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The use of green synthesized silver nanoparticles on leather

Kashif Ahmed*, **Niaz Ahmed, Irfat Ashraf**

Department of Chemistry, N.E.D. University of Engineering and Technology, Karachi, Pakistan

Key words: *Conocarpus erectus, Azadirachta indica, Nerium indicum,* Silver nanoparticles, Silver treated leather.

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Abstract

The present work shows the determination of total phenolic compounds in plant leaves extract of *Azadirachta indica, Conocarpus erectus* and *Nerium indicum* and then Silver nanoparticles (Ag NPs) were prepared by using plant leaf extract as reductant and their application on leather. Ag NPs were characterized by SEM (Scanning Electron Microscope) and XRD (X-Ray Diffractometer) methods. The size of Ag NPs size was assessed in the limit of 30-80 nm. UV-Visible spectroscopy and SEM was used to confirm that Ag NPs were set down on the collagen fibers surface and inner side of the skin collagen matrix of fibers (leather). The antibacterial and antifungal effect of Ag NPs was assessed by general microbiological test for seven days. The result shown power full strength of silver Nano particles against bacterial or fungal attack for long duration of time. This permits us to deliberate the assimilation of these Nano particles into leather as a feasible substitute of other than commercially available expensive products in order to gain leather with enhanced antimicrobial properties.

* **Corresponding Author:** Kashif Ahmed ✉ kashif25473@yahoo.com

Introduction

A number of methods have been developed to prepare the silver nano particles (Sergeev, G, 2006). Some methods involved the use of organic chemicals which are carcinogenic, toxic, expensive and required a lot of time as well as sophisticated machine which destruct the sample (yield decrease) and also produce worst environment impact, while some are green *i.e.* environment friendly, cheap and easy handling (Sudrik *et al*., 2006).

Use of leather as a garment is subjected in highly specific conditions. Because of direct contact with the body for long duration in a hot and poorly ventilated environment, the temperature and humidity conditions enhance the growth of micro-organisms. These microorganisms produce unpleasant smell by the degradation of leather components and produce sweat by the wearer's (Ara K *et al*, 2006). Now in recent years silver has been extensively used in biomedical field as well as in industrial level applications (garments and mostly in electrical appliances) as it provides excellent antimicrobial effect against the fungi and bacteria (Usman MS *et al*., 2013). Silver ions show significant decrease in microbial growth by using small amount.

It is reported the Ag cytotoxicity due to several possible mechanisms, like the large production of free radicals containing great oxidative stress, functionality of cell membrane modification, or binding of DNA and change to genetic units by damage (Panyam J and Labhasetwar V, 2003).The biocidal properties of silver compounds have been remarkably enhanced through nanotechnology in the form of Ag NPs in which the size of metal nanoparticles lead to enhance the stability of the colloidal mixture with controlled release of the silver nanoparticles (Pileni, M.1997). This property of Ag NPs protects it rom cytotoxic effects, control the Leather's shelf life, or minimize the direct release of Ag ions into the environment. The present work is the Green synthesis of silver Nano particles along with its application at leather, a study which is environment friendly and beneficial for leather industry.

Materials and methods

All chemicals which were consumed throughout the research work such as Silver nitrate were of analytical grade provided by Merck (Germany) and Sigma-Aldrich (USA) from local market. Equipment used were Analytical balance (Sartorius, Germany), UV-Visible Spectrophotometer (721 Vis spectrophotometer), SEM analyzer (Hitachi S4160, Japan) XRD analyzer (Karaltay, DX-2700 MIN), Magnetic stirrer/Hot plate (JJ78-1), vacuum filtration assembly (Thomas 4595D45), Thermostat/incubator (Seimens), grinder (West point).

Leaves Extract Preparation

Samples of *Nerium indicum, Conocarpus erectus* and *Azadirachta indica* leaves were collected from the vicinity of NED University Karachi (Main Campus), then they were naturally shaded air dried for the period of seven days and then 100 g of this leaves were grinded with the help of grinder to generate fine powder then it was mixed with 500 ml distillated/ deionized water in 1litre volumetric flask and shacked vigorously. The plant extract preparation was achieved by using hot plate/magnetic Stirrer (500 to 800 rpm) at 50° C for one hour .Then filtered by the help of vacuum filtration plant (Ahmed *et al* .2016).

Determination of Total Reducing Strength or Total Phenolic Compounds

Total phenolic compounds in plant extracts were determined with the help of spectrophotometer. Accurate 0.5 mL of extract mixed with 10 % Folin-Ciocalteu's solution (2.5 mL in equal volume of 7.5 % $NaHCO_3$). Blank was made by mixing methanol (0.5 mL), 10 % Folin-Ciocalteu's solution (It was mixed in water and 7.5 % $NaHCO_3$ in equal volumes of 2.5 mL). The reaction solutions were incubated at 45° C for 60 minutes. The solution absorbance was calculated at a wavelength of 765 nm with help of spectrophotometer. Gallic acid was taken as standard solution. (Ahmed *et al.* 2016).

Selection of Leather Samples

Leather samples of pickle stage were used. Firstly it was tanned with silver Nano particles then prepared dyed crust by the normal dyeing process of leather then applied silver Nano composite with the finishing chemical by normal leather spray finishing technique. Three different thicknesses of leather was used (0.04, 0.045 and 0.05,06 mm), which relate to leather thicknesses and mostly utilized in the leather garment industries.

Green Synthesis of Silver Nanoparticles

The Ag NPs were synthesized in a 250 ml conical flask, taking 50 ml of cent molar $AgNO_3$ solution was mixed by adding 10 ml of the plant leaf extract (100 g of dried plant leaves powder was mixed to 500 ml water and then make up to 1000 ml by deionized/ distillated water in one liter volumetric flask) along with continuous shaking on a hot plate at 50 C° till the appearance of reddish color.

In order to confirm the optimum reaction time, obtaining Nano size of silver particles the process was monitored by UV-Vis spectroscopy at different time frame. Nucleation proceeds with the stimulus of the agitation (500 and 800 rpm) during the method development of the Ag NPs.

Preparation of Silver Nano colloidal solution

As Ag NPs (appeared as silver powder) insoluble in water so AED SONO ultrasonic cleaner was used to disperse silver powder, in this regards silver powder was place along with 100 ml distill/deionized water at 50 °C for three hours silver powder was completely dispersed and became a colloidal solution which was then filtered by What-man filter paper No 41.

Characterization of Ag NPs

The total morphology of created Ag NPs was characterized by X-Ray Diffractometer (XRD), SEM (Scanning Electron Microscope) and UV-Vis 721 spectrophotometer.

Tensile and Tear Strength Test of Ag NP-Treated Leathers

All physical test of Ag NPs-treated leather were carried out on the basis of ISO standards. Test for the tear strength was carried out rendering to EN ISO 3377-2:2003. Test for the tensile strength was carried out rendering to EN ISO 3376:2003.

The thickness of leather was determined rendering to EN ISO 2589:2003. For tensile and tear strength was calculated of by applying synthesized Ag NPs and Ag Nano composites on 200×400 mm leather test-pieces on the grain side by spraying technique 400 µL above chemical were taken by using micro pipette along with normal finishing procedure. Two coats were applied (200 µL each, permitting it to dry between these two coat applications and used digital camera for image. For antimicrobial test same procegure is applied on grain and on flesh side of leather (Ag NPs and Ag Nano composites) and allow them to react well for at least 8 hours in open dry air between and after every application.

Assessment of Antibacterial Activity

A bacterial suspension was prepared by inoculating a loop full of bacterial colony into 10 ml 0.9 % normal saline and O.D was adjusted at 0.5 bacterial suspension, 300 ml was soaked into the leather and placed in petri plates and incubated at room temperature for seven days. The leather pieces were periodically moistened with mineral salts medium during the entire incubation periods. To this end, 2.5x2.5 cm leather test-pieces were used.

Assessment of Antifungal Activity

2.5x2.5 cm leather pieces were taken out, a spore suspension of fungal *Aspergillus* species, *Aspergillus niger* and *Aspergillus flavus* was prepared. 300 µL of the same fungal spore suspension was soaked into the leather pieces placed in petri plates. The petri plates were incubated for seven days at 25° C temperatures with periodic moistening of the leather pieces with mineral salts.

Result and discussion

Total phenolic compounds

Leaves extracts (water and methanol) of Neem leaves (*Azadirachta indica*), *Conocarpus erectus* and *Nerium indicum* were investigated for total phenolic compounds and results are reported in Table 1. It can be seen that the total phenolic compounds were found higher in methanol extracts (e.g. *Azadirachta indica*, 85.9 ± 4.0 µg/g) lower in water extract (e.g. *Azadirachta indica*, 48±8 µg/g).

Water extract of *Conocarpus erectus (59±8* µg/g*)* showed higher total phenolic compounds so it was used for the green synthesis. (El-Sayed *et al.* 2012) have reported that the total phenolic compound were remarkably higher in ethyl acetate fraction of flowers and fruits (301.15 and 303.45 mg/g GAE respectively) whereas they were lower (181.61 and 186.21 mg/g GAE) in stem and leaves. On the contrary our results show the methanol extract of leaves exhibit higher values which might be due to selection of solvent and environmental effect (Ahmed *et al.*, 2015). Vinayagam and Sudha, (2011) has described in his article that the total reducing strength or total phenolic compounds was found to be higher in *Azadirachta indica* flower extract (449 mg/100g), as compared to leaves 227mg/100g. Our selection of leaves extract as raw material for the green preparation of silver nanoparticles is only due to abundance of leaves throughout the year.

Table 1. Total phenolic compounds in leaves extract of *Azadirachta indica* and *Narium indicum and Conocarpus erectus*.

Plant	Total Phenolic Compounds (µg/g)	
	Water	Methanol
Azadirachta indica	52 ± 5	85.9±4.0
Nerium indicum	22 ± 2	180 ± 6
Conocarpus erectus	59±8	296±9

SEM analysis

Usually the structure of the Nanoparticles can be determined by SEM analysis (or reaction products). The SEM image (Fig. 1) presented a number of discrete Ag NPs as well as unique larger groups. The SEM image of Ag NPs also showed irregular as well as spherical shaped nanoparticles were appeared with the diameter range 30-80 nm whereas grouped particles were fashioned above the range 100nm. Various researcher also reported similar types of images for Ag NPs (Jana N R *et al.*, 2001)

Characterization of silver nanoparticles

The formation of silver nanoparticles by using plant leaves extract as reducing agents was evaluated by SEM and XRD. Fig. 1 shows the SEM image and Fig. 2 shows XRD. These values fairly agree with reported values for silver NPs. (Ahmed *et al.* 2016).

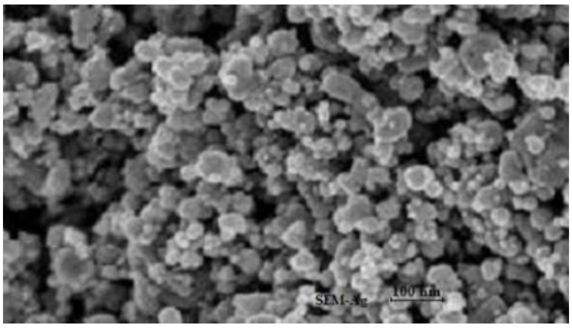

Fig. 1. Scanning Electron Microscope Image of Green synthesized Ag NPs by *Conocarpus erectus* (Ahmed *et al.* 2016).

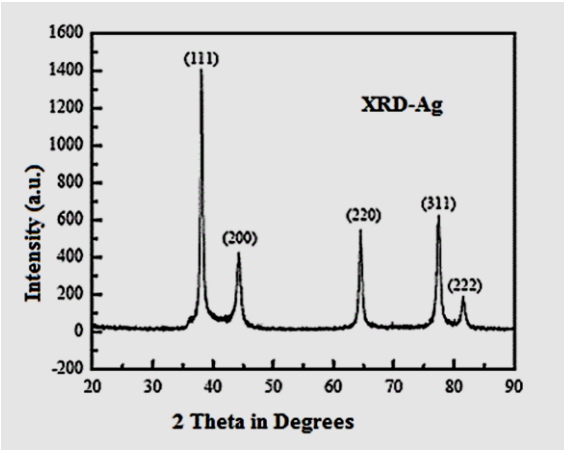

Fig. 2. XRD of Green synthesized Ag NPs by leaf extract of *Conocarpus erectus* (Ahmed *et al.* 2016).

The digital image (Fig. 3) carried out on the treated leather exposed the presence of colloidal emulsion on their surface and inside the leather matrix. The collagen fibers of Ag NP-treated leathers had a spotted appearance.

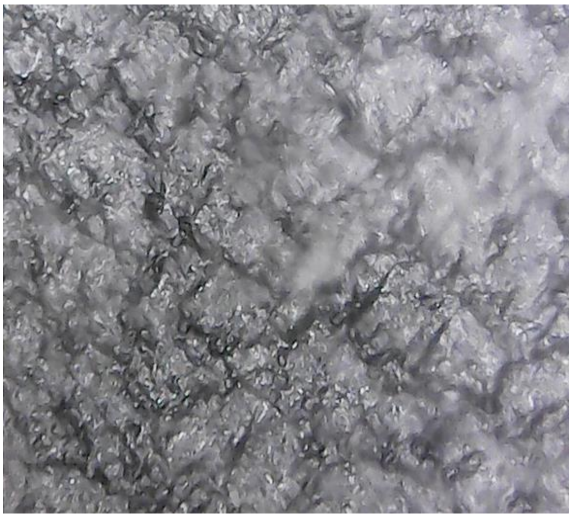

Fig. 3. The Digital image of Ag NPs treated leather.

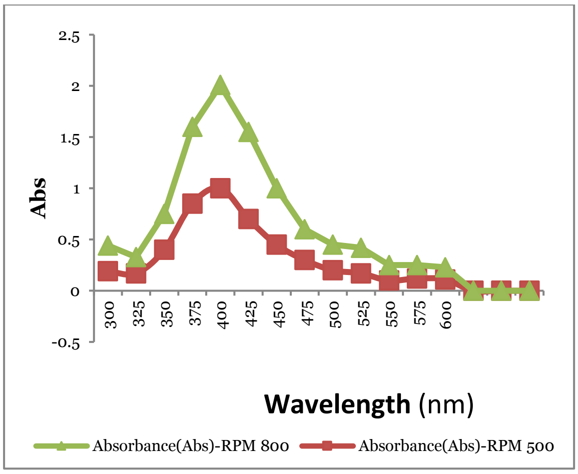

Fig. 4. UV-VIS spectra of synthesized silver nanoparticles obtained from water extract of *Conocarpus erectus* leaves.

Fig. 4 corresponds to Ag nanoparticle synthesized by using water extract of *Conocarpus erectus* leaves as a reducing agent at 500 and 800 rpm speed which is used as agitation function. The spectrum of the synthesized silver nano particle at 500 rpm estimated a maximum absorbance peak at 391 nm. As the agitation speed increased from 500 to 800 nm during the reduction process showed a slight shift towards higher absorbance wavelengths, which is corresponds to a slight increase in the diameter of Silver nanoparticle.

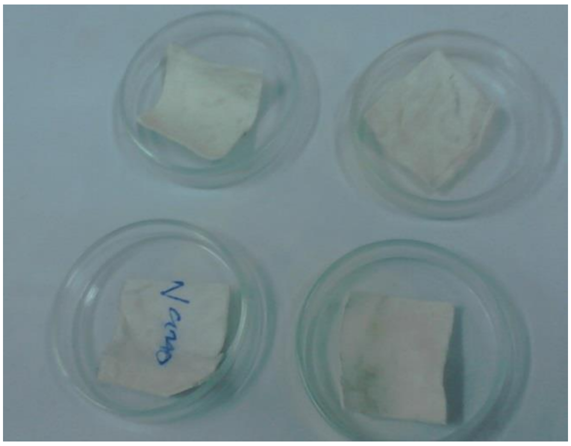

Fig. 5. Control (untreated leather).

Furthermore, a second peak distribution appeared at wavelengths around 500-525 nm, which may be due to the aggregation of Ag nanoparticles at higher rates of agitation. However In both cases the particle size average was between 30-80 nm. In addition, according to Fig. 4, a timely increase in the absorbance of the Plasmon resonance bands was appeared which is due to slower kinetics at 500 nm while higher kinetics at 800 nm, This effect might be corresponds to a higher rate of particle collisions in the reduction reaction enhancing nucleation process of Ag nanoparticle.

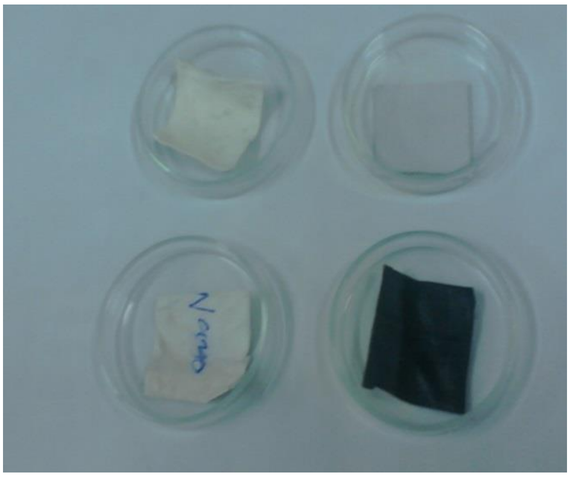

Fig. 6. After 36 h show microbial growth.

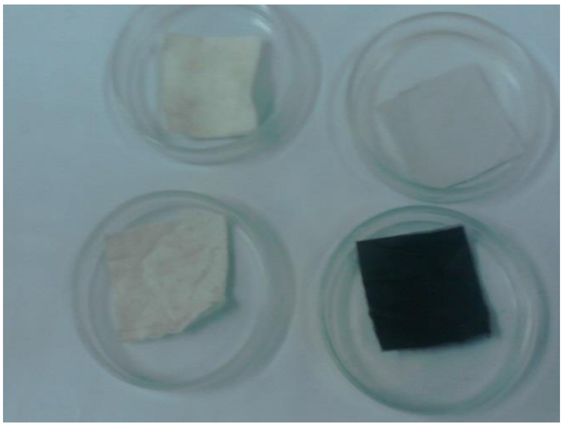

Fig. 7. Leather treated with Ag NPs showed no bacterial and fungal growth.

Tear and tensile strength

Tensile and tear strength tests (Tables 2, 3 ,4 and 5) were performed to determine whether the application of silver emulsions could alter the physical properties of leathers, which could have an result on their superiority and acquiescence with some standard requirements for certain types of garment leather.

Table 2. Tear strength of Untreated leather.

S.NO	Leather type	Thickness (Inch)	Tear strength (lbs)	Mean
1		0.04	12.2	
2	Normal	0.045	15.75	15.46
3		0.05	18.43	

Table 3. Tensile strength of Untreated Leather.

S.NO	Leather type	Thickness (Inch)	Tensile strength (PSI)	Mean
1		0.04	1282	
2	Normal	0.045	1534	1549.33
3		0.05	1832	

Table 4. Tear strength of Ag NPs treated leather.

S.NO	Leather type	Thickness (Inch)	Tear strength (lbs)	Mean
1		0.04	17.78	
2	Silver Nano applied leather	0.045	22.21	22.11
3		0.05	26.35	

Table 5. Tensile strength of Ag NPs treated leather.

S.NO	Leather type	Thickness (Inch)	Tensile strength (PSI)	Mean
1		0.04	1795	
2	Silver Nano applied leather	0.045	2194	2172.33
3		0.05	2528	

Table 2 and 3 listed the tensile strength and tear strength values of chrome tanning leather, and Table 4 and 5 shows the tensile strength and tear strength of treated leather. The results acquired specified that there were no significant differences with respect to appearance but strength of leather improved by 40-45 % which is the advantage of application of Silver Nano particles on leather production. The use of Nano silver emulsions has increased tear and tensile strength which is prerequisite for garment leather.

Assessment of antibacterial and antifungal activity

Sample showed no growth of fungi as well as bacteria except without applied pieces which showed growth just after 36 hour. This showed the confirming the potential use of these procedures in leather production. The similar results were also reported by N.Duran,P *et al.* (2007).

References

Ahmed K, Ahmed N, Siddiqui MT, Aziz AA. 2016. Green Synthesis of Silver Nano particles by plant leaf extract. FUUAST Journal of Biology **6(1),** 61-64.

Duran N, Marcarto PD, Souza GHD, Alves OL, Esposito E. 2007. Antibcterial effect of silver nano particles produced by fungal process on textile fabrics and their effluent treatment, Journal of Biomedicine and Nano technology **3,** 208.

El-Sayed, Abdel-Hameed S, Bazaid AS, Shohayeb MM, Sayed MM, El-Wakil EA. 2012. Phytochemical Studies and Evaluation of Antioxidant, Anticancer and Antimicrobial Properties of *Conocarpus erectus* L. Growing in Taif, Saudi Arabia. European Journal of Medicinal Plants **2(2)**, 93-112.

Jana NR, Gearheart L, Murphy CJ. 2001. Seeding growth for size control of 5-40 nm diameter gold nanoparticles. Langmuir **17(22),** 6782–6786.

Panyam J, Labhasetwar V. 2003. Biodegradable nanoparticles for drug and gene delivery to cells and tissue. Advance Drug Delivery Review **55,** 329-347.

Pileni M. 1997. Nano sized Particles Made in colloidal Assemblies. Langmuir **13,** 3266.

Sergeev G, Shabatina T. 2008. Colloids Surf. A Physicochem. Engineering Aspects **313,** 18.

Sudrik S, Chaki N, Chavan V, Chavan S, Sonawane HR, Vijayamohanan K. 2006. Silver nanocluster redox-couple-promoted nonclassical electron transfer: An efficient electrochemical Wolff rearrangement of alpha-diazoketones. Chemistry. A European Journal **12(3),** 859-864.

Usman MS, Zowalaty ME, Shameli K, Zainuddin N, Salama M, *et al.* 2013. Synthesis, characterization, and antimicrobial properties of copper nanoparticles. International Journal of Nano medicine **8,** 4467-4479.

Vinayagam A, Sudha PN. 2011. Antioxidant Activity of Methanolic extracts of Leaves and Flowers of *Nerium indicum*. International Journal of Pharmaceutical Sciences and Research **2(6),** 1548-1553.