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Novel precursors for green synthesis and application of silver nanoparticles in the realm of cotton finishing

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ABSTRACT

Innovative nano-silver colloidal solutions could be achieved using a newly prepared copolymer namely, β-cyclodextrin grafted with poly acrylic acid [βCD-g-PAA] using potassium persulphate as initiator. The copolymer was then used as reductant and stabilizer in the preparation of silver nanoparticles. The latter were monitored via color and UV–visible spectral analysis and transmission electron microscopy (TEM) to determine size and size distribution of these nanoparticles. Such monitoring and evaluation revealed that reduction of Ag^+ to Ag^0, coalesces of the latter to form cluster and the size of this cluster depends on the type and concentration of alkali, the graft yield of the copolymer, the concentrations of both silver nitrate and copolymer and the means of heating: thermal, ultrasonic or microwave. Thermal and ultrasonic methods are by far more effective than the microwave. The silver nanoparticles colloidal solution(s) was applied to cotton fabric. The innovative formulation in question results in fabrics with excellent and durable antibacterial properties.

1. Introduction

The synthesis and application of nano-sized particles to textiles have become of prime importance within the great priority given during the last decade to nanotechnology world-wide. This is advocated by the unique physicochemical properties and potentional applications of nanoparticles For example, nano-TiO_2 was applied for textiles for self-cleaning and in hygienic textiles (Fei, Deng, Xin, Zhang, & Pang, 2006; Shi, Neoh, & Kang, 2005) and ZnO nanoparticles for UV-blocking, antibacterial properties and applying in medical clothes, protective (Choi, Zhang, Gopalan, Lee, & Kang, 2005). On the other hand, silver nanoparticles attract an increasing amount of scientific and industrial interest from fields such as textile science (Lee & Jeong, 2005), medicine (Silver, Phung, & Silver, 2006), agriculture (Park, Kim, Kim, & Choi, 2006), and catalysis (Kensuke Nishioka, Tsuyoshi Sueto, & Nobuo Saito, 2009). It is well known that silver has a broad antibacterial activity while exhibiting low toxicity towards bacteria and fungus. Thus, nanostructure silver film deposited on textile substrates can be used to make ideal functional textiles.To prepare antimicrobial silver-treated cotton fabrics, research and developmental efforts were placed on preparations of silver nanoparticles with controlled size and developing routes to impart silver nanoparticles to cotton fabrics. Traditionally, in preparing silver nanoparticles, numerous reducing agents, such as sodium borohydride ($NaBH_4$), formaldehyde, sodium citrate, hydrazine, ascorbic acid, glucose and γ-ray or UV irradiation, were utilized to reduce the silver cations (Chou, Lu, & Lee, 2005; Shchukin, Radtchenko, & Sukhorukov, 2003), and some polymeric materials, such as poly(vinylpyrrolidone) (PVP), poly(ethylene glycol) (PEG), and some surfactants were used as stabilizers to prevent nanoparticles agglomeration and precipitation (Khanna and Subbarao, 2003; Qing, Xing, Kai, & Jinhuai, 2008).

The use of silver ion or metallic silver as well as silver nanoparticles can be exploited in medicine for burn treatment, dental materials, coating stainless steel materials, textile fabrics, water treatment, sunscreen lotions, etc. and posses low toxicity to human cells, high thermal stability and low volatility.

Chemical reduction is the most frequently applied method for the preparation of silver nanoparticles (Ag NPs) as stable, colloidal dispersions in water or organic solvents (Wiley, Sun, & Xia, 2007). Commonly used reductant is borohydride, citrate, ascorbate, and elemental hydrogen (Panáček et al., 2006). The reduction of silver ions (Ag^+) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers. 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. These clusters eventually lead to the formation of colloidal Ag particles (Morones et al., 2005). When the colloidal particles are much smaller than the wavelength of visible light, the solutions have a yellow color with an intense band in the 380–400 nm range and other less intense or smaller bands at longer wave length in the absorption spectrum. This band is attributed to collective exci-

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tation of the electron gas in the particles, with a periodic change in electron density at the surface (surface plasmon absorption) (Oates & Mucklich, 2005).

In some cases polysaccharides serve as both a reducing and a capping agent. For instance, synthesis of starch–Ag NPs was carried out with starch as a capping agent and β-D-glucose as a reducing agent in a gently heated system. The starch in the solution mixture avoids use of relatively toxic organic solvents. Additionally, the binding interactions between starch and Ag NPs are weak and can be reversible at higher temperatures, allowing separation of the synthesized particles.

Nowadays the increasing awareness about the environment has brought the concept "green chemistry" into focus. 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 (Desimone, 2002). Accordingly, natural polymers like chitosan (Hui-Chia, Wen-Hong, Kuo-Shien, & Min-Hsiung, 2010) and soluble starch (Raveendran, Fu, & Wallen, 2003), hydroxypropyl, carboxymethyl cellulose (Jing, Jing, Xin, Yeling, 2008) and fungi secreted enzyme and proteins (El-Rafie, Mohamed, Shaheen, & Hebeish, 2010) have been dealt with as reducing and stabilizing agent for preparation of silver nanoparticles.

Cyclodextrin molecules, as the biopolymer and biocompatible materials, have attracted lots of research effort both academic and practical applications. In solid or solution state, β-cyclodextrin (βCD) forms a cone shaped molecule with the hydroxyl groups on the outside of the molecule, providing a hydrophilic outside and a hydrophobic cavity. This results of maximum solubility 18.7 of BCD in water and the ability to host hydrophobic non-water-soluble substances in the hydrophobic cavity. Due to this special feature, cyclodextrins have been applied in textile industry, pharmaceuticals and cosmetics fields. A number of approaches in the surface of textiles modification by CDs have been reported in the literature (Martel et al., 2000; Rehmann, Yoshii, & Furuta, 2003). Also reported were graft copolymerizations of βCD with butyl acrylate (Hebeish et al., 2009) and the use of the copolymers obtained in synthesis of ZnO nanoparticles along with application of the latter to cotton fabrics (El-Shafei, Sharaawy, & Hebeish, 2009).

In this research paper we present a thorough investigation on the preparation of silver nanoparticles and utilization of the latter in rendering cotton textile antibacterial. The green strategy implemented to achieve this goal comprises three studies. The first is concerned with the factors affecting the synthesis of βCD, grafted with acrylic acid (βCD-g-PAA); the latter will be used to perform dual actions, viz a reducing agent and stabilizing agent during the preparation of silver nanoparticles. The second study is devoted to the conditions associated with new methods excercized for application of the silver nanoparticles to the cotton fabrics. The third study covers characterization of the surface morphology of antibacterial cotton fabrics and the relationship between the antibacterial property and the content of nano-sized silver on the treated fabric. Moreover, the laundering durability of the bacteriostasis of the silver nanoparticles-treated cotton fabric is examined.

2. Experiments

2.1. Materials

β-cyclodextrin (βCD) was purchased from Wacker Chemie GmbH and acrylic acid (AA) monomer, from Fluka. Mill desized, scoured and bleached print cloth, plain weave, style 400, 102 g/m2 was supplied by Misr El Mahalla El Kobra company, Egypt. The fabric was further purified in the laboratory by washing at 100 °C for 60 min using a solution containing 2 g/L, Na_2CO_3 and 1 g/L, nonionic surfactant. The fabric was then washed several times with boiling water then with cold water and finally dried at ambient conditions.

Potassium persulphate (KPS), sodium hydroxide, sodium carbonate, epichlorohydrin, silver nitrate, sodium citrate, and ethyl alcohol were of laboratory grade chemicals.

2.2. Methods

2.2.1. Graft polymerization procedures

Graft polymerization was carried out under various conditions including concentrations of βCD, AA and $K_2S_2O_8$ (initiator) as well as polymerization time and temperature with a view to obtain βCD copolymer having different grafts. Graft polymerization of βCD with AA was carried out in 100 ml stopper flask. βCD was firstly dissolved in a certain volume of water as desired then AA monomer was added and the flask placed in thermostatic water bath adjusted at 65 °C. The initiator KPS was introduced in the flask containing βCD and AA. At this end the polymerization reaction was allowed to proceed for different times (30–180 min) at different temperatures (30–80) °C. After the desired time, the contents of the flask (polymerization mixture) were poured in a large amount of ethyl alcohol where a precipitate was formed. The precipitate was filtered, washed thoroughly with acetone, and dried at 50 °C. Details of the ingredients concentration as well as other conditions are detailed in the text.

2.2.2. Synthesis of silver nanoparticles using βCD-g-PAA

Silver nanoparticles were prepared using silver nitrate and the newly prepared β-cyclodextrin as reducing and stabilizing agent in presence of sodium carbonate. Experimentally, βCD-g-AA (1%) was dissolved in water and after complete dissolution, sodium carbonate solution (2%) was added to attain pH 9 (solution A). In another conical flask silver nitrate solution with different concentrations in distilled water using heating magnetic stirrer was prepared (solution B). At this end, (solution A) was added dropwise (1 ml each) to (solution B). The reaction was allowed to proceed under continuous stirring and the temperature was maintained at 90 °C. As the reaction went on, the color of the solution changed from pale yellow to dark yellow. The appearance of the yellow color indicated the formation of silver nanoparticles in the reaction mixture. It is well-known that silver nanoparticles exhibit striking colors (light yellow to brown) due to excitation of surface plasmon vibrations in the particles. Preparation of the silver nano particles was also be carried out by making use of either microwave or ultrasonic radiation as described under.

2.2.2.1. Synthesis of silver-nano particle using ultrasonic wave. After addition of solution A to solution B the reaction mixture undergoes different time of sonication (5–20 min) at 70 °C in the ultrasonic water bath.

2.2.2.2. Synthesis of silver-nano particle using microwave technique. After addition of solution A to solution B the reaction mixture proceeds with different microwave power (200–600 W) for different time (3–7 min).

It is as well to note that UV–vis spectrum is quite sensitive to the formation of silver nanoparticles at different time for all reaction techniques.

2.2.3. Application of β-cyclodextrin copolymers onto cotton fabric

The prepared silver nanoparticles and the βCD grafted with AA were applied to cotton fabric incorporated with epichlorohydrin (non-formaldehyde finishing agent) at different concentrations as per two methods, either in the same bath or in two successive bathes by applying silver nano particle at different concentrations, to the cotton fabric before or after treatment with the βCD-g-PAA as described below.

2.2.3.1. Method 1. The cotton fabric was padded in an aqueous solution containing βCD copolymer 3%, ephichlorphydrin as a crosslinker 2% and NaOH (2%) and nano silver solution (20–50 mg). The fabric was then dried at 80 °C for 5 min followed by fixation at 140 °C for 3 min.

2.2.3.2. Method 2. Fabric samples were padded to 100% wet pickup in an aqueous solution containing the βCD copolymer 3% ephichlorphydrin as a cross linker (2%) and NaOH (2%), dried then immersed for 15 min in two different concentrations of freshly prepared nano silver solution (20, 50 mg). Alternatively, the samples were padded firstly in silver nano solution, dried at 80 °C for 5 min followed by padding in the βCD copolymer solution. For all the samples fixation was conducted at 140 °C for 3 min. Finally, the samples were washed several times with hot water and dried at ambient temperature.

2.3. Testing and analysis

Carboxyl group was determined according to a reported method (Daul, Reinhardt, & Reid, 1953).

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). Silver nanoparticles embedded in βCD-g-PAA were recorded in spectra 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. A solution containing βCD-g-PAA was used as the blank.

Transmission electron microscope (*TEM*): Particle shape and size were obtained with a JEOL-JEM-1200. Specimens for TEM measurements were prepared by dissolving 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 silver nanoparticles was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs.

Scanning Electron microscopy (*SEM*) of the treated fabrics was studied using a scanning electron probe microanalyzer (type JXA-840A) – Japan. The specimens in the form of fabrics were mounted on the specimen stabs and coated with thin film of gold by the sputtering method. The micrographs were taken at two magnifications, namely 1000 and 2500, using 30 kV accelerating voltage.

The antimicrobial activity of the treated fabrics was examined on *staphylococcus aureus*, and *Escherechia coli*, by antimicrobial agar diffusion test according to AATCC Test Method 147-1988.

3. Results and discussion

3.1. Factors affecting preparation of β-cyclodextrin copolymer

Grafting of a vinyl monomer such as acrylic acid (AA) onto β-cyclodextrin (βCD) is generally considered to involve two steps; (1) the generation of reactive sites on βCD backbone and addition of AA to βCD free radical to initiate the graft chain (2) propagation of the graft through addition of AA molecules to the initiated chain. Reactive sites on βCD backbone are perhaps generated by chemical and physical initiation methods in manner similar to those used for natural polysaccharides (Hebeish and Guthrie, 1981; Mondal, Farouqui, & Enamul Kabir, 2002). With this in mind, a systematic study is carried out with a view to optimize graft copolymerization of β-cyclodextrin with acrylic acid using potassium persulphate as initiator. Hence, parameters affecting the copolymerization under investigation are examined. Parameters studied included (i) monomer concentration, (ii) initiator concentration (iii) reaction time and (iv) reaction temperature. The graft yield expresses the increase in weight of βCD divided by its original weight whereas the carboxyl content, expressed as m eq/100 g βCD-g-PAA is determined as reported elsewhere (Mondal and Hoque, 2007). Given below are the results obtained along with their appropriate discussion.As already indicated graft polymerization of AA onto βCD was carried out using potassium persulphate as the initiator. In this system, graft polymerization is initiated by the decomposition of the inorganic agents ($K_2S_2O_8$) and the generation of the primary radicals $SO4^{\bullet -}$ and $^{\bullet}OH$ (Ibrahim, Mondal, Yasumitsu, Makoto, & Koki, 2008). The primary radicals, in turn, abstract hydrogen atoms from the βCD backbone to generate secondary radicals, the active sites for graft polymerization. The proposed mechanism of graft polymerization in this system is shown in Scheme 1 Scheme 1.

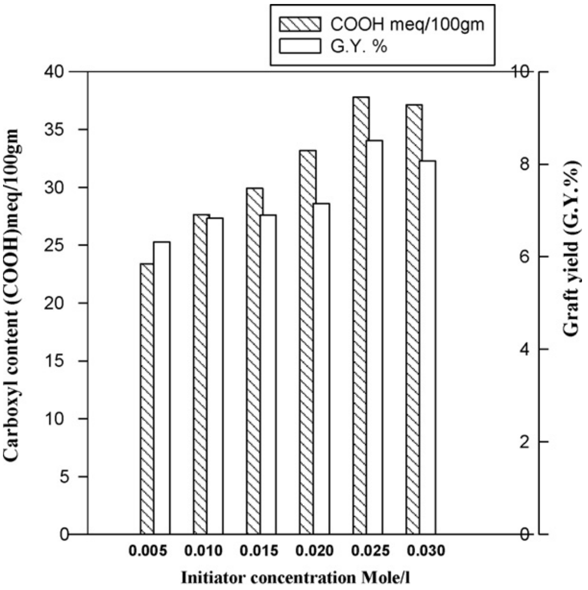

Fig. 1. Effect of initiator concentration on GY% and carboxyl content of β-cyclodextrin grafted wit AA condition used: [βCD], 0.351 mol/l; [AA], 2.8 mol/l; time 60 min; temperature, 65 °C.

Fig. 1 shows the effect of potassium persulphate ($K_2S_2O_8$) concentration on the graft yield and carboxyl content of βCD. The graft yield increases by increasing potassium persulphate concentration up to 0.025 mol/l. Further increase in initiator concentrations decreases the graft yield. Logically, the increase in initiator concentration causes an increase in the number of primary radicals generated. However, the primary radicals not only trigger the graft polymerization via hydrogen abstraction along the βCD backbone, but also homopolymerization of the acrylic acid as well as fast termination of the growing grafted chains. It is well known that high initiator concentrations lead to short chain polymers (low degree of polymerization). Thus higher amount of homopolymer formation on the charge of grafting as well as lower molecular weight of the graft upon using higher $K_2S_2O_8$ concentrations would account for lower grafting at higher $K_2S_2O_8$ concentrations.

As is evident, the graft yield substantially increases by increasing AA concentration up to 7 mol/l then tends to leveling off.

It is known that raising the graft polymerization temperature up to 65 °C causes substantial increase in graft yield and carboxyl content. This could be associated with (i) increase in the number of the free radicals formed on the βCD backbone, (ii) increase in propagation of the graft, (iii) increase in the mobility of monomer molecules and their collision with the βCD macroradicals, and (iv) enhancement of diffusion of monomer and initiator into the βCD structure.

On the other hand, temperature higher than 65 °C decreases the magnitude of grafting most probably due to the fast termination rates (Hebeish, El-Shafei, & El-Bisi, 2005) along with instability of the initiator.

The graft yield % and carboxyl content increases by prolonging the duration of polymerization up to 120 min then almost levels off. This indicates that the polymerization time exerts a favorable effect on grafting yield % and carboxyl content. The favorable effect of polymerization time on the polymer yield is a manifestation of better opportunity for the reactants to be in better contact and therefore reactions. That is, time creates a more favorable environment for reactions to occur. Current results disclose, however, that 60 min-polymerization time is enough to attain high graft yield and carboxyl content. Longer than 60 min. causes little extra increase in the graft yield. It is concluded; therefore, that major amount of polyacrylic acid graft occurred on βCD backbone in the first 60 min of the copolymerization reaction.

The characterization of the prepared graft copolymer was done using FTIR spectroscopy which improve the appearing of new peaks at 1720 cm^{-1} indicated the presence of –COOH in the back bone of B-CD.

3.2. *Utilization of grafted β-cyclodextrin copolymers (βCD-g-PAA) as reducing and stabilizing agent in preparation of silver nanoparticles*

In our method for preparation of Ag NPs we used the aforementioned βCD-g-pAA for studying factors that govern the preparation of silver nanoparticles e.g. type and concentration of alkali, concentration of βCD-g-pAA, silver nitrate concentration as well as temperature and duration. The preparation of silver nanoparticles was monitored via color change using UV–visible spectral analysis. Evaluation of the prepared silver nanoparticles was made using transmission electron microscopy (TEM). The polymer under investigation characterized by βCD backbone with its seven glucose units and Polyacrylic acid graft can do the dual polysaccharide function AgNPs is synthesized by the reduction of Ag^+ inside of nanoscopic βCD templates. The extensive network of hydrogen bonds in the templates provides surface passivation or protection against nanoparticle aggregation.

βCD-g-PAA i.e. β-cyclodextrin copolymers were synthesized having different grafts yields using different monomer concentrations based on weight of βCD (20%, 50%, 80%, 100%) these copolymers were used to perform dual role: as reducing agent and as stabilizing agent during the preparation 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.

Reaction mechanism for formation of silver nanoparticles: The β-cyclodextrin copolymers βCD-g-PAA was carried out in current work to provide products with specific properties which are needed for synthesis of silver nanoparticles. βCD-g-PAA consists of chemically modified βCD-g-PAA chains containing reducing groups and carboxyl groups. All these components with their anionic and reducing properties support the utilization of βCD-g-PAA as reducing and stabilizing agent for the synthesis of silver nanoparticles. The negatively charged solubilized βCD-g-PAA 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 βCD-g-PAA. 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).

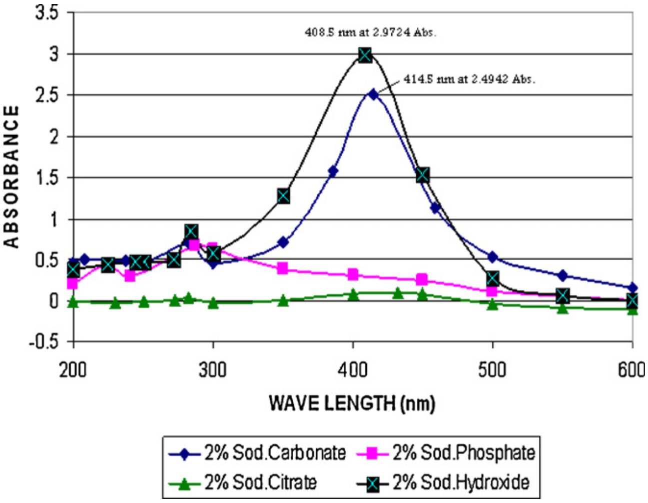

Fig. 2. Effect of type of alkali on preparation of silver nanoparticles. Conditions: (βCD-g-PAA), 1%; ($AgNO_3$), 20 mg; time, 10 min; temperature, 90 °C.

3.2.1. *Type of salts*

Fig. 2 shows the UV–vis spectra of silver nanoparticles prepared using βCD-g-PAA. As reducing and stabilizing agent in presence of different salts, namely, sodium hydroxide, sodium carbonate, sodium phosphate and sodium citrate at 2% each. It is observed that the use of different types of alkali is accompanied by noticeable changes in the electronic absorption spectra. The band becomes stronger and symmetrical, with pronounced bell-shape at λmax 408.5 nm and λmax 414.5 upon using sodium hydroxide and sodium carbonate, respectively; this band could be assigned to the plasmon excitation of silver nanoparticles as a result of collective excitation of the conduction electrons in the metal. It should be emphasized, however, that silver colloids were destabilized by sodium hydroxide and deposited. Furthermore, sodium phosphate and sodium citrate have failed to assist formation of silver nanoparticles by virtue of their unability to bring about the proper pH required for reduction of Ag^+ to Ag^0. It follows from this that sodium carbonate is the best alkali for affecting the reduction and conversion of Ag^+ to Ag^0.

3.2.2. *Concentration of sodium carbonate*

Obviously, the concentration of sodium carbonate plays an important role in the reduction of silver ion to silver nanoparticles. When 0.5% sodium carbonate was used no plasmon peak is observed. Increasing the concentration of sodium carbonate to 1% acts in favor of conversion of Ag^+ to Ag^0 though the intensity of the plasmon band is weak and very broaden around 423 nm indicating lower conversion percentage of Ag^+ to Ag^0. This situation remains almost unaltered when 1.5% sodium carbonate was used. Increasing the concentration of sodium carbonate to 2% causes unexpected enhancement in the absorption intensity and shift the band towards shorter wave length (414.5 nm at 2.4942 absorbance) which could be attributed to the enlargement in the size of silver nanoparticles. Increasing the concentration of sodium carbonate further to 3% exerts an adverse effect on the absorption intensity of the plasmon band which become broaden around 414.5 nm at 2.1425 absorbance, a point which may be taken to indicate depletion in formation of silver nanoparticles. It can, therefore, be

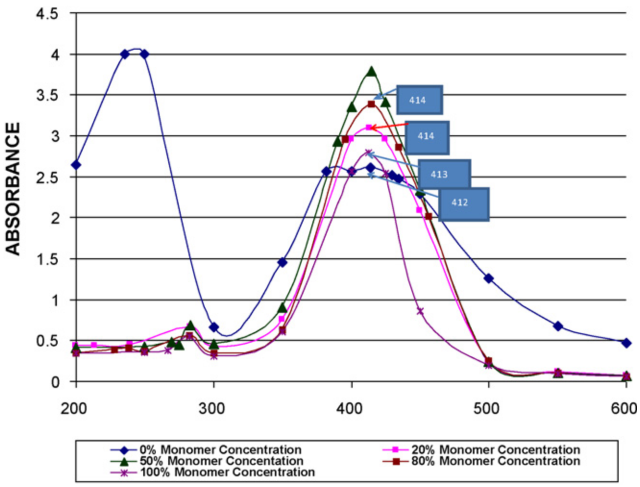

Fig. 3. Effect of graft yield of βCD-g-PAA on preparation of silver nanoparticles. Conditions: (βCD-g-PAA), 1%; ($AgNO_3$), 20 mg; sodium carbonate, 2% concentration; time, 10 min; temperature, 90 °C.

concluded that 2% sodium carbonate constitutes the optimal concentration as it enables attaining the proper pH 9.5 which required for effective reduction of Ag^+ to Ag^0.

3.2.3. *Nature of β-cyclodextrin copolymer*

As already emphasized, the β-cyclodextrin copolymer, i.e. βCD-g-PAA, plays dual rule during the preparation of nano-sized silver particles. The first is to generate complex compound with silver ions and control the reduction process. The second is to protect the silver atoms from a growth and agglomeration for silver nanoparticles to get embedded and stabilized. Stated in other words, complexation of silver ions to hydroxyl groups of β-CD accelerate the reduction process by the hemiacetal groups and secondary alcoholic groups and expand PAA graft molecules would make it more accessible for silver. Hence, it is advantageous to study the effect of the magnitude of grafting of β-cyclodextrin, which determines nature of the latter, on the reactions involved in preparation of silver nanoparticles. To achieve this target, β-CD copolymers containing different PAA grafts were firstly synthesized using AA monomer at concentrations of 20%, 50%, 80% and 100%, based on weight of β-CD and the so obtained copolymers were used in a second step for preparation of silver nanoparticles.

Fig. 3 shows the UV–vis absorption spectroscopy of the nano-sized silver particles prepared using the aforementioned copolymers at 1% concentration each at 90 °C for10 min. Obviously, when β-cyclodextrin prepared using 50% AA monomer for preparation of nano-sized silver particles, the latter acquire plasmon resonance band which is stronger and symmetrical, with a pronounced bell-shape with λmax 414.5 nm at 2.4249 absorbance. Similar situations are encountered with copolymer with copolymers prepared using AA concentrations of 20% and 80% but with lower intensity. On the other hand, higher AA concentration (i.e. 100% on weight of βCD) brings about copolymer with which the plasmon peak becomes broaden with the least intensity (λmax 412 nm at 1.6485 absorbance) within the range of the copolymers studied. In contrary of this, at 0% of monomer there is a broad band appear and there is sharp band indicate the formation of silver nanoparticle. This concluded that the βCD alone without grafting not efficient in the preparation of silver nanoparticles.

Based on the above, it may be concluded that nature of the β-cyclodextrin copolymers under investigation as determined by the magnitude of polyacrylic acid graft in the copolymer plays an important role in the preparation of silver nanoparticles. Reduction of Ag^+ to Ag^0, coalesces of the latter to form cluster and the size of this cluster seems to rely on the nature of the β-CD copolymer.

3.2.4. *Silver nitrate concentration:*

The study of the UV–vis absorption spectroscopy of silver nanoparticles prepared using 1% βCD-g-PAA as a reducing and stabilizing agent along with different concentrations of silver nitrate was clarify that variation in silver nitrate concentration causes appreciable changes in the electronic absorption spectra of the nanosized silver particles. A band at higher energy i.e. 285 nm, appears when silver nitrate at a concentration of 15 mg was used; the intensity of this band decreases at lower $AgNO_3$ concentration (5 mg/l) as well as higher $AgNO_3$ concentrations (20, 25 and 40 mg/l). Simultaneously other bands at relatively lower energy. i.e. 385–500 nm with plasmon peaks, 415 nm at 0.78 absorbance, 422 nm at 1.2 absorbance, 414.5 nm at 2.4942 absorbance and 412.5 nm at 2.6547 absorbance when $AgNO_3$ concentrations of 25, 5, 20 and 15 mg were used respectively. With higher $AgNO_3$ concentration (i.e. 40 mg), no plasmon peak could be observed indicating that nano-sized silver particles did not form. Greater availability of $AgNO_3$ molecules at its higher concentration seems to bring about strong complexes with the copolymer and exceeds the sites of interaction on the copolymer thereby offsetting the functions of the latter as reducing agent and stabilizing agent. It is also likely that higher concentration of $AgNO_3$ acts in favor of agglomeration of the silver particles rather than in the formation of capped silver nanoparticles in a colloidal solution.

3.2.5. *Concentration of β-cyclodextrin copolymer*

β-cyclodextrin copolymer (βCD-g-PAA) prepared using 50% AA, based on weight of βCD was used at different concentrations along with constant concentrations of $AgNO_3$ and Na_2CO_3 for preparation of silver nanoparticles. The UV–vis spectra of the so obtained nano-sized silver particles and their dependence on the concentration of β-cyclodextrin copolymer are illustrated that a band at higher energy (285 nm) appears when 0.5% and 1% of the copolymer were used. Higher copolymer concentration (2% and 3%) brings about bands which are coincided and their intensity is much lower.

Simultaneously other bands appear at relatively lower energy (350–500 nm) with different plasmon peaks at different absorbance. Most notably of this is the plasmon peak 411 nm at 2. 9548 absorbance obtained upon using 1% copolymer. It is as well to emphasize that 0.5% copolymer results also in a narrow plasmon peak but with less intensity compared to that obtained with 1% copolymer. This is not the case when the copolymer was used at concentrations of 2% and 3%. With such high concentrations the plasmon peaks are broaden with much lower intensity compared to their mates obtained upon using the copolymer at 0.5 and 1% concentrations.

3.3. *Application of microwave and ultrasound in preparation of silver nano-particles*

In the foregoing paragraphs, preparation of silver nanoparticles was carried out under the effect of thermal heating using β-cyclodextrin copolymer in alkaline medium as a reductant for conversion of Ag^+ to Ag^0 and stabilizer for capping the formed silver nanoparticles in order to prevent agglomeration. In this paragraph other heating sources, namely, microwave radiation and ultrasonic energy were practiced. UV–vis spectra of thus obtained silver nanoparticles along with those prepared under the influence of thermal heat (90 °C) are shown in Fig. 4.

Fig. 4 discloses that the silver nanoparticles obtained by thermal heating as well as by microwave exhibit bands at higher energy (285 nm) but with the certainty that the intensity of the former is higher than the latter. Concurrently other bands appear at relatively

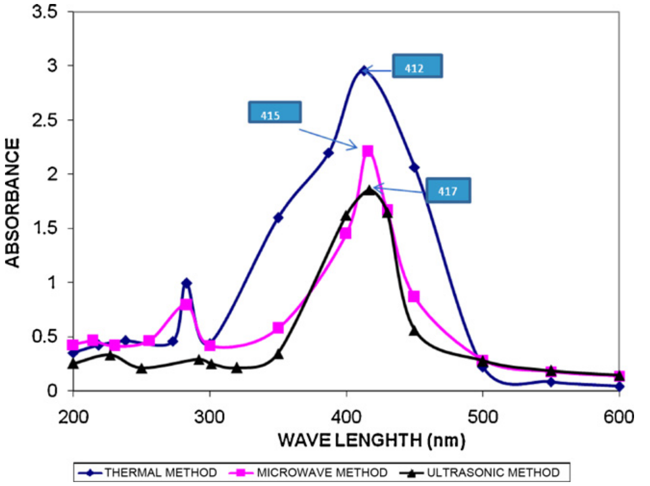

Fig. 4. Effect of different heating sources on preparation of silver nanoparticles. Conditions: thermal method:(βCD-g-PAA), 1%; ($AgNO_3$), 20 mg; sodium carbonate, 2%; time, 10 min; temperature, 100 °C. Microwave method: achieving the optimum condition for 4 min at power 200 W. Ultrasonic method: achieving the optimum condition for 12 min at 90 °C.

lower energy (350–500 nm) with different plasmon peaks when the particles become larger. While the sharp plasmon peak at 407 nm of silver nanoparticles prepared using the thermal method is narrow with higher intensity, plasmon peak of the nanoparticles prepared using the microwave method is broaden with much lower intensity. The same holds true for the ultrasonic method but the peak is more broaden with lower intensity as compared with the microwave method. Hence the thermal method is by far more effective than the microwave and ultrasonic methods though the microwave was reported to yield uniform nanoparticles (Siddharthan, Seshadri, & Sampath Kumar, 2005).

3.4. Characterization of silver nanoparticles

Silver nanoparticles prepared as per the three methods viz. the thermal method; the microwave method and the ultrasonic method were subjected to transmission electron microscopy (TEM) with a view to shed insight on the size, shape and distribution of those nanoparticles. The TEM images (Fig. 5a–c) signify that the mean size of silver nanoparticles amounts to 3–22 nm and they are spherical in shape irrespective of the method of preparation. On the other hand, silver nanoparticles prepared using the ultrasonic method are much more uniform than those prepared using either thermal or microwave radiation method. With the latter, some agglomeration of the nanoparticles occurs as is evident from the corresponding TEM image. The nanoparticles smaller than 10 nm interact with bacteria and produce electronic effects, which enhance the reactivity of nanoparticles. Thus, it is corroborated that the bactericidal effect of silver nanoparticles is size dependent. Uniformity of silver nanoparticles and smaller size are obtained using ultrasonic method than thermal and microwaves radiation. While the conventional thermal method is very comparable with those prepared by the microwave method though little agglomeration is observed with the thermal method.

3.4.1. Morphologies and surface characterizations of cotton before and after treatment with β-cyclodextrin copolymers with and without silver nanoparticles

The interactions between the fibers and the metallic silver result from: (a) the formation of a chemical bond between the silver and alcoholic groups of cotton and (b) the physical adsorption of the silver nanoparticles on the surface of the fabrics.

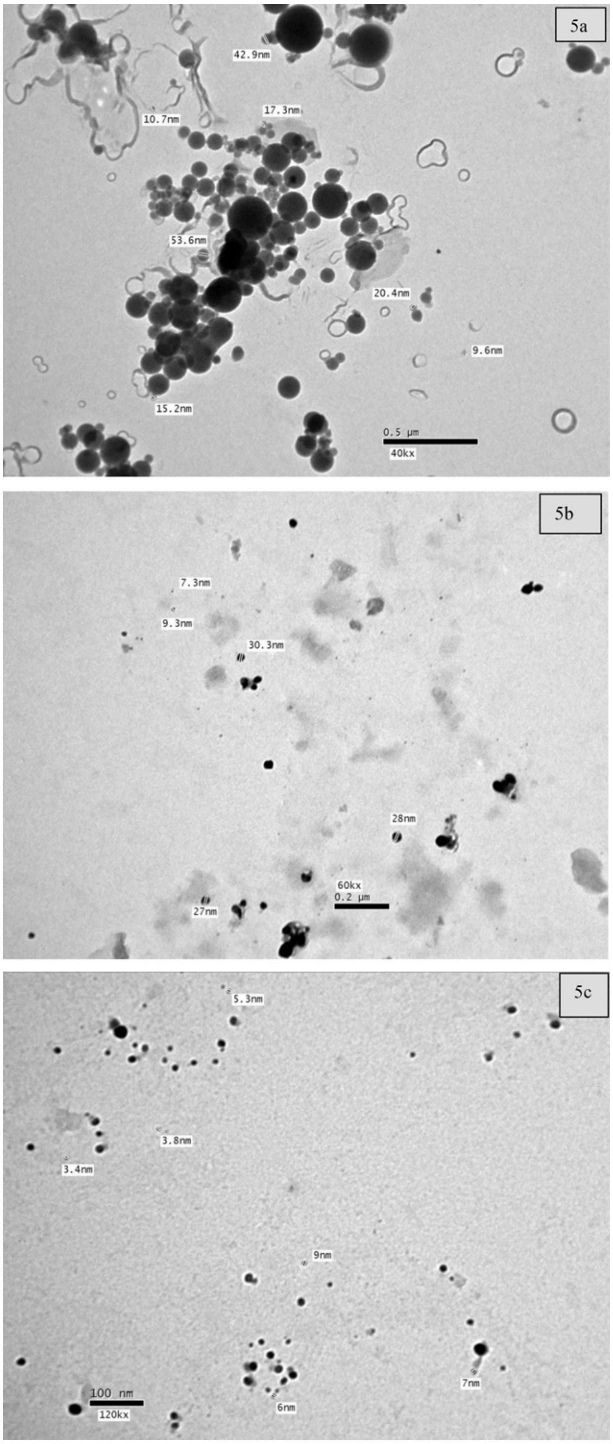

Fig. 5. (a–c) TEM micrograph of silver nanoparticles prepared using $AgNO_3$ at concentration of 50 mg using (a) thermal heating, (b) microwave, and (c) ultrasonic waves.

The scanning electron microscope (SEM) images of cotton fibers before and after treatment of the fabric with β-cyclodextrin copolymers along with epichlorohydrin with and without silver nanoparticles prepared using two different concentrations of silver nitrate are shown in Fig. 6(A–D).

The image of Fig. 6A demonstrates the smooth structure of the cotton fabrics before coating with the β-cyclodextrin copolymers. After treatment with the copolymer (i.e. βCD-g-PAA) along with epichlorohydrin homogeneous coating occurred as can be seen in

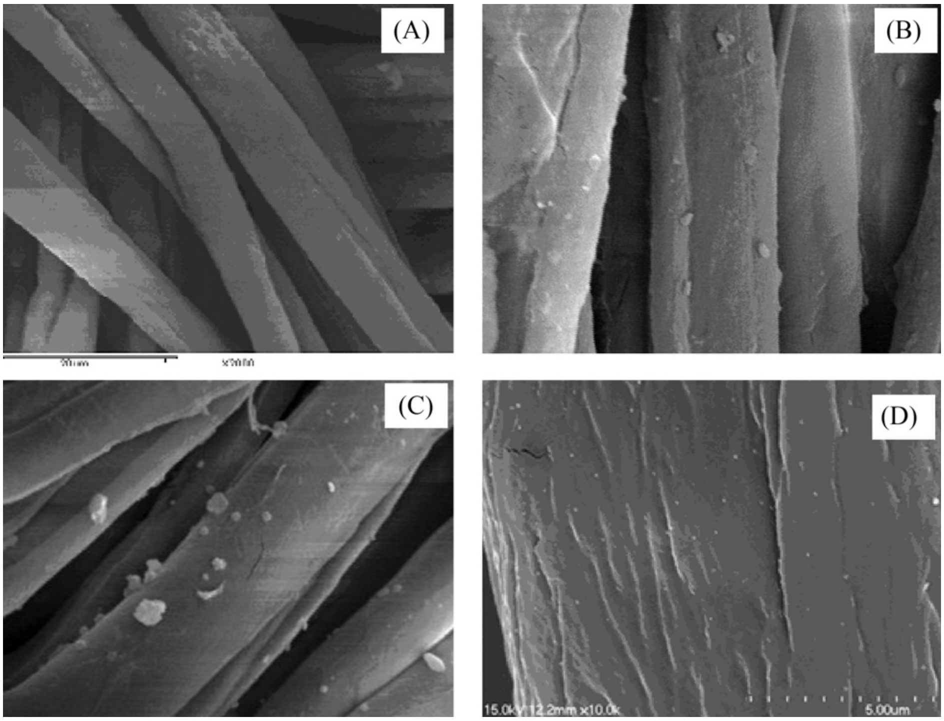

Fig. 6. SEM of cotton blank and cotton loaded with β-cyclodextrin copolymers with and without silver nanoparticles, blank cotton (A); βCD-g-PAA along with epichlorohydrin (B); βCD-g-AA along with epichlorohydrin and silver nanoparticles [Ag], 20 mg; βCD-g-PAA along with epichlorohydrin and silver nanoparticles [Ag], 50 mg.

Fig. 6B. Treatment with the same formulation but with additional silver nanoparticles colloid prepared using $AgNO_3$, (20 mg) brings about coated fabric with the nanosilver particles included therein as well as deposited on the surface of the fibers of the cotton fabric as shown in Fig. 6C. Stronger coating could be achieved using higher concentration of silver nanoparticles as is realized from Fig. 6D. In the latter the nano-sized silver particles are well dispersed on both the cotton surface and the grafted coating present thereon. It is understandable that presence of epichlorohydrin act to anchoring the said β-cyclodextrin copolymers to cotton cellulose as well as to effect crosslinking between adjacent cellulose chains for better fabric performance.

Mention should also be made of attachment of the silver nanoparticles to cotton fabric. Attachment can be induced through inclusion of the nanoparticles in the β-cyclodextrin cavities of the copolymer. Attachment of the nanoparticles can also occur by being embedded in the βCD-g-PAA. This is in addition to the aforementioned interactions including chemical reaction and physical absorption.

3.4.1.1. Qualitative determination of βCD molecules on the textile substrate. βCD molecules on the textile substrate were determined with phenol red and phenolphthalein (Voncina, Majcen, & Marechal, 2005). Phenol red forms a yellow complex with βCD, so phenol red changed color from red to yellow when βCD was present on the textile substrate (shown in Fig. 7). Fig. 7 presents the change in the color of phenolphthalein from carmine red for the untreated textile substrate to colorless for the βCD-g-PAA treated textile materials.

3.5. Antibacterial activity of cotton fabric loaded with silver nanoparticles

Two colloidal solutions containing 20 mg and 50 mg/l silver nanoparticles were prepared as previously described. Each solution (S) was applied along with βCD-g-PAA plus epichlorohydrin (composite, C) as per two treatment sequence. One treatment sequence involved padding the fabric with composite (C), drying then padding with silver solution (S) to establish C/S sequence. The other sequence of fabric treatment entailed padding with the silver solution (S) then drying followed by padding with the composite (C) to establish (S/C) sequence. After treatment, fabrics thus loaded with nano-sized silver particles were laundered 5 and 10 cycles simulated in an AATCC standard wash machine according to the AATCC test method 61-1996. This was done to clarify the durability of the silver nanoparticles as antibacterial finish which was realized through investigating the bacterial reduction rates of *Escherichia coli* and *Staphylococcus aureus* after 5 and 10 washing cycle of the treated fabrics. Results obtained with both sequences of treatment, i.e. C/S and S/C using silver nano particles at concentration of 20 mg and 50 mg/l are shown in Fig. 8a and b respectively.

Results of Fig. 8a and b signify the following features: (a) the untreated cotton fabric (blank) and fabric treated with the composite (βCD-g-PAA) in absence of the nano-sized silver particles exhibit no inhibition zone indicating no antibacterial activity; (b) treatment of the fabrics as per the C/S and S/C at the two used concentrations of silver nanoparticles render the fabric antibacterial irrespective of the bacteria used, (c) resistance of the treated fabric to *S. aureus* is, however, greater than *E. coli* as evidenced

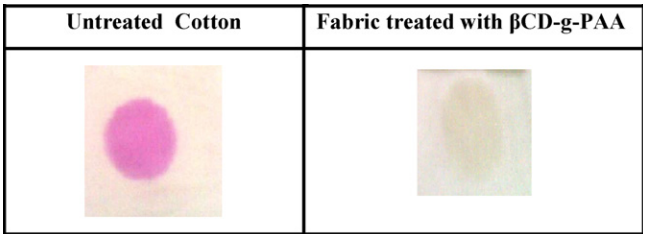

Fig. 7. Change in the phenol red color from red to yellow for fabrics treated in solutions containing βCD-g-PAA. (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Factors affecting fabric finished formulation βCD-g-PAA and epichlorohydrin.

Physical properties	Untreated fabric	Factors affecting fabric finished formulation βCD-g-PAA and epichlorohydrin															
		βCD-g-PAA concentration (%)				NaOH concentration (%)				Epichlorohydrin concentration (%)				Duration of thermofixation (min)			
		1.0	3.0	4.0	5.0	0.5	1.0	1.5	2.0	0.5	1.0	3.0	4.0	2.0	3.0	4.0	5.0
Dry CRA^0 (W + F)	126	160	179	167	159	163	182	210	208	190	196	210	186	190	212	198	195
Wet CRA^0 (W + F)	137	205	217	213	203	195	207	225	223	208	245	208	203	210	242	234	232
T.S (kg)	61	61.5	64	63	59	70.5	62.5	63.5	62	69	58	53.5	60	68.5	72.5	67.5	72
Elongation at break (%)	15	12	12	13	12	12	11	13	11	10	14	13	11	18	20	18	17

by comparing the inhibition zone for both bacteria, (d) similarly, the higher concentration of silver nanoparticles is accompanied by higher inhibition zone than the lower concentration reflecting the key role played by greater availability of silver nanoparticles within the fabric in the bacterial activity of the latter, (e) fabrics treated according to C/S sequence display lower antibacterial activity than those obtained with S/C sequence indicating greater fixation in concomitant with higher accessibility of the silver nanoparticles by the composite in S/C sequence than C/S sequence, (f) the inhibition zones are lower upon giving 5 washing cycles implying partial removal of the silver nanoparticles under repeated washing, (g) the retained antibacterial activity – after 10 washing cycles – as measured by inhibition zones advocate current treatment as durable finishing for production of antibacterial cotton and, (h) the finishing treatment under investigation is so effective that fabrics finished using current treatment formulation at silver nanoparticles as low as 20 mg/l acquire significant antibacterial properties even after 10 washing cycles.

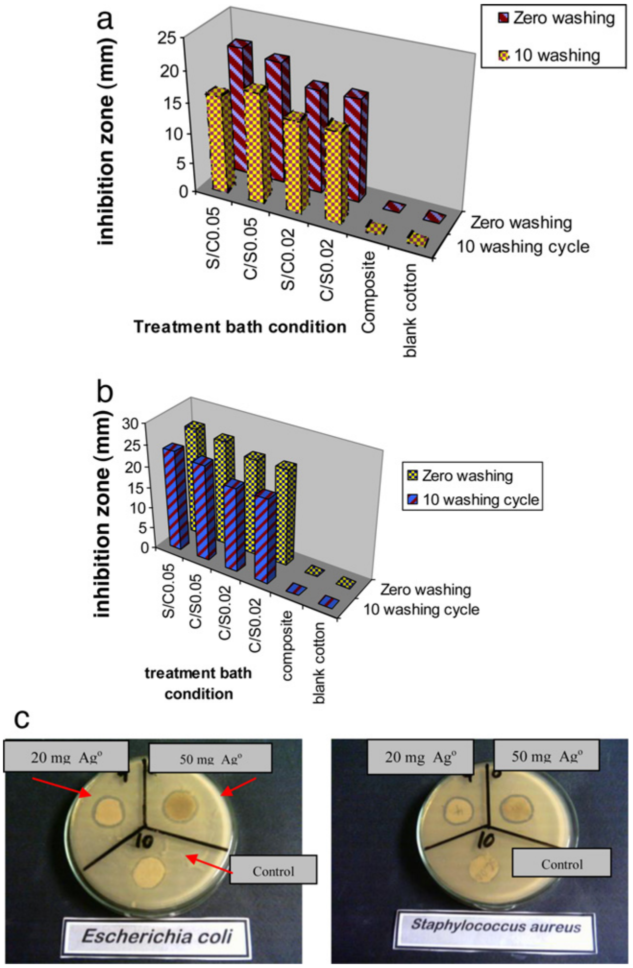

Fig. 8. (a) The bacterial reduction rates of *Escherichia coli* with different treatment sequences, (b) the bacterial reduction rates of *Staphylococcus aureus* with different treatment sequences, (c) antibacterial results of 20, 50 mg silver nanoparticles using two Scheme 1 Proposed mechanism for graft polymerization of vinyl monomers onto βCD using $K_2S_2O_8$ initiation system.

Fig. 8C shows the results of the antibacterial activity of cotton fabric loaded with silver nano particles (Ag-loaded fabric) as per the S/C sequence on the growth of *Escherichia coli* and *Staphylococcus aureus*. It is clear that the growth of the bacterial colonies around the Ag-loaded fabric is inhibited, whereas a dense population of bacterial colonies appears in the control set that contains pieces of control fabric in the petri dish (Fig. 8C). The observed inhibiting action of nano Ag-loaded fabric is due to the release of Ag^+ ions from the Ag nanoparticles present in the fabric. These Ag^+ ions come in contact with bacterial cells and kill them.

The bactericidal action of Ag-loaded fabric is shown above to depend upon the concentrations of Ag nanoparticle onto the fabric. To confirm this, two samples of fabric treated with βCD-g-PAA and epichlorohydrin were put in previously prepared colloidal solution containing 20 mg and 50 mg/l Ag nanoparticles. The antibacterial action of the so obtained treated samples as compared with the untreated fabric (control), is shown in Fig. 8C Obviously, fabric treated with 50 mg silver nanoparticles exhibit greater inhibiting power against growth of bacterial colonies as compared with fabric treated with 20 mg silver nanoparticles. This could be interpreted in terms of greater silver nanoparticles entrapped in the fabric due to the availability of a greater number of binding sites for Ag^+ ions. That is why Ag-loaded fabric with 50 mg Ag nanoparticles acquires more inhibiting power against bacteria. Hence, it may be concluded that the extent of Ag nanoparticles in the fabric plays a key factor in controlling its antibacterial activity. It is further noted that the control (untreated fabric) shows a dense population of bacterial colonies; a point which substantiates the key role of silver nanoparticles in the bacterial action of fabrics treated thereof.

Table 1 shows the effect of concentration of β-CD (1–5%), sodium hydroxide (0.5–2%), epichlorohydrin (0.5–4%) and fixation time (2–5 min) on fabric performance when the chemical finishing was carried out using βCD-g-PAA-Ag nano particle incorporation with epichlorohydrin as non formaldehyde finishing agents. Results of WRA advocate the use of 3% βCD-g-PAA-Ag nano particle. The same holds true for the tensile strength and elongation at break.

4. Conclusion

Synthesis of silver nanoparticles using a newly prepared copolymer namely, β-cyclodextrin grafted with poly acrylic Acid [βCD-g-PAA].were investigated The optimum condition were as follow: [βCD]0.351 mol/l, [A.A]2.8 mol/l; M:L.R(1:5); time 60 min; temperature 65 °C The copolymer was then used as reductant and stabilizer in the preparation of silver nanoparticles. The latter were monitored via color and UV–vis spectral analysis. Meanwhile thus obtained silver nanoparticles colloids were evaluated by making use of transmission electron microscopy (TEM) to determine size and size distribution of these nanoparticles. Investigation of the factors affecting the preparation process were focused on the type and concentration of alkali, the graft yield of the copolymer, the concentrations of both silver nitrate and copolymer and the means of heating, thermal, ultrasonic or microwave. The results signify that uniformity of silver nanoparticles and smaller size are obtained using ultrasonic method (3–6 nm) than thermal (9–42 nm) and microwaves radiation (7–30 nm). While the conventional thermal method is very comparable with those prepared by the microwave method though little agglomeration was observed with the thermal method.

Application of the prepared silver nanoparticle colloidal solution on to cotton fabric by the aid of the prepared copolymer along with epichlorohydrin were done in alkaline medium in two alternatives ways. The new finishing formulation results in fabrics with excellent and durable bacterial properties

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