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Synthesize of nano silver using cellulose or glucose as a reduction agent: the study of their antibacterial activity on polyurethan fibers

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Silver nanoparticles are used an increased attention for various biomedical and medical applications.In this paper, the synthesis of nano silver was investigated and compared to using chemical reduction of silver nitrate by glucose and cellulose in neutral and alkaline media. The reducing properties of glucose and cotton cellulose showed that cellulose acted as a strong reducing agent. The antibacterial activity of synthetized nano silver on polyurethane fiber using exhaustion method was measured. The synthesis of nano silver in an aqueous solution was illustrated with an adsorption spectrophotometer. Moreover, the TEM images demonstrated the size and shape of the nano silver particles. Silver nitrate salts were reduced using cellulose in alkaline media, and nano silver particles were subsequently synthesized with the sizes of 30-40nm. Antibacterial properties of treated polyurethane fibers with synthetized nano silver were good.

Keywords: Nano Silver, Chemical Reduction, Glucose, Cellulose, polyurethane fibers.

INTRODUCTION

Metal nano particles have attracted a great deal of attention in recent years due to their optical, physical and chemical properties that differentiates them from bulk material properties. There is wide application in various fields like catalysis, photonics, optoelectronics, information storage, antibacterial applications, etc. Silver powders, having ultra fine and uniformly distributed particle size, are of considerable use in the electronics industry as thick film conductors in integrated circuits due to their unique properties such as high electrical and thermal conductivity, high resistance to oxidation [1].

Silver is a safe and effective bactericidal metal because it is non-toxic to animal cells and highly toxic to bacteria such as Escherchia coli (E. coli) and Staphylococcus aureas. Colloidal silver, nano silver coated fabric, nano silver metal oxide granules and nano silver coated ceramic materials are used for antibacterial applications. Nano silver in the form of powders as well as suspensions, due to the high surface to volume ratios, has been used in the above said applications as it enables the loading of small quantities of silver and thus makes the product cost effective [2].

Many methods and approaches have been reported for the synthesis of AgNPs by using chemical, physical, photochemical and biological routes. Each method has advantages and disadvantages with common problems being costs, scalability, particle sizes and size distribution. Physical and photochemical methods to prepare nanoparticles are usually need the very high temperature and vacuum conditions, and expensive equipment [3].

There are several aqueous based chemical methods reported in the literature to produce nano silver. While most of these reports deal with inorganic bases such as NaOH to control the pH to above 9, the contamination of silver with metals ions will cause limitations in specific applications such as electronics, and hence organic bases are required in the nano silver synthesis, as reported by Hsu and co-worker [4].

Generally, nano silver particles is synthesised by chemical reduction of metal salt, using stabilizing agent, including a polymer or a surfactant. A great deal of studies was carried out on the effect of stirring, temperature control and pH, on the size of particles [5-9].

The chemical reduction method involves the reduction of $AgNO_3$ by a reducing agent in the presence of a suitable stabilizer, which is necessary in protecting the growth of silver particles through aggregation. In the formation of silver nanoparticles by the chemical reduction method, the particle size and aggregation state of silver nanoparticles are affected by various parameters, such as initial $AgNO_3$ concentrations, reducing agent/$AgNO_3$ molar ratios, and stabilizer concentrations [10].

In one of the methods of chemical reduction, high dispersed silver particles with size of 20–80 nm were prepared by reducing silver nitrate with glucose using protective agent as poly vinyl pyrrolidone (PVP). The addition of the sodium hydroxide enhanced the reaction velocity. The PVP

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has protected the silver particles from agglomeration. In another study, PVP was used as dispersant agent in the reaction between silver ions and glucose [11, 12]. An approach based on the polyol process for the large-scale synthesis of silver nanowires with uniform diameters was demonstrated.It was involved the reduction of silver nitrate by polyol in the presence of PVP as stabilizer. This method had been successfully illustrated with the production of silver nanowires 30-60 nm in diameter and 1-50μ in length [13].

In another work, silver nanoparticles were prepared by a green method from reduction of silver nitrate. Carboxymethyl cellulose sodium (CMS) was employed as both a reducing and a stabilizing reagent and silver ion can be reduced by hydrolyze of CMS to form silver nanoparticles. Results were also shown that the concentration of CMS has very small effect on the size distribution of silver and nanoparticles prepared was uniform and stable, which was stored at room temperature for 2 months without any visible change [14].

Polyurethane (PU) is one of the most important engineering polymers and widely used in commercial applications, including construction, automotive, food packaging and storage, transportation, textiles, foot- wear and wound dressing materials. With the growing public health awareness of the pathogenic effects and stain formations caused by microorganisms, there is an increasing need to develop antimicrobial PU for improving the properties. Besides antibiotics, silver salts and silver nanoparticles can be used as filler or coating material in the preparation of antimicrobial PU. Comparatively speaking, silver nanoparticles show more efficient antimicrobial property than silver salts due to their extremely large surface area. The effective biocide concentration of silver nanoparticles is at a nano molar level in contrast to a micromole level of silver ions. Therefore, application of nano silver antibacterial agent would be a better alternative. The silver nanoparticles coated PU could serve as water filter to remove bacteria from water [15].

In the present work, we have synthesised silver nanoparticles by an aqueous chemical method with cellulose or glucose. The size of synthetized nanoparticles compered and analysed. Electrospun polyurethane was treated nano silver colloid. The antibacterial activities of the fibers were assessed against both Gram-positive Staphylococcus aureus (*S. aureus*) and Gram-negative Escherichia coli (*E. coli*).

MATERIALS AND METHOD

The substances and materials used in this study, including cotton fabric as cellulosic substrate, electrospun polyurethane fibres from china, silver nitrate, glucose, sodium hydrosulphite and sodium hydroxide, were all catered by Merck Company, Germany. All experiments were carried out following with Table 1, using distilled water at 60^{o}C for one hour.

Table 1: The methods of experimental

Sample code	AgNO3 1%	Cellulose 322g/m^2	Glucose 1%	pH
NS	2 cc/l	0	0	12
NCS	2 cc/l	20 g/l	0	12
NG	2 cc/l	0	4.5 cc/l	7
NGS	2 cc/l	0	4.5 cc/l	12
NCG	2 cc/l	20 g/l	4.5 cc/l	7
NCGS	2 cc/l	20 g/l	4.5 cc/l	12

Then, after synthetizing of nano silver, polyurethane (PU) Samples were treated using 3 g/L nano silver colloid for 60 min at 70° C and pH = 7.

Adsorption spectra of synthesised samples were measured by Camspec UV-vis spectrophotometer; model M-350, England. Microscopic images were prepared from suspension samples by a transmission electron microscope (TEM), model EM 208, from Philips Company, Netherlands. The distribution range of particles of synthesised samples was obtained using a dynamic light scattering (DLC), Malvern model, England.

Quantitative experiments, investigating the strength and decrease in microbial agents, were conducted according to AATCC 100-2004 standard test method, using gram-positive Staphylococcus aureus, gram-negative Escherichia coli bacteria. In this method, the number of colonies of bacteria was counted according to colony forming unit (CFU) and the decrease in microbial agents (C) was determined using equation 1, where M1: the number of colonies in control microbial suspension and M2: the number of colonies existing in the suspension after being co-located adjacent to treated samples.

$$C = \frac{M_1 - M_2}{M_1} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Adsorption spectrophotometry

Figure 1 shows the UV-vis spectra of silver nitrate, reduced silver nitrate with cellulose in

alkaline media, and silver nitrate in alkali media in absence of the reducing agent.

The adsorption spectra illustrated in fig. 1 indicate that silver nitrate has created a peak at wavelength of 302nm, and then the silver nitrate reduced by cellulose in alkali media, shows a peak at 408nm. This peak prove the synthesis of nano silver in experiment conditions; while, the silver nitrate in alkaline media without cellulose is not reduced and it has no peak at 400nm. Thus, nano silver particles have not formed in the absence of cellulose. Figure 2 shows the UV-vis spectra of silver nitrate was reduced by cellulose and glucose in alkali media.

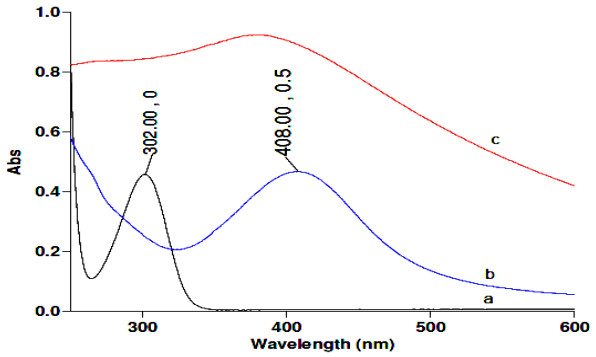

Fig. 1. Ddsorption spectra of silver nitrate in different condition, a :AgNO3 1% ،b :NCS،c:NS

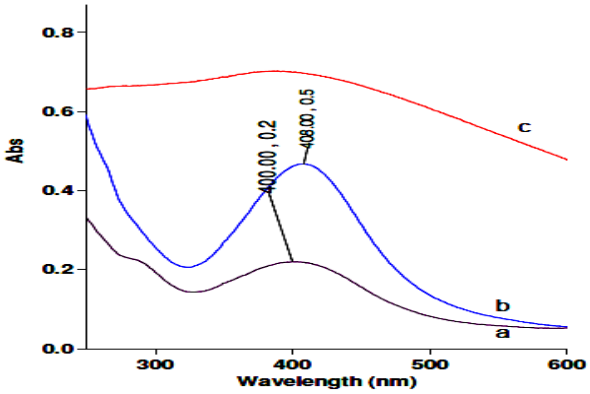

Fig. 2. Adsorption spectra of the silver nitrate, reduced by cellulose and glucose, a: NCGS, b: NCS, c: NGS

The adsorption spectra of silver nitrate in Figure 2 indicate that silver nitrate was reduced by both cellulose and glucose because of peak at 400nm. This indicates that presence of glucose and cellulose, was caused that silver nitrate was reduced in alkali media and nano silver particles is synthesised based on reaction has shown in figure 3. These results indicate the cellulose or glucose oxidation through reduction of silver nitrate, resulting in formation of nano silver.

Considering to adsorption spectra and previous studies, it seems that using of glucose in reduction reaction has helped avoiding the aggregation of particles and leads to the creation of an appropriate peak at 400nm.

DLS analysis, TEM and SEM

Dynamic light scattering (DLS) was used to determine the size distribution of small particles in solution. Fig 4 shows the distribution curve of nano silver particles, It could has founded from the curves, nano silver particles has synthesized by cellulose and are formed at a range lower than 100 nm (The measurement range of DLS is limited to the size range of hydrodynamic particles, which is 10% larger than the actual size). If silver nitrate is reduced by cellulose along with glucose using sodium hydroxide, the size of nano silver particles has decreased to 10nm.

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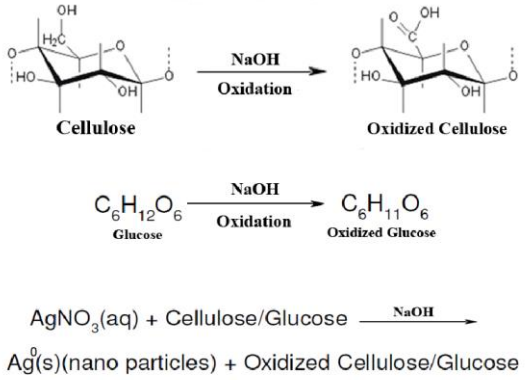

Fig. 3. Schematic reactions: Oxidation of cellulose and glucose and synthesis of nano silver by cellulose and/or glucose in alkaline media.

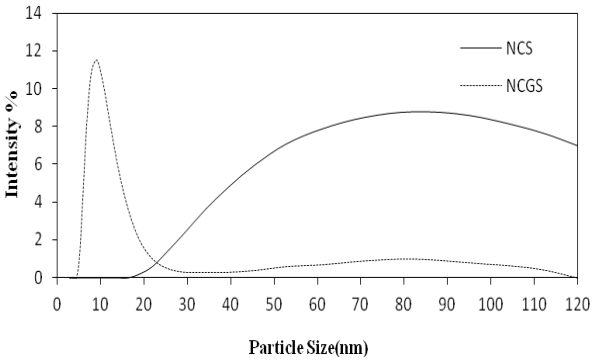

Fig. 4. Size range diagram of synthesized Nano silver particles

Figure 5 shows the TEM images of nano silver particles was synthesized by cellulose along with

glucose in alkali media. It is obvious that synthesized nano silver particles using cellulose and glucose have been less aggregated and the size of particles is less than 100nm. It seems that synthesized particles using cellulose alone were aggregated and size of them is more than 50nm; thus, Glucose acts as a stabilizing agent in reduction process of silver nitrate to nano silver.

Figure 6 shows the SEM images of untreated and treated substrate cellulosic (cotton). While the surface of untreated substrate (fabric) is smooth with no particles, the synthesized silver nanoparticles were uniformly distributed on the surface of the cellulosic substrate treated in reduction of silver nitrate. Thus, it proves that nano silver particles has been synthesized well by substrate cellulosic (cotton fiber) along with glucose.

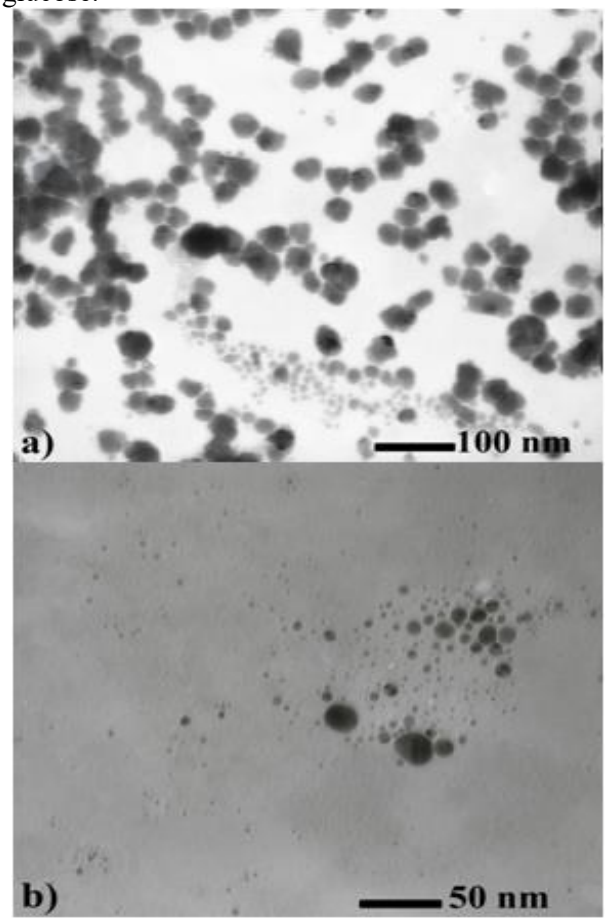

Fig. 5. TEM images of Nano silver particles, synthesized with cellulose in an alkaline media (a) and synthesized using cellulose and glucose at the same time (b)

SEM pictures and Antibacterial activity

The morphologies of untreated PU fiber, PU fiber treated with nano silver are shown in Figure 6. The SEM image of untreated fiber showed no particles on the surface of the fibers. However, the synthesized nano silver particles are well distributed on the surface of treated fibers. No agglomeration detected on the sample treated with nano silver, indicating the synthesis of silver nano particles with smaller size. Therefore, cellulosic material was acting as a stabilizer through nano silver synthesis preventing nano particles agglomeration.

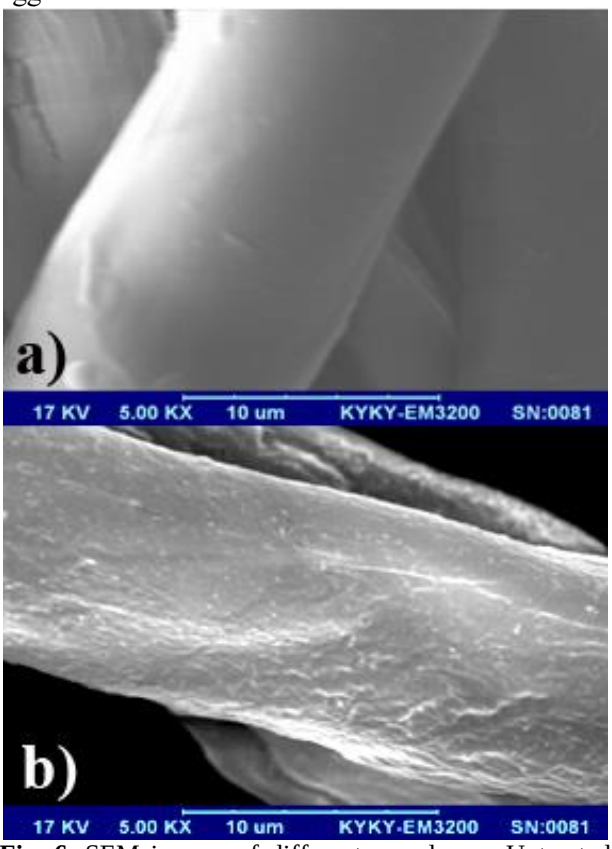

Fig. 6. SEM images of different samples, a: Untreated PU fiber, b: treated PU fiber with nano silver

The decrease in the number of colonies by the samples treated with nano silver nitrate after being placed adjacent to the Gram-negative and Gram-positive bacteria are presented in Table 2. Generally, textile goods without antibacterial modifications provide an excellent environment for microorganisms to grow. The PU fiber treated with nano silver indicated a good antibacterial activity thus they were effective in inhibitory and killing microorganisms. Treated sample with synthetized nano silver with cellulose have antibacterial activity than other samples, because of the small size of nanoparticles. the comparison of bacteria's colonies of PU fibers are shown figure 7.

Table 2: Antibacterial activities of different samples

Bacteria type samples	*E. coli*	*S. aureus*
Untreated	0	0
glucose	89.1	90.4
Cellulosic	97.6	96.2

material

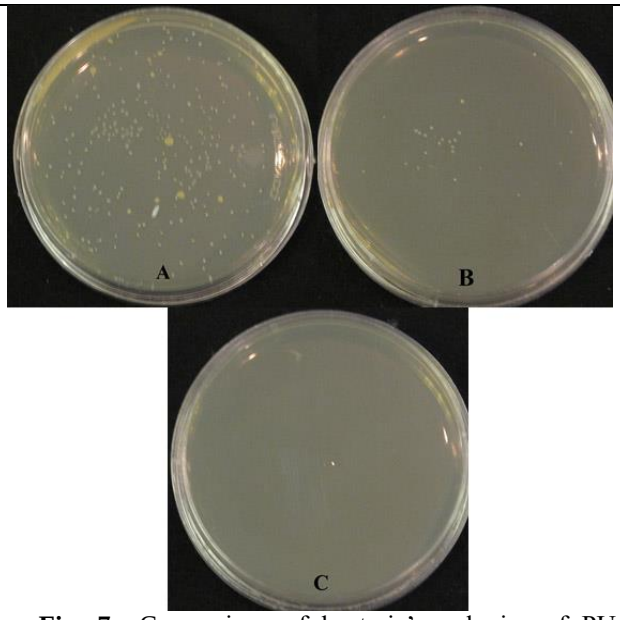

Fig. 7. .Comparison of bacteria's colonies of PU fiber, A: untreated sample, B: treated sample with synthetized nano silver with glucose, C: treated sample with synthetized nano silver with cellulosic material.

CONCLUSIONS

In this research, synthesise of nano silver particles through chemical reduction of silver salt has been studied and electrospun fiber PU was treated with synthetized nano silver. Nano-silver particles have been stable and not aggregated, with no sedimentation. In this study, nano silver particles were been successfully synthesized by cellulose and or glucose in an alkali media. The nano particles was synthesised through chemical reduction using cellulose along with glucose have had a size of 10nm. Thus glucose has prevented the aggregation of synthesized particles and acted as stabiliser in chemical reduction. Treated PU fibers with synthetized nano silver using cellulosic material have high antibacterial activity.

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