Synthesis of Silver Nanoparticles from Spent X-Ray Photographic Solution via Chemical Rreduction

Azarkhalil, Mohammad Saeed; Keyvani, Bahram*[+]

Chemistry Department, Islamic Azad University, Saveh Branch, P.O. Box 39187-366 Saveh, I.R. IRAN

ABSTRACT: *Silver metal was recovered primarily from spent X-ray photographic solution using a horizontal tube furnace. The X-Ray Diffraction (XRD) spectroscopy analysis approved almost 95 percent purity of the recovered silver metal. In the next step, the synthesis of silver nanoparticles from the recovered silver metal proceeded by using chemical reduction method. The proposed method uses ethanol as reducing agent and VinylTriMethoxySilane (VTMS) as stabilizer. Nitrogen gas may be used to provide dry and inert atmosphere. Upon optimized condition spherical nano-sized silver particles with approximately 68 nm diameter are formed. XRD and EDX spectroscopy studies confirmed the formation of silver nanoparticles. The morphology of the silver nanoparticles was studied by using scanning electron microscope.*

KEYWORDS: *Silver recovery; Silver nanoparticle; X-Ray photographic Fixing Solution; Chemical reduction; VinylTriMethoxySilane; Stabilizer*.

INTRODUCTION

Metallic silver with its remarkable thermal and electrical conductivities has found particular attractions in both research and industrial scale applications [1]. However, silver is among rare elements in the earth crust and there are serious limitations for its broad applications. In this view, the recovery of silver from spent chemicals is a focus of attention. Among various recycling sources for silver, photographic wastes is matter of importance [2]. There are different methods of silver recovery from spent X-ray photographic solutions including: chemical precipitation and metallic replacement [3], extraction and electrodeposition [4].

Modern industry however, accounts for the application of nano matter in various processing units. In response to such a need, there have been attempts addressing to the study of synthesis of nanoparticles. There are a number of chemical methods for the synthesis of nanoparticles. These include: chemical precipitation [5], sol gel [6], micro-emulsion [7], vapor phase condensation[8], biosynthesis [9,10] and chemical reduction [11,12]. The later has been addressing to the synthesis of silver nanoparticles [13]. There are a number of reducing agents reported for the synthesis of silver nanoparticles including; citric acid [14], ascorbic acid [15, 16], glucose [13] and sodium borohydride [17]. According to the literature [18], silver ions primarily dissolved in alcohol followed by reduction of silver ions to form silver atom. Alcohol facilitates the reduction process. Ultimately, the individual atoms are bond together to form nanoparticles. The use of stabilizer (VinylTriEthoxySilane) (VTES) [15,19] prevents the growth of the newly formed nanoparticles [19]. There are various fields of applications for silver nanoparticles;

* *To whom correspondence should be addressed.*

+ E-mail: bkeyvani@iau-saveh.ac.ir

1021-9986/2016/3/1-8 8/$/5.80

microfiltration [20] and nanofluid applications are to name but a few. The later accounts for antibacterial effect [21]. Nevertheless, for its remarkable thermal conductivity, silver nanoparticle is reported as active ingredient in nanofluid applications [22]. The use of nanofluids as opposed to conventional fluids in heat transfer operations has proven a dramatic improvement of thermal performance and better yields [23].

This work refers to the recovery of silver from silver containing municipal waste solutions and accounts for environmental considerations accordingly, paves the path to introduce silver nanoparticles with its potential applications in various industries.

EXPERIMENTAL SECTION

Equipments

The synthesis of silver nanoparticles was achieved by using a Carbolite horizontal tube furnace MTF 12/38/850 (UK). Ultrasonic sample preparations prior to size analysis completed with a Bandelin Sonopuls HD3200. The X-Ray Fluorescence (XRF) spectroscopy analysis carried out with a Philips PW 1480. At the same time, the X-Ray Diffraction (XRD) spectroscopy analysis performed with an Ital Structure MPD 3000. The elemental analysisof the sample was investigated by using Energy Dispersive X-Ray (EDX) spectroscopy with Tescan VEGA 3 LM. Morphology of the silver nano particles was studied by using a Tescan VEGA 3 LM Scanning Electron Microscope (SEM).

Materials

The spent X-ray film fixing solution used in this study was purchased from Social Insurance General Hospital of Shahryar District, Tehran Province, Iran. VinylTriMethoxySilane (VTMS) (Merck, 97%), ethanol (Merck, 99.5%), hydrochloric acid (Merck, 37%), nitric acid (Merck, 65%) and the remaining chemicals used in this work were purchased from Merck chemicals and purified, or prepared according to the literature methods.

The recovery of silver from spent X-ray film fixing solution

Concentrated hydrochloric acid (37%) was added in a beaker containing 1000 mL spent X-ray film fixing solution to adjust the pH to 2.6. Therefore, metal ions present in the solution converted into metal chloride. The solution was heated up to 65 ^{o}C while stirred vigorously for 1 hour to allow the formation of precipitates. It was then filtered, washed, dried out and weighed. A small segment was assigned for the XRF analysis while the remaining of the sample was smelted in a horizontal tube furnace at 1000 ^{o}C for 2 hours to obtain metallic silver(95% purity).

Preparation of silver nitrate

In a 1000 mL beaker, 10 g (92.71 mmol) the recovered silver was dissolved into 500 mL (7.17 mol) nitric acid (65%) at 40 ^{o}C. The solution was aged at 0 ^{o}C for 24 hours to form silver nitrate crystals. The solution was then filtered to obtain silver nitrate powder as precursor.

Synthesis of silver nanoparticles

In a double neck flask equipped with magnetic stirrer, nitrogen contact, 1.6 mg (9.42 µmol) newly formed silver nitrate (precursor) was dissolved in 18 mL ethanol under nitrogen atmosphere. After 50 minutes vigorous stirring and when the color of solution changed into pale Yellow, 17 µL (111.246 µmol) VinylTriMethoxySilane (VTMS) was gradually added to the mixture. The solution was then centrifuged at 4000 rpm. Accordingly, the solvent was evaporated and nano particles were collected.

Optimization of ethanol to VTMS molar ratio

Five samples in respective with ethanol to VTMS molar ratio in the range of 2.846 to 2.336 (mmol / µmol) were prepared to investigate the effect of solvent to stabilizer molar ratio on the variation of silver nanoparticle size. The optimization was performed in an array of synthesis to yield silver nanoparticles. Table 1 shows the molar ratio changes of ethanol against VTMS.

RESULTS AND DISCUSSION

The metallic silver recovery from spent X-ray film fixing solution

The results of XRF spectroscopy analysis concerning the precipitate obtained from spent X-ray film fixing solution is given in Table 2. Based on these results it is clear that the spent X-ray film fixing solution is a valid source for the recovery of silver. Fig. 1 shows the results of XRD spectroscopy analysis after precipitation of sample experienced smelting process at 1000 ^{o}C.

Table 1: Quantitative report of the components in the synthesis of five different silver nano samples.

Samples Number	Ethanol (mmol)	VTMS (μmol)	Ethanol(mmol) / VTMS (μmol)
1	307.1196	107.907	2.846
2	307.1196	114.282	2.635
3	307.1196	120.623	2.546
4	307.1196	126.965	2.419
5	307.1196	131.476	2.336

Table 2: The XRF report for the spent X-ray film fixing solution sample.

Compound	%	Compound	%	Compound	[ppm]	Compound	[ppm]	Compound	[ppm]
SiO_2	0.32	Ag	6.51	Cl	685	Cr	5	Rb	11
Al_2O_3	2.68	Br	5.02	Ba	8	V	5	Co	4
Fe_2O_3	0.09	TiO_2	0.006	Sr	126	Ce	11	As	2
CaO	0.96	MnO	0.002	Cu	117	La	5	U	2
Na_2O	16.85	P_2O_5	0.109	Zn	75	W	2	Th	8
K_2O	13.45	So_3	38.54	Pb	26	Zr	33	Mo	2
MgO	0.09	L.O.I	53.34	Ni	31	Nb	5	Ga	10

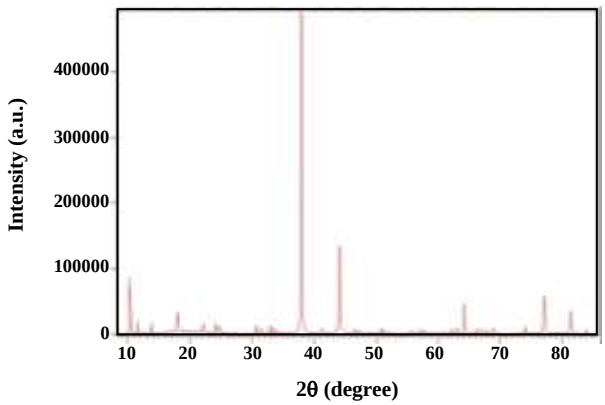

Fig. 1: The results of XRD analysis for the recovered silver from recycled X-ray film fixing solution.

According to Fig.1 the characteristic 2θ values equal to 38.4, 44.6, 64.6 and 77.9 are in good agreement with the JCPDS No. 01-087-0597 that refers to silver. Table 3 represents the possible compositions and the relevant percentage values in the test sample. It is evident from Table 3 that pure silver accounts for almost 95% and silver compounds account for less than 2% of the recovered sample. Gravimetric analysis indicated that approximately 24.8% of silver content in the spent X-ray film fixing solution sample was recovered.

Synthesis of silver nanoparticles

Fig. 2 depicts the SEM image of silver nanoparticles. The spherical like shape particles with ca. 50 to 70 nm diameter size are clearly shown in Fig. 2. The complementary EDX analytical results are given in Fig. 3. The chemical characterization based on Fig. 3, proves that the spherical nanoparticles are made of silver. Fig. 4 shows the XRD analytical results for silver nanoparticles. Formation of silver nanoparticles is confirmed according to the JCPDS No.01-087-0597. Table 4 represents the characteristic values derived from Fig. 4. According to Sherrer equation [24]:

$$L = \frac{K \times \lambda}{B \times (\cos\theta)} \quad (1)$$

For K (0.9) and λ (0.15406) for copper with B and θ values selected from Table 4, the size determination of silver nanoparticles (L) would be 66.8 nm.

The results of optimization of ethanol to VTMS molar ratio

The synthesis of silver nanoparticles by using chemical reduction method has been discussed elsewhere [25].

The use of Alcohol is recommended to dissolve silver nitrate. Nevertheless, alcohol potentially acts as reducing

Table 3: The XRD report of components from recycled X-ray film fixing solution.

Composition	JCPDS No. (www.ICDD.com)	(%)
Pure Silver (Ag)	0597-087-01	94.974
Silver Oxide (AgO)	1489-076-01	1.870
Potassium Peroxide (KO_2)	5956-089-01	1.417
Potassium Fluoride (KF)	0657-078-01	0.991
Sulfur Fluoride (SF_6)	0131-070-01	0.748

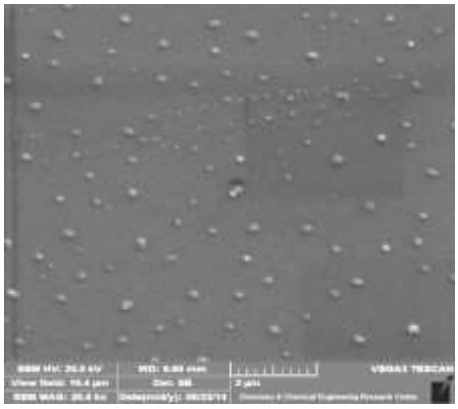

Fig. 2: The SEM image for silver nanoparticle synthesized with ethanol to VTMS respective molar ratio 2.419 (mmol / μmol).

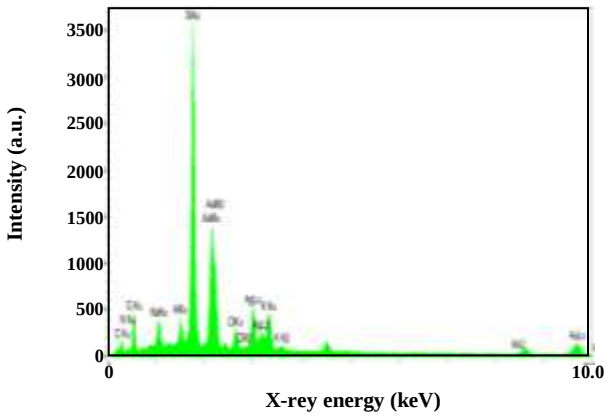

Fig. 3: The results of EDX analysis for silver nanoparticles with ethanol to VTMS respective molar ratio 2.419 (mmol / μmol).

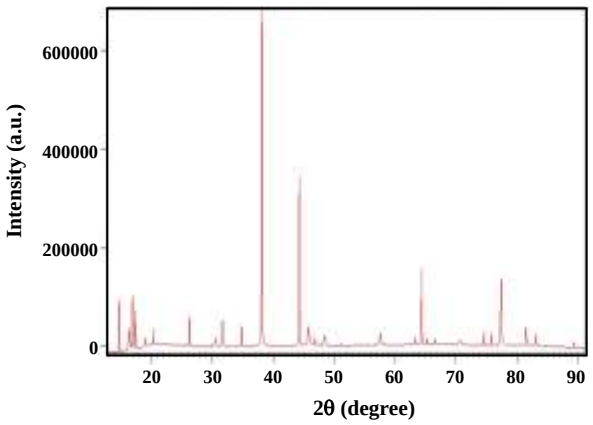

Fig. 4: The results of XRD analysis for silver nanoparticles with ethanol to VTMS respective molar ratio 2.419 (mmol / μmol).

agent to convert silver ions into atoms. In the next step atoms are bond together to form silver nanoparticles[18]. Fig.s 5 (a-d) show complementary SEM images for the four remaining silver nano samples formulated based on Table 1. The SEM images show that as the molar ratio of ethanol to VTMS increases the silver nanoparticles follow a trend of size enlargement. In Fig. 5a, the estimated mean silver nanoparticle size is equal to 230 nm. The corresponding mean silver nanoparticle size in Fig.s 5b, 5c and 5d are 160, 110 and 40nm respectively.

Silver nanoparticles with 230 nm mean size have VTMS concentration and molar ratio of ethanol to VTMS equal to 107.907 (μmol) and 2.846 respectively (Sample 1). The formation of relatively larger nanoparticles

Table 4: The numerical results of XRD analysis for silver nanoparticles with ethanol to VTMS respective molar ratio 2.419 (mmol / μmol).

Rel. Int.[%]	Height [cts]	d-spacing	Backgr.[cts]	Derivation	Area [cts*°2Th.]	FWHM [°2Th.]	Pos. [°2Th.]
100	605263.1	2.35881	27886.9	Pure K-Alpha1	44329.89	0.1216	38.1205
50	302631.6	2.35881	27886.9	Pure K-Alpha2	22164.95	0.1216	38.2189

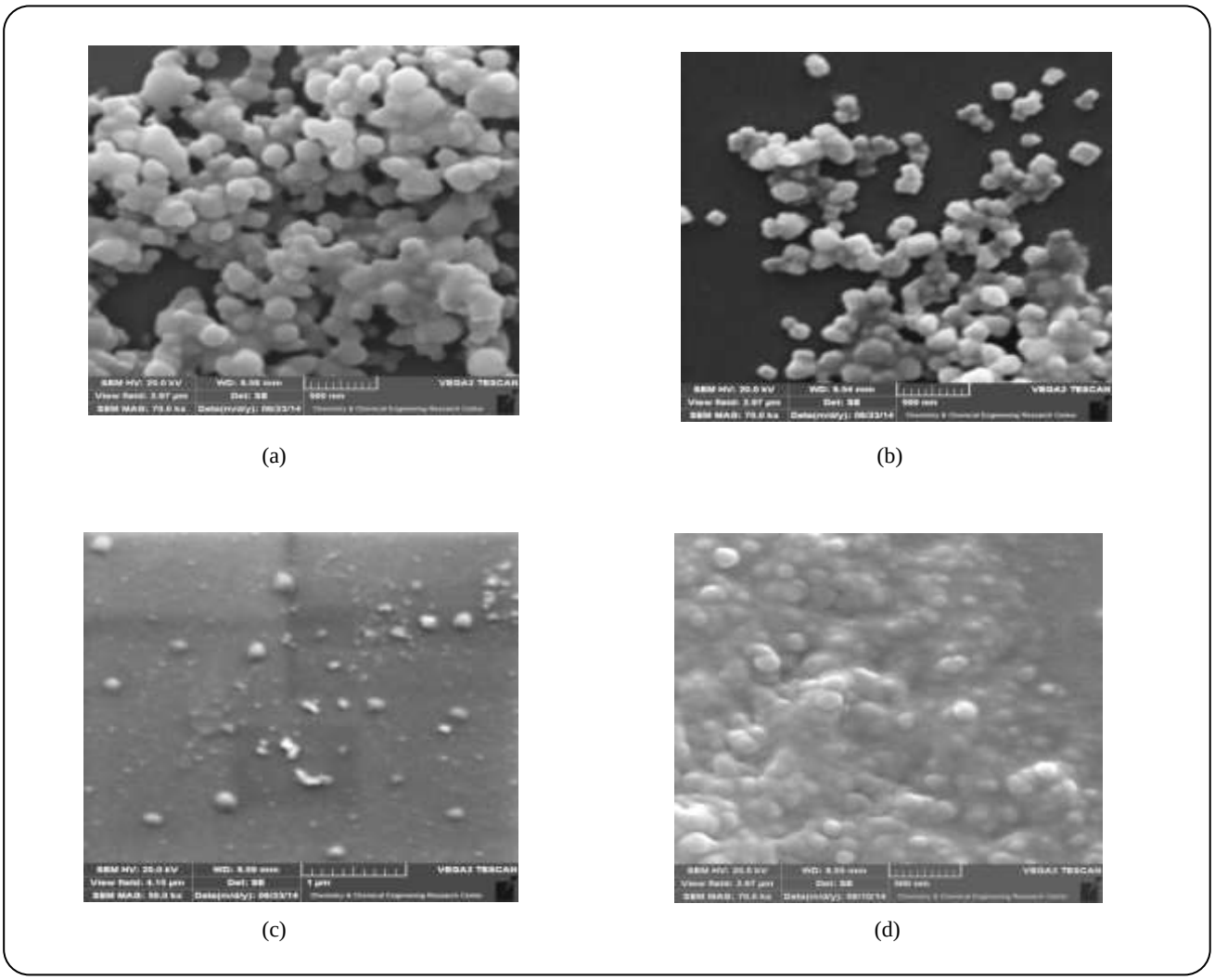

Fig. 5: The SEM images for silver nanoparticles synthesized at various ethanol to VTMS respective molar ratios. Agglomeration in nanoparticles is evident at lower VTMS molar ratio: (a) 2.846 (mmol / μmol), (b) 2.635 (mmol / μmol), (c) 2.546 (mmol / μmol), (d) 2.336 (mmol / μmol).

in sample 1 may be argued by the VTMS concentration. The use of stabilizer prevents the coalescence of the newly formed nanoparticles [19]. Therefore, by reducing the concentration of VTMS in the reaction mixture the risks associated with agglomeration in nanoparticles increases.

The morphology of sample 5; with the least ethanol to VTMS molar ratio (i.e. 2.336) was studied by using SEM image (Fig. 5d). The results show agglomeration of nanoparticles in sample 5. A convenient and apparently logical explanation would be to attribute the observed agglomeration to the surface to volume ratio of the nanoparticles. A comparison between sample 4 and sample 5 from Fig. 2 and Fig. 5d respectively, indicates that finer nanoparticles (40 nm) as compared with

Table 5: A summery of the effect of ethanol to VTMS molar ratio on the variation of silver nanoparticle size.

Samples Number	Ethanol (mmol) / VTMS (μmol)	Silver particle size (nm)
1	2.846	230
2	2.635	160
3	2.546	110
4	2.419	68
5	2.336	40

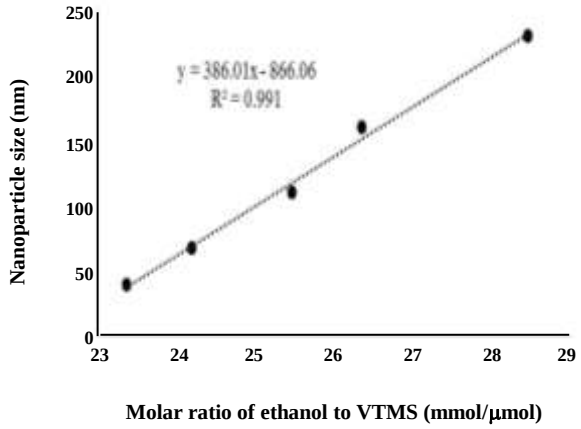

Fig. 6: Variation of mean silver nanoparticle size with respect to an increase in ethanol to VTMS molar ratio.

the coarser ones (68 nm) show substantial increase in surface to volume ratio. The interactive forces between finer nanoparticles are indeed more than those of the coarser nanoparticles. Therefore agglomeration in the finer nanoparticles (Sample 5) will occur. On this basis sample 4 with the ethanol to VTMS molar ratio equal to 2.419 provides optimum fine nanoparticle size. A summary of the above findings is given in Table 5.

Fig. 6 depicts the variation of silver nanoparticle size with respect to changes in the molar ratio of ethanol to VTMS. Based on Fig. 6 mean silver nanoparticle size is directly proportional to the solvent/stabilizer molar ratio. This dependency follows satisfactorily a linear trend (R^2=0.991).

CONCLUSIONS

The analysis of spent X-ray film fixing solution sample reveals 6.51% silver content. Gravimetric analysis shows that approximately 25% of silver content in the spent sample was recovered. Based on the XRD spectrometry analysis 95% purity (i.e. 22.8 karat) in metallic silver was achieved. Prior to the synthesis of silver nanoparticles, the recovered silver converted into silver nitrate. The synthesis of silver nanoparticle was based on chemical reduction method where, silver nitrate was used as precursor. As opposed to the research works addressed in the literature [19] the use of ethanol and VTMS was chosen in the present study. An optimization of the molar ratio of ethanol to VTMS indicated that finer silver nanoparticle sizes can be achieved by choosing 2.419 molar ratio of ethanol to VTMS. The SEM images confirmed the formation of spherical silver nanoparticles in the 50–70 nm size range.

Received : May 11, 2015 ; Accepted : Dec. 21, 2015

REFERENCES

[1] Kubik T., Bogunia-Kubik K., Sugisaka M., NanoTechnology on Duty in Medical Applications, *Curr. Pharm. Biotechnol*., **6** (1): 17-33 (2005).

[2] Modi A., Shukla K., Pandya J., Parmar K., Extraction of Silver from Photographic Waste, *International Journal of Emerging Technology and Advanced Engineering*, India, **2**(11): 599-606 (2012).

[3] Ratanamskul C., Lertviriyaprapa K., Saiyasitpanich p., Appropriate Technology for Silver Removal and Recovery from Spent Bleach-Fix Photographic Solution, "Ninth International Conference of Greening of Industry Network", Bangkok, Jan 21-25, (2001).

[4] Ekpunobi U.E., Okwukogu O.K., Anozie A.I., Ogbuagu A.S., Ajiwe V.I., Nweze C.I., Deposition and Characterization of Silver Oxide from Silver Solution Recovered from Industrial Wastes. *American Chemical Science Journal*, **3**(3): 307-313 (2013).

[5] Sosa Y.D., Rabelero M., Trevino M.E., Saade H., Lopez R.G., High-Yield Synthesis of Silver Nanoparticles by Precipitation in a High-Aqueous Phase Content Reverse Microemulsion. *Journal of Nanomaterials.* Hindawi, **2010**(2) (2010).

[6] Ahlawat D.S., Kumari R., Rachna., Yadav I., Synthesis and Characterization of Sol–Gel Prepared Silver Nanoparticles, *International Journal of Nanoscience*, **13**(01): 1-8 (2014).

[7] Zielińska-Jurek A., Reszczyńska J., Grabowska E., Zaleska A., Nanoparticles Preparation Using Microemullsion Systems, *Poland. Gdansk*, POI: 10.5772/36183, **10**(12): 229-246 (2012).

[8] Cushing B.L., Kolesnichenko V.L., O'Connor C.J., Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles, *Chemical Reviews*, **104**: 3893-3946 (2004).

[9] Saware K., Sawle B., Salimath B., Jayanthi K., Abbaraju V., Biosynthesis and Characterization of Silver Nanoparticles Using Ficus Benghalensis Leaf Extract, *International Journal of Research in Engineering and Technology*. **3** (05): 867-874 (2014).

[10] Lageswari P., Silambarasan S., Abraham J., Ecofriendly Synthesis of Silver Nanoparticles From Commercially Available Plant Powders and their Antibacterial Properties. *Scientia Iranica*. **20**(03): 1049-1054 (2013).

[11] Burda C., Chen X., Narayanann R., El-Sayed M.A., Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev*., **105**: 1025-1102 (2005).

[12] Lu Y.C., Chou K.S., A Simple and Effective Route for the Synthesis of Nano-Silver Colloidal Dispersions. *Journal of the Chinese Institute of Chemical Engineers*, **39**: 673–678 (2008).

[13] Mocanu A., Pasca R.D., Tomoaia G., Garbo C., Franqopol P.T., Horovitz O., Tomoaia-Cotisel M., New Procedure to Synthesize Silver Nanoparticles and their Interaction with Local Anesthetics, *International Journal of Nanomedicine*. **8**:3867-74 (2013).

[14] Kamali M., Ghorashi S.A.A., Asadollahi M.A., as Complexing Agent:Characterization of Nanopartciles and Effect of pH on Size And Crystallinity. *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **31**(4): 21-28 (2012).

[15] Yaqiong Q., Xiaohui J., Jing J., Hong L., Hongli W., Wensheng Y., Size Control Over Spherical Silver Nanoparticles by Ascorbic Acid Reduction, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **372**(1-3): 172-176 (2010).

[16] Debabrata S., Nabajeet B., Kalyanasis S., A Facile Synthesis of High Optical Quality Silver Nanoparticles by Ascorbic Acid Reduction in Reverse Micelles at Room Temperature, *Journal of Colloid and Interface Science*, **413**: 37-42 (2014).

[17] Polte J., Yuaev X., Wuithschick M., Fischer A., Thuenemann A.F., Rademann K., Kraehnert R., Emmerling F., Formation Mechanism of Colloidal Silver Nanoparticles: Analogies and Differences to the Growth of Gold Nanoparticles, *American Chemical Society Nano*., **6**(7): 5791-5802 (2012).

[18] Roucoux A., Schulz J., Patin H., Reduced Transition Metal Colloids: A Novel Family of Reusable Catalysts?, *Chem. Rev.*, **102** (10). 3757(2002).

[19] Farbod M., Batvandi M.R., Fabrication and Size Control of Ag Nanoparticles, *Iranaian Journal of Physics Research*, **12** (1): 77-83 (2012).

[20] Madaeni S.S., Akbarzadeh Arbatan T.,Preparation and Characterization of MicrofiltrationMembrane Embedded with Silver Nano-Particles, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **29** (4): 105-111 (2010).

[21] Rahaman Mollick M.M., Bhowmick B., Maity D., Mondal D., Roy I., Sarkar J., Rana D., Acharya K., Chattopadhyay S., Chattopadhyay D., Green Synthesis of Silver Nanoparticles-based Nanofluids and Investigation of their Antimicrobial Activities, *Microfluidics and Nanofluidics*, **16**(03) 541-551 (2014).

[22] Salehi J.M., Heyhat M.M., Rajabpour A., Enhancement of Thermal Conductivity of Silver Nanofluid Synthesized by a One-step Method with the Effect of Polyvinylpyrrolidone on Thermal Behavior, *Applied Physics Letters*, **102** (23) (2013).

[23] Aghayari R., Madah H., Keyvani B., Moghadassi A., Ashori F., The effect of Nanoparticles On Thermal Efficiency of Double Tube Heat Exchangers in Turbulent Flow, *ISRN Mechanical Engineering*. Hindawi, Article ID 274560, **2014**(10): 1-5 (2014).

[24] Akbari B., Pirhadi Tavandashti M.,Zandrahimi M., Particle Size Characterization of Nanoparticles – A Practical approach, *Iranian Journal of Materials Science & Engineering*, **8**(2): 48-56 (2011).

[25] Aashritha SH., Synthesis Of Silver Nanoparticles by Chemical Reduction Method and their Antifungal Activity, *India*. *International Research Journal of Pharmacy*, ISSN 2230-8407, **4**(10): 111-113 (2013).