

Synthesis of Silver Nanoparticles using Facile Wet Chemical Route

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ABSTRACT

Stable aqueous monodispersed silver nanoparticles were synthesised by reducing silver nitrate using various sugars such as glucose, fructose, lactose, and sucrose at 55-60 °C. A mixture of two stabilising agents, polyvinyl pyrrolidone (PVP) of molecular weight (MW 40, 000) and gelatin plays a decisive part in controlling size and shape of superfine silver nanoparticles. Using PVP, better control of particle size was obtained, whereas a mixture of PVP, and gelatin resulted in sea urchin kind of structure. Effects of several processing parameters such as pH, quantities of alkaline solution, reaction time, concentration of stabilising agent, and the metal/dispersant ratio were investigated. The suspensions were stable for at least one week. Silver nanoparticles can be easily collected by centrifugation on mixing with sufficient amount of acetone. Structural characterisation of synthesised silver nanoparticles was carried out by X-ray diffraction (XRD), which shows that the as-synthesised silver nanoparticles are face-centered cubic crystalline. Chemical characterisations of as-synthesised silver nanoparticles were done using inductively-coupled plasma-optical emission spectrometry (ICP-OES) and LECO gas analysers. The optical properties of silver nanoparticles were monitored using UV-Vis spectrophotometer. Role of stabilising agent in protecting the silver nanoparticles was studied using fourier transform infrared spectroscopy (FTIR). Particle size and distribution were characterised using small-angle X-ray scattering (SAXS), zeta particle size analyser (PSA), scanning electron microscopy, and transmission electron microscopy. The average particle size of the as-synthesised silver nanoparticles was 35 nm.

Keywords: Chemical synthesis, silver nanoparticles, monodispersed, stabilising agents, nanotechnology, polyvinyl pyrrolidone (PVP), gelatin

1. INTRODUCTION

The development of uniform nanometer sized particles has been intensively pursued because of their technological and fundamental scientific importance¹⁻⁶. These nanoparticulate materials often exhibit very interesting electrical, optical, magnetic, and chemical properties, which cannot be achieved by their bulk counterparts⁷⁻¹¹. Synthesis, chemical and physical properties of metal nanoparticles are currently of considerable interest because of their potential application in material science and commercial industries. Owing to the small size of the building blocks and high surface-to-volume ratio, these materials are expected to demonstrate unique properties.

1.1 Synthesis of Nano materials: Different Approches

There are two approaches for synthesis of nanomaterials, bottom-up approach and top-down approach. The top-down approach involves chopping down the bulk metals by mechanical means and the resulting particles are subsequently stabilised by colloidal protecting agents^{12,13}. Application of metal vapour techniques¹⁴⁻¹⁶, which works on this principle, provides a versatile route for the production of a wide range of nanostructured metal colloids on a

preparative laboratory scale^{17,18}. However, this method has a few drawbacks in that it is difficult to obtain a narrow particle size distribution, and installation of metal vapour machines is highly demanding.

On the other hand, bottom-up approach of wet chemical nanoparticle preparation basically relies on the chemical reduction of metal salts, electrochemical pathways, or the controlled decomposition of metastable organometallic compounds in solution. Control over the growth of the primarily formed nanoclusters and their agglomeration is effected using a variety of stabilisers, in the form of donor ligands, polymers, and surfactants. Current nanomaterial research rests heavily on bottom-up approach compared to the top-down approach. The bottom-up approach offers better flexibility and versatility in terms of material design.

The synthesis of nanomaterials from atomic or molecular sources depends on the control of variety of nanoscale attributes desired in the final product. Though a plethora of methods have been reported for the synthesis of metallic nanoparticles, some of them have been extensively studied, because of their ease to apply for large-scale production and also to a wide range of materials. Chemical

synthesis of nanomaterials is a rapidly growing research area with a great potential to make technologically advanced and useful materials. Chemical methods have been widely used to produce nanostructured materials due to their straight forward nature and their potential to produce large quantities of the final product. There are several synthetic procedures for synthesising monodisperse nanoparticles. The particle sizes of the nanoparticles can be controlled by systematically adjusting the reaction parameters, such as time, temperature, and the concentration of reagents and stabilising agents.

Metallic silver, either in bulk or finely dispersed form, displays unique properties normally associated with the noble metals such as chemical stability, excellent electrical conductivity, catalytic activity along with other more specific ones like antibacteriostatic effects, nonlinear optical behavior etc¹⁹⁻³⁰.

1.2 Methods of Preparation of Nanostructured Fibres

Several methods have been used in the past to prepare nanostructured silver particles, including chemical reduction of silver ions in aqueous solutions with or without surfactants^{31,33} electrochemical reduction^{34,35} heat evaporation^{36,37} thermal decomposition in organic solvents³⁸ polyol process³⁹ chemical and photoreduction in reverse micelles⁴⁰⁻⁴⁶ and radiation chemical reduction⁴⁷⁻⁴⁹. All these methods of preparation involve the reduction of relevant metal salts in the presence or absence of surfactants, which is necessary in controlling the growth of metal colloids through agglomeration. From a practical point of view, the method of chemical reduction from aqueous silver nitrate solution is the most preferred for obtaining silver nanoparticles.

Envisaging the various possible defence applications of silver nanoparticles such as anti-microbial fibres for quick healing of wounds and burns, preparation of coloured fabrics and electrically conducting polymer films with interconnected silver particle network for sensor applications^{50,52}. An attempt has been made to synthesise silver nanoparticles using low cost and environmentally friendly chemical route and their further application in preparing polymer based nanocomposites by spin and solution casting are in progress.

The present process yields concentrated and stable dispersions of monodispersed silver nanoparticles in a simple and cost-effective manner, by the reduction of concentrated aqueous solutions of silver nitrate with sugars in aqueous medium. Polyvinyl-pyrrolidone (PVP) and gelatin were selected as suitable dispersants based on preliminary evaluations of the protective ability of several classes of stabilising agents. Effects of alkaline concentration and protective agents on the conversion and subsequent stability of silver colloids were also included. The produced silver nanoparticles were mainly characterised for their particle size distribution to provide information on the optimal conditions of synthesis and sufficient stability against coagulation.

The synthesis of silver nanoparticles was carried out using standard synthetic chemical procedure and commercially available reagents. Silver nitrate ($AgNO_3$) (99.9%), sugars like glucose (99.5%), fructose (99.5%), lactose (99.5%), and sucrose (99.5%) were of high purity grade purchased from Alfa Aesar. Sodium hydroxide (99%), sodium carbonate (99%), acetone, gelatin and PVP (MW ~ 40,000 g/mol) were used as received from Loba Chemie, India. For preparation of all the samples, purified water with cartridges from millipore with a resistivity of 18 Ω M cm was used.

2. EXPERIMENTAL PROCEDURE

Silver nitrate solution of 0.01 M was used as precursor. A predetermined quantity of (1%) PVP (MW~40,000) was then added to silver nitrate solution. The following molar concentrations of various reagents $[Sugars]/[AgNO_3] = 2$, $[NaOH]/[AgNO_3] = 1$ and $[Na_2CO_3]/[AgNO_3] = 0.5$ were kept constant during the reactions. The pH of the reaction solution was kept in between 8.5 to 9.0 throughout the reaction using $NaOH$ and Na_2CO_3 . The reaction mixture was heated in a water bath at 55 °C to 60 °C for 1 hr with vigorous agitation by magnetic stirrer.

On completion of the reduction process, acetone (30 ml) was added to precipitate silver nanoparticles. After washing several times with acetone, the precipitated silver nanoparticles were separated by centrifugation at 6000 rpm for 10 min and subsequently allowed to air dry in a desiccator. The dry silver particles were re-dispersed in de-ionized water using an ultrasonic bath to obtain concentrated dispersions.

Elemental analysis of as-synthesised silver nanoparticles was carried out using inductively coupled plasma-optical emission spectrophotometer (ICP-OES) model (JYULTIMA) and LECO Gas Analysers of model CS-444 and TC-136. The crystal structure of the as-synthesised silver nanoparticles were obtained using PHILIPS-PW3020 diffractometer with a Cu K α radiation source ($\lambda = 1.5418$ Å).

The optical property of silver hydrosol was monitored with a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer. The presence of the polyvinyl-pyrrolidone (PVP) at the surfaces was assessed by fourier transform infrared spectroscopy (FTIR, using Perkin-Elmer FT-IR system, Spectrum GX) in the range of 400-4000 cm^{-1} . The dried silver nanopowders were thoroughly mixed with KBr before the spectrum of the pellet was recorded.

SAXS (Anton Paar-PW3830) was used to calculate size, shape, and size distribution of the silver nanoparticles. The particle size and size distribution of the silver nanoparticles were examined by taking silver dispersions in a quartz tube using Malvern zetasizer 3000 HSA.

The morphology of the particles was examined by Scanning Electron Microscopy (SEM). The samples for SEM analysis were prepared by drying a dispersion of silver nanoparticles on brass holder. The particles were imaged by LEO 440i (SEM) at an accelerating voltage of 20 kV. Elemental analysis of as-synthesised silver nanoparticles were conducted using energy dispersive X-ray microanalysis (EDX).

The samples for TEM were prepared by drying a dispersion of the silver nanoparticles on amorphous carbon-coated copper grids. The particles were imaged using Philips, TECHNAI FE 12 microscope at an accelerating voltage of 120 kV.

3. RESULTS AND DISCUSSION

On reaction with the reducing sugars at 55°C to 60°C for 1 h, the colourless silver nitrate solution turned yellowish, indicating the reduction of Ag^+ to Ag^0 . The nanoparticles were analysed for chemical composition using ICP-OES and silver content was found to be 99.5 per cent. Carbon, nitrogen, and oxygen were found as the main impurities in the produced silver nanoparticles. Elemental analyses of the as-synthesised silver nanoparticle powder were performed by LECO instruments. The carbon, nitrogen, and oxygen content were in the range of 0.1–0.3 per cent, 0.01–0.02 per cent, and 0.01–0.03 per cent, respectively.

Fig. 1 shows that the XRD pattern of the as-prepared silver nanoparticles capped with surfactants. The XRD patterns of the silver nanoparticles synthesised using various sugars exhibit five sharp peaks in the diffractogram which indicates that the silver nanoparticles are crystalline in nature. The peaks at $2\theta = 38.36, 44.55, 64.69, 77.54$, and 81.54 reveal that it is a facecentered cubic (fcc) structure. The discernible peaks can be indexed to (111), (200), (220), (311) and (222) planes of a cubic unit cell, which corresponds to cubic structure of silver (JCPDS card. No. 89-3722). Crystallite size calculations were done using Scherrer equation and results are given in the Table 1. The crystallite size was the least when lactose was used as reducing agent. Therefore, lactose was employed as a reducing agent for further studies.

These are two possible mechanisms can occur during the reaction.

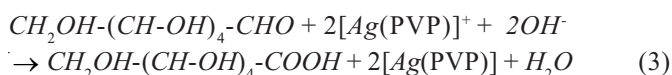
Table 1. Crystallite sizes of synthesised silver nanoparticles in the presence of PVP as protecting agent using, (a) glucose, (b) fructose, (c) lactose, and (d) sucrose

Sugars used	Crystallite size (nm)
Glucose	18
Fructose	17
Lactose	14
Sucrose	18

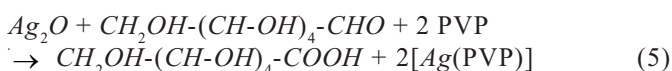
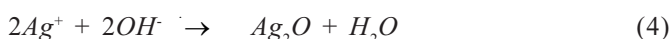
Possible Reaction Mechanism

The stoichiometric reaction between sugars and silver ion in an alkaline solution can be written as

• Reaction Path I



• Reaction Path II



In reaction path I, eqns (1) and (2) show that PVP was compounded with Ag^+ and H^+ respectively and then hydroxyl ion may undergo a nucleophilic addition reaction to $-CHO$ group producing hydride and $-COO^-$ ions⁵³. The hydride ions then reduce silver ion to silver atom. In reaction path-II, Ag^+ reacts with OH^- ions to form Ag_2O , which subsequently gets reduced by sugars to produce silver nanoparticles, as shown in eqns (4) and (5)⁵⁴. The relative molar ratio of sugars-to-silver precursors was kept at 2 throughout this study to allow the reaction to complete.

3.1 Effect of pH

The pH of the reaction mixture plays an important role during the reaction process. At acidic pH, path I of the reaction mechanism is followed and with increase of the pH path II becomes dominant. Therefore, to obtain a uniform particle size and narrow distribution, the pH of the reaction was maintained between 8.5–9.0 throughout this study.

3.3 Effect of Sodium Hydroxide Concentration

When $NaOH$ was used to promote the reduction reaction, it had an adverse effect on particle agglomeration. The precursor solution would quickly turn to yellow, colour upon $NaOH$ addition and then gradually change into light brownish as the reaction proceeds. Presumably the yellow colour suggested that the silver ion was reduced into extremely fine silver particles, and its slow change to brown colour indicates the gradual agglomeration into certain stable size distribution in the presence of PVP molecules.

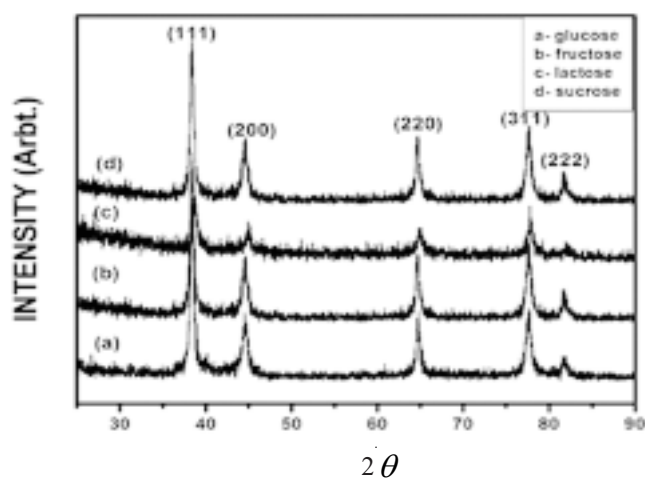


Figure 1. XRD diffraction patterns of the synthesised silver nanoparticles in the presence of PVP as protecting agent using (a) glucose, (b) fructose, (c) lactose, and (d) sucrose.

When only $[NaOH]/[AgNO_3] = 1$ was added, the pH decreased to 5.8. The reducing power of sugars was poor under this condition. For comparison, when $[Na_2CO_3]/[AgNO_3] = 0.5$ was added in addition to $NaOH$, the pH of the solution remained in between 8.5 to 9.0. These results demonstrate the importance of solution alkalinity to the reducing power of sugars.

3.4 Effect of Sodium Carbonate Concentration

The reduction pathway significantly alters upon the addition of sodium carbonate. First, a white precipitate is observed which indicates the formation of Ag_2CO_3 . Later, the carbonate ion gets hydrolyzed, releasing the Ag^+ ion which is subsequently reduced to Ag^0 . Now that the carbonate concentration has reduced, further dissolution of Ag_2CO_3 to their respective ions is facilitated. This process continues till all the Ag^+ converts to Ag^0 . This mechanism has an added advantage over the reduction in only alkaline solution. In alkali solution reduction, all the silver ions get reduced quickly, thereby PVP does not have enough time to protect the particles efficiently, whereas in the Ag_2CO_3 complex, a time lag in reduction enhances the effective binding of the polymer onto the surface, and henceforth, a better control over particle size and distribution is achieved.

Although a higher pH is favoured for higher reducing power, however, it showed an adverse effect on particle size. When large amount of $NaOH$ was added to the reaction system the silver colloids became larger precipitate and settled at the bottom. As a compromise, a weak base such as sodium carbonate was added along with $NaOH$. The intention here was to release hydroxyl ions only when the pH becomes lower. When more Na_2CO_3 was added, the solution pH would become higher and that was detrimental to the stability of the silver colloid.

3.5 Effect of Reaction Temperature

The influence of temperature on the reducing ability of sugars is obvious. The particle sizes of the as-synthesised silver nanoparticles with varying reaction temperature were measured using zeta particle size analyser. In Fig. 2 the average particle sizes of the silver nanoparticles were plotted against the reaction temperature. As reaction temperature increased from 30 °C to 60 °C, the particle size decreased. This could be attributed to the increased reduction capability of sugars at higher temperatures. Therefore, more amounts of silver nuclei were occurred, and then smaller particles were formed. The influence of reaction temperature on dispersibility of silver nanoparticles is ignorable.

3.6 Effect of Stabiliser

For preparing ultrafine powder using chemical reduction method, it is important to choose appropriate stabiliser. The stabiliser adsorbs on the solid-liquid interface and forms a layer of molecular membrane to hinder the intercontact between the particles. At the same time, it reduces surface tension by reducing the absorption capability. In this work,

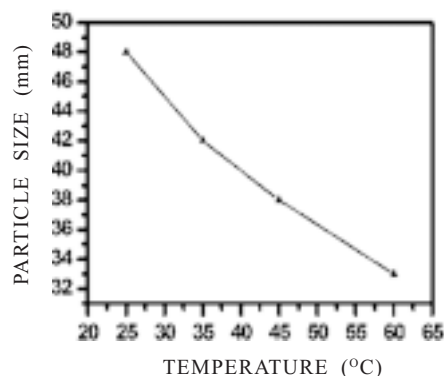


Figure 2. Particle size vs temperature plot for silver nanoparticles synthesised in the presence of PVP using lactose as reducing agent at pH =8.5-9.

the water-soluble polymer polyvinyl-pyrrolidone (PVP) was employed as a stabilising agent. The use of dispersant served two purposes, one is to generate complex compound with silver ion, and control the process of the reaction; to protect the particles from growth and agglomeration. The average particle size of silver powder decreases linearly with increase in PVP concentration.

When PVP was added to the silver nitrate solution, it was noticed that the pH would decrease to some extent as PVP is actually a weak acid. This result suggested that PVP molecules are capable of combining with hydroxyl ions. This interaction would then reduce the effective quantity of PVP towards protection of silver nanoparticles. This possible competition may explain that under a high pH condition, the silver nanoparticles would agglomerate into larger particles due to less free PVP molecules.

On addition of gelatin, the morphology of the silver particles changed from spherical to sea urchin kind of shape [(Fig. 7 b)] and the stability period of the silver nanoparticles increased to one month.

3.7 Effect of Mixing Speed of Reactants

When the reactants are mixed, the generated silver nanoparticles needed time to disperse in the solution, and surfactants also needed time to form a protecting layer. If mixing speed is too high, larger particles are formed.

When the speed is about 1 drop per second, the nanoparticles can disperse sufficiently before the new particles are generated, but if the speed was too slow, the reaction time increases and the particles will impact with each other and agglomeration due to Brownian motion will occur.

Due to smaller size, the colloid was quite difficult to separate from the mother solution by ordinary centrifuge. These colloids were easily be separated from the solution through centrifugation after the solution was mixed with at least the same amount of acetone. Due to poor solubility of PVP in acetone, the PVP protected silver nanoparticles agglomerate under this condition and make the separation easier. This study has demonstrated that stable dispersions of silver nanoparticles can be rapidly prepared by reduction of silver nitrate with reducing sugars in the presence of

a mixture of stabilisers - gelatin and polyvinyl-pyrrolidone (PVP).

The formation of silver nanoparticles is characterised further in terms of the optical absorption spectrum, as shown in Fig. 3. On addition of reducing sugars to the silver solution containing PVP a broad band with average absorption maximum wavelength at 420 nm appears, which shows the surface electrons on the surface induced by incident light.

Figure 4 shows the FT-IR spectra of polyvinyl-pyrrolidone (PVP) and silver nanoparticles protected by PVP. From figure it can be observed that the resonance peak of $C=O$ at 1643 cm^{-1} in pure PVP and PVP protected silver

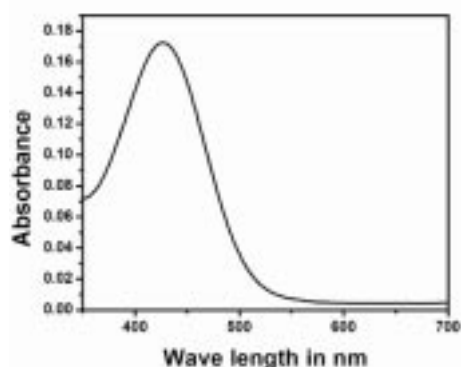


Figure 3. UV-Vis spectrum of silver nanoparticles synthesised in the presence of PVP using lactose as reducing agent at $60\text{ }^{\circ}\text{C}$ ($\text{pH} = 8.5\text{--}9$).

nanoparticles have no considerable change. The band at 1020 and 1075 cm^{-1} in pure PVP corresponds to the C-N bending modes and the same were strengthened and shifted to 1035 and 1077 cm^{-1} respectively in case of PVP protected silver nanoparticle spectra. Even the $N-O-H$ peak at 1286 cm^{-1} has reduced intensity when compared to pure PVP. From these observations it could be inferred that the oxygen atom of $C=O$ is free in both the cases, but shift in C-N bond indicates the coordination of nitrogen atom to the silver nanoparticles surface. This is because of the ease of donation of lone pair electrons of nitrogen when compared to the oxygen as the latter being more electronegative. As a result the nitrogen atom has coordinated to the silver nanoparticles, and henceforth providing stability to the nanoparticles and preventing it from further growth and agglomeration.

The SAXS experiment was carried out for the aqueous dispersion of silver nanoparticles. Pair distance distribution function (PDDF) $p(r)$ has been calculated from the scattering data using the programme GIFT. The $p(r)$ is the fourier inversion of the scattering curve and defined as $[(1/2p^2) * \int_0^r I(q) \cdot q \cdot dq]$, where r is the distance or radius of the particles.

Fig. 5 (a) shows the pair distance distribution functions as a function of r . The shape of the $p(r)$ vs r curves also resembles that the particles are spherical. The PDDF curves also reveal that the shape of the silver nanoparticles is

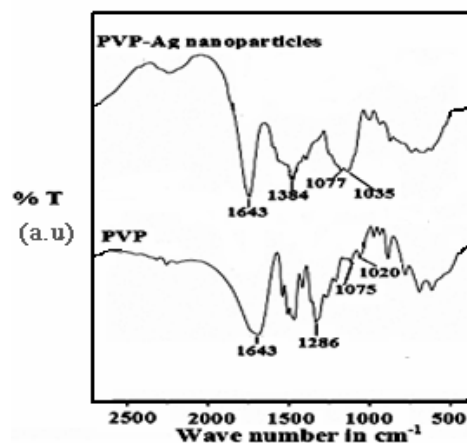


Figure 4. FT-IR spectrum of PVP and silver nanoparticles synthesised in the presence of PVP using lactose as reducing agent at $60\text{ }^{\circ}\text{C}$ ($\text{pH} = 8.5\text{--}9$).

spherical and average particle size is around 33 nm . It is to be noted that the PDDF curve does not show the presence of inhomogeneity in the as-synthesized silver nanoparticles. The approximation curve of the silver nanoparticles is shown in Fig. 5(b). The solid line is the best fit to the data. This value is in good agreement with the average particle size obtained from TEM measurement. The particle size and size distribution of the PVP protected silver nanoparticles were examined using zeta particle size analyzer. Fig. 6 shows the particle size distribution of PVP protected silver nanoparticles obtained from zeta particle size analyzer. The average particle size is around 32 nm which is in good agreement with SAXS results.

The main advantage of SAXS over particle size analyzer is that particle size analyzer can only provide the information on the size of particles present in the sample, whereas SAXS gives the additional information of particle shape and morphology. It can detect regular shapes such as sphere, rods from irregular shapes. When compared to TEM the advantage lies in the fact that larger quantities of the samples are analyzed in SAXS, so it gives a better representation of the whole sample.

Figure 7 (a) shows the SEM images of silver nanoparticles prepared using PVP only. From SEM images it is observed

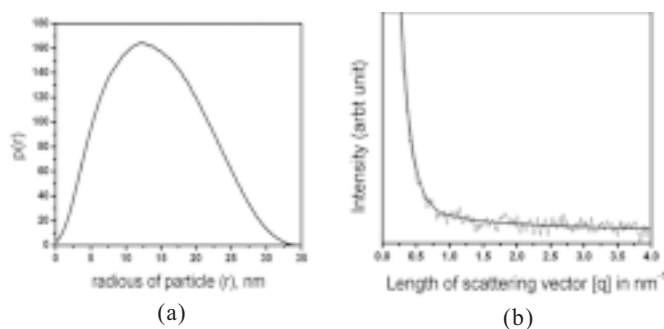


Figure 5. (a) Pair distance distribution function curve of silver nanoparticles synthesised in presence of PVP using lactose as reducing agent at $60\text{ }^{\circ}\text{C}$ ($\text{pH} = 8.5\text{--}9$), and corresponding (b) approximation curve.

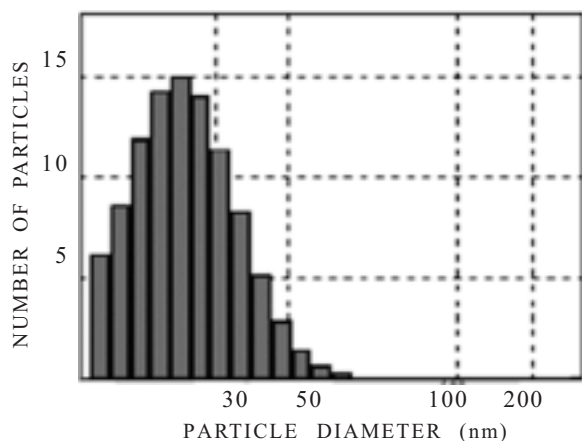


Figure 6. Particle size distribution of silver nanoparticles synthesized in presence of PVP using lactose as reducing agent at 60 °C (pH =8.5-9).

that the silver nanoparticles had a relatively narrow size distribution and a shape close to spherical. Fig. 7 (b) is the EDX spectrum excited by an electron beam with 20kV. It shows the elemental peaks of Ag, C and O. From EDX it was confirmed that there is little amount of C and O impurities. The appearance of C and O peaks can be attributed to the presence of PVP coating on the surface of silver nanoparticles.

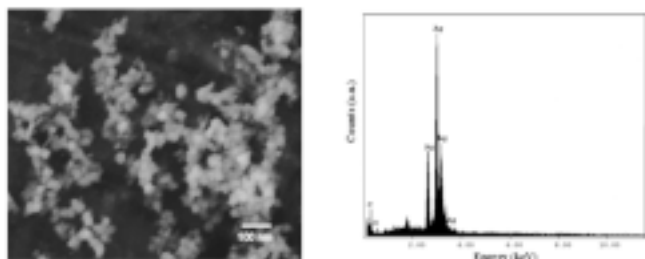


Figure 7. SEM image of the silver nanoparticles synthesized using lactose as reducing agent at 60 °C (pH = 8.5-9) in presence of (a) PVP as surfactant and (b) EDX spectrum.

Figure 8 (a) shows the SEM images of silver nanoparticles prepared using a mixture of surfactants PVP and gelatin and they show a sea urchin shape with relatively narrow size distribution. 8(b) is the EDX spectrum which shows the elemental peaks of Ag, O and C. From EDX it was confirmed that there is no other impurities except carbon and oxygen. The appearance of C and O peaks are due to mixture of surfactants PVP and gelatin present on surface of silver nanoparticles.

Figure 9 shows TEM images of the silver nanoparticles with PVP as stabilizer. The silver nanoparticles obtained are very uniform in size and spherical in shape. The average size of the prepared silver nanoparticles was 35 nm.

4. CONCLUSIONS

Well-dispersed crystalline silver nanoparticles were successfully synthesized by chemical reduction of silver

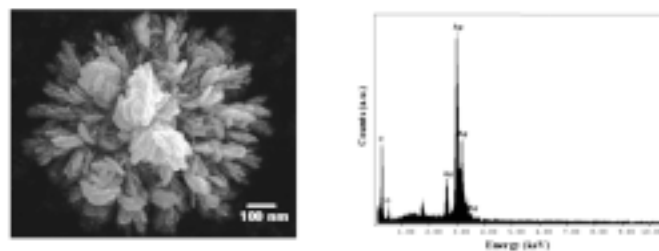


Figure 8. SEM image of the silver nanoparticles synthesised using lactose as reducing agent at 60 °C (pH =8.5-9) in presence of; (a) mixture of surfactants PVP and gelatin, and (b) EDX spectrum

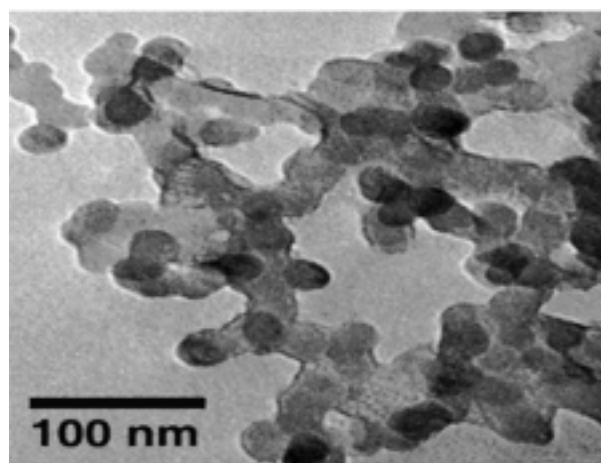


Figure 9. TEM image of the silver nanoparticles synthesized in presence of PVP using lactose as reducing agent at 60 °C (pH = 8.5-9).

nitrate using reducing sugars in presence of protective agents. The addition of sodium hydroxide enhanced the reaction speed. It was found that the addition of sodium carbonate played an important role in determining the particle size and stability. Increase of solution pH increased the reducing power of sugars. However, more alkaline solution would reduce the effectiveness of the protective agent. When the mixing speed of the reactant was about 1 drop per second, the colloid got excellent dispersing ability. The obtained silver nanoparticles are crystalline fcc structure. The average particle size of silver nanoparticles produced by sugars is around 50-to-100 nm as evidenced from the literature, compared to an average particle size of 35 nm by the present method.

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