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Environmental synthesis of silver nanoparticles using hydroxypropyl starch and their characterization

M.H. El-Rafie[b], M.E. El-Naggar[a,b], M.A. Ramadan[b], Moustafa M.G. Fouda[a,b,*], Salem S. Al-Deyab[c], A. Hebeish[b]

[a] Strategic Center for Diabetes Research, Nanotechnology Department, King Saud University, P.O. Box 245, Riyadh 11411, Saudi Arabia
[b] Textile Research Division, National Research Center, P.O. Box 12622, Dokki, Giza 12522, Egypt
[c] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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ABSTRACT

Silver nanoparticles (AgNPs) were synthesized in an alkaline aqueous solution of silver nitrate ($AgNO_3$)/hydroxypropyl starch (HPS) using chemical reduction method. HPS is water soluble/biocompatible starch derivative which play a dual rule as reducing agent for silver ions and as stabilizing agent too for the formed AgNPs. The influences of the reaction parameters, such as the concentrations of HPS and $AgNO_3$, pH, temperature, and duration of the reaction medium on the size and agglomeration of the formed AgNPs were studied. The formation of AgNPs has been confirmed with ultraviolet–visible spectra and transmission electron microscopy (TEM) images. The diameter range of well stabilized AgNPs solution with a concentration of 500 ppm of a diameter of 6–8 nm was obtained. The obtained AgNPs remain without aggregation for more than six months. The advantage of this methodology is that it is possible to prepare AgNPs without any organic solvents or other reducing agents.

1. Introduction

Nowadays special focus on “green chemistry” by researchers is strongly created as a result of increasing awareness about the environment. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy (Poliakoff & Anastas, 2001; Raveendran, Fu, & Wallen, 2006). Nanomaterials have wide-ranging implications in a variety of areas, including physics, chemistry, electronics, optics, materials science and the biomedical sciences (Alivisatos, 1996). The success of nanomaterials relies not only on the size and shape-controlled distribution but also on the preparative routes. Regardless of the preparative method, metal nanoparticles have the tendency to form large clusters or aggregates that lead to precipitation.

The AgNPs form exhibits strong cytotoxicity towards a broad range of microorganisms and its use as an antibacterial agent is well known (Frattini, Pellegri, Nicastro, & De Sanctis, 2005; Textor, Fouda, & Mahltig, 2010). Recently researchers developed a skin gel made of AgNPs that improve the treatment of burns and speed up healing (Jain et al., 2009). Research indicates that silver is also effective in purification of water or air (Palapparambil, Debajyoti, & Prafulla, 2010; Qilin et al., 2008). The reduction of silver ions (Ag^+) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers (Virender, Sharma, Yngard, & Yekaterina, 2009). Initially, the reduction of various complexes with Ag^+ ions leads to the formation of silver atoms (Ag^0), which is followed by agglomeration into oligomeric clusters (Kapoor, Lawless, Kennepohl, & Meisel, 1994). These clusters eventually lead to the formation of colloidal Ag particles (Kapoor et al., 1994).

A variety of preparation routes have been reported for the preparation of metallic nanoparticles (Pal, Shah, & Devi, 2007), notable examples include, reverse micelles process (Xie, Ye, & Liu, 2006), salt reduction (Pillai & Kamat, 2004), microwave dielectric heating reduction, ultrasonic irradiation (Salkar, Jeevanandam, Aruna, Koltypin, & Gedanken, 1999), radiolysis (Soroushian, Lampre, Belloni, & Mostafavi, 2005), solvothermal synthesis (Starowicz, Stypula, & Banaoe, 2006), electrochemical synthesis (Zhu, Liao, Zhao, & Hen, 2001).

Most of the synthetic methods reported to date rely heavily on the use of organic solvents and toxic reducing agents like hydrazine (Sakai, Kanda, Shibata, Ohkubo, & Abe, 2006), N,N-dimethylformamide (Pastoriza-Santos & Liz-Marzan, 2002), and sodium borohydride (Van Hyning, Klemperer, & Zukoski, 2001). All these chemicals are highly reactive and pose potential envi-

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[*] Corresponding author at: Strategic Center for Diabetes Research, Nanotechnology Department, King Saud University, P.O. Box 245, Riyadh 11411, Saudi Arabia. Tel.: +966 560773127; fax: +966 14725682.
E-mail addresses: mmfoudah@ksu.edu.sa, m_gaballa@yahoo.com (M.M.G. Fouda).

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ronmental and biological risks. Earlier reports have dealt with natural polymers like chitosan (Huang & Yang, 2004), heparin (Huang & Yang, 2008) and soluble starch (Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006) as reducing and stabilizing agent for preparation of AgNPs.

The aim of the present work is to develop a simple and effective one-pot totally green approach towards the rapid synthesis and stabilization of AgNPs with well-defined size using HPS as reducing agent for silver ions and in the same time as stabilizing agent for the synthesized AgNPs. It is possible to synthesize nanoparticles with size 4–8 nm even at relatively low temperatures in short reaction time (15 min) without using complicated systems and without any other intermediate steps.

2. Experiment

2.1. Chemicals

Hydroxypropyl starch (HPS) with molar substitution (MS = 0.84), silver nitrate ($AgNO_3$, 99%), were provided from Sigma–Aldrich/Germany. All glassware was washed by ultrasonication in a mixture of distilled water and non-ionic detergent, followed by thorough rinsing with distilled water and ethanol for many times to get rid of any remnants of non-ionic detergent and dried prior to use.

2.2. Characterization techniques of silver nanoparticles

2.2.1. Ultra violet–visible (UV–vis) spectra

Ultra violet–visible (UV–Vis) spectra have been proved to be quite sensitive to the formation of silver colloids because AgNPs exhibit an intense absorption peak due to the surface plasmon excitation (it describes the collective excitation of conduction electrons in a metal). AgNPs embedded in HPS were recorded in spectra 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. A solution containing HPS was used as the blank.

2.2.2. Transmission electron microscope (TEM)

Particle shape and size were obtained by means of TEM; JEOL-JEM-1200. Specimens for TEM measurements were prepared by placing a drop of colloid solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average diameter of the AgNPs was determined from the diameter of 100 nanoparticles found in several arbitrarity chosen areas in enlarged microphotographs.

2.3. Synthesis of Ag nanoparticles

Silver nanoparticles were prepared by a simple wet chemical method. Water soluble hydroxypropyl starch (HPS) having molar substitution (MS; 0.84 (at this value, HPS becomes completely soluble in H_2O)) was dissolved in 100 mL distilled water and brought to heating at different temperature for some minutes; then different amounts of prepared $AgNO_3$ solution was added dropwise to it. Synthesis of HPS is described previously in details by El-Naggar (2008). Factors affecting the reduction efficiency and stability as well as shape and size of the formed silver nanoparticles along with mechanisms involved are given below.

3. Results and discussion

3.1. Reaction mechanism of nano-sized silver colloid

Previous reports (Goia, 2004; Guang, 2007) have disclosed that the solutions of polymers can be used for the synthesis and stabilization of nanoparticles. Linear as well as denderitic polymers have been successfully used for nanoparticles synthesis. Polyhydroxylated macromolecules present interesting dynamic supramolecular associations facilitated by inter- and intra-molecular hydrogen bonding resulting in molecular level capsules, which can act as templates for nanoparticles growth.

Hydroxypropylation of starch has impact depression on its gelatinization tendency, resistance to dispersion breakdown and complete solubility in water. Hydroxypropyl starch macromolecules consist of chemically modified linear polymeric polysaccharide (amylose) and highly branched one (amylopectin) in addition to reducing aldehydic end groups and the newly introduced secondary alcoholic groups. All these components with their anionic and reducing properties support the utilization of hydroxypropyl starch as reducing and stabilizing agent for the synthesis of AgNPs.

For the synthesis of AgNPs, the generally accepted mechanism suggests a two-step process, i.e. atom formation and then polymerization of the atoms. In the first step, a portion of metal ions in a solution is reduced by a suitable reducing agent. The atoms thus produced act as nucleation centres and catalyze the reduction of the remaining metal ions present in the bulk solution. Subsequently, the atoms coalesce leading to the formation of metal clusters. Since the binding energy between two metal atoms dimerize or associate with excess ions. The surface ions again reduce and in this way the aggregation process does not cease until high values of nuclearity are attained, which results in larger particles. The process is stabilized by the interaction with the polymer so preventing further coalescence and aggregation (Goia, 2004).

3.2. Effect of pH of reaction medium

Hydroxypropyl starch (HPS) plays dual role during the preparation of nano-sized silver particles. The first is to generate complex compound with the silver ions and control the reduction process. The second is to protect the particles from agglomerations. Different concentrations of HPS as well as molar substitutions (MS) were studied (El-Naggar, 2008) and the optimum condition for HPS was 9 gm/l and 0.84 MS. It was observed that using this concentration can reduce all silver ions in addition to formation of more stabilized AgNPs. Contrary, using HPS concentrations of 3 or 6 gm/l cannot either reduce silver ions completely or protect the formed AgNPs from aggregation.

HPS (0.9 g) was dissolved in distilled water using heating magnetic stirrer. After complete dissolution, the pH was adjusted to: 2, 5, 9 and 12 respectively using dilute sulphuric acid and sodium hydroxide while the temperature was maintained. At this end, silver nitrate (0.1 N) was added dropwise (1 ml each). Keeping in mind that the total volume of the reaction is 100 ml. The reaction was allowed to proceed under continuous stirring whereby silver colloids were obtained and the latter was monitored by UV–vis absorption spectroscopy after 15 min of its preparation.

Fig. 1 shows the UV–vis spectra of the AgNPs obtained using HPS as reducing and stabilizing agent at different pH's. The results bring into focus a number of observations which may be summarized as follows: (a) increasing the pH of the solution is accompanied by appreciable changes in the electronic absorption spectra; (b) a band at higher energy i.e. 285 nm appears at pH 2, the intensity of this band decreases by increasing the pH up to 9, (c) further increase in the pH of the reaction medium up to pH 12 leads to disappearance of this band, (d) simultaneously another band at 405 nm starts to appear and reaches its maximum intensity at pH 12, and (e) when the range of pH 9–12 is targeted, the band becomes stronger and symmetrical, with a pronounced bell shape at λ_{max} 405 nm. This band could be assigned to the plasmon resonance of AgNPs.

The behavior caused by the observations stated above could be attributed to: (i) the formation of various ionic states of silver

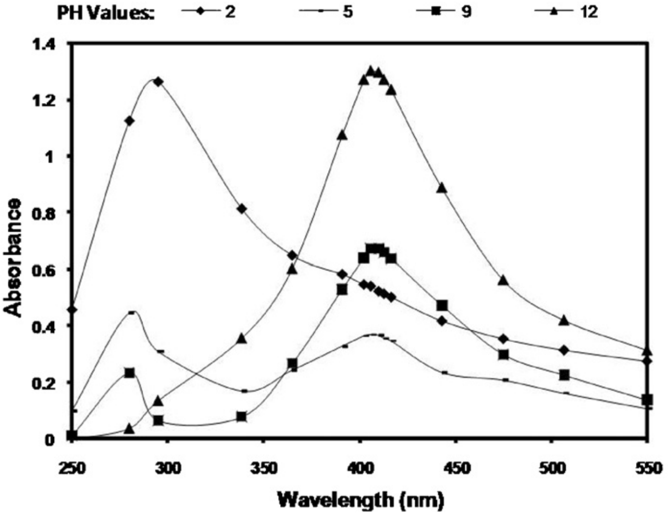

Fig. 1. UV–vis spectroscopy of silver nanoparticles prepared at different pH's.

such as Ag^+, Ag^{2+} and Ag^{3+} (Khanna, Singh, Kulkarni, Deshmukh, & Charan, 2007) bound to negatively charged surface of HPS polymer which appears as the absorption band 285 nm, (ii) increasing the pH enhances the reduction of silver ions to Ag^0, (iii) the reductive properties of HPS are substantially enhanced owing to the base hydrolysis with the formation of low molecular weight reducing fragments, and (iv) maximum intensity of the plasmon peak (405 nm) at pH 12 indicate full reduction of Ag ions (Raveendran et al., 2006) and, therefore, reflecting the dual role of HPS as stabilizing and efficient reducing agent in alkaline medium.

3.3. Reaction duration and temperature

Fig. 2 shows the UV–vis absorption spectroscopy of AgNPs prepared at different temperatures (30, 70, and 90 °C) using initial pH 12 for 15 min. It is clear from the data that (a) the temperature plays the important role to both reduction reaction and particle size, (b) when the reaction temperature was 30 °C the colour of the solution was light yellow, and the intensity of the plasmon band was weak and very broaden around 405 nm which indicate lower conversion percentage of Ag^+ to Ag^0, (c) raising the reaction temperature up to 70 °C is accompanied by formation of deep yellow colour and the absorption band at 405 nm becomes stronger and narrower which means higher conversion of Ag^+ to Ag^0 with smaller nanoparticles size and (d) further increases in the reaction temperature to 90 °C leads to higher absorption intensity with concomitant wavelength shifted towards larger wavelength band (415 nm), indicating that larger nanosized silver were formed.

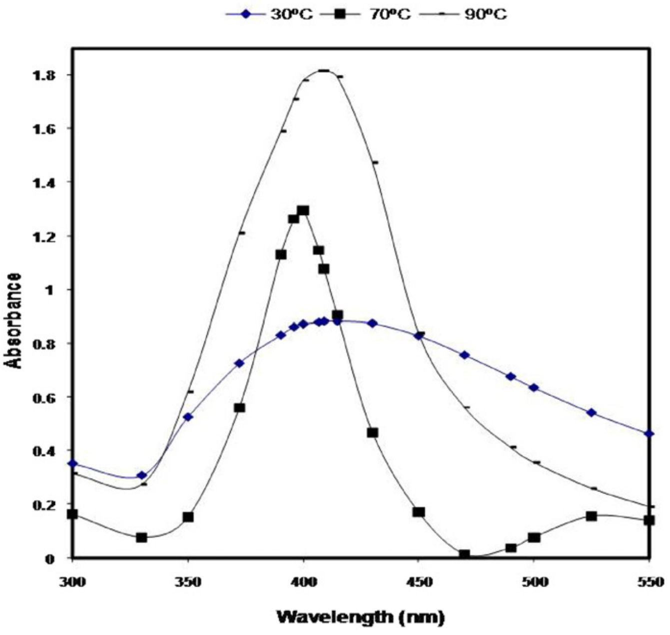

Fig. 2. UV–vis absorption spectroscopy of the silver nanoparticles prepared at different temperatures.

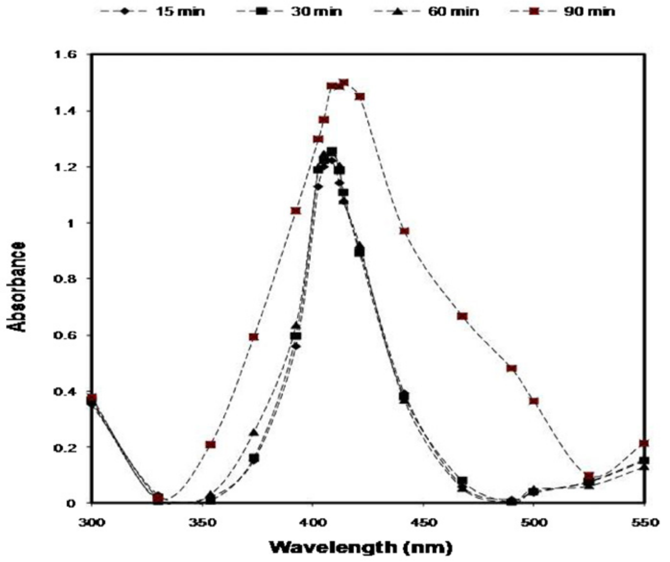

Fig. 3. Shows the UV–vis absorption spectroscopy for silver nanoparticles at different duration.

Fig. 3 shows the UV–vis absorption spectroscopy for AgNPs at different durations: 15, 60 and 90 min. Prolonging the reaction duration from 15 to 60 min for samples prepared at 70 °C leads to marginal increase in the plasmon intensity indicating that all silver ions are reduced and are used for cluster formation, (iii) further increase in the reaction duration up to 90 min is accompanied by unexpected enhancement in the absorption intensity and shift the band towards longer wavelength (415 nm) which could be attributed to enlargement in the AgNPs size.

3.4. TEM and histogram of silver nanoparticles prepared at different durations

To confirm the results obtained from the UV–vis absorption spectroscopy, the size determination and size distribution of AgNPs were further established by recording TEM of silver colloids prepared by HPS as reducing and stabilizing agent.

Fig. 4 shows TEM images of AgNPs prepared at 70 °C for different duration, viz., 15, 60 and 90 min respectively. TEM images of AgNPs at an earlier stage, i.e., 15 min, exhibit smaller sized spherical particles (Fig. 4a and b). The histogram (Fig. 4b) clearly illustrate that the prepared particle size seem to be around 2–8 nm. Fig. 4c and d shows that AgNPs prepared at 70 °C for 60 min exhibit particles of diameter 10–15 nm. Fig. 4e, on the other hand, discloses that AgNPs prepared at 70 °C for 90 min have particle size around 50 nm but highly aggregated. Fig. 5a and b shows the TEM image and the histogram of the size distribution of AgNPs prepared at temperature 90 °C for 15 min. The figures depict that the AgNPs are not homogeneous in size and about 55% ranges from 10 to 200 nm.

Obviously, the reaction duration and temperature play an important role in the reduction and stabilization processes involved

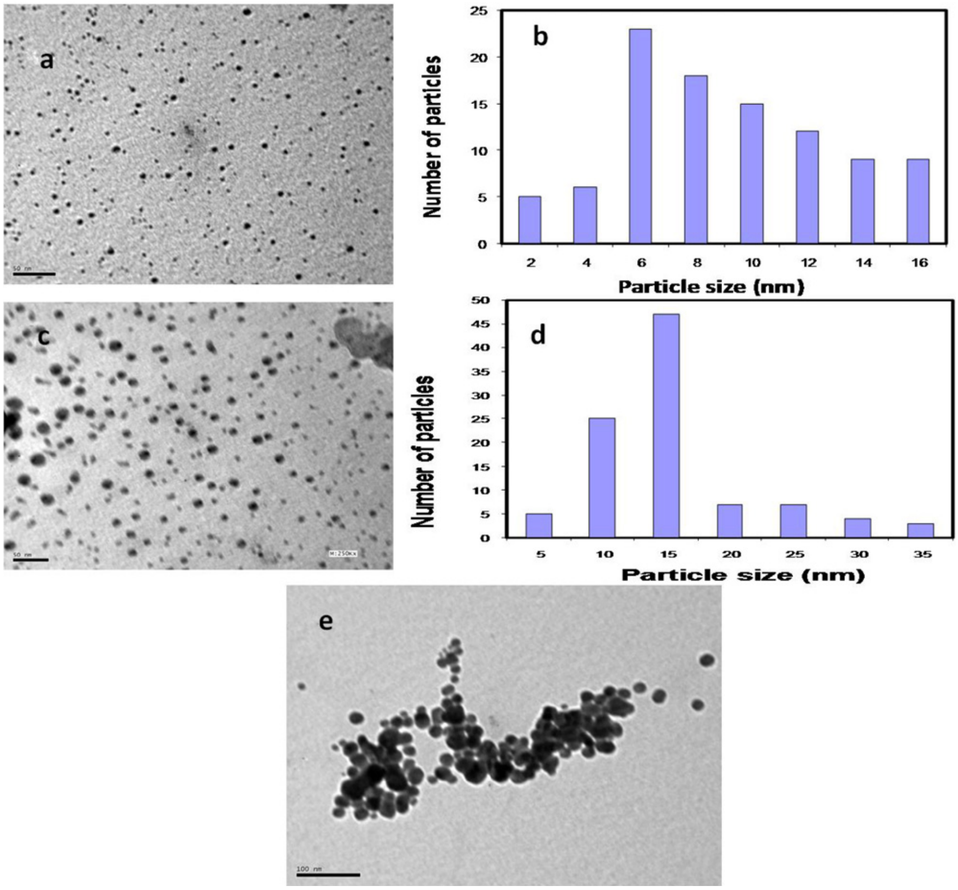

Fig. 4. TEM micrograph and histogram of the silver nanoparticles: (a and b) 15 min, (c and d) 60 min, and (e) 90 min.

in preparation of nano-sized silver particles. The following statements speak of this: (1) at low temperature (30 °C) the reduction efficiency is low even by prolonging the duration of reaction; (2) higher temperature (70 °C) for 15 min facilitates the complexation of silver ion to hydroxyl groups of the molecular matrix, accelerate the reduction process by aldehyde and secondary alcoholic groups and expand HPS molecules making it more accessible for AgNPs to get embedded and stabilized with the formation of particle size within the range of (2–8 nm) and; (3) prolonging the duration and raising the temperature above this limit leads to increase in the kinetic energy of the newly formed silver nanoparticles, as a result the collision frequency between the particles also rises and this leads to higher rate of agglomerations.

3.5. *Concentration of silver nitrate*

Results of the foregoing section made it possible to prepare silver nanoparticles solutions with a concentration (100 ppm). This concentration is rather low for industrial applications. Interest in preparation of AgNPs solutions, which acquire higher concentrations of the nano-sized silver particles are, therefore, stimulated. Thus a study was undertaken where silver nitrate ($AgNO_3$)

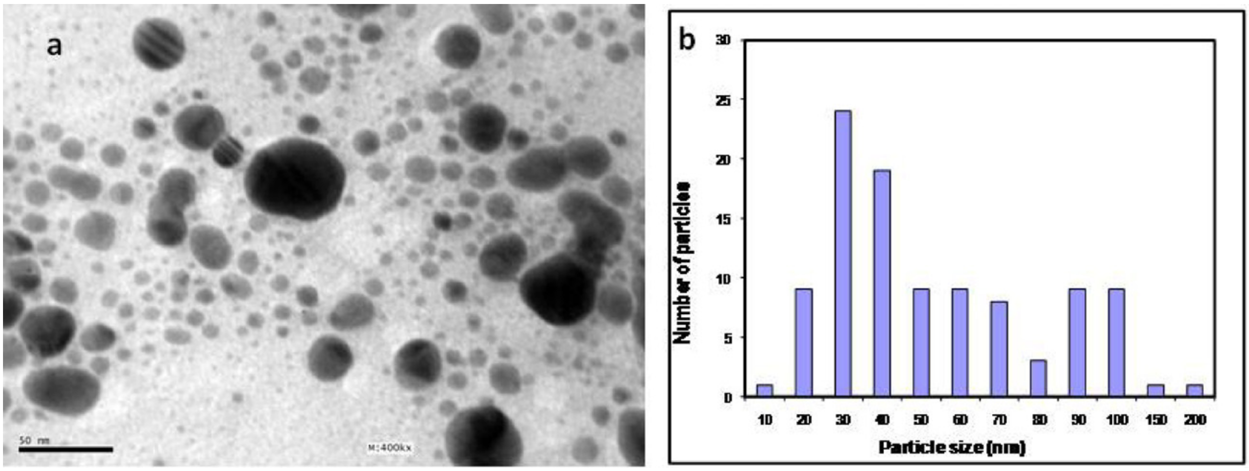

Fig. 5. (a) TEM micrograph and (b) histogram of silver nanoparticles prepared at 90 °C.

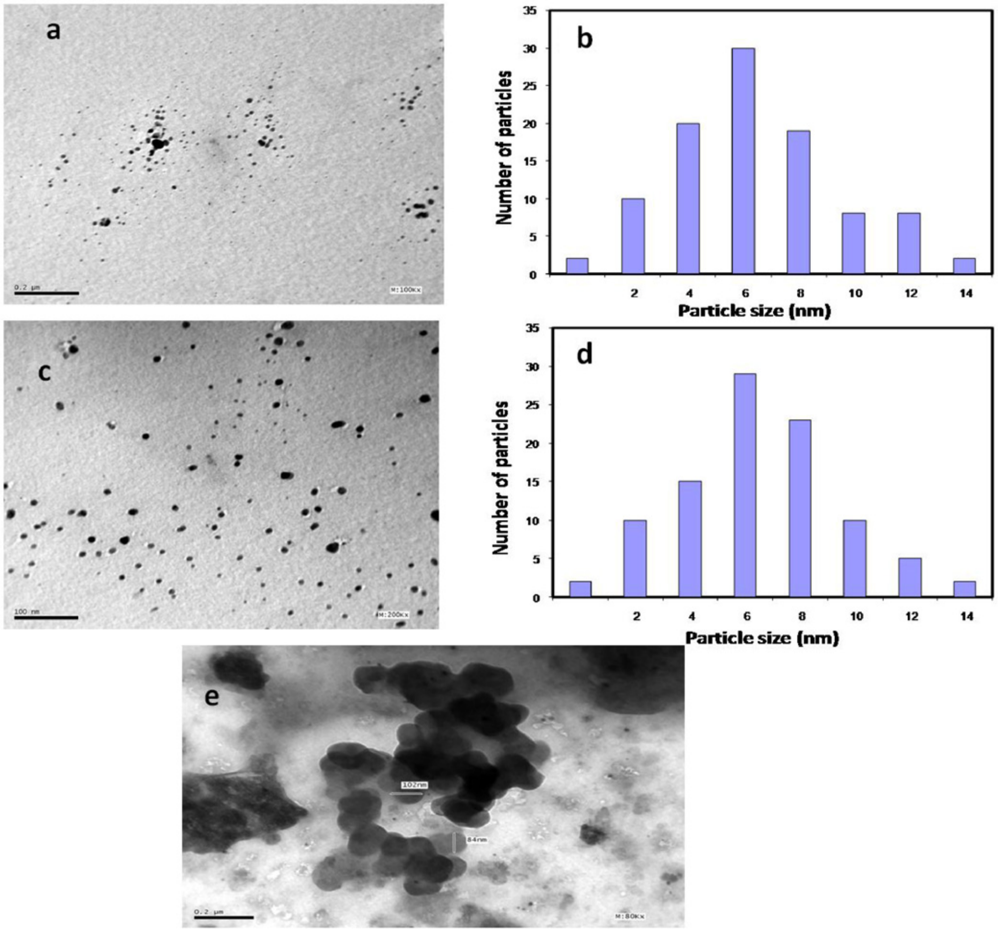

Fig. 6. TEM micrograph and histogram showing the particle size and particle size distribution of silver nanoparticles prepared at different concentrations of silver nanoparticles: (a and b) 250 ppm, (c and d) 500 ppm, and (e) 750 ppm.

was incorporated at different concentrations in the reaction medium.

Fig. 6a shows TEM micrograph of AgNPs with a concentration of 250 ppm. The reaction solution was prepared containing 0.9 g HPS having MS of 0.84 and 0.39 g $AgNO_3$. pH of the reaction medium was adjusted to pH 12 and the reaction was allowed to proceed at 70 °C for 15 min. Fig. 6b illustrates a histogram showing the particle size and particle size distribution of AgNPs at a concentration of 250 ppm using the same reaction conditions of Fig. 6a. Fig. 6c shows TEM micrograph of AgNPs with a concentration of 500 ppm. Here, the reaction conditions are identical to those outlined above using double concentration of silver nitrate which in this case increased to 0.078 g. Fig. 6d illustrates a histogram showing the particle size and particle size distribution of AgNPs at a concentration of 500 ppm using the same reaction conditions of Fig. 6c.

At higher concentration more than 500 ppm, aggregation occurs and the formed AgNPs were precipitated in large size as shown in Fig. 6e. So the most suitable concentration of AgNPs is prepared with 500 ppm which is suitable for industrial applications.

4. Conclusion

A highly facile, simple, safe, cost effective, and green approach to the preparation of AgNPs without use of any reducing agent, in the presence of HPS polymer, has developed. HPS acted as a reducing agent and stabilizer for the formed AgNPs. The use of environmentally benign materials (HPS) offers numerous benefits ranging from environmental friendly to ready integration of these nanomaterials to biologically relevant systems. The preparation of the nanoparticles relied on a concentration of HPS as well as silver nitrate concentration in addition to pH, temperature and duration of the reduction reaction. The optimum conditions for preparation of AgNPs colloids with excellent size and size distribution within the range of 6–8 nm were as follows: 0.9 g HPS (MS: 0.84), $AgNO_3$; 0.078 g, pH; 12, temperature; 70°C, duration; 15 min. The so obtained AgNPs colloidal solution with a concentration of 500 ppm was stable and remained without aggregation for more than six months. AgNPs colloidal solution with such unique characteristics will certainly be feasible for industrial applications. This methodology can also be adapted to the preparation of other metal nanoparticles.

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