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Facile size-regulated synthesis of silver nanoparticles using pectin

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ABSTRACT

Monodispersed silver nanoparticles capped by pectin were prepared by the reaction of silver nitrate with alkali hydrolyzed pectin at 70 °C for 30 min. Spherical and size-regulated silver nanoparticles were prepared using alkali hydrolyzed pectin as a reducing and particle-stabilizing agent. This approach is facile, effective, rapid, and convenient for the large scale preparation of silver nanoparticles. UV–visible spectral analysis confirmed that the nanoparticles consisted of metallic silver. Transmission electron microscopy (TEM) was used to estimate particle size and size distribution of the produced silver nanoparticles. Transmission electron microscopy and size distribution analysis revealed the presence of spherical silver nanoparticles with a main diameter of 5–10 nm and have a narrow size distribution. The concentration of reducing sugars was monitored by using dinitrosalicylic acid. A comprehensive schematic mechanism for the formation of silver nanoparticles using pectin is proposed.

1. Introduction

Natural fiber products, especially cotton fabrics, are highly popular with people and widely applied in daily life because of their excellent properties, such as softness, hygroscopicity, affinity to skin, bio-degradability and regeneration property (Lu, Lin, Chen, Wang, & Hua, 2007; Saravanan, Vasanthi, & Ramachandran, 2009). However, these products could be easily damaged by microorganisms on account of its natural feature and ability to retain moisture, which not only cause discoloration, mechanical strength loss and foul odor generation of the products but also result in a series of negative health effects to human beings (Zhang, Chen, Ling, & Zhang, 2009).

With increasing awareness of consumers toward health and hygiene, demand for antibacterial textiles is now expanding. Therefore, many antibacterial agents have been applied to fabricate antibacterial textiles, such as quaternary ammonium compounds (Sun, Li, Qiu, & Qing, 2005), chitosan (Ali, Joshi, & Rajendran, 2011), triclosan (Kalyon & Olgun, 2001), nanoparticles of noble metals and metal oxides (Abdel-Mohsen, Aly, & Hrdina, 2012; Abdel-Mohsen et al., 2014; El-Rafie, Ahmed, & Zahran, 2014; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Jiang, Liu, & Yao, 2011; Joshi, Ali, & Rajendran, 2007; Mary, Bajpai, & Chand, 2009; Montazer & Seifollahzadeh, 2011; Vasilev, Sah, Goreham, Ndi, Short, & Griesser, 2010; Xia, Cai, Jiang, & Yao, 2011; Zahran, Ahmed, & El-Rafie, 2014; Zahran, Ahmed, & El-Rafie, 2014b), and bioactive plant-based products (Alemdar & Agaoglu, 2009), in which silver nanoparticles (AgNPs) has been widely used due to its broad spectrum of antibacterial activity and low toxicity toward mammalian cells (Hebeish et al., 2010; Kim, Sung, Suh, Moon, Choi, & Kim, 2009).

Over the past two decades, dendrimers and hyperbranched polymers have been widely developed due to their unique chemical and physical properties together with their potential application in additives, drug and gene delivery, nanotechnology, and supramolecular science (Gao & Yan, 2004; Menjoge, Kannan, & Tomalia, 2010). With numerous interior cavities as well as inward and outward oriented functional groups, they can be utilized as templates to control synthesis of nanoparticles with small size, good monodispersity and stability, such as Ag NP, Au NP, ZnO NP, etc. (Castonguay & Kakkar, 2010; Richter, Schüler, Thomann, Mülhaupt, & Ludwigs, 2009; Scott, Wilson, & Crooks, 2005). Biodegradable and biocompatible polymers are suitable for human use and can be prepared as particle complexes of various sizes.

Pectins are anionic, soluble, non-starch polysaccharides extracted from the primary cell walls of plants. Pectins, a heterogeneous complex polysaccharide of linear 1, 4-linked α-D-galacturonic acid, are used as gelling and thickening agents in food industries (Rolin, 1993). In recent years, the polymer has also been explored as a pharmaceutical excipient (Pillay & Fassihi, 1999). The functional properties of pectin are determined by the percentage of carboxyl groups that have been esterified or amidated, denoted

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as the degree of esterification (DE) and degree of amidation (DA), respectively. Amidated low methoxy pectin (DE < 50%) forms more rigid gels by the action of calcium, which cross-links the galacturonic acid chains, than does only methoxy pectin.

Pectin is known as a miracle polymer of natural origin because of its excellent biodegradable and biocompatible nature. Pectin is commercially extracted from different citrus products like apple, pomace, and oranges under mildly acidic conditions. Pectin is a high value functional food ingredient which is widely used as a gelling agent and stabilizer in food industries. Pectin has been widely investigated for different potential biomedical applications.

Several researchers successfully incorporated protein or peptide into calcium pectinate beads for a colonic delivery system (Atyabi, Inanloo, & Dinarvand, 2005; Bourgeois, Gernet, Pradeau, Andremont, & Fattal, 2006; Bourgeois, Laham, Besnard, Andremont, & Fattal, 2005; Kim, Park, Kim, & Cho, 2003; Sriamornsak, 1999). Cheng and Lim (2004) have succeeded in formulating insulin-loaded calcium pectinate nanoparticles by adapting an ionotropic gelation method reported for the manufacture of calcium pectinate beads. This method is advantageous by virtue of being a simple method that does not involve expensive equipment, harsh processing conditions, or organic solvent systems.

In this study, in order to fabricate AgNPs treated cotton fabric with excellent antibacterial property and laundering durability, pectin was employed to prepare Ag NPs by one-step reaction in aqueous alkaline medium without any other reducer and stabilizer. In this part, the interaction between pectin and AgNPs was confirmed by UV–visible spectroscopy, Monitoring of the concentration of reducing sugars in the reaction medium by using dinitrosalicylic acid reagent (DNS) was preceded, and the average size and size distribution of the produced nanoparticles were shown by TEM micrographs. This process is a “green” approach

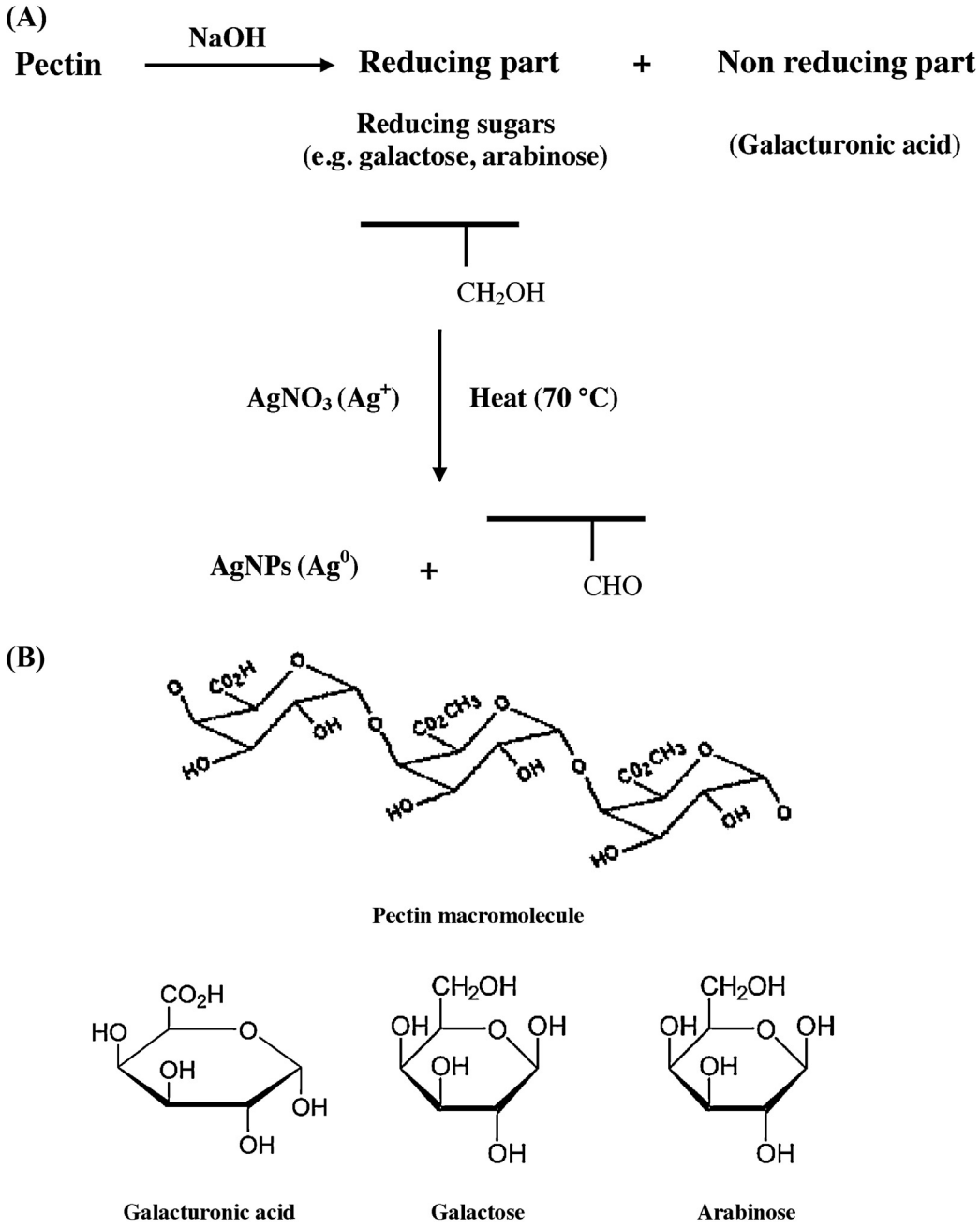

Fig. 1. (A) Schematic diagram represents preparation of silver nanoparticles by pectin and (B) chemical structures of pectin and its fragments results from alkaline hydrolysis.

because it does not involve any toxic materials or any other undesirable impurities.

2. Experimental

2.1. Materials and chemicals

Silver nitrate (99.5%from Panreac, Barcelona, Spain), pectin (M.W. = 300,000–1,000,000) supplied from (Alpha Chemika Company, Mumbai, India), sodium hydroxide, 3,5-dinitro salicylic acid (DNS), sodium sulphite, potassium sodium tartarate, glucose, phenol, and sodium carbonate monohydrate (from the Egyptian company for chemicals and pharmaceuticals, 10th 99 of Ramadan, Egypt) were all used without any further purification.

2.2. Method

Different weights of pectin (1–6 g/l) were treated with sodium hydroxide solution (20 g/l) using magnetic stirrer to prepare different solutions of alkali hydrolyzed pectin with pH value nearly12 in order to serve the dual role as a reductant of silver nitrate and stabilizer for the produced nanosilver. After complete dissolution, the temperature of the reaction medium was raised to the desired degree (60–80 °C). In this moment, certain amount from silver nitrate solution (0.1 mol/l) was added dropwise (keeping in mind that the total volume of the reactants is 100 ml).

The reaction was kept under continuous stirring for different durations (1–60 min). After addition of silver nitrate, the reaction medium acquires a brownish color indicating that silver nanoparticles may be produced. The progression of the reaction was controlled by UV–visible absorption; aliquots from the reaction bulk were withdrawn at given time intervals and evaluated.

2.3. Experimental analysis

2.3.1. Determination of the concentration of reducing sugars

The dinitrosalicylic acid reagent (DNS) was used for the determination of concentrations of reducing sugars. This method was carried out to detect the free carbonyl groups of the so-called reducing sugars remained after the redox reaction between silver nitrate and alkali hydrolyzed pectin. This involves the oxidation of the aldehydic and/or ketonic groups presented in the sugar to the carboxylic group and 3,5-dinitrosalicylic acid are reduced to 3,5-diaminosalicylic acid under alkaline conditions.

The reagent is composed of dinitrosalicylic acid, Rochelle salt (sodium potassium tartarate), phenol, sodium bisulfite, and sodium hydroxide. According to Sumner (1921), Rochelle salt is added to prevent the reagent from dissolving oxygen, phenol is used to increase the amount of color produced, and bisulfite to stabilize the color obtained in the presence of phenol. Also the alkali is required for catalyzing the reducing action of sugar on dinitrosalicylic acid.

The test was carried out with 3 ml of DNS reagent which is added to 3 ml of different colloidal silver nanoparticles solutions under different conditions in capped test tubes. The mixture was heated at 90 °C for 15 min to develop the reddish brown color. 1 ml of Rochelle salt is added to stabilize the color. After cooling at room temperature in a cold water bath, the absorbance was recorded spectrophotometerically at 575 nm (Sumner, 1921).

2.3.2. UV–visible spectroscopy

Silver nanoparticles solutions exhibit an intense absorption peak due to the surface plasmon resonance (SPR). Thus the UV–visible absorption spectra were used to prove the formation of AgNPs colloidal solutions. The UV–visible absorption spectra of AgNPs colloidal solutions were measured using a multi channel spectrophotometer (T80 UV–visible, $d = 10$ mm, PG Instruments Ltd., Japan) at wavelengths 250–600 nm.

2.3.3. Transmission electron microscope (TEM)

For more characterization of the prepared silver nanoparticles, two drops of the silver nanoparticles colloidal solutions were placed on a 400 mesh copper grid coated by carbon film. The morphology and the distribution of AgNPs were characterized by means of a JEOL-JEM-1200 transmission electron microscope.

2.3.4. Particles size distribution

The diameter and distribution of silver nanoparticles were calculated by 4 pi analysis software using TEM photos. The average

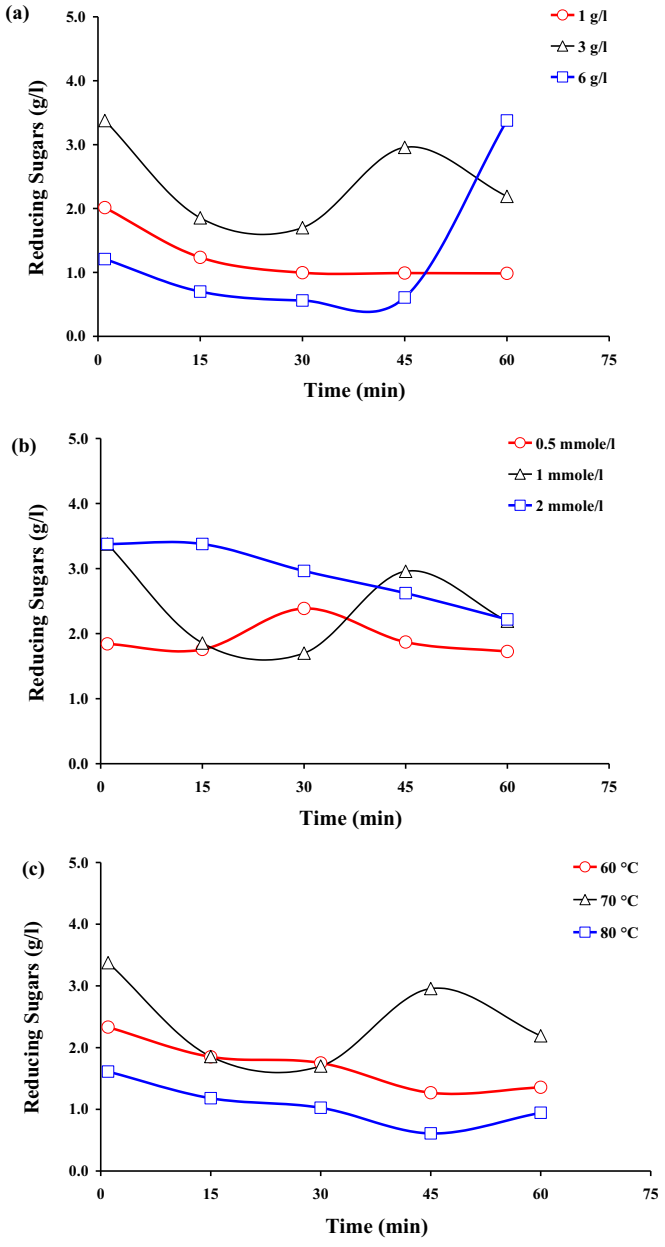

Fig. 2. (a) Effect of pectin concentration on the amounts of reducing sugars produced in the reaction medium, using 1 mmol/l $AgNO_3$ at pH 12 and 70 °C temperature. (b) Effect of $AgNO_3$ concentration on the amounts of reducing sugars produced in the reaction medium, using 3 g/l pectin at pH 12 and 70 °C temperature. (c) Effect of temperature on the amounts of reducing sugars produced in the reaction medium, using 1 mmol/l $AgNO_3$ and 3 g/l pectin at pH 12.

diameter of the silver nanoparticles was determined from the diameter of at least 20–100 nanoparticles.

3. Results and discussion

Small metallic particles exhibit a high optical absorbance due to the existence of discrete energy levels of electron and particularly of specific states. Silver particles with diameters below 5 nm have a rather high absorbance band with a maximum at about 400 nm. This band is broadened and shifted toward higher wavelengths with increasing particle diameter (Sanchez & Garcia, 1995). Silver particles with diameters of 10 nm exhibit absorption bands at 410–450 nm depending on their chemical environment (Chumanov & Sokolov, 1995).

In the alkaline medium, polysaccharides are known to undergo diverse transformations such as depolymerization, alkaline hydrolysis, and oxidizing destruction (Nadezhda, Natalya, Lydmila, & Vasilyi, 2012).

Also Nadezhda indicated that, these processes take place during the interaction of pectin with Ag (I) in the alkaline medium, to give galacturonic acid and monosaccharides of arabinose, galactose, rhamnose, glucose, mannose, and (in minor quantity) xylose. Dominating monosaccharides are galactose and arabinose in a ratio of 2.7: 1 (Fig. 1a and b) (Nadezhda et al., 2012).

Also, it has been reported that, the comparison of structural characteristics of the initial pectin with those of "pectin-Ag (0)" nanobiocomposites allows one to assume that pectin as a polysaccharide acts a reducing agent and also undergoes destructive changes. Pectin carboxy-groups and other groups (–OH, =O) are contained in structure of side chains of pectin fragments were participated in formation of AgNPs (Nadezhda et al., 2012).

3.1. Determination of residual reducing sugars

Alkali treatment of pectin was performed in the current work to increase the solubility and provide fragments lower in molecular weight with higher affinity and reducibility, which are required for synthesis of well dispersed and stable silver nanoparticles.

Due to the high polarity of water, silver nanoparticles usually agglomerate immediately and form larger particles. In our approach, pectin is added into the solution and bind with silver molecules with COO^- and CH_2 groups in a hydrogen bond system to restrain the formed silver nanoparticles from further agglomeration by the action of steric hindrance. After a long time reaction, the pectin-wrapped silver nanocomposites are formed.

This method is used to determine the concentration of reducing sugars in the reaction medium, as this method tests for the presence of free carbonyl groups, of reducing sugars produced from pectin hydrolysis (Miller, 1959).

During the redox reaction between sugars (products of pectin hydrolysis) and silver nitrate, sugars are turned to the oxidized form with more aldehydic and/or ketonic groups, and simultaneously, 3,5-dinitrosalicylic acid is reduced to 3,5-diaminosalicylic acid.

Increasing the concentration of reducing sugars means that the redox reaction between alkali hydrolyzed pectin and silver ions is running, and so means increasing in the affinity of producing spherical AgNPs, and building of nanosilver clusters.

3.1.1. Pectin concentration

Fig. 2a shows the change in the concentration of the produced reducing sugars by increasing pectin concentration, and it could be observed that, by raising concentration of pectin to 3 g/l, the concentration of reducing sugars is increased. However, further

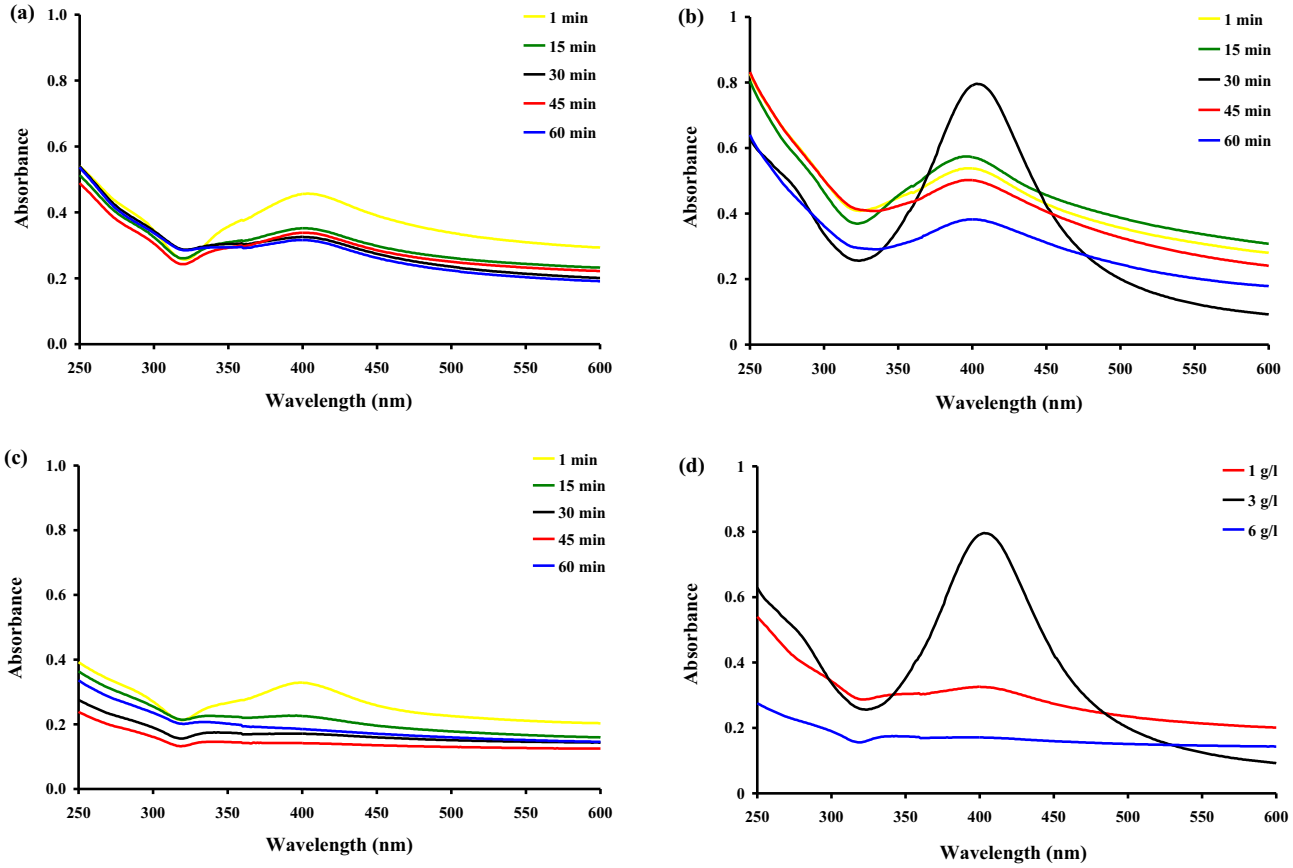

Fig. 3. UV–visible absorption spectroscopy of silver nanoparticles (AgNPs) prepared at different durations. Reaction conditions:1 mmol/l $AgNO_3$,pH 12, temperature 70 °C, (a) 1 g/l pectin,(b) 3 g/l pectin, (c) and (d) effect of pectin concentration on preparation of silver nanoparticles under the preceding conditions at 30 min.

increase to 6 g/l leads to decrease the amounts of the produced sugars. It could be explained, as by increasing the concentration of pectin, the amounts of galacturonic acid units produced due to alkaline hydrolysis of pectin chain is higher than that of monosaccarides' units (Nadezhda et al., 2012).

Thus, 3 g/l of pectin is suggested to be the optimum concentration in order to have the maximum concentration of reducing sugars, required for generating the highest concentration of spherical AgNPs.

3.1.2. Silver nitrate concentration and temperature

From Fig. 2b, it could be clarified that, when the concentration of silver nitrate was increased than 1 mmol/l, the concentration of reducing sugars was decreased, as reported by the studies of Nadezhda, which confirmed that, when the concentration of silver nitrate becomes higher than 1 mmol/l, the net monosaccarides' fragments produced due alkaline hydrolysis of pectin is indirectly proportional to the concentration of silver nitrate, and acidic fragments (galacturonic acid) were the dominating form in the reaction medium (Nadezhda et al., 2012).

From Fig. 2c, the maximum concentration of reducing sugars was approached at 70 °C from the first minute, and further increase in reaction temperature resulted in a decrease in concentration of residual reducing sugars, which also can be explained to the production of greater amounts of galacturonic acid in reaction medium, than monosaccarides' units (Nadezhda et al., 2012).

So, it could be decided that, reaction temperature plays an important role in accelerating the redox reaction between silver ions and pectin macromolecules.

3.1.3. UV–visible spectroscopic analysis

The preliminary detection of AgNPs was carried out by visual observation of the color changes of the reaction solutions. These changes were attributed to the excitation of surface plasmon resonance (SPR) in the metal nanoparticles (Natarajan, Selvaraj, & Murty, 2010). Typically, UV–visible absorption is used to investigate SPR.

Initially, the influence of pectin concentration, silver nitrate concentration and temperature on the synthesis of spherical AgNPs by our simple and novel method was investigated by measuring UV–visible spectra of the reaction solutions at different durations.

3.1.4. Pectin concentration

As shown in Fig. 3a–d, the peak area and height of the UV–visible spectrum obtained for the reaction solutions which contain 1, 3 and 6 g/l of pectin by time.

It was clarified that, the colloidal solution which contained 3 g/l pectin was characterized by considerably higher absorbance values than those for the others, which is an indication of the higher productivity of the method at this concentration of pectin.

Also, by increasing the concentration of pectin, the absorbance value starts to decrease, this behavior could be explained according to the data shown in monitoring of reducing sugars, as by increasing of pectin concentration more than 3 g/l, it resulted to produce greater amounts of galacturonic acid, which cannot take a place in the redox reaction with silver nitrate to give a zerovalent metallic silver.

Hence, 3 g/l pectin was selected to be the optimum concentration for the synthesis of spherical AgNPs using our method. These results revealed that the efficiency of the synthesis of AgNPs depends on the concentration of the generated reducing sugars, and consequently, on pectin alkali hydrolysis.

Also in Fig. 3, strong SPR is observed near 409 nm. This band is considered to be in the ideal wavelength range for AgNPs colloidal solutions (Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006). SPR is affected by the size and shape of the synthesized AgNPs. On the other hand, the lower-wavelength region implies the formation of smaller nanoparticles (Prathna, Chandrasekaran, Raichur, & Mukherjee, 2011). Thus, Fig. 2 indicates that the use of our novel method results in the formation of very small spherical AgNPs.

Fig. 3b shows the effect of reaction time on the Ag^+ reduction, in which the experiments were performed at 70 °C, with 1 mmol/l $AgNO_3$ and 3 g/l pectin. After 15 min of reaction, a slight absorption band around 409 nm was appeared, this became a clearly visible peak after 30 min, suggesting the presence of spherical Ag nanoparticles. The absorption peak intensity decreased rapidly with the increase of reaction time to 1 h, due to the formation of enlarged Ag nanoparticles (Wei, Wang, Sun, Song, Sun, & Guo, 2007), suggesting a period of predominant crystal growth of Ag nanoparticles in the reaction system by the assemble and amalgamation of small particles.

3.1.5. Silver nitrate concentration

The silver nitrate concentration in the reaction system is surely affecting the reduction rate of Ag^+, as it acts as the generator of silver nanoparticles in the reaction medium. Fig. 4a shows the effect of silver nitrate concentration on the Ag^+ reduction by UV–visible spectroscopy while keeping the pectin concentration unchanged (3 g/l), in which the experiments were performed at 70 °C and pH ≈12 for 30 min.

It could be observed that, the absorption peak intensity is increased by increasing the concentration of silver nitrate from 0.5

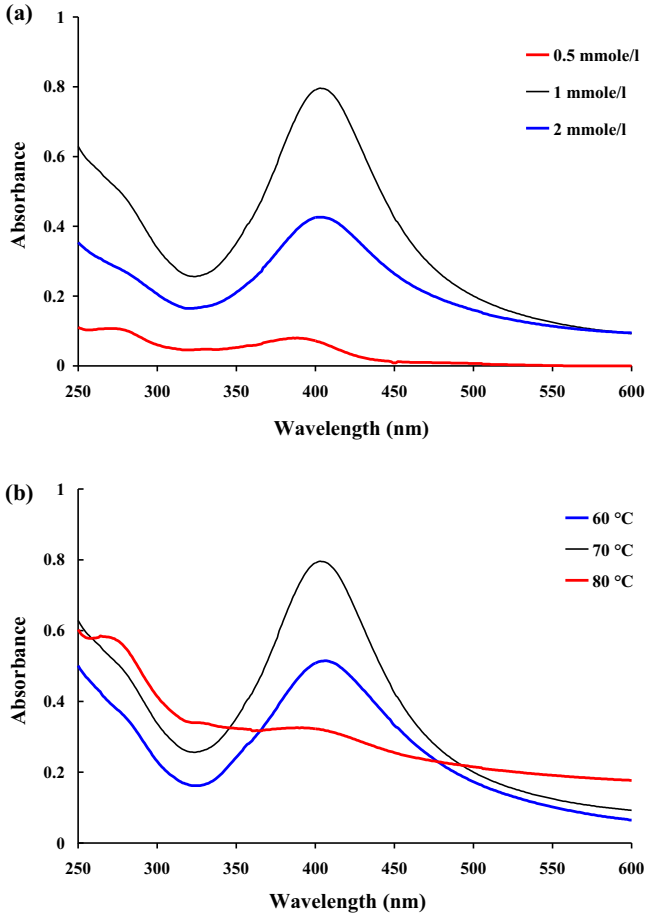

Fig. 4. (a) UV–visible absorption spectroscopy for AgNPs prepared by using different concentrations of $AgNO_3$ (0.5–2 mmol/l), reaction conditions: 3 g/l pectin, pH 12 at 70 °C for 30 min. (b) UV–visible absorption spectroscopy for AgNPs prepared at different temperatures, reaction conditions: 3 g/l of pectin, pH 12, 1 mmol/l $AgNO_3$ after 30 min.

to 1 mmol/l and then starts to decline with the increase of $AgNO_3$ concentration from 1 to 2 mmol/l, which suggests that a part of the resulting Ag (0) is not involved in formation nanobiocomposites, and were consumed in the production of well-formed crystalline cubic structure (Nadezhda et al., 2012).

3.1.6. Temperature of reaction medium

The synthesis was made at different temperatures. Fig. 4b shows the UV–visible spectra of samples obtained in a reaction medium at 60, 70 and 80 °C. In the spectrum of the sample prepared at 60 °C, a weak plasmon resonance band was observed; this is due to a low yield. When the reaction was made at 70 °C an intense band centered at 409 nm appeared, indicating the formation of Ag nanoparticles with a sharp size distribution.

At higher temperatures, the absorbance values started to decrease that is correlated with the fact supported by Hebeish, that by raising reaction temperature, the produced nanoparticles tended to aggregate and starts to precipitate (Hebeish et al., 2010).

Thus, it could be suggested, 70 °C allowed obtaining a good yield in short times with a good size distribution of particles, and this is also confirmed from the data obtained by monitoring the amounts of reducing sugars, as mentioned before.

3.1.7. TEM images

Typical TEM images and size distributions for spherical AgNPs obtained at 70 °C by using 3 g/l alkali hydrolyzed pectin with 1 and 2 mmol/l of silver nitrate are shown in Figs. 5(a and b) and 6(a and b), respectively. In both cases, particles appeared spherical, well dispersed and well-separated, however the particles obtained with 2 mmol/l were larger in size (8–12 nm).

Also, Fig. 7(a and b) shows the spherical silver nanoparticles prepared at 80 °C with 3 g/l alkali hydrolyzed pectin and 1 mmol/l silver nitrate, and it could be observed that, by raising temperature, enlarged nanoparticles were obtained (20–30 nm). Thus, TEM data have confirmed the suggestions which were supposed previously to explain UV–visible spectra.

The smaller particle size of spherical AgNPs in experiment carried out with 3 g/l alkali hydrolyzed pectin and 1 mmol/l silver nitrate at 70 °C for 30 min (5–10 nm), may be due to the fact that silver ions are ionically bound to anionic groups within the pectin macromolecules prior to reduction as opposed to being more loosely adsorbed onto the alkali hydrolyzed pectin matrix.

However, by increasing the concentration of silver generator ($AgNO_3$), the greater amounts of synthesized nanoparticles tended to collapse and then started to aggregate to enlarged particles. Also by raising temperature, the produced spherical AgNPs gained higher kinetics and tended to collapse and then aggregated to bigger clusters.

It has been shown that smaller spherical AgNPs diameters provide better antimicrobial performance than larger ones (Morones, Elechiguerra, Camacho, Holt, Kouri, & Ramirez, 2005). Therefore, the optimum conditions for producing AgNPs with

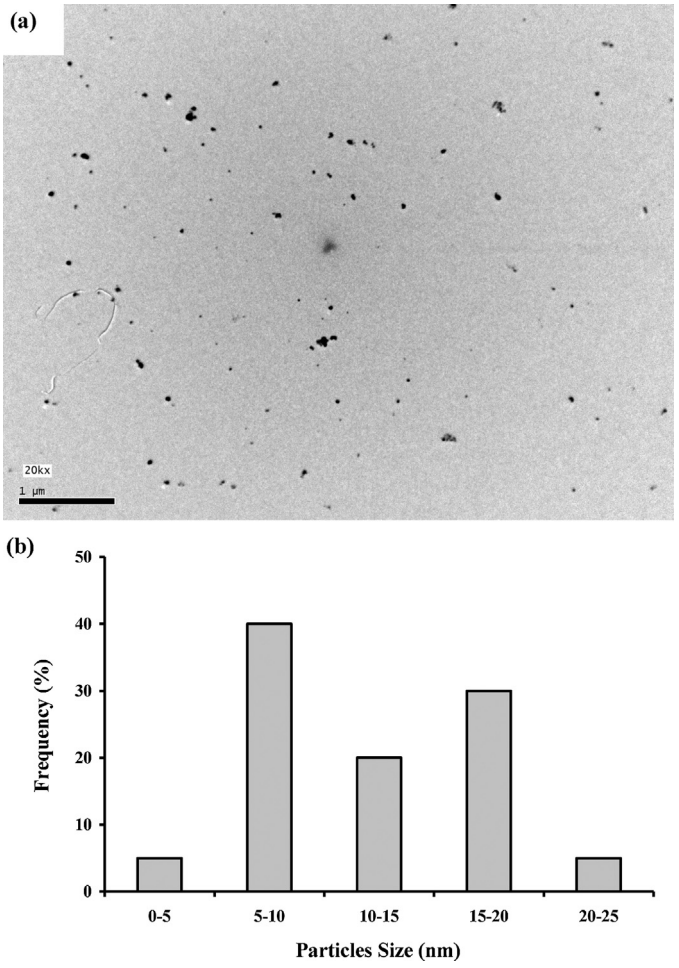

Fig. 5. (a) TEM image silver nanoparticles prepared by 1 mmol/l $AgNO_3$ (reaction conditions: 3 g/l pectin, pH 12 at 70 °C for 30 min). (b) Size distribution histogram for silver nanoparticles in the viewed TEM image.

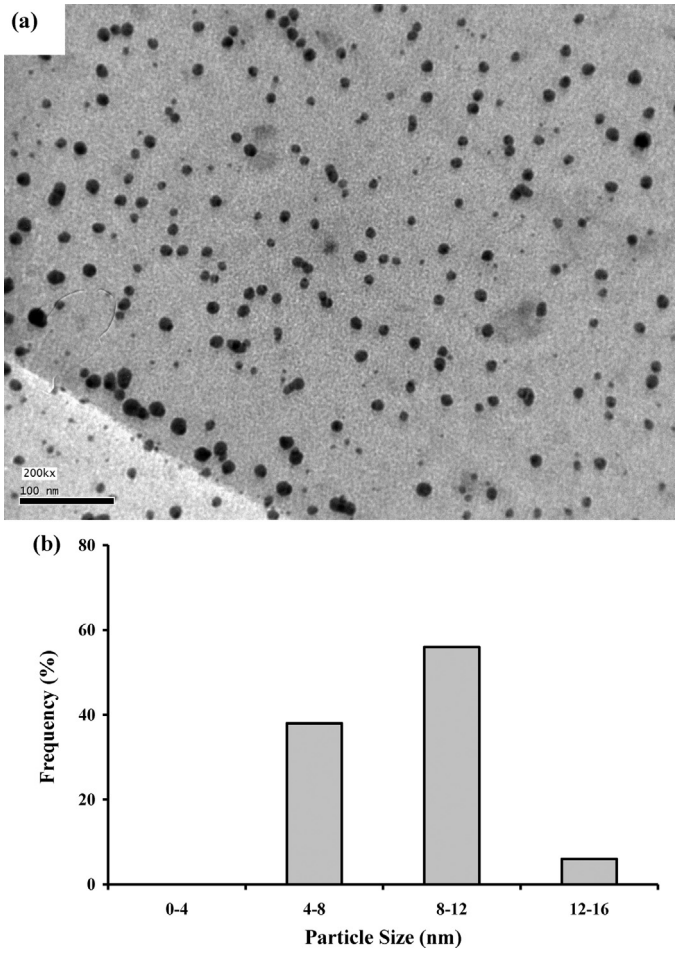

Fig. 6. (a) TEM image of silver nanoparticles prepared by 2 mmol/l $AgNO_3$ (reaction conditions: 3 g/l pectin, pH 12 at 70 °C for 30 min). (b) Size distribution histogram for silver nanoparticles in the viewed TEM image.

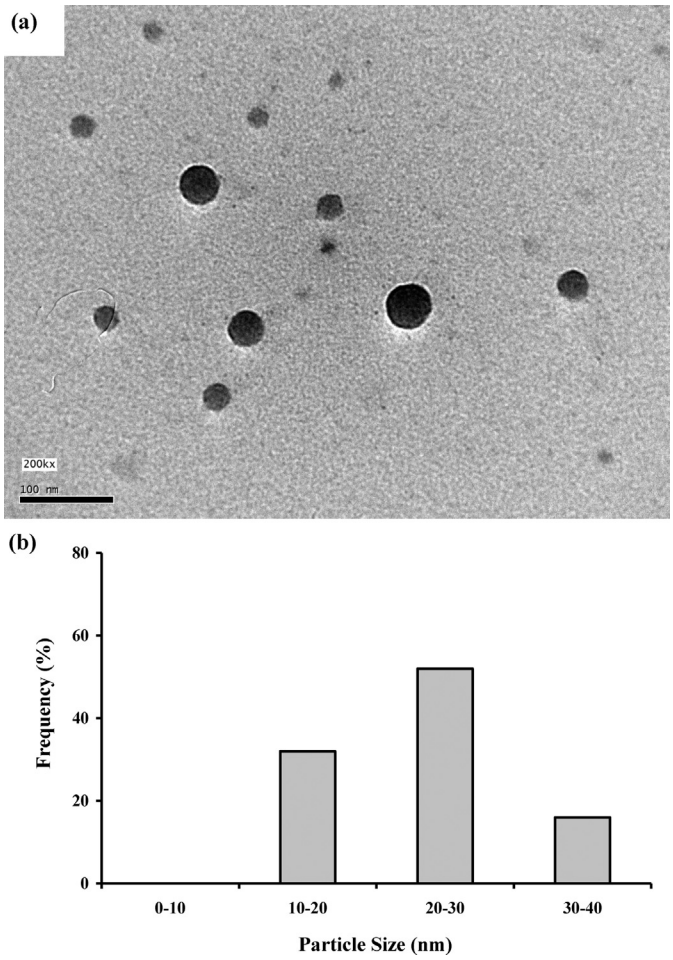

Fig. 7. (a) TEM micrograph of silver nanoparticles prepared at 80 °C (reaction conditions: 1 mmol/l $AgNO_3$, 3 g/l pectin, pH 12 for 30 min). (b) Size distribution histogram for silver nanoparticles in the viewed TEM image.

particle size 5–10 nm were, 3 g/l alkali hydrolyzed pectin, 1 mmol/l silver nitrate at 70 °C for 30 min.

4. Conclusion

Spherical silver nanoparticles (AgNPs) were successfully prepared by using alkali hydrolyzed pectin as reductant and stabilizing agent. The formation of spherical AgNPs was firstly indicated by changing the color of solution to golden yellow giving absorbance peak around 409 nm. Secondly, the presence of spherical shaped AgNPs was confirmed by transmission electron microscope. The size distribution of spherical AgNPs was detected using transmission electron microscope photos. At the optimum condition used, the average size of spherical AgNPs was 5–10 nm. The reduction process of Ag^+ to Ag^0 was confirmed by measuring the reducing sugars in the reaction mixture using DNS reagent. This study reveals that a novel green method was used for synthesis of spherical AgNPs. The method used in the current work shows significant advantages which making it suitable for different industrial applications compared with the traditional methods for preparation of AgNPs, as it is a quite simple technique, with low chemical consumption and energy-saving as well as no hazard organic solvents or reducing agents were used. Application of AgNPs based on these findings may be used for production of valuable textile products beneficial in various purposes such as medical dressings and antimicrobial garments.

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