Copper Nanoparticles Synthesis and its coating for antimicrobial applications with improved durability

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ABSTRACT

The present work describes the synthesis of copper nanoparticles by chemical reduction method and its coating over pre-treated cotton fabric by Pad-Dry-Cure method. Plasma treatment followed by acrylic acid grafting was adopted as pre-treatment over cotton fabric to improve the adhesion between Copper nanoparticles (Cu-NP) over cotton fabric. The deposition of Cu-NPs was analyzed by SEM EDX as well as antibacterial activity. Developed Cu-NP coated cotton fabric showed excellent antibacterial activity as well as durability towards washing.

1. INTRODUCTION:

Bacterial and viral infections are a major concern nowadays, which has been arising from adhesion, growth and proliferation of bacteria/virus on the surfaces. Significant research has been carried out to get novel antibacterial solution through effective use of nanotechnology and its applications [1,2].The cheaper copper nanoparticles with high effectiveness and long durable properties could match the requirement of antibacterial materials for industrial production. Antibacterial activity of NPs is varied depending on the taxonomical location of microorganisms. For example, it was shown that Cu NPs have higher affinity to the amines and carboxyl groups on the surface of Bacillus subtilis than Ag NPs and therefore show higher antibacterial activity [2].

The most common process of conferring the copper nanoparticles to fabrics materials is utilizing some adhesion and cross-linked agents, such as acrylate and polyurethane, to form a composite coating on the substrate [1,3]. Consequently, only the exposed copper nanoparticles on the external surface can be released and show antibacterial property subsequently; meanwhile the majority of nanoparticles are blocked in the inner of composites by adhesion agents[1,4].

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In this paper, method of impregnation of CuNP over plasma activated and acrylic acid grafted cotton fabric is proposed in order to get better antimicrobial activity as well as wash durability.

2. EXPERIMENTAL:

2.1 Material & Method:

Light weight, ready for dyeing 100% knitted cotton fabric was used for the coating of Copper Nanoparticles. Copper (II) Sulphate pentahydrate (*Merck India, > 98%*) and Ascorbic acid (SDFCL India) were used for the synthesis of CuNP. All the chemicals were of analytical grade and were used as-received. De-ionized (DI) water was used to conduct all the experimental procedures.

2.2 Preparation of Cu NP:

1.6% copper sulphate solution was prepared in distilled water and was heated at 80° C for 10 minutes. Later the 4% ascorbic acid solution was added in the same copper sulphate solution, drop wise with vigorous magnetic agitation. The colour of the copper sulphate solution slowly changes from light blue to light green initially and after 10-15 minutes turns to brown due to suspension of CuNP's.

The reaction condition was then maintained at 80°C for 5hrs. After the reaction, it was allowed to cool at room temperature. The resultant solution containing the nanoparticles was centrifuged for 10 min at 4000 rpm and resulting suspension was redispersed in distilled water. The centrifugation and redispersation process was

repeated twice with water and finally with ethanol to remove any unreacted agent. Brown suspension of Cu-NPs was allowed to dry at room temperature. Finally, the dried nanoparticles of CuNP were used for further coating over Cotton substrate.

2.3 Fabric Treatment:

The knitted cotton fabric sample was pre-treated using dielectric barrier discharge- atmospheric pressure plasma treatment with helium + oxygen gas. The treatment was conducted on equipment PLATEX-600 (make GRINP S.R.L., Italy). Fabric sample of 50cm width was passed in continuous manner through plasma zone under 1.5 kW plasma power. Plasma treatment time and interelectrode spacing was maintained constant at 60sec and 1.0mm respectively for all experimental trials. This plasma treated sample was immersed in to acrylic acid solution (20% V/V). In order to remove the air trapped inside the flask, nitrogen gas was purged in to the solution. Reaction flask was then heated for 60 min at 65° C. Fabric was then removed, washed and dried in open atmosphere.

2.4 Cu NP coating over Cotton fabric:

Untreated cotton and pre-treated cotton fabric were dipped in solution containing CuNP (0.5%), and allowed to pass through padding process (2 dip-2 nip) with maintaining 75% pick up. Then samples were dried in 80°C for 15 min and cured at 110°C for 1 min. These CuNP coated fabrics were further analyzed for antibacterial activity, SEM EDX investigations and their durability towards washing.

2.5 Antibacterial Properties: An antimicrobial property of CuNP's coated cotton fabrics was studied by AATCC-100 procedure which gives a quantitative estimate of the antibacterial activities of the fabrics.

2.6 Wash Durability: The durability of CuNP coated fabrics towards washing was analyzed by gentle washing of samples as per AATCC LP2-2018 method with 5 and 10 numbers of washes.

2.7 SEM & EDX investigation: Scanning electron micrographs and Energy dispersive X-ray (EDX) scans were recorded using JEOL JSM IT 200 & Element make EDX, to confirm the surface morphology and elemental composition of the CuNP's coated fabrics

3.0 RESULTS & DISCUSSION:

Cu particles in nano scale have been shown to have antibacterial effect on the bacterial cell, functions in multiple ways, including adhesion to gram negative bacterial cell wall due to electrostatic interaction, having effect on protein structure in the cell membrane, denaturation of the intracellular proteins and interaction with phosphorus and sulphur containing compounds like DNA[5].

In our study, it was found that both (with and without plasma pre-treated) Cu NP coated fabrics showed excellent antibacterial activity towards Gram positive (Klebsiella Pneumoniae) and Gram negative bacteria (Staphylococcus aureus). In case of control (without pre treated) CuNP coated fabric, the antibacterial rate reached to 99.44% towards bacteria Klebsiella Pneumoniae and 99.96% towards bacteria Staphylococcus aureus after 24 hrs duration. Whereas for plasma pre-treated CuNP coated fabrics, it reached to 99.93% and 99.96% for Klebsiella Pneumoniae and Staphylococcus aureus respectively.

Wash durability of CuNP coated fabrics (with and without plasma treatment) was then assessed in terms of change in antibacterial activity with 5 and 10 number of washes. It was found that for control CuNP coated samples, complete loss of antibacterial activity due to poor adhesion between substrate and CuNP [Table-1]. For practical use, it is very important to have wash durability in antibacterial textiles. Hence to overcome this, fabric was activated with plasma and grafting treatment in order to improve the adhesion between fabric and antibacterial finish.

Table-1 : Poor adhesion between substrate and CuNP

Sample No.	Bacterial Reduction, (%)	
	Klebsiella Pneumoniae ATCC 4352	*Staphylococcus aureus* ATCC 6538
Cu-NP 0-Wash	99.44 %	99.96 %
Cu NP - 5 Wash	No reduction	No reduction

These pre-treated CuNP coated samples showed negligible change in antibacterial activity, even after 10 no. of washes [table-2]. This improvement in wash durability of CuNP coated fabric, after pre-treatment of functionalisation and grafting is due to physical interaction and formation of chemical bonding respectively. Interaction of plasma and grafting of acrylic acid leads to formation of more hydrophilic groups(such as C=O, COO) on the surface[6,7], resulting in improved functionality of the fabric, leads to improvement of adhesion of CuNP's over substrate.

To confirm the presence of CuNP's on the fibre surface, Scanning electron micrographs and energy dispersive X-ray (EDX) spectra were generated. Surface morphology of the CuNP coated cotton sample shows the uniform distribution of Cu nanoparticles over the substrate (Fig.1).

Whereas the EDX spectra (Fig.2) shows the signals for Cu along with oxygen and carbon. The appearance of carbon

Table-2 : Wash durability of Pre-treated Cu-NP coated fabrics

Sample No.	Bacterial Reduction, (%)	
	Klebsiella Pneumoniae ATCC 4352	*Staphylococcus aureus* ATCC 6538
Cu -Np 0-Wash	99.93 %	99.96 %
Cu Np – 5 Wash	99.87 %	99.93 %
Cu Np – 10 Wash	99.90 %	99.94 %

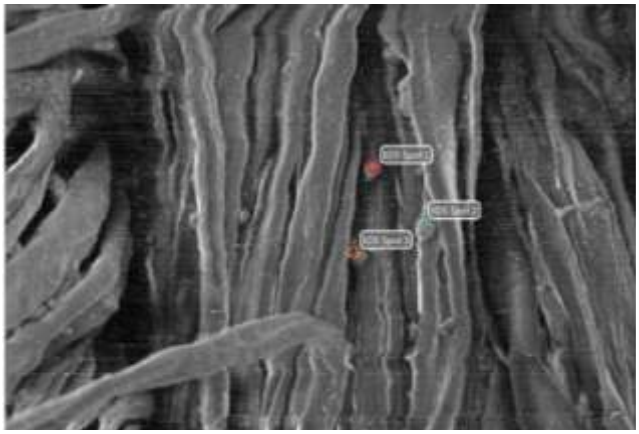

Fig. 1Scanning electron micrograph (SEM) of CUNP coated sample

and oxygen peaks in the spectrum may attribute to the cotton fabric over which Cu-nanoparticles are coated. The elemental analysis of prepared CuNP coated sample is shown in Table-3.

Overall uniform distribution and improved adhesion of

Table-3 Energy dispersive X-ray (EDX) of CUNP coated samples

Elemental analysis weight by weight percentage	
Carbon	70.9
Oxygen	26.3
Cupper	2.8

CuNP's over pre-treated cotton fabric leads to excellent antibacterial activity and wash durability in cotton fabric rendering them suitable for commercial applications.

4. CONCLUSION:

Highly efficient antimicrobial cotton fabric was obtained by coating CuNP over pre-treated cotton fabric by Pad-Dry cure method. The sample was characterized by SEM, EDX spectra, which confirms the Cu deposition over cotton substrate. Developed Cu-NP coated cotton fabric showed excellent antibacterial activity as well as its durability towards washing as pre-treatment of atmospheric pressure plasma followed by acrylic acid grafting resulted in improved adhesion between CuNP over cotton fabric.

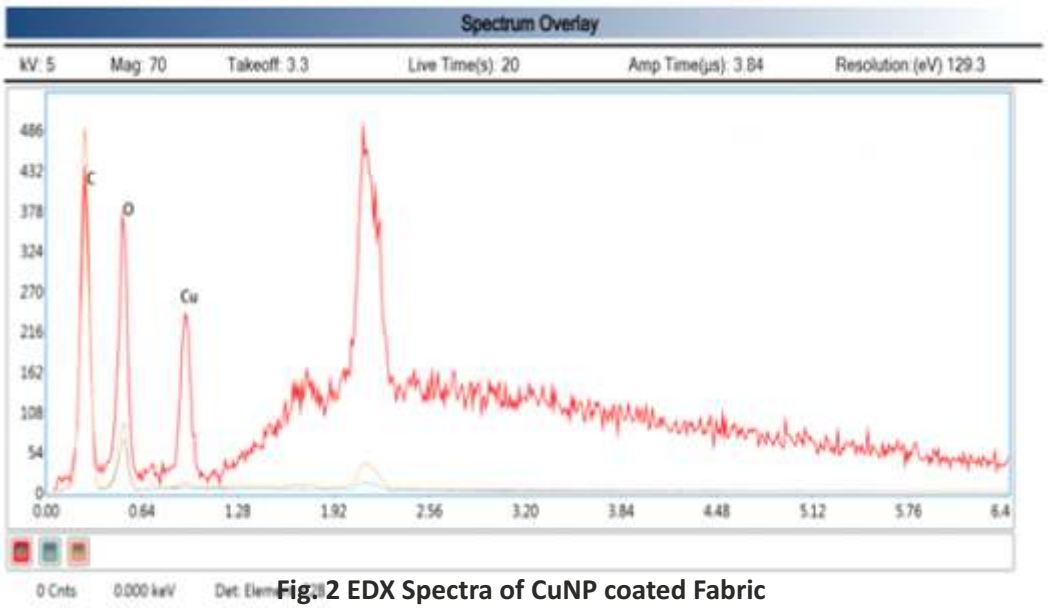

Fig. 2 EDX Spectra of CuNP coated Fabric

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