Synthesis of copper nanoparticles on cellulosic fabrics and evaluation of their multifunctional performances

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Abstract Two different kinds of copper nanoparticles (CuNPs) (brown colour and greenish colour) were synthesised by using simple solution route and applied by exhaust method to achieve multidimensional functionalization on one of the most popular cellulose materials e.g., cotton fabric. The synthesised CuNPs imparted different colours to the said textile due to different conditions of synthesis and localized surface plasmon resonance. Physico-chemical characterizations of the synthesized nanoparticles were performed by using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis whereas the optical properties of the nanoparticles were studied using UV–visible spectroscopy. The prepared CuNPs of both the types demonstrated very good antimicrobial activity up to 97%. In addition, cotton fabric treated with CuNPs showed very high catalytic activity for reduction of 4-nitroaniline (4-NA) in presence of sodium borohydride to phenylene diamine (4-PD). Washing durability and rubbing fastness of the treated fabric have also been measured by following standard testing methods and found to be very good with a rating 4.

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Introduction

Recent advancement in nanomaterials plays a major role in science and technology. Nanomaterials have been used in various applications such as sensor, catalyst, energy storage, energy harvesting and many more (Sharma et al. 2016; Chawla et al. 2017; Bairagi and Ali 2019, 2020a, b, c). Numerous techniques have been used in the recent past to apply nanomaterials on different natural substrate for useful value addition. Treatment and functionalization of cotton with natural materials and application of nanomaterials to textile have attracted extensive attention, with the aim of imparting various functional properties such as flame retardancy using bulk as well as nanomaterial (Alongi et al. 2014a, b; Alongi et al. 2015; Sharma et al. 2018; Shukla et al. 2019; Durrani et al. 2020; Rajpoot et al. 2021), hydrophobicity (Leng et al. 2009), ultraviolet-protection (Dhineshbabu et al. 2016; Shaheen et al. 2016) and antimicrobial (Sedighi et al. 2014; El-Shishtawy et al. 2011; Mohamed et al. 2017; Sharma and Ali 2022) properties. Different methods of incorporation of the functional materials into textile substrates have been demonstrated. Among them, electrostatic assembly, chelation by active groups, plasma treatment and in situ synthesis are most common and much explored process routes for generation or synthesis of nanoparticles (Alongi et al. 2014a, b; Cady et al. 2011; Dong and Hinestroza 2009; Gorjanc et al. 2010; Tang et al. 2012, 2013).

Among the mostly available and explored nanoparticles, copper nanoparticles (CuNPs) attract more attention due to their low production cost and they are free from toxicity. Copper complexes, metallic copper and copper oxide have been used from centuries in various processes such as disinfection of liquid, solid,
and human tissues, etc. (Perelshtein et al. 2013). Copper based materials have also been used in heat transfer systems (Eastman et al. 2001) as antimicrobial agents (Esteban-Cubillo et al. 2006; Cioffi et al. 2005a), sensors (Kang et al. 2007; Male et al. 2004; Xu et al. 2006), as an excellent-resistant material (Wang and Gao 2007; Kang et al. 2007) and as catalysts. Recently, various types of nanoparticles have been applied on the fabric to impart multifunctionalities on cellulose (like to act as catalyst, antimicrobial activity, for imparting coloration, self-cleaning action, ultraviolet ray protection, etc.). In the same way, cellulose materials also attract more attention for the application of nanoparticles due to their exceptional biocompatibility, no or low toxicity, and potential biological activities (Mary et al. 2009). Various scientific techniques have been reported on the synthesis route of CuNPs including gas-phase evaporation, vacuum vapor deposition, chemical–mechanical, hydrothermal radiation, ultrasonic, reverse microemulsion, electrolysis, electron beam irradiation, sol–gel, and mostly used chemical reduction methods, (Cheng et al. 2006) etc. As per report, chemical reduction technique used for the synthesis of nanoparticles has certain advantages of tuning the process parameters such as the pH, temperature, stabilizing agent, reducing agent, and solvent quantity. As a result, particle size of the synthesized material can be controlled in a proper manner, and also the process provides a grip for addressing the aggregation challenge of nuclei (Wang and Gao 2007). CuNPs have been used in various organic synthesis processes such as cyclization of azides with terminal alkynes and to catalyse the multicomponent synthesis of 1,2,3-triazoles (Alonso et al 2009, 2011). In the similar context, CuNPs have also been used as catalyst in reduction of 4- nitrophenol to 4-aminophenol (Deka et al. 2014). Recently, Kottappara et al. (2020) have reported a review context on the copper based nano catalysts for nitroarene reduction.

So, nanoparticles are also gaining a lot of interest in synthesis and transformation of various organic moieties as emerging field. Very recently one literature reveals that CuNPs could be synthesized by green synthesis route using cotton (Alvarez et al 2021). Aladpoosh et al. 2014 have reported the synthesis of silver nanoparticles. In the present study, CuNPs have been synthesised using two routes and integrated on cotton textile. Further properties of these CuNPs functionalized textiles were studied step by step. Firstly, imparted colour value has been measured and wash fastness properties was studied, followed by physical property like tensile strength was analysed. Afterwards, antimicrobial properties of the functionalized fabric were evaluated. Finally, the catalytic properties of treated textile were studied systematically using UV–visible spectrophotometer. Present technique of functionalization of cellulosic fabrics having advantage of integration of the synthesized nanoparticles in the same reaction bath (whereas nanoparticles generated separately in solution is not stable because of their agglomeration tendency and its overall properties get diminished). In this way well-dispersed synthesized nanoparticles on cellulose fabric have been explored for various purposes which was not possible using as such particles generated in a separate solution.

**Experimental**

**Materials**

Copper sulphate (CuSO₄.5H₂O), phenylene diamine, disodium citrate, sodium hydroxide (NaOH, Assay-98%), 4-nitroaniline, and sodium borohydride
(NaBH₄ 98%), dimethylsulphoxide (DMSO) were purchased from Merck, India. Agar–agar and Luria broth were purchased from Central Drug House Fine chemicals (CDH). ECE non phosphate reference detergent without optical brightening agent was purchased from Subsidiary of the Society of Dyers and Colourists (SDC) Enterprises Ltd. All chemicals used for the experimental purposes were of analytic-grade reagents and further purification was not required. Entire study was carried out on pure cotton cellulosic fabric of density of 180 g/m². Deionised water was used throughout the process.

Synthesis of CuNPs on cotton fabric

**Synthesis of light brown coloured CuNPs on cotton fabric**

First 0.5 g copper sulphate was added into a neat and clean beaker containing 200 mL distilled water. 0.5 g of disodium citrate was added in it and stirred to form clear solution. A piece of cotton having dimension 25 cm x 15 cm was put in solution beaker. Drop-wise addition of sodium borohydride solution (40 mg in 50 mL water) was done in the beaker with a continuous stirring at 30 °C. After complete addition, absorption of formed dispersion was measured in spectrophotometer and beaker was transferred to hot water bath at 80°C for nearly 30 min for further treatment. Afterwards, with fabric was rinsed with water and dried in oven at 100 °C for 2 h. This sample is named as ‘Cot-Cu-1’.

**Synthesis of greenish coloured CuNPs on cotton fabric**

0.5 g copper sulphate was added into a neat and clean beaker containing 200 mL distilled water. 0.5 g of disodium citrate and 150 mg of sodium hydroxide were added into it and stirred to form clear dark sky-blue solution. A piece of cotton having dimension 25 cm x 15 cm was put in solution beaker. Then sodium borohydride solution (40 mg in 50 mL water) was poured dropwise in the beaker with a continuous stirring at 30 °C. After complete addition, absorption of the formed dispersion was measured in spectrophotometer and transferred the beaker in hot water bath at 80°C for nearly 30 min.

Thereafter, the fabric was rinsed with water and dried in oven at 100 °C for 2 h. This sample is named as ‘Cot-Cu-2’.

Zeta potential and particle size analysis of CuNPs

Zeta potential and particle size distribution were measured using a particle size analyser (Malvern Pan Analytical Instrumentation, Model Zetasizer Nano ZS). Particles were dispersed well in water before taking the measurements.

UV–visible spectroscopy for analysis of CuNPs

UV–Visible spectra of the synthesized nanoparticles and also the eluted particles from the fabric samples were studied using UV–visible spectrophotometer Model no 2450 of Shimadzu company. Diluted dispersion of the synthesized particles was taken to study its absorbance in UV–visible spectrophotometer.

Functional group analysis of the fabric treated with CuNPs

Functional group analysis of treated and control sample was accomplished using a Fourier Transform IR spectroscopy (Thermo Fisher Scientific instrument, Model: Nicolet iS50 FTIR). The samples were scanned in the range of 500 to 4500 cm⁻¹ wave number.

Surface morphology of nanoparticles and treated cotton fabric

The surface morphology of CuNPs prepared by both the routes and the treated cellulosic fabric with these nanoparticles was investigated by scanning electron microscope (SEM) (made by ZEISS EVO) model QuanTax 200 which is based on the software development and digital (SDD) technology and provides an energy resolution of 127 eV at Mn K alpha.

Colourfastness to washing

Washing fastness of the treated fabric samples was analysed in accordance with the standard test method. Cotton fabrics (1% add-on) treated with CuNPs were washed at 50 °C for 45 min in presence of ECE non
phosphate reference detergent (4 gL\(^{-1}\)) using a Laun-der-o-meter. Gregteg Color i7 7000 spectrophotometer was used to record the values of lab colour coordinates (L*, a*, and b*) for the CuNPs treated samples before and after the washing operation where L* represents the lightness/darkness, a* value corresponds to the red or green chroma, and b* corresponds the chromaticity coordinate for yellow/blue.

Colourfastness to rubbing

Rubbing fastness of CuNPs incorporated fabrics was analysed as per the standard (AS 2001.4.15–2006). Fabric treated with CuNPs was rubbed using a ready for dyeing (RFD) cotton cloth. Grey scale was used to evaluate the staining on RFD cotton cloth.

Tensile strength of the fabric

ASTM D5034, grab test method was used to evaluate the tensile strength of control and copper treated cotton fabrics using tensile testing machine (Tinius Olsen, Model: H5KS). Treated and control samples of dimension 200 mm × 50 mm were analysed at a speed of 300 mm/min. Three replicates of each sample were tested, and the average results are represented in the manuscript with CV%.

Evaluation of antimicrobial activity

Antimicrobial activity of copper treated cotton samples was tested using the standard colony counting method (AATCC 100). Digital colony counter was used to calculate the number of colonies of control and treated cotton fabrics and bacterial cell reduction (BCR) was calculated by using the following formula:

\[
\text{BCR} \% = \frac{\text{No. of colonies in control sample} - \text{No. of colonies in treated sample}}{\text{No. of colonies in control sample}}
\]

Catalytic activity

Catalytic activity of the CuNPs treated cotton fabric was analysed by monitoring the conversion of 4-NA to 4-PD in presence of sodium borohydride (NaBH\(_4\)). Catalytic activity was performed in presence of control and treated fabric by using Shimadzu 2450 UV spectrophotometer. In a typical experiment, 2.0 mL sodium borohydride (NaBH\(_4\)) solution (3.0 M) was added into 30 mL 4-NA aqueous solution (0.025 mM). Subsequently, 30 mg cotton fabric (control cotton, Cot-Cu-1 to Cot-Cu-2) was added into the mixed solution of 4-NA and NaBH\(_4\) under vigorous stirring. In case of control cotton, there was no change in yellow colour of the solution which was not the case for cot-1 and cot-2 sample. UV–Visible absorption spectra were monitored during the conversion of 4-NP to 4-PD and thus catalytic efficiency of treated fabrics was analysed.

Results and discussion

Mechanism of preparation of nanoparticles

Two types of CuNPs have been generated using two different conditions. The equation of preparation of both types of nanoparticles was written below and possible mechanism for the reaction is represented in Eq. 1.

\[
\text{CuSO}_4 + \text{Na}_2\text{C}_6\text{H}_6\text{O}_7 + \text{NaBH}_4 \rightarrow \text{CuNPs (Cu – 1, stabilized by citrate ions)}
\]

\[
\text{CuSO}_4 + \text{Na}_2\text{C}_6\text{H}_6\text{O}_7 + \text{NaOH} \rightarrow \text{Cu(OH)}_2 + \text{NaBH}_4 \rightarrow \text{CuNPs}
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size analyser. Zeta potential (ZP) of Cu-1 particle and Cu-2 particles was observed as -16.6 mV and -35.5 mV with standard deviation 3.01 and 8.8, respectively. High ZP implies highly charged particles, which prevents aggregation of the particles due to electric repulsion. If the ZP is low, attraction overcomes repulsion, and it is likely that the mixture forms coagulates (Samimi et al. 2019). The ZP value of −30 mV is considered optimum for good stabilization of a nanoparticles (Samimi et al. 2019). Nanoparticles with high ZP values, between 20 and 40 mV provide the system’s stability and are less prone to form aggregates or increase in particle size. Cu-2 particles having zeta potential value −35.5 mV showed that these particles have good stability than Cu-1 particles. Therefore, agglomeration of Cu-1 particles is more to form bigger particles. This may be due to the presence of sodium hydroxide (in case of Cu-2

**Table 1** EDX analysis data: elemental composition of Cot-Cu-1 and Cot-Cu-2

| Name of the element | Cot-Cu-1 | Cot-Cu-2 |
|---------------------|----------|----------|
| Carbon              | 45.24    | 45.97    |
| Oxygen              | 53.85    | 50.58    |
| Copper              | 0.91     | 3.44     |

**Fig. 1** SEM image of a Cu-1 and b Cu-2 particles taken from dispersion c Cu-1 particle size histogram d Cu-2 particle size histogram
particle dispersion) which additionally can act as stabilizing agent in addition to disodium citrate.

Surface morphology of Cu NPs and EDX of the CuNPs treated fabrics

Surface morphology of synthesized Cu-1 and Cu-2 nanoparticles were studied using SEM instrument and presence of copper was elucidated using SEM EDX. It was observed that in both the cases morphology of particles remains spherical. In case of Cu-1 uniformity of particle was observed whereas in Cu-2 non uniform distribution was found. However, due to a greater number of smaller particle size of Cu-2, reduction of 4-NA was faster which was discussed in later section. Figure 1a shows SEM image of Cu-1 particles whereas Fig. 1b depicts SEM image of Cu-2 particles.

Size measurement of 50 particles of Cu-1 from SEM analysis was done and histogram is presented in Fig. 1c. Similarly, size measurement of 50 particles from Cu-2 SEM image was carried out and is also presented in form of histogram in Fig. 1d. It was observed that the average size of Cu-1 nanoparticles is nearby 100 nm whereas for Cu-2 nanoparticles the average size is nearby 60 nm.

Cotton fabric treated in first formulation (Cot-Cu-1) is light brown and the same is greenish for second formulation (Cot-Cu-2), implying presence of CuNPs on the cotton fabric. The colour of the cotton fabric treated with CuNPs (Cot-Cu-2) has been changed from light brown to red to dark greenish brown as the sodium hydroxide is added to the second formulation.

Elemental analysis of both the treated samples has been performed using EDX technique and date is presented in Table 1. It has been observed that copper content gets increased on the fabric which has been treated at basic pH. This may be due to more swelling of the treated cotton at basic pH which in turn
helps to penetrate higher amount of CuNPs inside the cotton fabric and supports faster reduction by Cot-Cu-2 sample than Cot-Cu-1. Percentage of CuNPs is around 1% in Cot-Cu-1 sample whereas the same is ~3% in Cot-Cu-2 when applied at basic (pH 11) pH using sodium hydroxide. As presented in Fig. 2, SEM EDX image (Fig. 2e, captured on a single thread) also demonstrates smaller size of particles in case of Cot-Cu-2 image as compared to Cot-Cu-1 (Fig. 2b) which also justifies the incorporation of the formed nanoparticles on the cotton substrates simultaneously as and when these are formed in the reaction solution. SEM–EDX images have been taken at different parts of treated fabric and it has been observed that CuNPs are present all over the fabric as indicated by their uniform colour also.

UV–visible analysis of CuNPs

UV–Visible absorption of CuNPs formed in reaction mass was measured using UV–Visible spectrophotometer. It is clearly observed that peak at 584 nm is responsible for brown colour CuNPs and absorbance at 578 nm is due to green coloured nanoparticles (Cu-2) which is also in agreement with the findings reported by other researchers (Salavati-Niasari and Davar 2009) and reported in Fig. 3. The treated fabric with Cu-1 and Cu-2 particles was further analyzed...
to confirm the presence of copper in its nanoparticle form. For this assessment, 2 inch × 2 inch cotton treated sample was put in a test tube containing DMSO and the same was heated for 30 min at 50 °C so that particles present in the fabric can elute to DMSO solution. The absorbance of the DMSO suspension was measured using UV–visible spectrophotometer which clearly confirms that CuNPs remain in metallic form on fabric samples as represented in Fig. 3c and d wherein the absorbance peak was observed for Cu-1 and Cu-2 particles, respectively.

FTIR analysis

FTIR spectra of the raw and treated cotton fabric with CuNPs have been analysed and are presented in Fig. 4. It is observed that some new peaks have been appeared in the FTIR curve of the treated fabric, at about 1500 to 1700 cm⁻¹. This phenomenon has been occurred may be because of the oxidation of cellulose due to reduction of copper ion (Quinian et al. 2011). CuNPs treated cotton fabric (Cot-Cu-2), in presence of sodium hydroxide, shows less intense peak near this region. Tensile strength also follows the same order (as discussed in the later part of this article) as strength gets decreased due to oxidation of the treated cotton while the strength loss is even more in absence of sodium hydroxide. This observation substantiates that CuNPs get attached to cellulosic structure physically. Stretching observed around 1500–1700 cm⁻¹ in the treated samples is due to oxidation of cellulose whereas OH stretching has been observed in all three samples in the region of 3200–3500 cm⁻¹ (Sedighi et al. 2014). Cotton fabric shows intense peak ranging from 1000 to 1100 cm⁻¹, could be associated with the vibration of pyran structure (–C–O–C stretch) and C–O group stretching of cellulose. However, Cu nanoparticle treated cotton fabric (Cot-Cu-2) also shows less intense and broader peak at 1000–1100 cm⁻¹, may be assigned with the oxidation of the some of the pyran groups of cellulose, and also may be due to cellulosic interaction with CuNPs as broadening of the peak is observed. However, no significant peak has been observed in the treated cotton fabric as the percentage loading of copper is very less on the fabric surface. The physical presence of copper on the fabric surface is observed due to colour shade and chemically from the EDX analysis of the treated cotton fabric, depicted in Fig. 2.

Influence of pH value

The original pH value of the CuSO₄ aqueous solution has been around 2.8. It has been investigated

| Sr No | Fabric Type          | L     | a*    | b*    | c*    | H     |
|-------|----------------------|-------|-------|-------|-------|-------|
| 1     | Pure cotton          | 81.78 | -0.11 | 2.85  | 2.85  | 92.27 |
| 2     | Cot-Cu-1             | 71.41 | 1.26  | 9.67  | 9.75  | 82.59 |
| 3     | Cot-Cu-2             | 38.44 | -0.33 | 5.45  | 5.56  | 93.45 |
| 4     | Cot-Cu-1 after wash  | 77.13 | 1.69  | 7.07  | 7.27  | 76.53 |
| 5     | Cot-Cu-2 after wash  | 41.26 | -0.34 | 5.33  | 5.34  | 93.63 |
that pH plays an important role in the formation of CuNPs as without sodium hydroxide treated sample has shown more strength loss than the sample treated in presence of sodium hydroxide. The pH value of the reaction system of Cot-Cu-1 has been around 2.8 as such which has been made 11 by addition NaOH aqueous solution for Cot-Cu-2. Two different colours have been observed after addition of sodium borohydride solution to above solutions due to the formation of different size nanoparticles.

Assessment of colour fastness of the CuNPs treated cotton substrates

Colourfastness is one of the important aspects to assess the properties and performance of the treated textile products. Cot-Cu-1 and Cot-Cu-2, both the treated fabric samples have been tested for colourfastness to washing. Treated samples have been washed using Lissapol N detergent at 50 °C for 45 min. Thereafter, L, a*, b*, c*and h* values of the treated fabric have been measured before and after the washing operation and the concerned data is represented in Table 2. Value obtained after wash clearly demonstrates that both the cotton fabrics coloured with CuNPs possess reasonably good colourfastness to washing. Treated fabrics have also been
examined for colour fastness to rubbing. The grey scale rating has been used to demonstrate the DE values of Cot-Cu-1, Cot-Cu-2, under dry and wet rubbing conditions. The dry rubbing colour fastness has been rated as 4 for both the treated fabrics whereas wet rubbing data for Cot-Cu-1 and Cot-Cu-2 are 3 and 3.5, respectively. Therefore, from the fastness data, it has been confirmed that the copper treated fabrics retain CuNPs even after laundering and rubbing. However, only physico-absorption of CuNPs on cotton takes place in both the cases. In future wash fastness test up to various cycles will be performed and if there is poor washability, then some cross-linker like sodium hypophosphite (SHP) and citric acid can be used for improved durability. Images of untreated and treated fabric with Cu-1, Cu-2 as well as solution of Cu-1 and Cu-2 are represented in Fig. 5a–e.

The images of the treated samples are also represented in Fig. 5.

Mechanical properties of treated cotton fabric

Physical effect of CuNPs integration on cotton fabrics has been analysed by studying the tensile strength of the control and treated cotton fabrics, depicted in Fig. 6. Control cellulosic fabric has shown the tensile strength of around 604 N (CV%-3.04) whereas CuNPs treated cotton fabric has displayed the tensile strength of around 624 N (Cot-Cu-2) (CV%-2.23) and 330 N (Cot-Cu-1) (CV%-2.52). CuNPs have adverse effect on the strength of the treated fabric especially while the treatment is carried out in absence of sodium hydroxide (Cot-Cu-1 in this case). However, the tensile strength has remained almost same in which the treatment is performed in presence of sodium hydroxide (Cot-Cu-2 in this case). It has also been reported in literature that if cellulosic substrate is treated in basic pH, then there should not be any detrimental effect on the fabric properties (Sharma et al. 2018). However, strength falls to a significant extent is a known phenomenon once the treatment is done in acidic pH. It is obvious that cotton gets degraded in acidic pH due to depolymerisation which is promoted by acid attack on cellulosic backbones. In our case FTIR analysis also supports the same where-in there is a significant loss in tensile strength due to degradation of cellulosic structure as represented by increased formation of aldehyde groups after the treatment process (in case of Cot-Cu-1).

Antimicrobial activity of the treated fabrics

It is well known that the cellulosic materials are prone to microbial attack. Usually they act as accumulator, spreader, and assist to multiply microorganisms in nearby environment (Dastjerdi and Montazer 2010). It has already been reported in the

![Fig. 7 Bacterial colony growth on Agar plate (A) control cotton, (B) Cot-Cu-1, (C) Cot-Cu-2 (D) Agar plate for diffusion test, CC-control cotton, whereas Cot-Cu-1 and Cot-Cu-2 represent Cu-1 NPs and Cu-2 NPs treated sample, respectively](image)
literature that cellulosic fabrics treated with various metal, metal oxide nanoparticles exhibit antibacterial properties (Sedighi et al. 2014). The results of the antibacterial tests, represented in Table 3, demonstrate the excellent antibacterial efficacy of the cotton fabrics containing CuNPs. Both the treated fabric samples have exhibited an efficient antibacterial effect against Gram-negative, E coli bacteria. Table 3 represents the reduction of colonies of treated sample [Cu-Cot-1 and Cu-Cot-2] and bacteria colony reduction (BCR) percentage with respect to control cotton sample whereas Fig. 7 represents the picture of various Agar plates showing the growth of microorganism. Also, diffusion test has been performed, and it has been observed that there is a significant growth of bacteria colony on and around the untreated sample whereas no visible bacterial growth has been observed on both the treated cotton fabrics (with Cu-1 and Cu-2) as shown in Fig. 7D. Cot-Cu-2 fabric showed bigger zone of inhibition than the Cot-Cu-1 sample as the size of copper nanoparticle is smaller in case of Cot-Cu-2 (resulting in enhanced surface interaction with bacterial cell) as compared to Cot-Cu-1 sample.

Antimicrobial activity of untreated and treated fabrics against S. aureus (Gram-positive bacteria) was also studied and the picture of the respective Agar plates with bacteria colony forming unit are represented in Fig. 8 A, B, C. It was observed that CuNPs treated fabric showed very good antimicrobial activity against S aureus bacteria. Table 4 represents the reduction of colonies of the treated sample [Cu-Cot-1 and Cu-Cot-2] and bacteria colony reduction (BCR) percentage with respect to control cotton sample. Cot-Cu-2 fabric showed bigger zone of inhibition than the Cot-Cu-1 as depicted in Fig. 8D. The reason behind the enhanced activity of Cot-Cu-2 fabric has already been discussed in the earlier paragraph.

Antimicrobial activity of metal nanoparticles is a proven phenomenon which occurs in multiple mode as these can penetrate inside the cell wall of bacteria due to its very small size and eventually inhibit the activity of bacteria to multiply. Nano copper shows
antibacterial activity due to various aspects as they can adhere to the cell wall of bacteria because of electrostatic force, disturb cell membrane protein structure and accelerate the process of denaturation of protein (Sedighi et al. 2014).

Investigation of catalytic activity of the treated fabrics

Metal and metal oxide nanoparticles have widely been used as catalyst in various applications from long back (Sharma et al. 2018). Metals have been used as reducing agent and its oxides have been exploited as oxidising agent (Sharma et al. 2016). Recently, silver (Ag), gold (Au) nanoparticles have been widely used by the researchers as catalyst in various organic reactions (El-Shishtawy et al. 2011, Tang et al. 2017). In the present research, CuNPs are bound to cotton fabrics after their synthesis at higher temperature and for the first time it has been used in the reduction of 4-NA to 4-PD as a model reaction, depicted in Fig. 9.

UV–visible absorption spectra of standard 4-NA and 4-PD have also been recorded. From the experimental analysis, it is clear that 4-PD and 4-NA absorb at different wavelength i.e., 300 and 380 nm. Cellulose acts as support and after reaction CuNPs remain with cellulose fabric and this copper functionalized cellulose fabrics can again be used for reduction. CuNPs treated cotton samples have shown catalytic activity which has been monitored in reduction at initial, 1, 3, 5, 10, 20, 30, 45, 60 min, (E) Cot-Cu-2 nanoparticles used at initial, 1, 3, 5 min

Fig. 10 UV–Visible spectra of (A) 4-nitroaniline, 380 nm, (B) phenylene diamine, 300 nm, (C) 4-nitroaniline (380 nm) and phenylene diamine (300 nm). (D) Cot-Cu-1 nanoparticles used in reduction at initial, 1, 3, 5, 10, 20, 30, 45, 60 min, (E) Cot-Cu-2 nanoparticles used at initial, 1, 3, 5 min
by taking UV–Visible absorption spectra of aqueous solution during reduction of 4-nitroaniline (4-NA) using NaBH₄. It has been observed that there is a change in colour of 4-nitroaniline (4-NA) solution from light yellow to brown after reduction. In general nitro compounds are inert to NaBH₄ in absence of catalyst. However, metal nanoparticles on cellulose fabric are acting here as an electron transfer agent from NaBH₄ to nitro compound to accelerate the reduction reaction. Absorption peak observed at 300 nm in UV–Visible absorption may be assigned to phenylene diamine (4-PD) and 380 nm in UV–Vis absorption may be denoted for 4-nitroaniline (4-NA). It has also been observed that the absorption peak intensity at 300 nm is increased and peak intensity at 380 nm is decreased during the reaction in presence of the treated fabric. However, peak intensity remains almost same whatever has been observed for only 4-NA in presence of control sample. Further, it also has been observed that CuNPs treated sample in presence of sodium hydroxide shows enhanced activity than without sodium hydroxide treated samples.

The absorption peak observed at 380 nm due to 4-NA is rapidly decreasing due to excellent catalytic activity of CuNPs treated cotton fabric. However, Cot-Cu -2 reduces 4-NA faster (5 min) than the Cot-Cu-1 system (60 min) (as shown in Fig. 10) whereas no reduction phenomenon is observed in case of control cotton even after 30 min as represented in Fig. 11. 4-NA reduction is generally considered to be a pseudo-first-order kinetic reaction on account of excess NaBH₄ used (Tang et al. 2017).

However, it has been noted that when control cotton is used as catalyst for reduction of 4-NA, no additional peak is observed for 4-PD. The observation directly indicates that no reaction takes place in this case and as a result there is no visible change in yellow colour of solution also.

Correlation between the two different cottons produced and the properties

In this study, cotton fabrics have been treated with two different types of CuNPs (as and when it’s formed in the reaction mixture itself) i.e. Cot-Cu-1 (in absence of NaOH) and Cot-Cu-2 (in presence of NaOH). Both the cases, the cotton fabrics are furnished with efficient antimicrobial property as well as catalytic activity which can be used for either of the applications or both. In both the cases, the particles distributed in the cotton fabric have shown efficient catalytic activity as these are not agglomerated unlike the nanoparticles in bulk or powder form. But, if we compare the results among the two types of the treated cotton fabrics, Cot-Cu-2 has significantly higher efficiency as compared to Cot-Cu-1. In fact, both the fabrics can be used for intended applications, but Cot-Cu-2 renders better efficacy. On the other hand, Cot-Cu-1 is also gone through acidic degradation during nanoparticle preparation and its deposition on the fabric (in absence of NaOH). Thus, this category of treated fabric may not be very suitable where there is a need of higher strength of the fabric for usages but for the other one (Cot-Cu-2) the tensile strength is perfectly intact without any loss. Thus, the study expresses two different solutions for specific need of adjusting the pH for synthesis and integration of Cu nanoparticles where the other required chemicals may not be compatible with acidic or basic pH and accordingly someone can choose the right one (either Cu-1 or Cu-2 route).

Conclusions

This research work represents the synthesis of two types of CuNPs on cotton fabric. Two different types of colours (light brown and greenish) have been obtained on the treated fabric. Both the treated fabrics
have shown an excellent antimicrobial efficacy (more than 97%) against Gram-negative \((E\ coli)\) bacteria. SEM investigation has depicted homogeneous distribution of CuNPs on both the cotton fabrics. Both the fabrics treated with CuNPs have shown catalytic activity, as measured by reduction of 4-NA to 4-PD and observed in UV–Visible spectroscopy analysis. Greenish coloured cotton fabric (CuNPs synthesized in presence of NaOH) has demonstrated significantly higher catalytic activity toward reduction of 4-nitroaniline because of distribution of smaller and a greater number of CuNPs size particles on the fabric surface. The mechanical property of cotton fabrics treated with CuNPs in absence of sodium hydroxide has registered remarkable decrease in tensile strength (i.e., 40–45%) of fabric (treated in acidic pH) due to degradation of cellulosic structure whereas there is no loss of tensile strength has been observed in case of fabric treated with CuNPs which are synthesized in presence of NaOH. The study successfully has demonstrated that beside other developed functionalities (such as antimicrobial activity, fabric colour, etc.) on the treated fabric, the nanoparticles can also be exploited as efficient catalyst on surface of fabric so that the problem of agglomeration of separately as-synthesized nanomaterials (in bulk or powder form) can be avoided and more efficient catalytic activity can be achieved.

Declarations

Conflict of interest The authors declare no conflict of interest in publishing this research article in this journal.

Human and animal rights This research article does not involve any human participants and/or animals for studies by any of the authors.

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