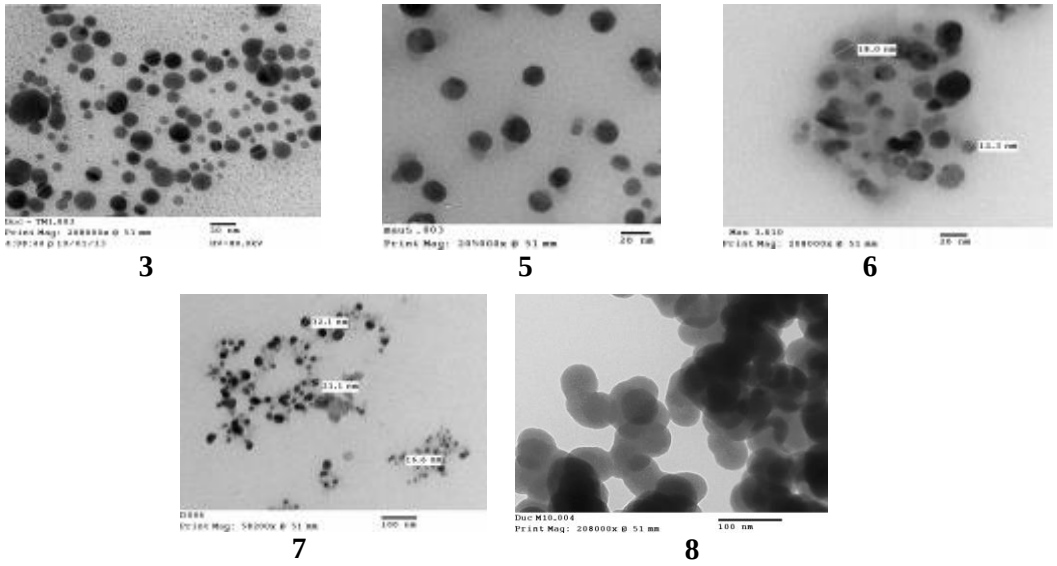


Fig. 7: TEM images of nano-Ag product obtained at different glucose concentrations.
Liquid flow rate L_A = 800ml/m; L_B = 200 ml/m; [$AgNO_3$] = 0,01 M; m_{PVP}/m_{AgNO3} = 1; [NaOH] = 0,05M; Rotation speed of spinning disc = 1500 v/m).

UV-vis absorption spectrum of samples 3, 5, 6, 7 shown in fig. 6 indicated that wave length and intensities of the maximum peaks as bellows:

- Sample (3): wave length of absorption peak: 397 nm - absorption value (ABS): 1.348
- Sample (5): wave length of absorption peak: 399 nm - absorption value (ABS): 1.483
- Sample (6): wave length of absorption peak: 402 nm - absorption value (ABS): 1.465
- Sample (7): wave length of absorption peak: 409 nm - absorption value (ABS): 1.472

The wave length of absorption peaks was in a range of 397 nm - 409 nm, corresponding with typical tawny color of nano-silver colloid. The absorption intensities (ABS) of maximum absorption peaks of three samples 5, 6, and 7 changed negligibly in range of 1.465 - 1.483 ABS. The spectrum shown in Fig. 6(3) indicated that, when glucose

concentration was low, the maximum absorption intensity was lower than that of sample 7, 6 and 9. When particle size increased, the square of UV-vis spectrum tended to be widened and the peak of maximum absorption spectrum moved slowly toward long wavelength.

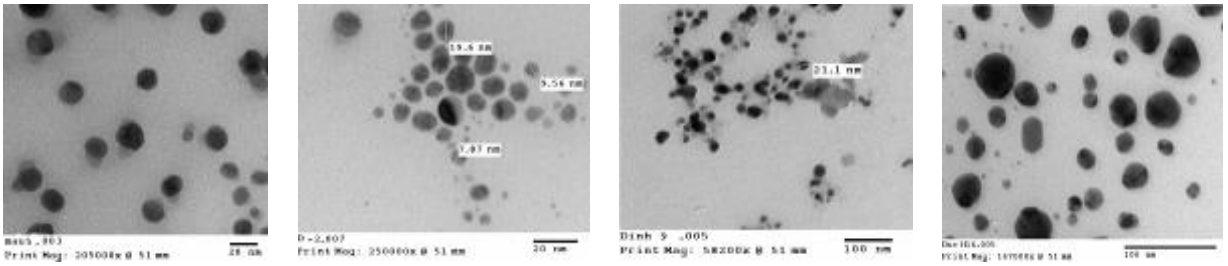
Based on assessing experimental data, glucose concentration = 0.02 M has been selected as optimal glucose concentration for the following experiments.

C. Effect of $AgNO_3$ concentration on quality of nano-silver product

In order to investigate the effect of $AgNO_3$ concentration on silver particle size, experiments were set up with experimental conditions as below (Table III and Figure 8):

Table III: effect of $AgNO_3$ concentration on nano-silver particle size.

Samples	5	9	10	11
Concentration of $AgNO_3$ (M)	0,01	0,015	0,02	0,03
Silver particle size (nm)	16,03	17,43	19,56	32,15



5 **9** **10** **11**

Fig. 8: TEM images of nano-silver colloids prepared at different $AgNO_3$ concentrations.
(Liquid flow rate L_A = 800 ml/m; L_B = 200 ml/m; [glucose] = 0,02 M; Weight rate of PVP/$AgNO_3$ = 1; [NaOH] = 0,05 M; Rotation speed of disc = 1500 rpm).

From the results shown in table III, it can be seen that, when increasing AgNO3 concentration, the mean size of nano-silver particles increased gradually. The mean size of nano-Ag particle was in range of 16.03 - 32.15 when $AgNO_3$ concentration increased from 0.01 M to 0.03 M.

From TEM images of nano-silver colloids in Fig. 8, it can be seen that almost synthesized nano-silver particles were spherical. With $AgNO_3$ concentration bigger than 0.01 M, TEM images in Fig. 8, 9, 10, 11 indicated that nano-silver particle size distribution was quite large.

With $AgNO_3$ concentration = 0.01 M (sample 5), the TEM results shown in Fig. 8(5) indicated that nano-silver particles were quite uniform with the mean particle size was about 16.03 nm.

From reaction equation (1), it can be found that during preparation reaction, H^+ ions were formed. These ions will neutralize OH^- ions presented in aqueous solution, reducing reaction speed. When increasing $AgNO_3$ concentration, the amount of H^+ ion in the solution increased, causing reaction yield to reduce.

Based on assessing experimental results, $AgNO_3$ concentration = 0.01 M was selected as the optimal $AgNO_3$ concentration for following experiments.

D. Effect of rotation speed of spinning disc on quality of nano-silver product

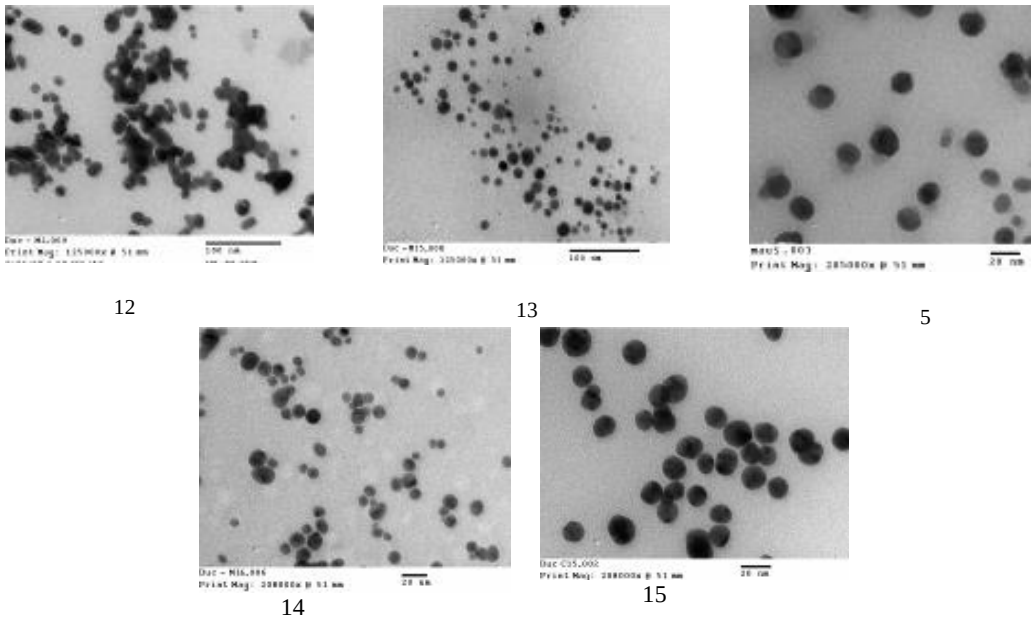
The results in Table IV indicated that when increasing rotation speed of disc, nano-silver size decreased. The rotation speed increased from 1000 to 2500 rpm, particle size decreased from 18.15 nm to 12.00 nm.

When rotation speed was about 500 rpm, silver particles were aggregated because micro-mixing effect was not strong enough.

With rotation speed was 2000 and 2500 rpm, the mean particle size changed insignificantly, about 12 nm. This can be explained as follows: The rotation speed of spinning disc of 2000 rpm was strong enough for impacting on liquid, causing liquid to flow into reaction area as thin films and droplets, leading to big liquid-liquid contact area. If rotation speed of disc continues to increase to 2500 rpm, liquid would flow into reaction area as small wire or droplet, leading to higher mass transfer rate and smaller silver particle size.

Table IV: Effect of rotation speed of spinning disc on nano-silver particle size

Samples	12	13	5	14	15
Rotation speed of disc (rpm)	500	1000	1500	2000	2500
Particle size (nm)	-	18,15	16,03	12,67	12,00



12 13 5 14 15

Fig. 9: TEM images of nano-silver product.
(Liquid flow rate L_A = 800ml/m; L_B = 200 ml/m; [Glucose] = 0,02 M; Weight rate of PVP/$AgNO_3$ = 1; [NaOH] = 0,05 M; [$AgNO_3$] = 0,01 rpm).

TEM images shown in Fig. 9(14) and 9(15) of nano-silver colloids indicated that the mean size of nano-silver product was quite uniform, about 12 nm with narrow particle size distribution.

From analyzing experimental data, the optimal rotation speed of 2000 rpm has been selected for next experiments because with this rotation speed, nano-silver product met technical requirements but still ensuring safety of the equipment.

Therefore, , it is possible to synthesize nano-silver colloid with the mean particle size less than 20 nm and narrow particle size distribution using spinning disc reactor.

E. Stability of nano-silver solution by time.

From observing color of nano-silver colloid after reaction (Fig. 10) and color of nano-silver colloid after keeping for 42 days (Fig. 11), it can be seen that, the colors of nano-Ag solution were almost same, meaning that nano-Ag solution system was stabilized for a long time.

Figure 12 was UV-vis absorption spectrum of nano-Ag solution (sample 16) after reaction and after 42 days. It can be seen that the positions of peak were almost same and ABS value changed insignificantly, the absorption peak moved slowly toward longer wave length. UV-vis spectrum shown in Fig. 12 indicated that position of peak was stabilized, meaning that aggregation of silver particles did not take place, so the mean particle size increased negligibly.

Figures 13 and 14 were TEM images of nano-Ag solution (sample 16) after reaction and after 42 days, indicating that nano-Ag particle size after 42 days increased, some silver particles aggregated, forming bigger silver particles. However, the mean particle size changed insignificantly. This indicated that nano-silver particles in nano-silver solution were stabilized for a long time (more than 42 days).

Fig. 10: Color of nano-silver solution after reaction (M16)..

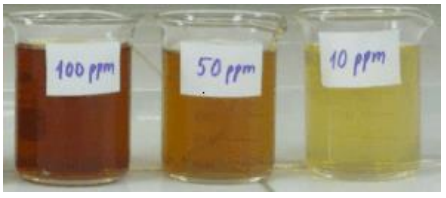


Fig. 11: Color of nano-silver solution after 42 days (M16)..

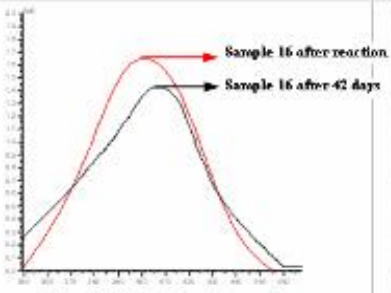


Fig. 12: UV-vis absorption spectrum of sample 16 after reaction and after 42 days.

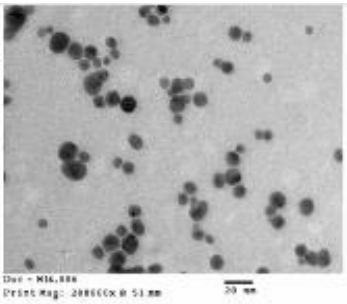


Fig. 13: TEM image of nano-silver solution after reaction (M16).

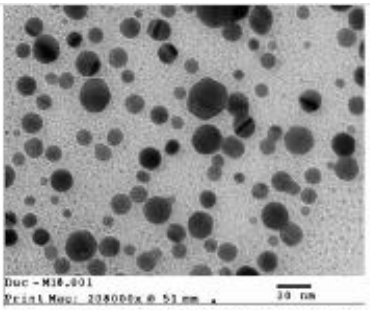


Fig. 14: TEM image of nano-silver solution after 42 days (M16).

IV. CONCLUSION

1- The technological factors that affect on nano-silver particle size has been investigated.

2- The optimal experimental conditions for preparation of nano-silver by spinning disc reactor have been suggested as follows:

- $AgNO_3$ concentration: 0,01 M
- Glucose concentration: 0,02 M
- Selected protecting agent: PVP K30
- Weight rate of PVP/$AgNO_3$: 1
- Liquid flow rate L_A: 800 (ml/p)
- Liquid flow rate L_B: 200 (ml/p)
- Rotation speed of disc: 2000 (v/p)

3- With optimized experimental conditions, nano-silver particle solution with the mean particle size of 12 nm, narrow particle size distribution has been synthesized. The stability of nano-silver solution was more than 42 days.

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