Carboxymethyl cellulose for green synthesis and stabilization of silver nanoparticles

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ABSTRACT

Cotton samples having different degrees of polymerization (DPs) were prepared and used for synthesis of carboxymethyl cellulose (CMC) derivatives with different degrees of substitution (DSs). Thus obtained CMC products were, in turn, used for preparation of silver nanoparticles using silver nitrate under different conditions. UV–vis spectra of the silver colloidal solution reveal that increasing the pH of the latter causes appreciable changes in the absorption spectra and reaches its maximum at pH 12.5 indicating full reduction of silver ions. Prolonging the reaction time from 30 to 60 min brings about outstanding enhancement in the plasmon intensity indicating reduction of larger amounts of silver ions. Complete transformation of silver ions into silver nanoparticles occurs at 70 °C. Dispersion of silver nanoparticles improved upon increasing the DS of CMC from 1.22 to 2.2. The DP of CMC has significant effect on reduction efficiency, particle size and stabilization by CMC macromolecules. Silver nanoparticles colloidal solutions with concentrations higher than 100 ppm could be prepared by using $AgNO_3$:CMC ratio 0.017 g:0.3 g per 100 ml solution.

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1. Introduction

Preparation of metals nanoparticles has been extensively studied by virtue of their attractive optical and electronic properties related with the quantum size effect as well as their promising applications in such areas as optics, optoelectronics, catalysis, nanostructure fabrication and chemical/biochemical sensors (Watanabe, Menzel, Nilius, & Freund, 2006). A variety of routes have been reported for the preparation of metallic nanoparticles (Pal, Shah, & Devi, 2007), notable examples include, reverse micelles process (Song et al., 2007; Xie, Ye, & Liu, 2006), salt reduction (Fan et al., 2008; Khanna & Subbarao, 2003; Pillai & Kamat, 2004; Sondi, Goia, & Matijevi, 2003), without any reductant in an autoclave (Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006), irradiation (Kassaee, Akhavan, Sheikh, & Beteshobabrud, 2008) and electrochemical synthesis (Starowicz, Stypuła, & Banaś, 2006; Zhu, Liao, Zhao, & Chen, 2001). Nanomaterials have wide range of applications in a variety of areas, including physics, chemistry, electronics, optics, materials science and biomedical sciences.

In spite of the novel properties exhibited by the metal nanoparticles due to quantum size effects, their synthesis protocol poses a major environmental problem (Alivisatos, 1996). 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-Marzán, 2002) and sodium borohydride (Van Hyning, Klemperer, & Zukoski, 2001). All these chemicals are highly reactive and pose potential environmental and biological risks. With the increasing interest in minimization/elimination of waste and adoption of sustainable processes, the development of green chemistry approaches is desirable. Earlier reports have dealt with natural polymers like chitosan (Huang & Yang, 2004), heparin (Yanli & Hongtao, 2008) and soluble starch (Vigneshwaran et al., 2006) as reducing and stabilizing agent for preparation of silver nanoparticles.

Increasing the awareness towards green chemistry and other biological processes evoked the interest to develop an eco-friendly approach for the synthesis of nanoparticles which has several advantages such as simplicity, cost effectiveness, compatibility for biomedical and pharmaceutical application as well as for large-scale commercial production. Currently, many interesting methods involve green preparation of nanosized metal particles (El-Rafie, Mohamed, Shaheen, & Hebeish, 2010; Hebeish, El-Rafie, Ramadan, & El-Naggar, in press; Liu, Qin, Raveendran, & Yukata, 2006; Lu, Gao, & Komarneni, 2005, 2006; Raveendran, Fu, & Wallen, 2003; Shin, Bae, & Exarhos, 2009; Shin, Blackwood, Bae, Arey, & Exarhos, 2007).

The present work is undertaken within the framework of a research program at our laboratories which addresses nanotechnology for production of multifunctional and smart textiles. Specifically, current work is pertaining to the preparation of silver

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Table 1
Chemical properties of untreated, scoured, bleached and oxidative degraded cotton substrates.

Cotton substrate	Degree of polymerization	Carbonyl content (mequiv./100 g)	Carboxyl content (mequiv/100 g)
Untreated	2250	4.8	3.7
Scoured	2150	7.5	6.7
S1	1800	22.3	17.6
S2	950	31.2	24.2
S3	350	45.4	35.3

S1 is bleached cotton substrate and S2, S3 are oxidative degraded cotton substrates.

Table 2
Effect of cotton substrate DP on efficiency of carboxymethylation.

	Degree of polymerization (DP)							
	350				950		1800	
Theoretical DS	1.75	2	2.5	3	2	2.5	2.5	3
Experimental DS	1.22	1.8	2.2	2.6	1.4	1.9	1.26	1.6
Reaction efficiency (%)	70	90	88	87	70	76	50	53

nanoparticles using CMC as reducing and stabilizing agent. Emphasis is placed on synthesis of CMC with tailored properties along with other factors controlling the preparation of the nanoparticles. The formation of silver nanoparticles was monitored via color and UV visible spectral analysis, whereas their evaluation was made by making use of Transmission Electron Microscope (TEM).

2. Experimental

2.1. Materials

Cotton sliver, Giza 85 was kindly supplied by Cotton Research Institute, Giza. It was subjected to purification and degradation treatments as given in Sections 2.2–2.4. Monochloroacetic acid, sodium hydroxide, sodium carbonate, sodium perborate, urea, sodium chlorite, isopropyl alcohol and silver nitrate were all laboratory grade reagents.

2.2. Alkaline treatment

In order to remove all impurities except the natural coloring matters, cotton sliver was boiled in an aqueous solution containing 2.5 g/l sodium hydroxide and 2 g/l nonionic wetting agent, under reflux for 60 min using a material to liquor ratio of 1:20. The cotton sliver was then washed three times with boiling water, twice with cold water and finally air dried.

2.3. Perborate treatment

Alkali scoured cotton sliver was boiled in an aqueous solution containing 2.5 g/l sodium perborate, 0.5 g/l urea and 2 g/l nonionic wetting agent, under reflux for 60 min using a material to liquor ratio of 1:20. The sliver was then washed three times with boiling water, twice with cold water and finally air dried. Perporate treatment was done with a view to remove the coloring matters and, in turn, obtaining purified cotton cellulose.

2.4. Molecular degradation treatment

The purified cotton sliver obtained as described above was treated with 6% sodium chlorite solution at pH 8 for 24 h using a material/liquor ratio of 1:20. Two samples were treated separately at two different temperatures, namely 55 °C and 70 °C and the degraded samples were found to have DPs of 950 and 350, respectively.

2.5. Carboxymethylation

Perborate bleached cotton sliver [S1 (DP 1800)] and the two degraded samples resulting from the oxidative chlorite treatment [S2 (DP 950) and S3 (DP 350)] were carboxymethylated as per the slurry method (Dapía, Santos, & Parajó, 2003). The DS was theoretically calculated with the aim of just having water soluble product. Finely ground cotton substrate (3 g) was dispersed in isopropyl alcohol (180 ml) and kept under mechanical stirring for 30 min at 25 °C. Calculated volume of 50% NaOH (w/v) was added drop wise in about 10 min and the mixture was left under continuous stirring for 60 min at 25 °C. Calculated weight of monochloroacetic acid dissolved in 15 ml of isopropyl alcohol was neutralized with the equivalent amount of Na_2CO_3 and added to the mixture portion wise. The temperature was raised to 60 °C and the mixture was allowed to react under stirring for 60 min. The mixture was then filtered, suspended in 150 ml of 80% methanol and neutralized with acetic acid. The final product was washed three times with 70% methanol and dried at 60 °C.
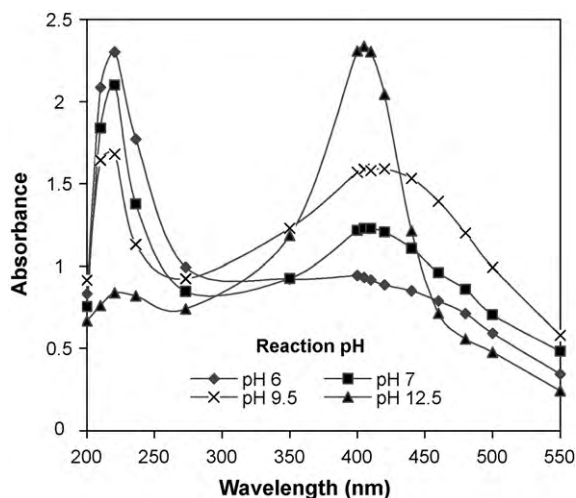
2.6. Preparation of silver nanoparticles

Definite weight of CMC was dissolved in distilled water using heating magnetic stirrer. After complete dissolution, the pH of the solution was adjusted within the range 6–12.5, followed by raising the temperature of the reaction medium to the desired temperature (30–90 °C). Certain amount of silver nitrate solution was then added drop wise (keeping in mind that the total volume of the reaction medium is 100 cm^3). The reaction mixture was kept under continuous stirring for different durations (15–90 min). Short time after addition of silver nitrate, the reaction medium acquires a clear yellow color indicating the formation of silver nanoparticles. The progression of the reaction was controlled by UV–vis absorption; aliquots from the reaction bulk were withdrawn at given time intervals and evaluated.

2.7. Testing and analysis

Degree of polymerization (DP), carbonyl content and carboxyl content of untreated, scoured, perborate bleached and oxidative degraded cotton were measured according to the following reported method, respectively (Mattisson & Legendre, 1952; Nelson & Tripp, 1953; Tihlérik & Pašteka, 1992).

Degree of substitution (DS) of carboxymethyl cellulose (CMC) was calculated as follows. The carboxyl content of CMC was measured according to a reported method (Mattisson & Legendre, 1952)

Fig. 1. UV–vis spectroscopy of silver nanoparticles prepared at different pHs. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 1.22); 1 ml (0.1 N) AgNO$_3$; temperature, 70 °C; duration, 60 min.

and the DS was calculated from the carboxyl content as follows:

$$DS = \frac{162X}{1 - 58X}$$

where X = number of carboxymethyl group in 1 g of CMC, 162 = molecular weight of the anhydroglucose unit of cellulose, 58 = net increase in molecular weight of anhydroglucose unit for each carboxymethyl group substituted.

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

Transmission Electron Microscope (TEM) was used for characterization of silver nanoparticles. Thus the shape and size of the synthesized silver nanoparticles were characterized by means of a JEOL-JEM-1200 Transmission Electron Microscope. The samples were prepared by placing a drop of the colloidal solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average
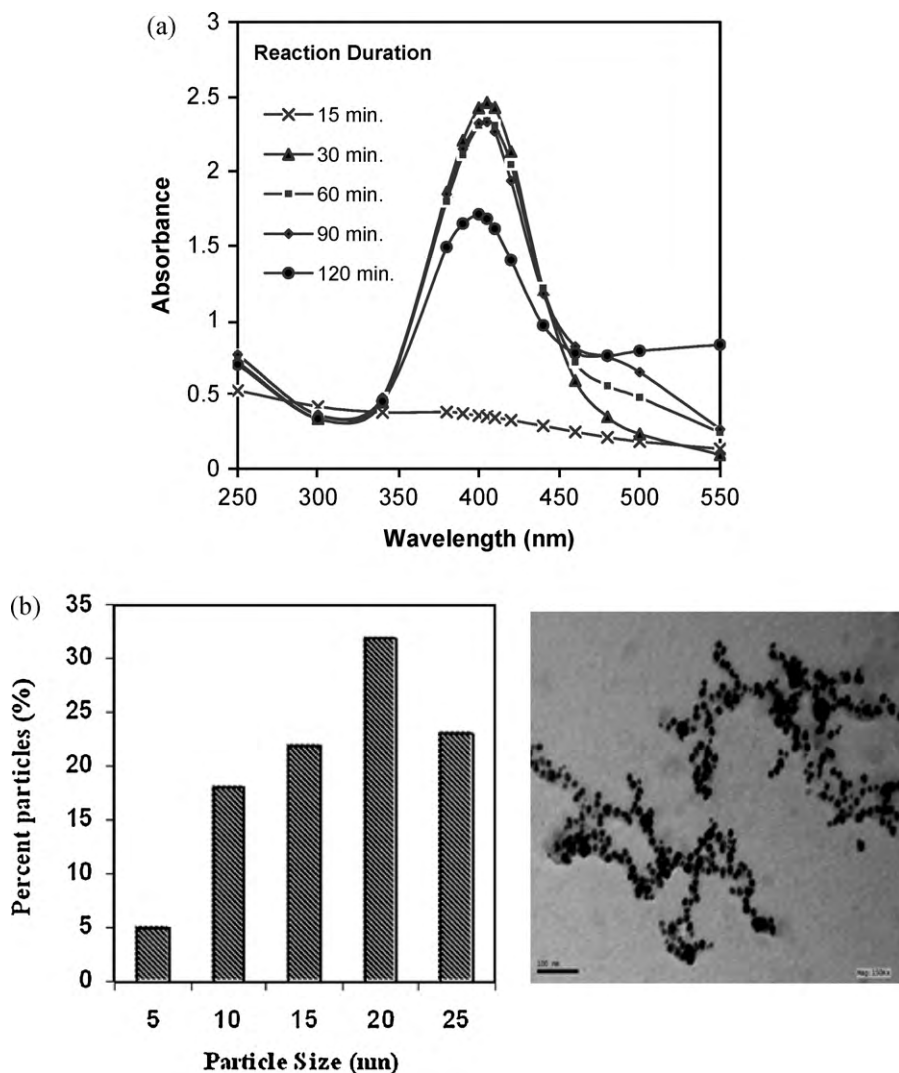
Fig. 2. (a) UV–vis spectroscopy of silver nanoparticles prepared at different durations. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 1.22); 1 ml (0.1 N) AgNO$_3$; pH 12.5; temperature, 70 °C. (b) TEM image and particle size distribution histogram of silver nanoparticles formed after 60 min. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 1.22); 1 ml (0.1 N) AgNO$_3$; temperature, 70 °C; pH 12.5; duration, 60 min.

diameter of the silver nanoparticles was determined from the diameter of 100 nanoparticles found in several chosen areas in enlarged microphotographs.

3. Results and discussion

3.1. Synthesis of carboxymethyl cellulose (CMC)

It is understandable that utilization of natural polymers for preparation of colloidal silver nanoparticles is governed by variety of parameters such as water solubility, degree of polymerization and reduction power. With this in mind, cotton cellulose was subjected to successive scouring, bleaching, oxidative degradation and carboxymethylation processes. This was done with a view to have tailored CMC products which can better serve as reducing and stabilizing agents during the preparation of silver nanoparticles.

Table 1 shows the chemical properties of untreated, scoured, bleached and oxidative degraded cotton substrates. Obviously the said successive treatments cause reduction in the DP while increasing the carbonyl and the carboxyl contents.

Systematic study was carried out to prepare water soluble CMC from the bleached and oxidative degraded cotton substrates (S1–S3). Results of Table 2 signify that the reaction efficiency is higher the lower the DP of cotton cellulose. This means that water soluble CMC can be prepared from low molecular weight cotton substrate at milder carboxymethylation conditions.

3.2. Utilization of CMC as reducing and stabilizing agent in preparation of silver nanoparticles

CMC products having different DPs and DSs, listed in Table 2 were used to perform dual role: as reducing agent for silver ions and as stabilizing agent during the formation of silver nanoparticles. 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.

3.2.1. Reaction mechanism for formation of silver nanoparticles

Previous reports (Goia, 2004; Hebeish et al., in press; Yu, 2007) have disclosed that the solutions of polymers can be used for the synthesis and stabilization of nanoparticles. Linear and dendritic 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.

Carboxymethylation of cotton sliver was carried out in current work to provide products with specific properties which are needed for synthesis of silver nanoparticles. CMC macromolecules consist of chemically modified cellulose chains containing reducing groups and carboxyl groups. All these components with their anionic and reducing properties support the utilization of CMC as reducing and stabilizing agent for the synthesis of silver nanoparticles. The negatively charged solubilized CMC facilitates the attraction of the positively charged silver cations to the polymeric chains followed by reduction with the existing reducing groups.

For the synthesis of silver nanoparticles, 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 the available reducing groups of the CMC. The atoms thus produced act as nucleation centers 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. The surface ions are again reduced 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 (Goia, 2004).

3.2.2. Effect of pH of reaction medium

0.3 g CMC (DP, 350; DS, 1.22) was dissolved in distilled water using heating magnetic stirrer. After complete dissolution, the pH was adjusted to 6, 7, 9.5 and 12.5 using dilute sulphuric acid or sodium hydroxide while the temperature was raised to 70 °C. At this end, silver nitrate (0.1 N) was added drop wise (1 ml each), keeping in mind that the total volume of the reaction medium is 100 ml. The reaction was allowed to proceed under continuous stirring for 1 h whereby silver colloid was formed.

Fig. 1 shows the UV–vis spectra of the silver colloid obtained using CMC as reducing and stabilizing agent at different pHs. The results reveal 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. 220 nm appears at pH 6, the intensity of this band decreases by increasing the pH up to 9.5; (c) further increase in the pH of the reaction medium up to pH 12.5 leads to disappearance of this band; (d) simultaneously another band at 405 nm starts to appear and reaches its maximum intensity at pH 12.5 and; (e) when the range of pH 12.5 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 silver nanoparticles.

The behavior caused by the observations stated above could be attributed to: (i) the formation of various ionic states of silver such as Ag^+, Ag^{2+} and Ag^{3+} (Khanna & Subbarao, 2003) bound to negatively charged surface of CMC polymer which appears as the absorption band at 220 nm, (ii) increasing the pH enhances the reduction of silver ions to Ag^0, (iii) the reductive properties of CMC are substantially enhanced owing to the oxidative degradation with the formation of low molecular weight reducing chains (DP 350) and, (iv) maximum intensity of the plasmon peak (405 nm) at pH 12.5 indicates full reduction of Ag ions (Raveendran et al., 2003) and, therefore, reflecting the dual role of CMC as stabilizing and efficient reducing agent in alkaline medium.

3.2.3. Effect of reaction duration

Fig. 2a shows the UV–vis absorption spectra of silver nanoparticles colloidal solutions prepared at different durations. The data reveal several important findings which can be presented as follows: (i) at the early stage reaction duration (after 15 min) the plasmon band is broaden and simple test for silver ion using NaCl solution indicates low conversion of silver ions to metallic silver nanoparticles at this duration, (ii) prolonging the reaction duration up to 30 min leads to outstanding enhancement in the plasmon intensity indicating that large amounts of silver ions are reduced and used for cluster formation, (iii) further increase in the reaction duration up to 90 min is accompanied by marginal decrement in the absorption intensity which could be attributed to some aggregation of the formed silver nanoparticles, (iv) increasing the reaction duration up to 120 min leads to significant decrease in the absorption intensity.

Fig. 2b shows the TEM images and the particle size distribution histograms of silver nanoparticles formed after 60 min. TEM image shows small size spherical particles. The corresponding size distribution histogram clearly illustrates that the size of the formed particles seem to be in the range of 10–25 nm.

3.2.4. CMC concentration

Fig. 3 shows the UV–vis absorption spectra of silver nanoparticles prepared using CMC (DP, 350; DS, 1.22) in different
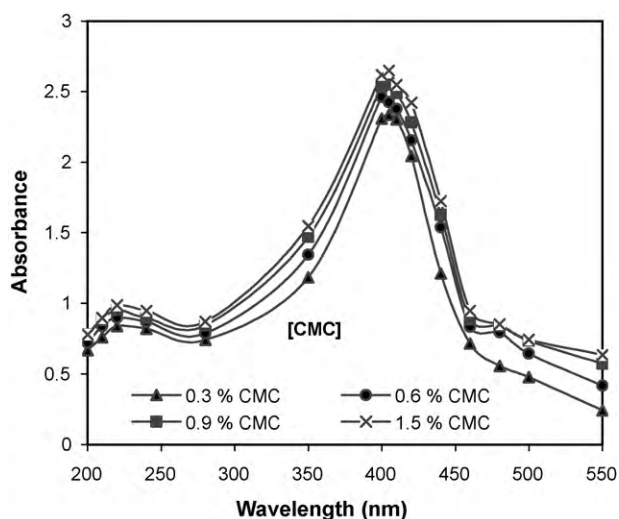
Fig. 3. UV–vis spectroscopy of silver nanoparticles prepared at different carboxymethyl cellulose concentrations. Reaction conditions: CMC (DP, 350; DS, 1.22); 1 ml (0.1 N) $AgNO_3$; pH 12.5; temperature, 70 °C; duration, 60 min.

concentrations (0.3–1.5%, w/v), at initial pH of 12.5 and temperature of 70 °C for 1 h. The data reveal that regardless of the CMC concentration used, similar plasmon bands are formed at wavelength 405 nm with the formation of the ideal bell shape

which is characteristic for the formation of Ag^0 nanoparticles. It is clear also that there is a gradual increase in the absorption intensity, by increasing the CMC concentration up to 1.5% which could be ascribed to the enhancement in the stabilization efficiency of the formed silver nanoparticles. It should be also mentioned that the least amount of CMC in the reaction medium (0.3%) is enough for full reduction of the Ag^+ to Ag^0 nanoparticles.

3.2.5. Effect of temperature

Fig. 4a shows the UV–vis spectra of silver nanoparticle prepared at different temperatures. The data indicate that at 50 °C the reduction efficiency is not enough for complete transformation of Ag^+ into silver nanoparticles (strong peak characteristic for Ag^+ is found at wavelength 220 nm). Increasing the reaction temperature above this limit, 70–90 °C leads to the disappearance of the peak characteristic for Ag^+, indicating its complete transformation into Ag^0. On the other hand, there is significant enhancement in the absorption band by rising the temperature up to 90 °C.

It is also clear from the data that preparation of silver nanoparticles at 70 °C represents the optimum condition, taking in mind the TEM images and particle size distribution histograms of silver nanoparticles prepared at 70 °C and 90 °C (Figs. 2b and 4b, respectively). The obtained data illustrate that the number of nanoparticles formed in the range of 10–25 nm is grater in case of 70 °C compared with that formed at 90 °C.
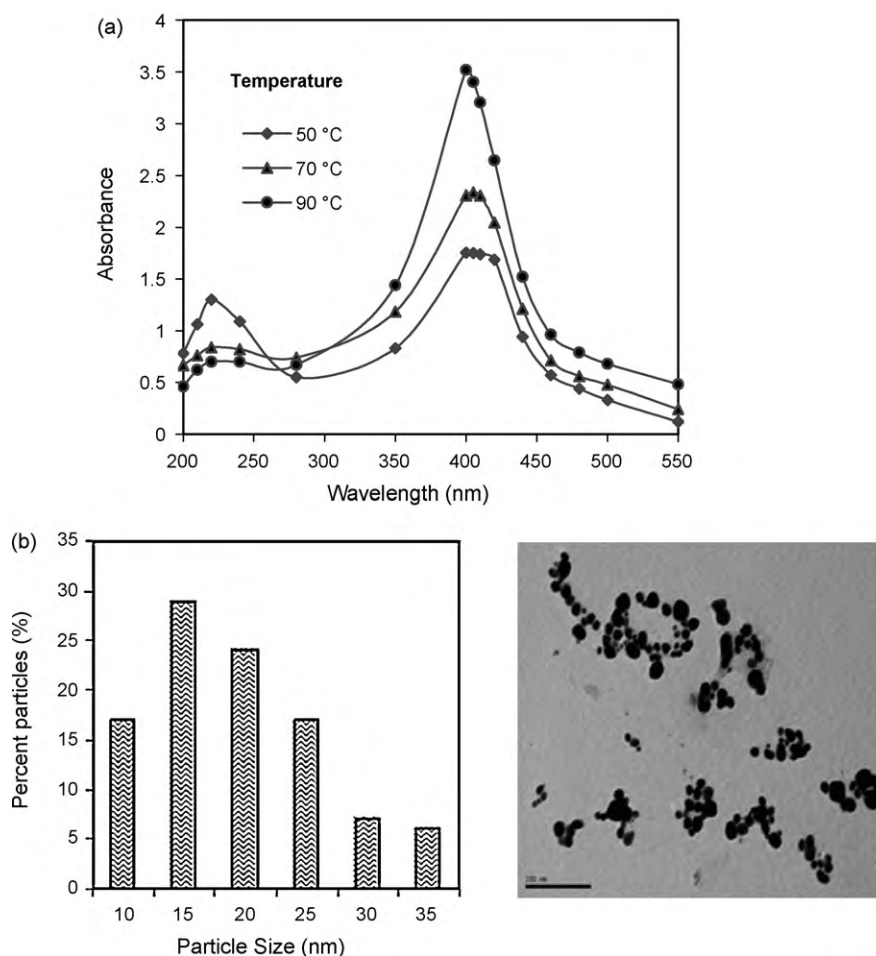
Fig. 4. (a) UV–vis spectroscopy of silver nanoparticles prepared at different temperatures. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 1.22); 1 ml (0.1 N) $AgNO_3$; pH 12.5; duration, 60 min. (b) TEM image and particle size distribution histogram of silver nanoparticles prepared at 90 °C. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 1.22); 1 ml (0.1 N) $AgNO_3$; temperature, 90 °C; pH 12.5; duration, 60 min.
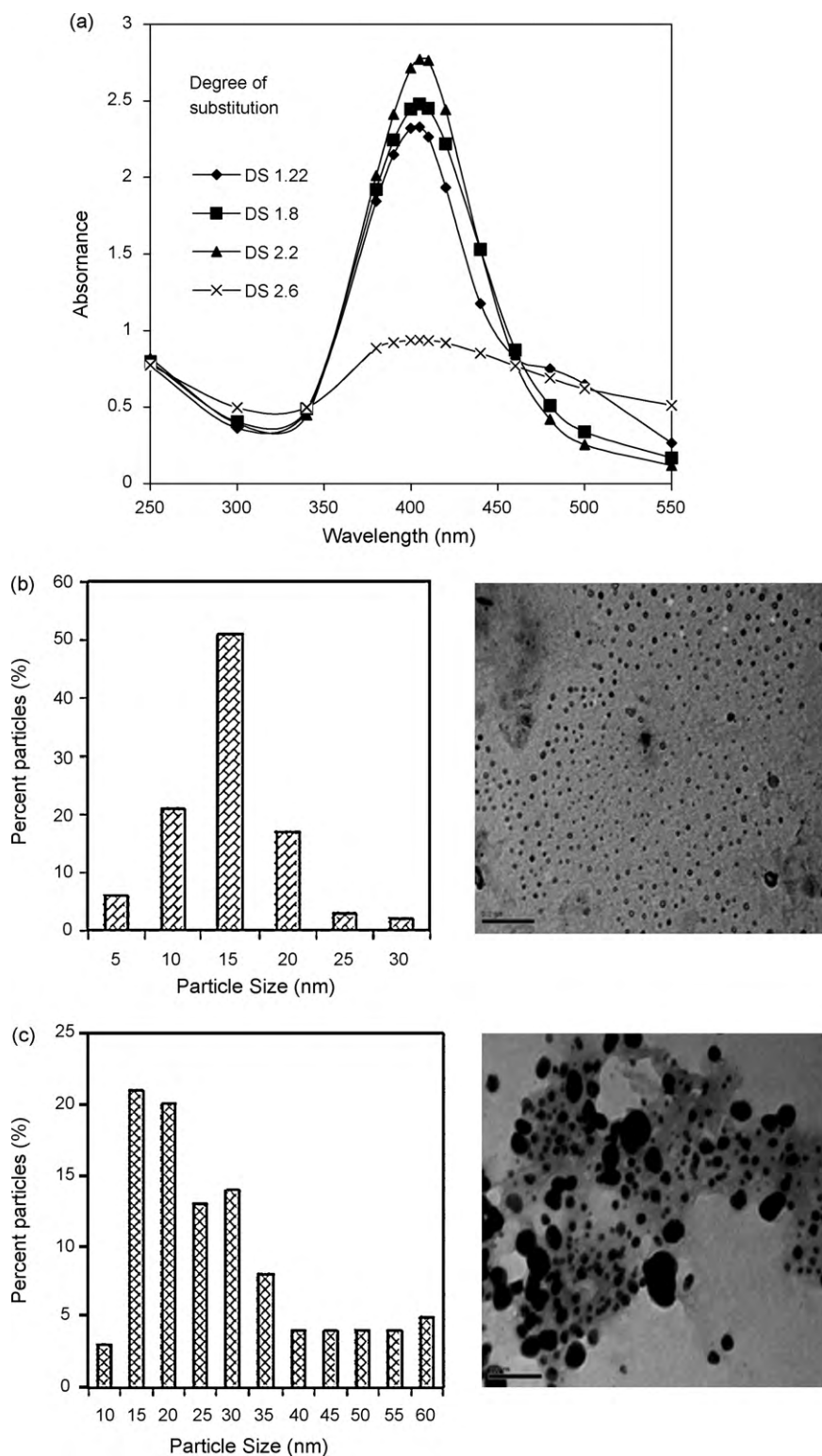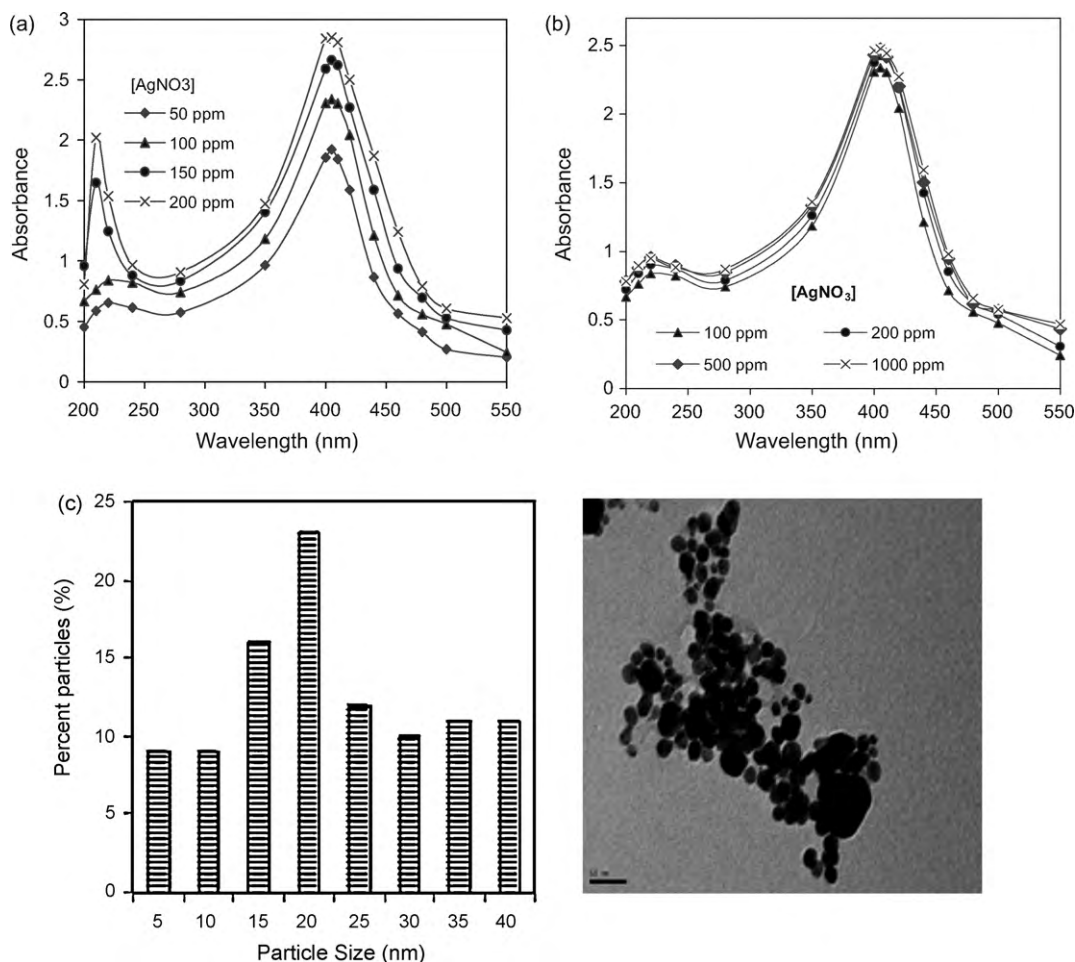
Fig. 5. (a) UV–vis spectroscopy of silver nanoparticles prepared using carboxymethyl celluloses having variable degrees of substitution. Reaction conditions: 0.3% (w/v) CMC (DP, 350); 1 ml (0.1 N) $AgNO_3$; pH 12.5; temperature, 70 °C; duration, 60 min. (b) TEM image and particle size distribution histogram of silver nanoparticles prepared using CMC with DS of 2.2. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 2.2); 1 ml (0.1 N) $AgNO_3$; temperature, 70 °C; pH 12.5; duration, 60 min. (c) TEM image and particle size distribution histogram of silver nanoparticles prepared using CMC with DS of 2.6. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 2.6); 1 ml (0.1 N) $AgNO_3$; temperature, 70 °C; pH 12.5; duration, 60 min.

3.2.6. Effect of degree of substitution

To evaluate the dual role of CMC as reducing and stabilizing agent during preparation of colloidal silver nanoparticles from silver nitrate solution, CMC having different amounts of carboxymethyl groups were used (DS 1.22–2.6).

Fig. 5a shows the UV–vis spectra of silver nanoparticles colloidal solutions prepared using 0.3% CMC solution having fixed DP of 350 and variable DS (1.22–2.6) under similar conditions (1 ml, 0.1 N $AgNO_3$; 70 °C; pH 12.5 for 1 h). The results reveal that (i) regardless of the DS of CMC used, all tested samples show plasmon peak at

Fig. 6. (a) UV–vis spectroscopy of silver nanoparticles prepared using different concentrations of AgNO$_3$. Reaction conditions: 0.3% (w/v) CMC (DP, 350; DS, 1.22); pH 12.5; temperature 70 °C; duration, 60 min. (b) UV–vis spectroscopy of silver nanoparticles prepared using different concentrations of AgNO$_3$ and CMC, keeping the ratio between them always constant. Reaction conditions: CMC (DP 350, DS, 1.22); [AgNO$_3$]:[CMC], 0.3:0.017; pH 12.5; temperature, 70 °C; duration, 60 min. (c) TEM image and particle size distribution histogram of silver nanoparticles prepared using 3% CMC and 1000 ppm AgNO$_3$. Reaction conditions: 3% (w/v) CMC (DP, 350; DS, 1.22); 10 ml (0.1 N) AgNO$_3$; temperature, 70 °C; pH 12.5; duration, 60 min.

wavelength 405 nm which is characteristic for silver nanoparticles colloidal solution, (ii) the absorption intensity increases by increasing the degree of substitution from 1.22 up to 2.2 with formation of the bell shape, which indicates improvement in dispersion of silver nanoparticle clusters in the reaction medium, (iii) increasing the DS above this limit (DS 2.6) leads to significant decrement in the absorption intensity and the curve is broaden which indicates less stability and higher aggregation of silver nanoparticles.

Figs. 2b, 5b and c show the TEM images and particle size distribution histograms of silver nanoparticles colloidal solutions using CMC having DS of 1.22, 2.2 and 2.6, respectively. As is evident the extent of aggregation of silver nanoparticles clusters with wide range of particle size distribution decreases by increasing the DS of CMC up to 2.2, where ideal condition is obtained with the formation of 15 nm silver nanoparticles which represents 50% of the formed nanoparticles. Increasing the DS up to 2.6 leads to the formation of silver nanoparticles with higher aggregation and scattered particle size ranges from 10 to 60 nm. These results are in agreement with the expected data obtained from the UV–vis spectra (Fig. 5a).

3.2.7. Concentration of silver nitrate

Results of the foregoing section made it possible to prepare silver nanoparticles with concentration of ca. 100 ppm. This concentration is rather low for industrial applications. Interest in preparation of silver nanoparticles solutions, which acquire higher concentra-

tions of the nanosized silver particles are, therefore, stimulated. Thus a study was undertaken where silver nitrate (AgNO$_3$) was incorporated at different concentrations in the reaction medium.

Fig. 6a shows the UV–vis spectra of Ag^0 resulting from incorporating different amounts of AgNO$_3$ (50–200 ppm) and keeping CMC concentration constant at 0.3% for all AgNO$_3$ concentrations. Fig. 6a reveals that similar absorption spectra are obtained at wavelength 405 nm and that the intensity of the absorption peak increases by increasing AgNO$_3$ concentration in the reaction medium. The existence of silver ion on incorporating AgNO$_3$ concentrations higher than 100 ppm is also observed indicating that the amount of CMC in the reaction medium is closely related to the amount of silver nitrate.

It could therefore be concluded that in order to obtain silver nanoparticles colloidal solutions with concentrations higher than 100 ppm, one should use AgNO$_3$:CMC ratio of 0.017 g:0.3 g per 100 ml solution.

In order to achieve better stability and efficient reduction for conversion of silver ions to silver nanoparticles with extremely small sizes, certain ratio of silver nitrate to CMC in the reaction medium must be established. Hence, preparation of silver nanoparticles was carried out using higher concentrations of both AgNO$_3$ and CMC (DP 350 and DS 1.22). Increasing the concentrations of both AgNO$_3$ and CMC was done while keeping the ratio of silver nitrate to CMC constant.
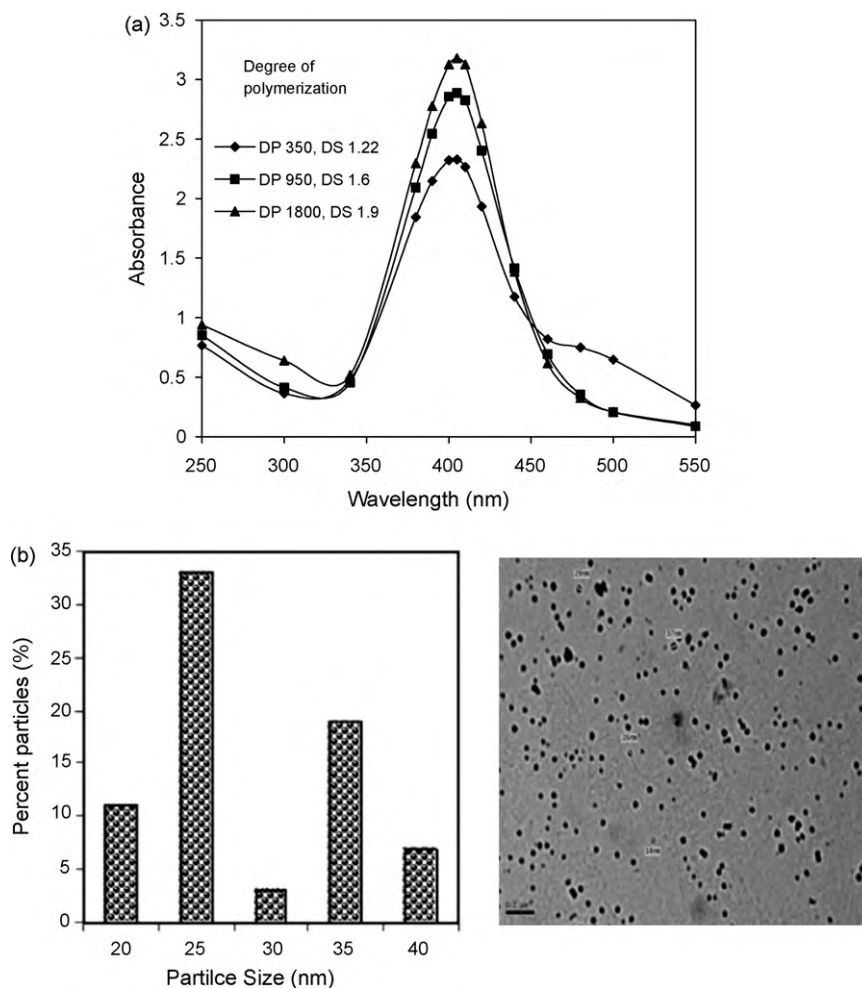
Fig. 7. (a) UV–vis spectroscopy of silver nanoparticles prepared using carboxymethyl celluloses having different degrees of polymerization. Reaction conditions: 0.3% (w/v) CMC; 1 ml (0.1 N) AgNO$_3$; pH 12.5; temperature, 70 °C; duration, 60 min. (b) TEM image and particle size distribution histogram of silver nanoparticles prepared using CMC with DP of 1800. Reaction conditions: 0.3% (w/v) CMC (DP, 1800; DS, 1.9); 1 ml (0.1 N) AgNO$_3$; temperature, 70 °C; pH 12.5; duration, 60 min.

Fig. 6b shows the UV–vis spectra of Ag^0 resulting from incorporating different concentrations of silver nitrate and CMC while keeping the ratio between them always constant. Fig. 6b reveals that similar absorption spectra are obtained at wavelength 405 nm with marginal increase in the intensity of the absorption peak by increasing amounts of AgNO$_3$ and CMC incorporated in the reaction medium. In addition to that, the UV spectra showed nearly disappearance of the peak characteristic for silver ion.

Fig. 6c shows the TEM micrograph and the particle size distribution histogram when silver nanoparticles were prepared using [AgNO$_3$]:[CMC] ratio of (0.17 g:3 g) per 100 ml reaction medium.

The output of this research calls for preparation of well stabilized silver nanoparticles colloidal solution with concentration of ca. 1000 ppm and particle size of nearly 25 nm. Silver nanoparticles with such unique characteristics are unequivocally feasible for valuable industrial applications.

3.2.8. Effect of degree of polymerization

Cellulosic substrates having variable degrees of polymerization (350, 950 and 1800) were prepared via oxidative degradation. These cellulose substrates were subjected to carboxymethylation reaction to obtain water soluble CMC. It is understandable that the higher the DP of the cellulose substrate, the higher the DS needed to obtain water soluble carboxymethyl cellulose. The substrates obtained have DP/DS as follows 350/1.22, 950/1.6 and 1800/1.9. The substrates were evaluated as reducing and stabilizing

agent for preparation of colloidal solution of silver nanoparticles.

Fig. 7a shows the UV–vis spectra of silver nanoparticles prepared using CMC having different DPs. Figs. 2b and 7b show TEM micrographs and the particle size distribution histograms of silver nanoparticles obtained on using CMC of DP of 350 and 1800, respectively.

The results signify that (a) the DP has significant effect on the reduction efficiency, particle size and stabilization by CMC macromolecule, (b) the UV–vis spectra indicate that the intensity of the peak increases by increasing the DP of CMC, (c) the TEM images and particle size distribution histograms indicate that the homogeneity of the formed silver nanoparticles increases by increasing the DP.

4. Conclusion

Green synthesis of silver nanoparticles using carboxymethyl cellulose (CMC) having different DPs and DSs could be accomplished through investigations into factors affecting the synthesis operation. The onset of DP and DS of CMC as well as pH, duration, temperature and ratio of silver nitrate to CMC on transformation of silver ions to silver nanoparticles via reduction by CMC and stabilization of these particles in their colloidal solution assisted by CMC macromolecules were studied. The formation of silver nanoparticles was monitored via color and UV visible spectral analysis, whereas their evaluation was made by making use of Transmission

Electron Microscope (TEM). Results obtained conclude that silver nanoparticles of concentration as high as 1000 ppm could be prepared using the following conditions: 3% CMC (DP, 350; DS, 1.22); 10 ml (0.1 N) AgNO$_3$; temperature, 70 °C; pH 12.5; duration, 60 min. The size (10–25 nm) and shape (spherical) of the silver nanoparticles advocate the latter for many applications, as antimicrobial agents for textiles.

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