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Stabilization of nano-structured ZnO particles onto the surface of cotton fibers using different surfactants and their antimicrobial activity

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Keywords: ZnO nanoparticles (ZnO NPs); Surfactants; Ultrasonic irradiation; Antimicrobial activity; Coated cotton fabric.

Abstract

ZnO NPs were prepared and deposited onto cotton fibers via ultrasound irradiation successfully. Different surfactants (SDS, HY, CTAB,TX-100) have been used to stabilize, homogenize the coated ZnO NPs and control their shape and size as encapsulated species. The use of surfactants has improved the durability of ZnO NPs and decreased its leaching in particular SDS. The small mean crystallite size for ZnO particles due to the use of surfactants is the main reason for decreasing the leached of ZnO particles from cotton substrate. SEM and XRD analysis revealed information about the shape and size of the coated ZnO nanopaticles. The use of SDS and HY surfactants in the synthesis of ZnO NPs coated fabrics showed the highest antibacterial and antifungal activities against different pathogenic bacterial and fungal species with high reduction reached over 90%.

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1. Introduction

Textile fabric provides an excellent environment for the growth of microorganisms because of their large surface area and the ability to retain moisture. Increasing microbial resistance have emerged as a major challenge to the healthcare systems and despite the wide range of the available antimicrobial therapies, microbial infections remain high, due to the ability of these organisms to develop resistance to virtually all antimicrobial therapies. A large number of chemicals have been used to impart antimicrobial activity to textile materials. More attention has been paid on the preparation and applications of nanometal oxide coatings onto cotton substrate due to their promising applications [1-7]. The nanometal oxide films deposited on cotton fabrics have exhibited excellent antimicrobial activity against bacteria [5-10]. There is a growing awareness of the use of antibacterial fabrics in the form of medical clothes, protective garments, and bed spreads to minimize the chance of the nosocomial infections [4, 11]. Inorganic metal oxides have attracted a great interest as alternative antimicrobial agents. This was due to their safety and selective toxicity against bacteria, stability, heat resistance and their ability to withstand intensive and harsh processing condition [12-16]. Nowadays, metal oxides nanoparticles coated onto cotton fibers represent important composites that are increasingly being developed for use in novel health-related applications [5,7, 17-20]. These coated fabrics protect against UV radiation and do not possess skin irritation and sensitization properties [7, 21]. Several researches have reported the synthesis and applications of zinc oxide nanoparticles coated onto textile substrates [5,7,8, 17-19]. The main challenge is to develop ZnO-NPs coated cotton composites with stable, less leachable, and effective in the elimination of both bacteria and fungi. The use of natural biodegradable and biocompatible biopolymers chemically link with transition metals to enhance the nanoparticles stability [22-24]. More recently Perelshtein et al. have used biocatalytic enzyme as tool for activation of textile surfaces for in-situ synthesis of zinc oxide nanoparticles on the cotton fabric. The finished cotton fabric showed a good photocatalytic activity on degradation of methylene blue and 100% antimicrobial properties against Staphylococcus aureus, Escherichia coli and Candida albicans [25,26]. The use of the enzyme, chemicals or binding agents as tools for activation of textiles may results of changes in

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the nature of the cotton fibers. In this work we have not used any harsh chemicals, enzymes or binding agent in-situ synthesis of ZnO NPs onto cotton fibers, instead of that, we have used several types of surfactants include: cationic, anionic and nonanionic (SDS, CTAB, TX-100% and HY) in the coating process. The surfactants are used to modify and improve the interaction between the substrate (cotton fibers) and the zinc oxide nanoparticles. Surfactants were used to stabilize ZnO-NPs by controlling their shape and size as encapsulated species, as well as modification of the surface of textile to improved the adherence properties between the textile surface and the inorganic particles in particular the SDS and HY. The morphology of the cotton coated metal oxides nanoparticles and their chemical structure have been analyzed by UV-vis, FTIR, TGA, SEM, XPS and XRD.

2. **Materials and Methods**

2.1 **Materials**

Zinc sulfate hepta-hydrated ($ZnSO_4.7H_2O$) , sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) andhydrochloric acid (HCl) were purchased from (HiMedia, India) and used in preparation of samples without further purification. Surfactants, sodium dodecyl sulfate (SDS) (Merck, 99%), cetyl tri-methyl ammonium bromide, $C_{19}H_{42}BrN$ (CTAB)(Merck, 99%), triton X-100, $C_8H_{17}C_6H_4O$ $(CH_2CH_2O)_9.5H$ (TX-100))(Merck, 99%) and alkyl hydroxy-ethyl dimethyl ammonium chloride, $C_{16}H_{36}NOCl$. $C_{18}H_{40}NOCl$ (Praepagen HY, Clariant 40%) (HY) were used in preparation of the samples. Deionized distilled water (D.D.W) was used to prepare all the solutions used during the coating of cotton material. Cotton was purchased from local market as a Turkish cotton product (100% cotton) and was pretreated before used.

Dehydrated nutrient agar powder, nutrient broth powder, Sabouraud Dextrose Agar (SDA), Di-Chloran Rose Bengal Chloramphenicol (DRBC) agar, Potato Dextrose Agar (PDA), were purchased from (HiMedia, India) and used to prepare culture media, and the manufacturer's instructions were followed for media preparations.

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2.2 **Methods**

Optical analysis of the ZnO-NPs coated cotton fibers was obtained by Ultraviolet-Visible (UV/VIS) Spectrophotometer using SHIMADZU-1601 model, Fourier transform spectroscopy (FTIR) are obtained using Thermo Fisher Scientific, USA, scanning electron microscopy (SEM) are obtained using Carl Zeiss AG - EVO® 60) and X-ray diffraction (XRD) for the samples are obtained using EQuniox 3000, INEL, France. Zn ions concetrations in aqueous solutions were determined using a Perkin Elmer Atomic Analyst-100, Spectrometer.

XPS spectra were recorded using aK Alpha apparatus (Thermo) fitted with a monochromatic Al Kα X-ray source (1486.6 eV, spot size: 400 µm). The pass energy was set to 200 and 50 eV for the survey and the narrow regions, respectively. Additional C1s spectra were recorded at a pass energy of 20 eV in order to accurately calibrate the spectra against the C-C/C-H C1s component set at 285 eV. The composition was determined using the manufacturer sensitivity factors.

2.3 **Coating process**

Cotton fibers were first washed in a warm solution of 1% of sodium dodecyl sulfate (SDS) at 50 °C for one hr. After rinsing with distilled water several times, the fibers were dried at 80°C for 24 hr. The ZnO-coated cotton materials were prepared as follow: of $ZnSO_4.7H_2O$ (1.44 g, 0.05 mol) was dissolved in 50 ml solution of each surfactant (SDS, CTAB, TX-100%, HY) (0.001M). NaOH (0.4 g, 0.01 mol) was then added and the mixture was stirred thoroughly in presence of 0.50 g of dry cotton, The mixture was irradiated using an Ultrasonicator (Model US-150 Ti-horn ,20kHz, output 10 Turning 7) for about 60 minutes with stirring from time to time to ensure coating of all the cotton material with ZnO-NPs. During the sonication, the flask was placed into a cooling bath keeping a constant temperature between (35-40°C). The ZnO-NPs coated cotton was then washed thoroughly several times with distilled water and dried at 80 °C overnight **(Fig. 1)**. ZnO coated cotton free of surfactant was prepared by same method. These coated materials are donated hereafter as ZnO+no surfactant, ZnO+CTAB, ZnO+SDS, ZnO+HY, ZnO-TX-100.

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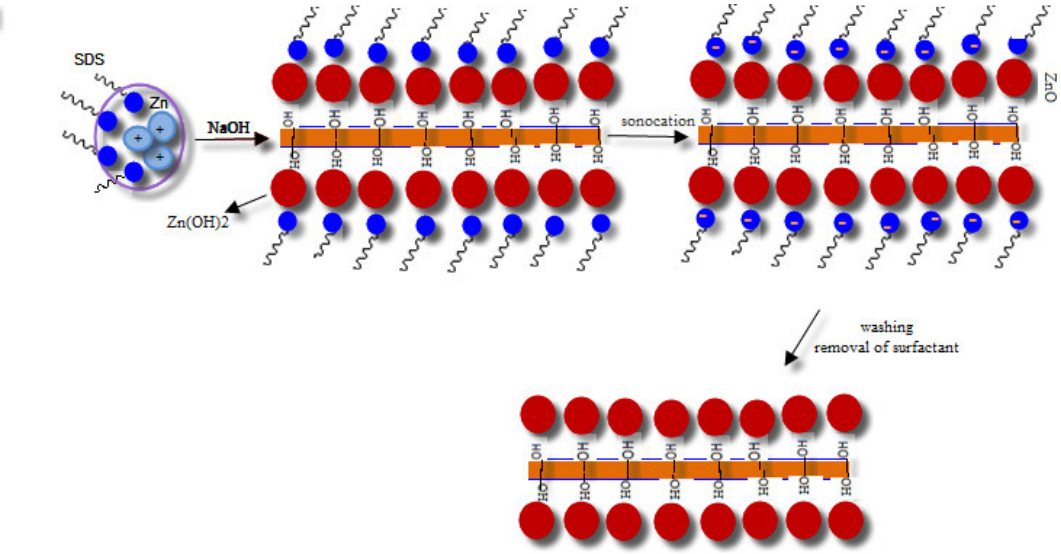


Fig. 1 Chemical process of formation coated ZnO NPs/cotton composite

2.4 **Wash durability tests**

The wash durability tests of all coated cotton samples were carried out using distilled water at ambient temperature. ZnO-NPs coated cotton material (100 mg) of each coated sample was washed with 20 ml D.D.W using Memeret shaker on 120 rpm at the room temperature for 25 minutes (5 cycles) and for 50 minutes (10 cycles). The samples were then dried at 80 °C for overnight. These samples were assessed for Zn content remained using Atomic Absorption Spectrometer (AAS) (Fig.2).

2.5 ZnO-NPs Content

The content of ZnO-NPs in percentage (%) was estimated in all coated samples by treatment the coated cotton materials (10 mg) with 5 ml of the concentrated solution (2M) of HCl: H_2SO_4 3:1 volume ratio. They are subjected to vortex for about 3-5 min to insure a complete removal of the ZnO-NPs from the cotton material. The cotton material was removed from solution and the content of ZnO was determined by AAS analysis. This was done for all ZnO-NPs coated samples before and after washings (5 and 10 washing cycles). The results are given in Table 1.

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2.6 Antimicrobial activity tests

The cotton fabrics were subjected to the assessment of their antibacterial activity before and after washing processes. The antimicrobial activity of ZnO-NPs coated cotton was tested against the Gram negative *Escherichia coli* and the Gram positive *Staphylococcus aureus*, and against the fungal isolates *Candida albicans* and *Microsporum canis*. These clinical isolates were kindly provided by the Microbiology laboratory of Al-Shifa' Hospital.

The antimicrobial activity was tested according to the standard quantitative test (AATCC 100, 2004) with some modifications, where a piece of the coated cotton was tested against a known concentration of bacterial or fungal suspension and the reduction in the viable cells in standard time was calculated. A dry piece of coated or uncoated cotton material (100 mg) was used for the antimicrobial test, the pieces were sterilized by autoclave and by UV- sterilization before testing the antimicrobial activity. The cotton materials "Test and Control "were soaked in sterile normal saline and incubated for a standard time without shaking. A preliminary antibacterial test was carried out for ZnO-NPs-coated cotton material treated with the different surfactants where the cotton materials were washed with water very well and then allowed to dryness. These samples were tested against the bacterial cultures on nutrient agar plates to ensure that the surfactant is completely removed by washing after the coating stage and any decrease in bacterial number was likely due to the exposure to ZnO-NPs coated cotton material not from the used surfactant.

2.6.1 Testing the antibacterial activity of the coated cotton

Two cotton pieces "Test and Control "were inoculated with 500 µL of the bacterial suspension and then each piece was inserted in a vial containing 20 ml of sterile physiologic saline solution (NaCl 0.9%). The vials were tightly closed and allowed to vigorous shaking for about 1 min. and then incubated at 37 °C for 24 hr. After incubation, 1000 µL of each sample was taken and serially diluted with (0.9%) NaCl solution and 100 µL of each dilution was transferred onto nutrient agar plates. The plates were allowed to grow overnight at 37 °C and the viable bacteria were counted..

2.6.2 Testing the anti-fungal activity of the coated cotton

Two cotton pieces " Test and Control "were inoculated with 100 µL of the *Candida* suspension or *M. canis* spore suspension and then each piece was inserted in a vial containing 30 ml of sterile saline solution. The vials were tightly closed and allowed to vigorous shaking for about 1 min and then incubated at 30°C for 48 hr. (*C. albicans*) or for 5 days (*M. canis).* After

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incubation, 1 mL of each sample was taken and serially diluted with (0.9%) NaCl solution and 100 µL of each dilution was transferred onto SDA plates (*C. albicans*) or onto (PDA) plates supplemented with chloramphenicol (*M. canis*). The plates were allowed to grow for 48 hr. (*C. albicans*) or for 72 hr. (*M. canis*)at 30 °C and the viable yeast or fungal cells were counted.

3. .**Results and Discussion.**

3.1 Synthesis

The ZnO-NPs coated cotton fibers were obtained by deposition of the ZnO-NPs onto the cotton fibers via the ultrasound irradiation of the zinc oxide [26]. The formation mechanism of the ZnO-NPs by adding $ZnSO_4.7H_2O$ into solution containing a surfactant and sodium hydroxide is probably involve three or four steps, first interaction between Zn^{2+} and surfactant, second formation of stable $Zn(OH)_2$ which is absorbed onto the cotton surface. Thirdly transformation of $Zn(OH)_2$ to ZnO-NPs by irradiation energy and finally removing the excess of reactants including the surfactant by washing process (**Fig. 1**). The role of surfactants is not only to control the size and shape of ZnO nanoparticles, but also to modify the cotton fabric surface to obtain small stable ZnO nanoparticles that well dispersed and adhered better to the cotton surface [6, 27].

Wash durability tests were carried out for ZnO-NPs coated cotton fabrics showed, that different washing cycles resulted in significant release of ZnO-NPs out of the cotton material. The reason for this behavior is that excess uncoated ZnO-NPs are leached out from the cotton fabrics.

The results showed that the use of surfactants generally have reduced the leaching of ZnO-NPs. Of the four different surfactants used, SDS was the most effective surfactant in minimizing the leaching of ZnO-NPs due to its smallest particle size (XRD results, Table 2) followed by HY. This can be explained that particles of smallest size leached less in comparison with larger particles. While CTAB has the lowest effect and TX-100 has almost minor effects (Fig. 2).

3.2 X-ray photoelectron spectroscopy (XPS)

Typical survey regions are displayed in Fig. 3, the XPS for untreated cotton(blank) showed two main peaks centered at 285 eV and 533 eV (Fig.3a). The XPS for ZnO/CTAB sample exhibits additional peaks due to Zn2p at 1021 eV and Zn LMN along with the C 1s and O 1s peaks (Fig

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3b)[28,29]. This provides strong evidence for the immobilization of zinc oxide nanoparticles onto the cotton fibers.. All other samples prepared with any of HY, SDS and TX-100 exhibit similar spectra with prominent Zn2p doublets centered at 1021 eV. High resolution C1s peaks were fitted with three components centered at 285, ~286.6 and ~288,2 assigned to C-C/C-H, C-O and O-C-O, respectively (Figs. 4a). Figure 3b depicts high resolution O1s spectra for the untreated cotton and ZnO/CTAB. For cotton, a single peak centred at 533 eV accounts for C-O-H and C-O-C groups. In the case of ZnO/CTAB-coated fabrics, an additional intense O1s peak centred at 530.2 eV is observed assigned to ZnO NPs.

Table 1 reports the surface composition of the different components present in the composites. The O/C ratio for the reported original untreated cotton fibers is 0.62 comparable to 0.65 reported for woven cotton fabric [29]. There was a decreasing in the atomic concentration of carbon, whereas the there was a minor decreasing of the atomic concentration of oxygen. The presence of minor content of N% is probably that traces of surfactant is present. The high Zn content in case of ZnO/SDS in comparison with other samples is probably due to the strong interaction between SDS and ZnO-NPs.

Table 1: Surface composition of for ZnO-coated cotton fabrics and reference materials ZnO and blanck cotton.

Materials	Zn	C	O	N
cotton	0.00	61.6	38.4	0.0
ZnO	23.4	38.1	38.5	
ZnO/SDS	20.8	40.2	38.4	
ZnO/CTAB	16	46.6	36.8	0.6
ZnO/HY	11.0	49.5	39.0	0.5
ZnO/TX	11.3	51.4	37.3	

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3.3 UV/Vis Spectra.

The UV visible spectra of all samples showed an absorption band at 362-371 nm in ethanol (Fig. 5)[28]. There was a blue shift of the peak maximum from 371 to 362 nm dependent on surfactant used, where the least blue shift of the peak maximum is found at 371 nm when SDS surfactant was used and the highest red shift is found when HY was used. This is in consistence with XRD results which proved that the use of SDS surfactant results of the smallest particle size in comparison with other samples (XRD results, Table 2). The gap energy was calculated according to the Planck's constant are 3.4-3.8 eV. There was slight change of gap energy based on the nature surfactant used.

3.4 FTIR Spectra

The FTIR spectral patterns of blank cotton and its ZnO-NPs coated cotton are shown in Fig. 6. The broad band at 3330-80 cm^{-1} is due the ν(O-H) vibration. This value is closed to the one at 3337 cm^{-1} reported by Azizi and her colleagues [28,31]. The strong band at (1050-1080 cm^{-1}) is assigned to asymmetric stretching vibration of ν(Zn-O-Zn) bridging. This is closed to the one at 1090 cm^{-1} reported previously by El-Nahhal and his team [6]. The absorption band at 1640 cm^{-1} is due to δ(O-H) vibrations of the hydroxyl groups of some physically adsorbed water molecules, this is almost similar to the one at 1637 cm^{-1} reported δ(O-H) vibration [32]. The FTIR spectrum showed an absorption band at 465 cm^{-1} which is typically due to the lattice stretching vibrations ν(Zn-O)[6,33]. There were no new peaks were observed due to the use of surfactant in all samples, this implies that almost complete removal of surfactants was achieved by washing process. That was also confirmed by TGA results discussed later.

3.5 Scanning Electron Microscopic (SEM)

The morphology of ZnO-NPs deposited into cotton fibers in the presence of different surfactants is examined by SEM and is presented in Fig. 7. The agglomerates ZnO-nanoparticles were dense and compact. The SEM image of blank cotton fiber (Fig. 7, image a) shows grooves and fibrils on the surface of the fiber. Fig. 7, image b shows that ZnO-NPs (absence of surfactant) were

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well covered all fiber surface. Some of the agglomerates of ZnO-NPs can be seen as intereconnected nano-flakes as vine leaves of no defined boundaries. It is obvious that the morphology of the ZnO-NPs coated cotton has changed based on the nature of surfactant used. In case of using HY, cationic surfactant, a less dense particle structure and a mixture of ZnO agglomerates were observed. Some particles are seen as flakes of different sizes or interconnected nano-sheets, others were seen as nano-flowers (Fig. 7, image c).. In the case of using SDS anionic surfactant, the ZnO-nanoparticles were seen as layered nano-sheets stacks with more uniform as hexagonal shape (Fig. 7, image d). In case of using CTAB, cationic surfactant, the surface of the fabric was fully covered with a layer of ZnO-NPs, these particles have grown as interconnected nano-leaves which were adhered themselves to the surface of the fiber (Fig. 7, image e). In the case of TX-100, nonionic surfactant, interconnected nano-sheets were observed (Fig. 7, image f). The different morphologies of ZnO-NPs were similar to those reported [31]

3.6 X-Ray Diffraction (XRD) Analysis

The XRD patterns for ZnO coated cotton materials prepared in absence and in presence of different surfactants are displayed in Fig. 8. All the diffraction peaks were well indexed to the hexagonal ZnO wurtzite structure [28,33]. The major three peaks at $2\theta = 31.5$, 35 and 37 can be indexed to the lattice planes at 100, 002 and 101. Interestingly, when HY surfactant was used, each peak splits into a doublet of two peaks, one peak matches the peak, when CTAB was used and the other peak matches the peak when SDS was used. This can be explain that HY surfactant is probably interacted with ZnO-NPs through two cites nitrogen & oxygen cites, whereas CTAB or SDS each interacted with ZnO-NPs through one cite (nitrogen cite for CTAB & oxygen cite for SDS) (Fig, 8) . The diffraction peaks at diffraction angle below 30 are characteristic with cellulosic cotton material [34]. Diffraction peaks corresponding to the impurities were not found in the XRD patterns, confirming a high purity of the synthesized composites. The mean crystallite size of ZnO particles was determined by Scherrer's equation, the crystallite particle sizes are given in Table 2. As shown in the Fig.8, there was a significant shift of all peaks to lower angle with broadening in the line width when surfactants were use. This led to a slight decrease in the mean particle crystallite size of ZnO-NPs. Therefore the average mean crystallite particle size of ZnO-NPs estimated by XRD data (8.00-12.8 nm, Table 2) are smaller than the

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reported values (12-38 nm) of similar ZnO-coated cotton material prepared without using surfactants [6,31,35,36]. The reason for this change is probably that the used surfactants act as capping agents that can limit the growth of ZnO-NPs during their formation. The small size obtained for ZnO particles upon using the surfactants is the main reason for decreasing the leaching of ZnO-NPs from cotton substrate. This was more obvious in case of SDS and HY which showed the highest antibacterial activities in comparison with CTAB and TX-100..

Table 2 : Particle size of ZnO-NPs coated cotton composites prepared in presence of different surfactants.

Material	**ZnO**	**ZnO/SDS**	**ZnO/HY**	**ZnO/CTAB**	**ZnO/TX-100**
Particle size(nm)	12.84	8.00	10.02	11.06	12.14

3.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) and (DTA) for blank cotton, ZnO-NPs coated cotton and ZnO-NPs coated cotton after 5 washing cycles are presented in **Figs. 9 a-c**. The total weight loss were found 90%, 75% and 80%, respectively. This reveals that around 15% of ZnO nanomaterial was adsorbed onto cotton fibrics and that about 10% remain onto the cotton fiber after 5 washings. These results are in consistance with the results obtained using atomic absorbtion spectrophotometer (AAS).

3.8 Antimicrobial activity of the coated cotton

Antimicrobial Tests Against bacteria

Reduction percentage (%) of microbial cells by the treated cotton material was calculated by the following formula: R= 100 (B – A)/B, where R = reduction percentage (%), A = the number of microbial cells recovered from the inoculated coated cotton material incubated over (24 hrs.) contact period. B = the number of microbial cells recovered from the inoculated uncoated cotton material immediately after inoculation (at “0” contact time). The treated cotton fabrics show a

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significant antibacterial activity even after 10 washes (Figs. 10 & 11). The greatest antibacterial activity was observed when HY and SDS surfactants was used. The uncoated fabrics (control) have negative values for the percentage reduction test because the final number of cells will be much higher than the initial number of cells, so it has no bactericidal activity and the results were found to be zero.

From Figs. 10 & 11, it is clear that the nano coated cotton fabric has the ability to withstand its antibacterial activity against both bacterial species (*E. coli* & *S. aureus*) even after 10 washes. However, this activity (% reduction) is reduced as the number of washing cycles increased.
The antimicrobial finishes durability in our study match very well the previous results of the wash durability test that carried out by Rajendra and his colleagues [10] who stated that a significant antimicrobial activity was retained in the ZnO-NPs coated cotton fabrics even after 10 washes. They also reported that the % bacterial reduction after 10 washes was very low and there was no activity found in the fabrics after 20 washing cycles.

It is also noticed that ZnO-NPs-coated cotton has greater antimicrobial activity against *S. aureus.* This matches very well the results [10, 37,38] about ZnO-NPs and their microbial toxicity.We suggested that these findings may be due to the differences in the structure of the bacterial cell wall and the cell membrane which controls the access of different molecule inside the cell [29]. The concentration of NPs and their distribution along the cotton surface has a significant contribution to the activity. Moreover, the impact of nanoparticle size and shape on the antimicrobial activity can't be ignored.

Figs. 10 & 11 also showed that the coated with ZnO-NPs in the presence of HY and SDS have the maximum antibacterial activity against both bacterial strains whereas cotton coated in presence of CTAB and TX-100 and that of the coated in absence of any surfactant have less activities. We suggested that the maximum antimicrobial activity of ZnO-HY and SDS was due to the highest concentration of ZnO-NPs. The size and morphology of coated particles cannot be also ignored.

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Antimicrobial Tests Against Fungi

Figs. 12 &13 showed that ZnO-NPs coated cotton has greater antimicrobial activity against the bacterial species (*E. coli &S. aureus*) compared with the fungal species (*C. albicans&M. canis*). Moreover, it's obvius from the previous figures that ZnO-NPs coated cotton showed greater antifungal activity against *C. albicans* compared with *M. canis*. In addition, the figures showed that ZnO-NPs coated cotton fabric was able to withstand the antifungal activity against *C. albicans* and *M. canis* even after 10 washes. However, this activity (% reduction) reduced as the number of washes increased. It was found that the cotton fabric which was coated with ZnO-NPs in the presence of HY and SDS have the maximum antifungal activity against the tested fungal species. Whereas those coated using CTAB and TX-100 have less antifungal activity.

Conclusion

It is concluded that ZnO-NPs were prepared and subsequently deposited onto cotton fibers via ultrasound irradiation successfully. Surfactants were used as stabilizing and homogenizing agents for the zinc oxide controlling its shape and size as encapsulated species. The durability of the ZnO-NPs coated fabric results showed that there was subsequent decrease of leaching of ZnO-NPs accompanied with reduction in the antibacterial efficiency even after ten washing cycles. ZnO-SDS and ZnO-HY were the most effective ones among the used surfactants in reduction of antimicrobial activity due to their smaller size. SEM and XRD analysis revealed important information about the shape and morphology of the coated nanopaticles. The physical and chemical characteristics of the cotton coated material prepared in presence of surfactants were markedly different from those prepared in absence of surfactants. It's also shown that the size of the ZnO-NPs which obtained in presence of surfactants is smaller than those obtained in absence of surfactants.

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References

ACCEPTED MANUSCRIPT

1. Perelshtein, G. Applerot, N. Perkas, E. Wehrchuetz-Sigl, A. Hasmann, G M. Guebitz , A.Gedanken, Sonochemical co-deposition of antibacterial nanoparticles and dyes on textiles, Surf Coat Technol. 204(2009)54–57.

DOI:10.1016/j.surfcoat.2009.06.028

2. J P. Borah, J .Barman, KC. Sarma ,Structural and optical properties of ZnSNanoparticles, Chalcogenide Lett 5(2008)201–208,

3. H.Wang, A.Zakirov, SU.Yuldashev, J.Lee,D. Fu,T. Kang , ZnO filmsgrown on cotton fibers surface at low temperature by simple two-stepprocess, Mater Lett 65(2011)1316, http://dx.doi.org/10.1016/j.matlet.2011.01.072

4. G. Borkow,J. Gabbay ,Copper, an ancient remedy returning to fightmicrobial and viral infections, Curr Chem Biol 3(2009)272-278, https://doi.org/10.2174/187231309789054887

5. OV. Abramov,A. Gedanken, Y.Koltypin, N. Perkas, I. Perelshtein, E. Joyce,TJ.Mason Pilot scalesonochemical coating of nanoparticles ontotextile to produce biocidal fabrics, Surf Coat Technol 204(2009)718–722, http://dx.doi.org/10.1016/j.surfcoat.2009.09.030

6. I. M. El-Nahhal,S. M.Zourab,F. S. Kodeh, A. A.Elmanama, M.Selmane,I. Genois, andF. Babonneau, Nano-structured zinc oxide–cotton fibers: synthesis, characterization and applications. Journal of Materials Science, Materials in Electronics 24(2013)3970-3975, DOI: 10.1007/s10854-013-1349-1

7. I. M . El-Nahhal, S. M. Zourab, F. S. Kodeh, M. Selmane, I. Genois, and F. Babonneau, Nanostructured copper oxide-cotton fibers: synthesis, characterization, and applications, International Nano Letters 2(2012)1-5, DOI: 10.1186/2228-5326-2-14

8. I. Perelshtein, G.Applerot,N.Perkas, Sigl E. Wehrschetz, A.Hasmann,G. Guebitz, A.Gedanken , CuO-cotton nanoparticles: formation, morphologyand antibacterial activity, Surf Coat Technol 204(2009)54, http://dx.doi.org/10.1016/j. surfcoat.

ACCEPTED MANUSCRIPT

2009 .06 .028

9. Ug˘ur SS, MerihSarıısık, HakanAktas A, ig˘demUc¸ar MC (2010) EmreErden Nanoscale Res Lett 5:1204–1210.

10 R. Rajendran, C. Balakumar,A.Hasabo, M. Ahammed,S.Jayakumar, K. Vaideki, E .Rajesh , Zinc oxide nanoparticles for production of antimicrobial textiles, Int J EngSciTechnol 2(2010)202, http://dx.doi.org/10.4314/ijest.v2i1.59113

11. S.Wang,W.Hou, L. Wei, H. Jia, X. Liu, B. Xu, Antibacterial activity of nano-SiO2 antibacterial agent grafted on wool surface, Surf Coat Technol, 202(2007)460, http://dx.doi.org/10.1016/j.surfcoat.2007.06.012

12. L. Fu,Z. Liu,Y. Liu,B. Han,P. Hu,L. Cao,D. Zhu, Beaded Cobalt Oxide Nanoparticles along Carbon Nanotubes: Towards More Highly Integrated Electronic Devices. Advanced Materials 17(2005) 217-221, DOI: 10.1002/adma.200400833

13. S. Makhluf,R. Dror,Y. Nitzan,Y. Abramovich,R. Jelinek,A. Gedanken, Microwave-Assisted Synthesis of Nanocrystalline MgO and Its Use as a Bacteriocide. Advanced Functional Materials 15 (2005)1708-1715, DOI: 10.1002/adfm.200500029

14. Manna A C. Synthesis, characterization, and antimicrobial activity of zinc oxide nanoparticles. Nano-Antimicrobials, Springer (2012)151-180, DO:I10.1007/978-3-642-24428-5_5

15. S.Ravikumar, R.Gokulakrishnan and P.Boomi, In vitro antibacterial activity of the metal oxide nanoparticles against urinary tract infectious bacterial pathogens, Asian Pacific Journal of Tropical Disease 2 (2012) 85-89, http://dx.doi.org/10.1016/S2222-1808(12)60022-X

16. G.Singh, EM.Joyce, J.Beddow and T J.Mason, Evaluation of antibacterial activity

ACCEPTED MANUSCRIPT

of ZnO nanoparticles coated sonochemically onto textile fabrics. J Microbiol Biotechnol Food Sci , 2 (2012)106-120.

17. M J.Firdhouse andP. Lalitha, Fabrication of Antimicrobial Perspiration Pads and Cotton Cloth Using Amaranthusdubius Mediated Silver Nanoparticles, Journal of Chemistry, 2013 (2013) 1-5, http://dx.doi.org/10.1155/2013/741743

18. A. Abramova, A .Gedanken, V. Popov, EH .Ooi, TJ. Mason, E M.Joyce, J.Beddow, I.Perelshtein and V.Bayazitov,A sonochemical technology for coating of textiles with antibacterial nanoparticles and equipment for its implementation, Materials Letters 96 (2013).121-124. http://dx.doi.org/10.1016/j.matlet.2013.01.041

19 O.L. Galkina , A. Sycheva, A. Blagodatskiy, G. Kaptay ,V.L. Katanaev, G.A. Seisenbaeva, V.G. Kessler,A.V. Agafonov, The sol–gel synthesis of cotton/TiO2 composites and their antibacterial properties, Surface & Coatings Technology 253(2004) 171–179, http://dx.doi.org/10.1016/j.surfcoat.2014.05.033

20. I.Perelshtein, A.Lipovsky, N.Perkas, A. Gedanken, EMoschini, andP.Mantecca , The influence of the crystalline nature of nano-metal oxides on their antibacterial and toxicity properties, Nano Research 8(2015) 695–707, DOI: 10.1007/s12274-014-0553-5

21. R M. El-Shishtawy, A M. Asiri, N A.Abdelwahed and M M.Al-Otaibi, In situ production of silver nanoparticle on cotton fabric and its antimicrobial evaluation, Cellulose 18 (2011)75-82, DOI: 10.1007/s10570-010-9455-1

22. A. El Shafei, Abou-Okeil, ZnO/carboxymethyl chitosan bionano-composite to impart antibacterial and UV protection for cotton fabric, Carbohydr. Polym. 83 (2011) 920–925,http://dx.doi.org/10.1016/j.carbpol.2010.08.083

23. M.I. Rosca, G.Popa, G.C. Lisa, Chitanu, Interaction of chitosan with natural or synthetic anionic polyelectrolytes. 1. The chitosan–carboxymethylcellulose complex, Carbohydr. Polym, 62 (2005) 35–41, http://dx.doi.org/10.1016/j.carbpol.2005.07.004

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

24. K. Varaprasad, G.M. Raghavendra, T. Jayaramudu, J. Seo, Nano zinc oxide–sodium alginate antibacterial cellulose fibres, Carbohydr. Polym, 135 (2016) 349–355, http://dx.doi.org/10.1016/j.carbpol.2015.08.078.

25. S. Ghayempour, M.Montazer, Ultrasound irradiation based in-situ synthesis of star-like Tragacanthgum/zinc oxide nanoparticles on cotton fabric,UltrasonicsSonochemistry, 34 (2017) 458–465, http://dx.doi.org/10.1016/j.ultsonch.2016.06.019

26. P.Petkova, A.Francesko, I.Perelshtein, G. Aharon, T.Tzanko, Simultaneous sonochemical-enzymatic coating of medical textiles with antibacterial ZnO nanoparticlesUltrasonicsSonochemistry,29 (2016) 244–250, http://dx.doi.org/10.1016/j.ultsonch.2015.09.021

27. Y .Wang, C. Ma, X. Sun,H. Li, Preparation of nanocrystalline metal oxide powders with the surfactant-mediated method,Inorg. Chem. Commun, 5(2002)751–755,http://dx.doi.org/10.1016/S1387-7003(02)00546-4

28. P .Li, Y.Wei, H.Liu, XK. Wang,Growth of well-defined ZnOmicroparticles with additives from aqueous solution, J. Solid State Chem. 178 (2005)855–860, http://dx.doi.org/10.1016/j.jssc.2004.11.020

29. MF.Attia , T.Azib, Z.Salmi , A.Singh, P. Decorse, N.Battaglini, H.Lecoq , M.Omastová, A. Higazy, A M . Elshafei ,MM Hashem, MM.Chehimi , One-step UV-induced modification of cellulose fabrics by polypyrrole/silver nanocomposite films. Journal of Colloid and Interface Science 393 (2013) 130–137, http://dx.doi.org/10.1016/j.jcis.2012.11.008

30. S. Azizi, M.Ahmad, M. Mahdavi and S.Abdolmohammadi, Preparation, characterization, and antimicrobial activities of ZnO nanoparticles/cellulose nanocrystal nanocomposites, BioResources 8(2013)1841-1851.

31. V.Parthasarathi, and G .Thilagavathi, Synthesis and characterization of zinc oxide nanopartilce and its application on fabrics for microbe resistant defence clothing,

ACCEPTED MANUSCRIPT

International Journal of Pharmacy and Pharmaceutical Sciences 3 (2011)392-398.

32. T.Thilagavathi and D .Geetha, . Nano ZnO structures synthesized in presence of anionic and cationic surfactant under hydrothermal process,Applied Nanoscience 4(2014).127-132, DOI: 10.1007/s13204-012-0183-8

33. A A .Al-Owais, Synthesis and magnetic properties of hexagonally packed ZnO nanorods. Arabian Journal of Chemistry 6(2013)229-234, http://dx.doi.org/10.1016/j.arabjc.2011.11.001

34. E N J .Ford, S K .Mendon, S F .Thames and J W .Rawlins, X-ray diffraction of cotton treated with neutralized vegetable oil-based macromolecular crosslinkers, Cellulose 9(2010)18-23.

35. I .Perelshtein, G .Applerot, N.Perkas, Sigl E.Wehrschetz, A .Hasmann, G .Guebitz and A .Gedanken, Antibacterial properties of an in situ generated and simultaneously deposited nanocrystalline ZnO on fabrics. ACS applied materials & interfaces 1(2008)361-366,DOI: 10.1021/am8000743

36. N.Vigneshwaran, S. Kumar, A. Kathe, P .Varadarajan and V. Prasad, Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites. Nanotechnology 17(2006).5087, DOI: 10.1007/s12034-006-0017-y

37. K M. Reddy, K. Feris, J. Bell, D G.Wingett, C. Hanley, and A. Punnoose, Selective toxicity of zinc oxide nanoparticles to prokaryotic and eukaryotic systems,Applied physics letters 90 (2007) 213902—213903, http://dx.doi.org/10.1063/1.2742324

38. Y-W.Baek and Y-J.An, Microbial toxicity of metal oxide nanoparticles (CuO, NiO, ZnO, and Sb 2 O 3) to Escherichia coli, Bacillus subtilis, and Streptococcus aureus, Science of the total environment **409**(2011)1603-1608,

doi: 10.1016/j.scitotenv.2011.01.014. Epub 2011 Feb 18

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Figure Captions

Fig.1 Chemical process of formation coated ZnO NPs/cotton composite

Fig. 2 ZnO-NPs content in percentages (%) before and after washings.

Fig. 3 Typical XPS survey spectra of (a) pristine cotton, and (b) ZnO/CTAB.

Fig. 4 Typical high resolution (a) C1s spectrum for cotton/ZnO (b) O1s narrow regions from cotton and ZnO/CTAB.

Fig. 5 UV/Vis Spectra of ZnO-NPs sol obtained for the various samples.

Fig. 6 FTIR spectra of blank cotton and cotton coated ZnO-NPs of the various samples.

Fig. 7 SEM images (a) blank cotton (b) ZnO/cotton, (c) ZnO-SDS/cotton, (d) ZnO-HY/cotton, (e) ZnO-CTAB /cotton, (f) ZnO-TX-100/cotton.

Fig. 8 XRD pattern of ZnO-coated cotton fibers prepared in presence or absence of surfactants

Fig. 9 Thermogravimetric analysis for a) blank cotton, b) ZnO coated cotton, and c) ZnO coated cotton after 5 cycles of washing.

Fig. 10 Antimicrobial effect of ZnO coated cotton against *S. aureus.*

Fig. 11 Antimicrobial effect of ZnO coated cotton against *E. coli.*

Fig.12 Antimicrobial effect of ZnO coated cotton against *C. albicans*.

Fig. 13 Antimicrobial effect of ZnO coated cotton against *M. canis.*

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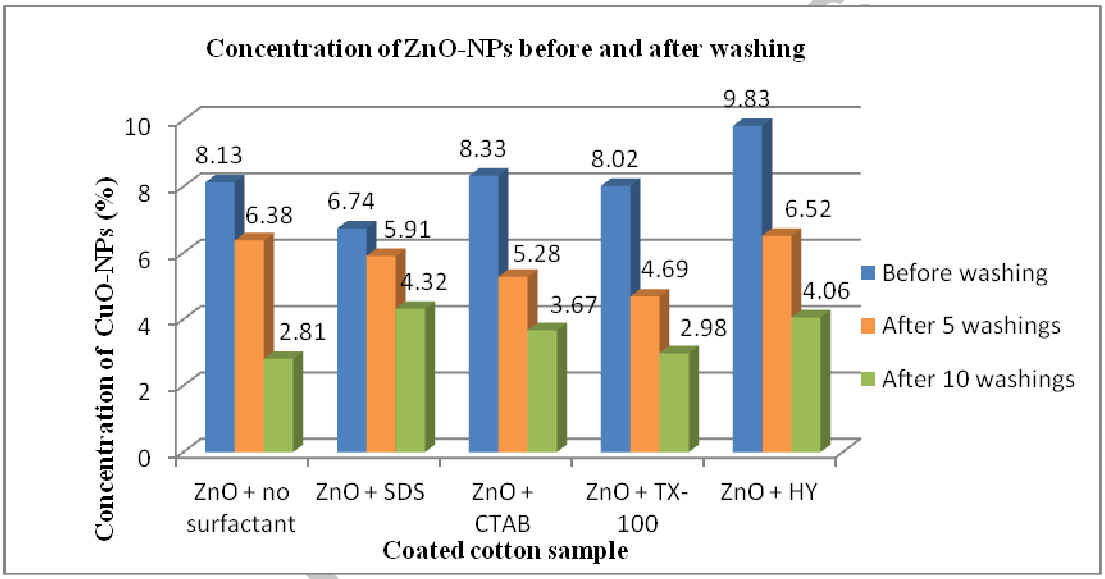


Fig. 2

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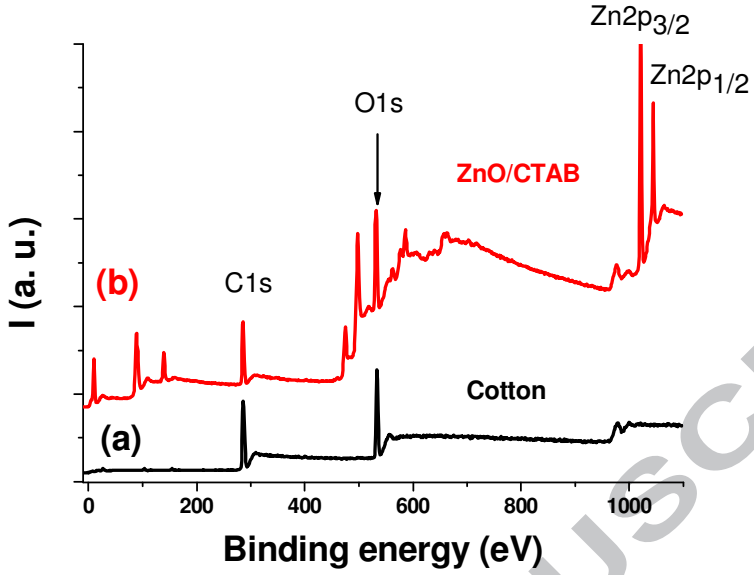
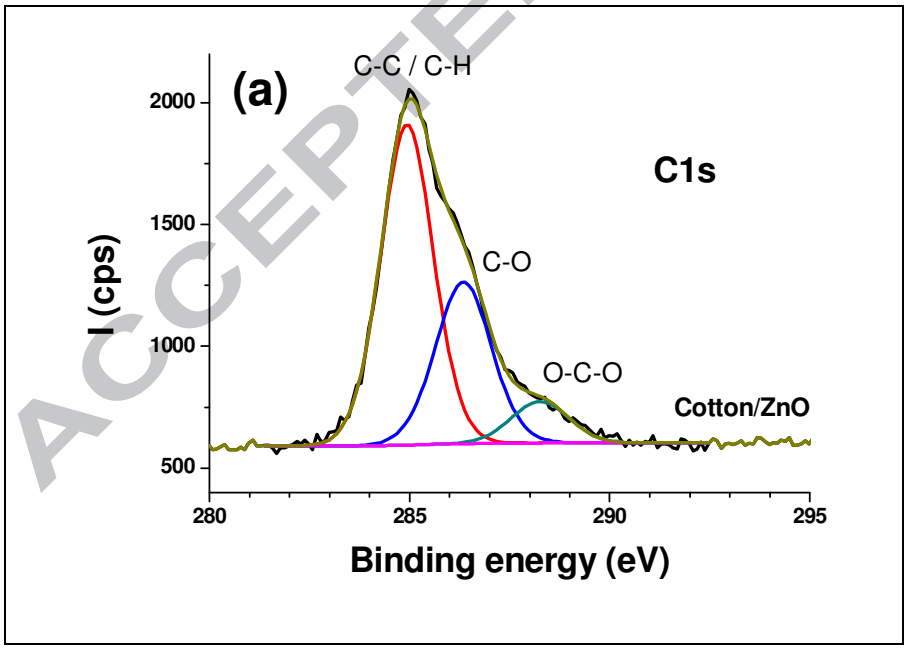


Fig. 3



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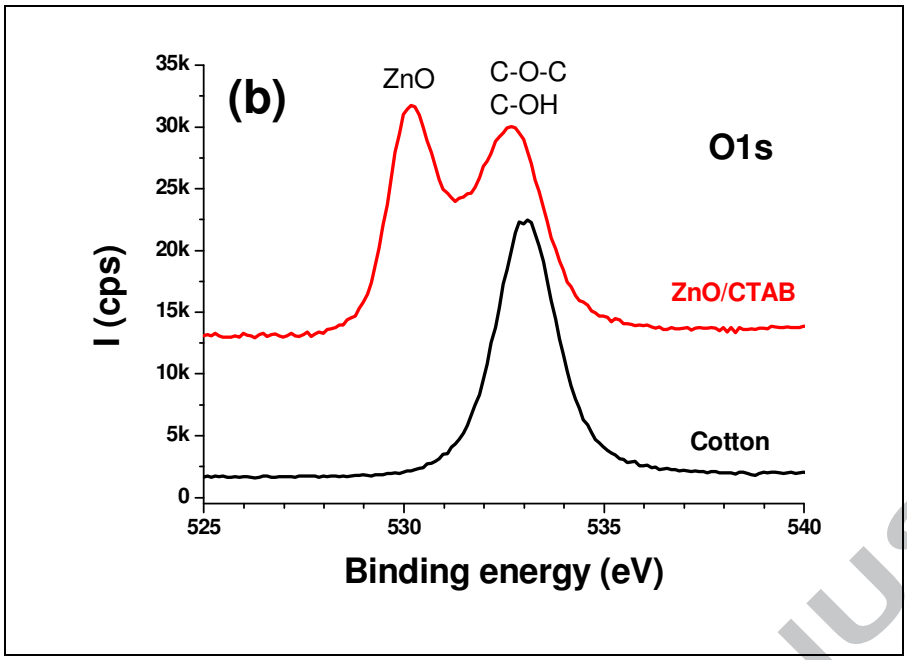


Fig. 4

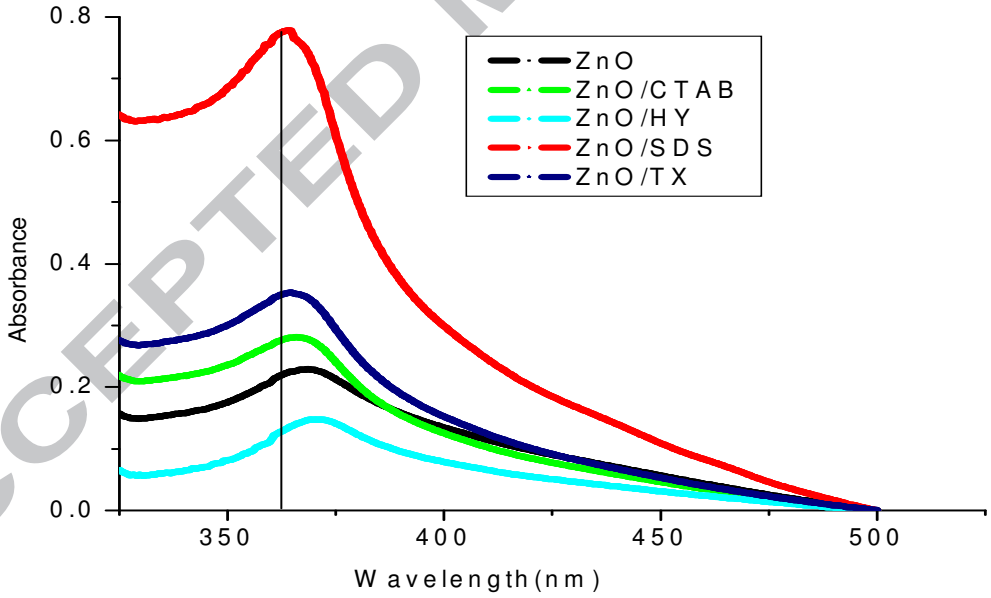


Fig. 5

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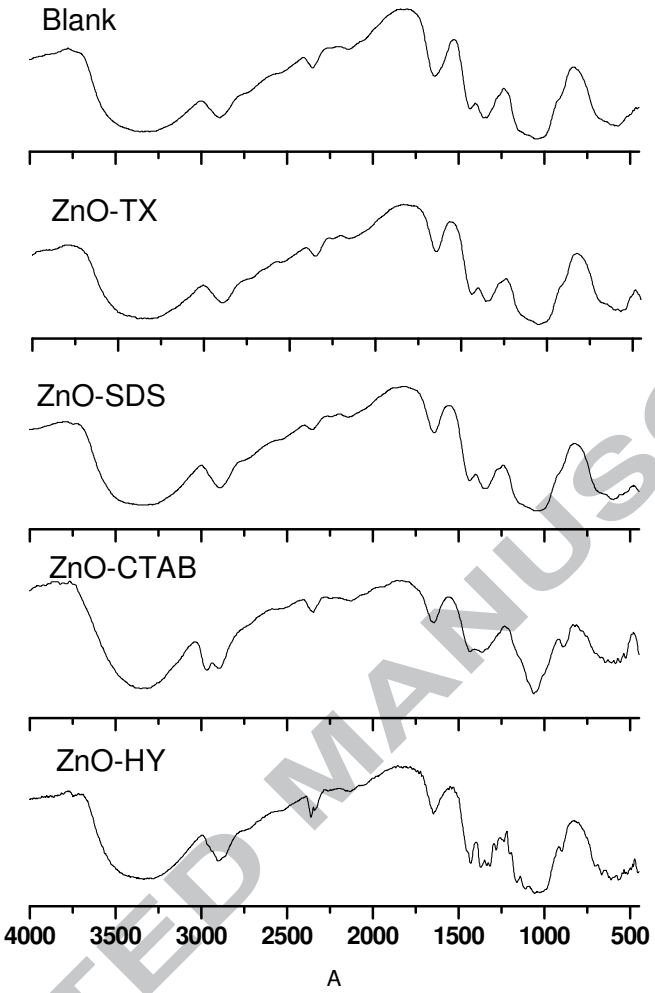
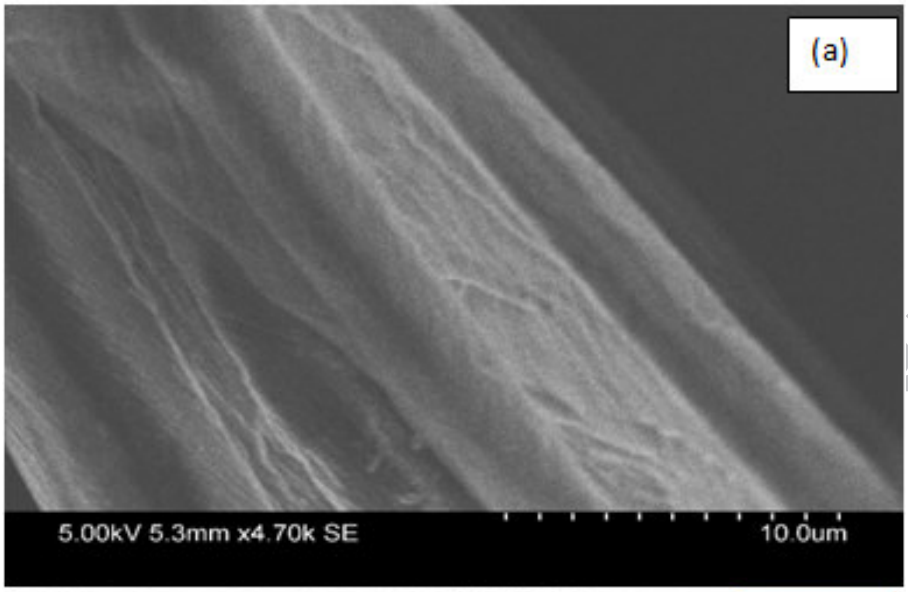
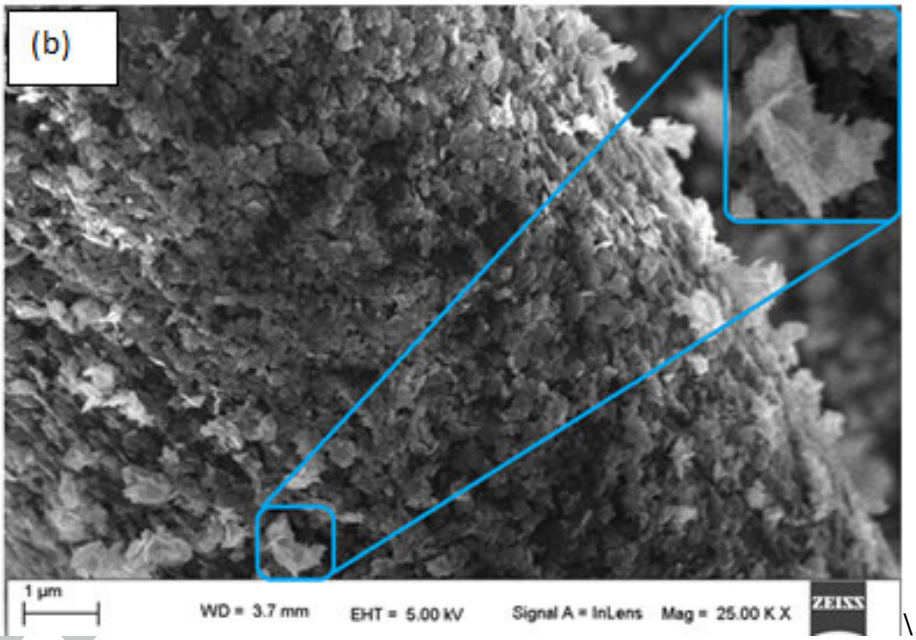


Fig. 6

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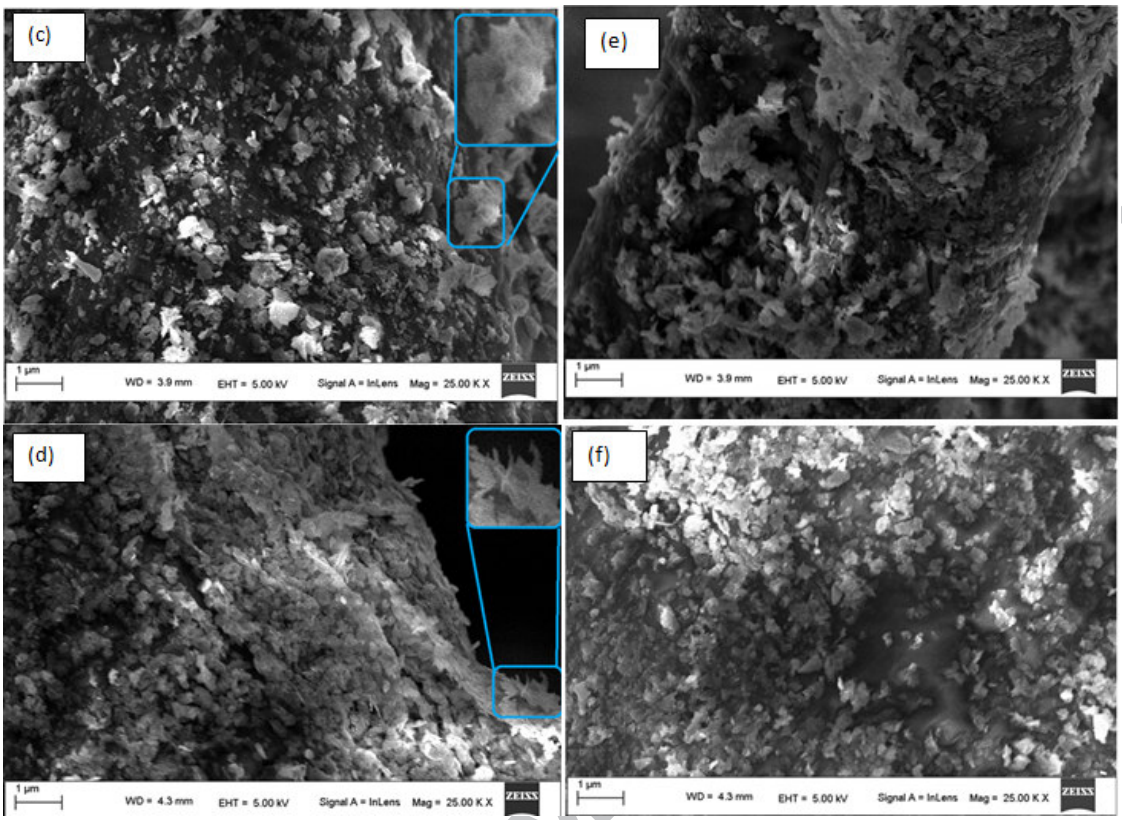


Fig. 7

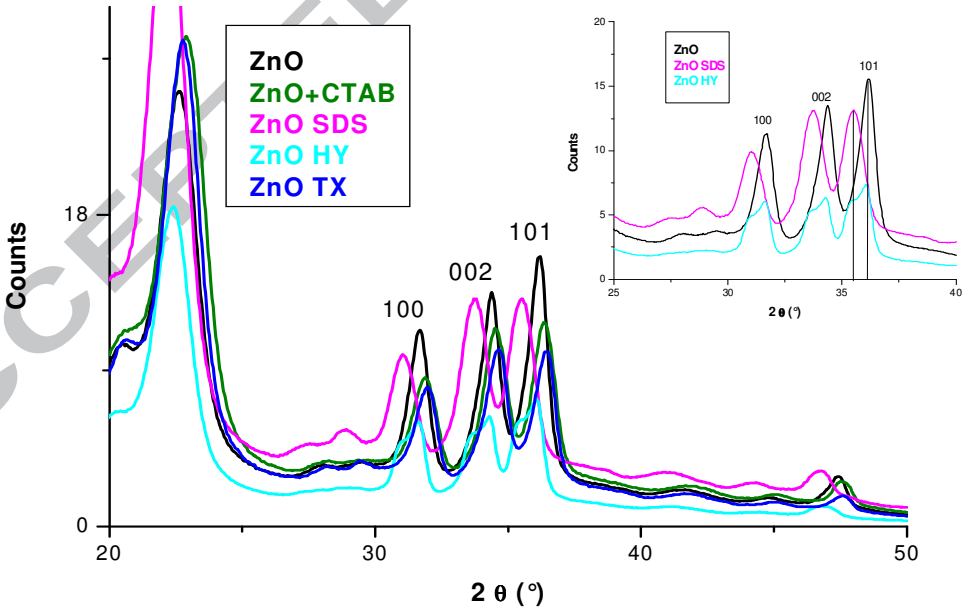
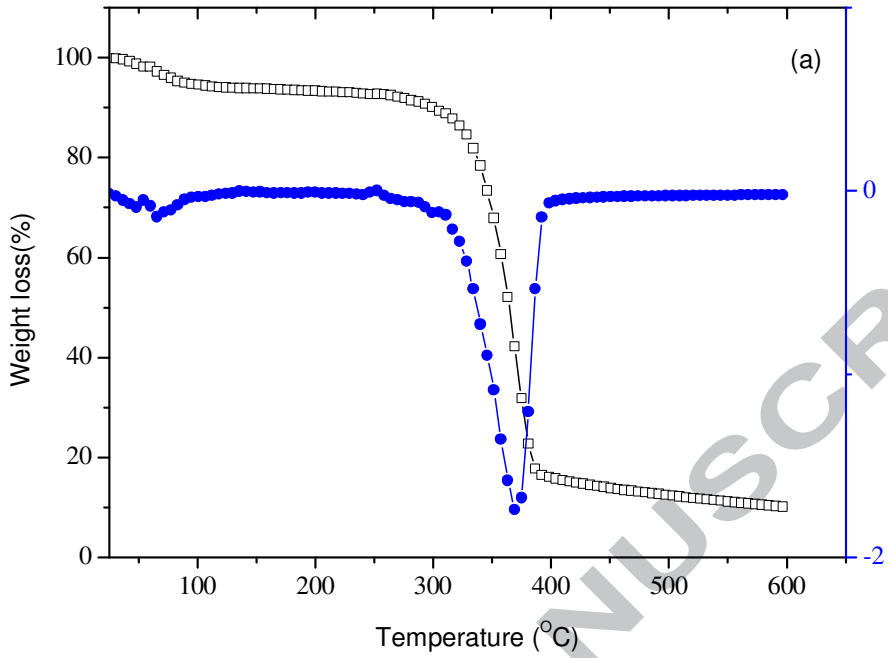
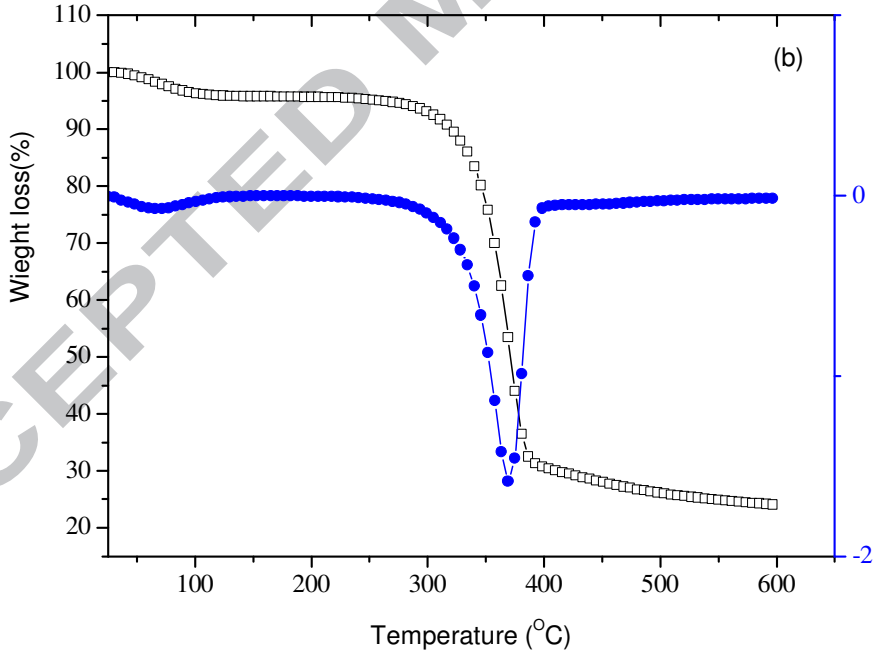


Fig. 8

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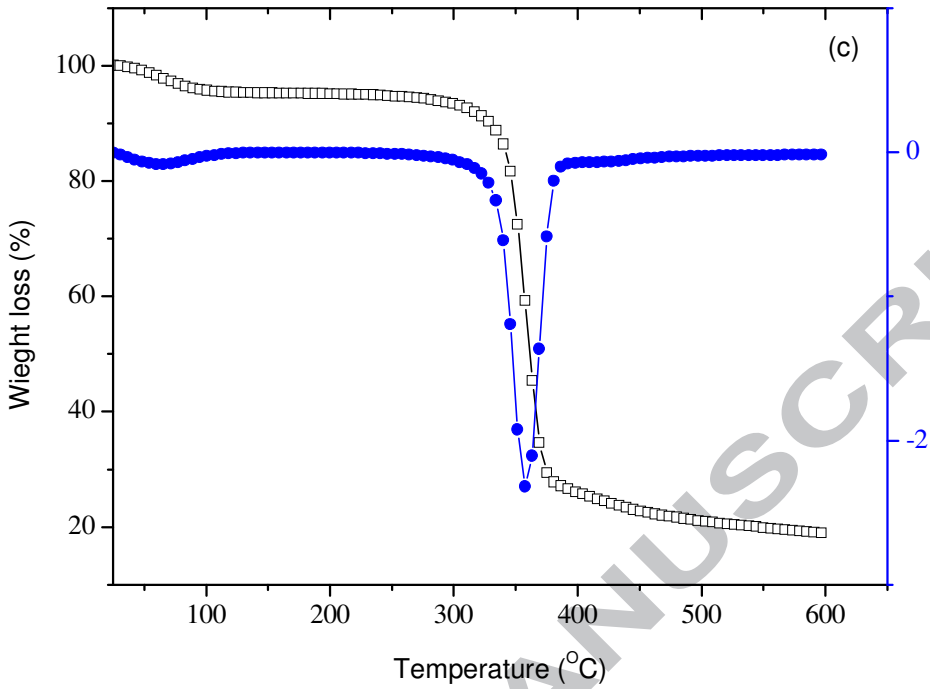


Fig. 9

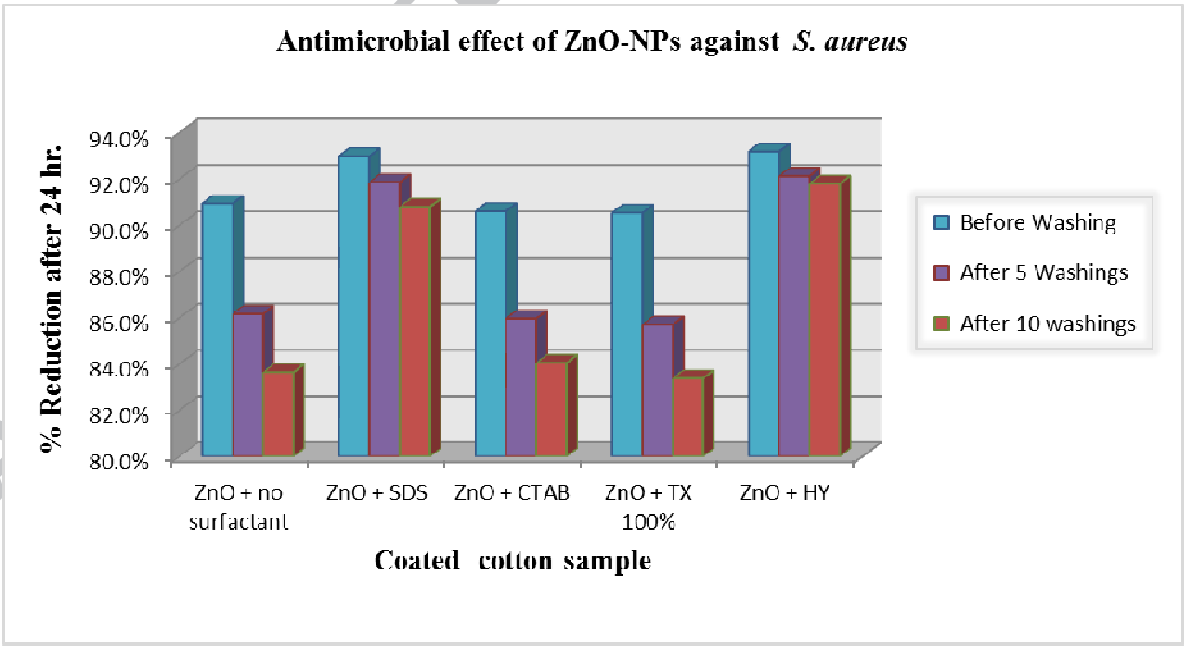


Fig. 10

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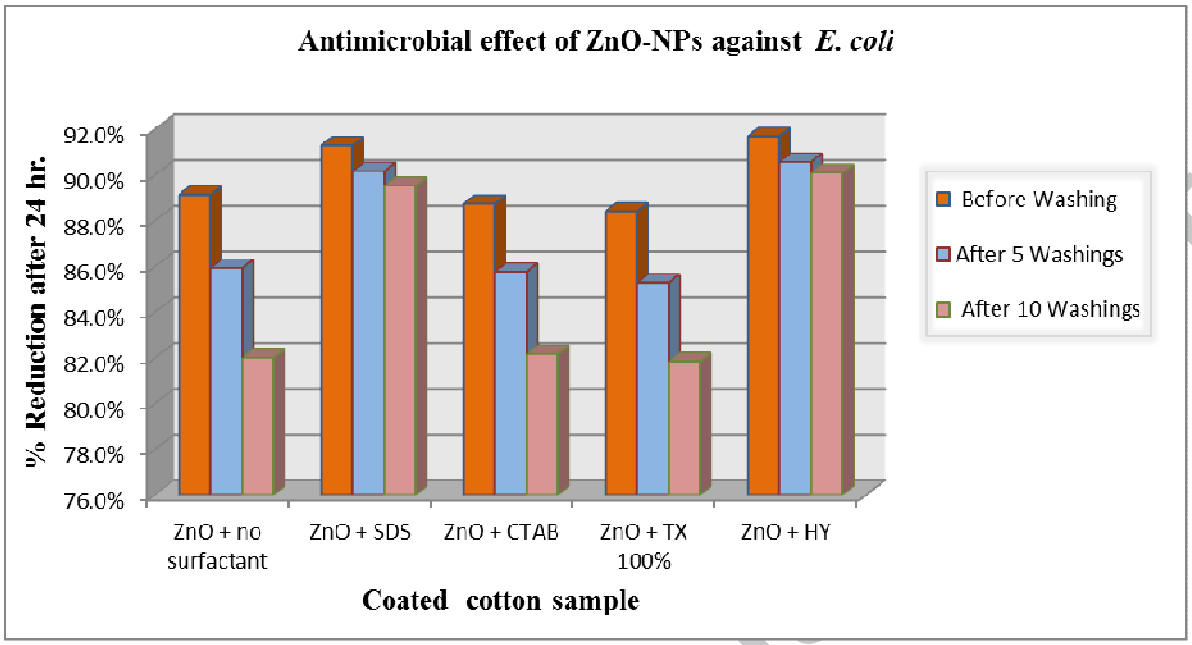


Fig. 11

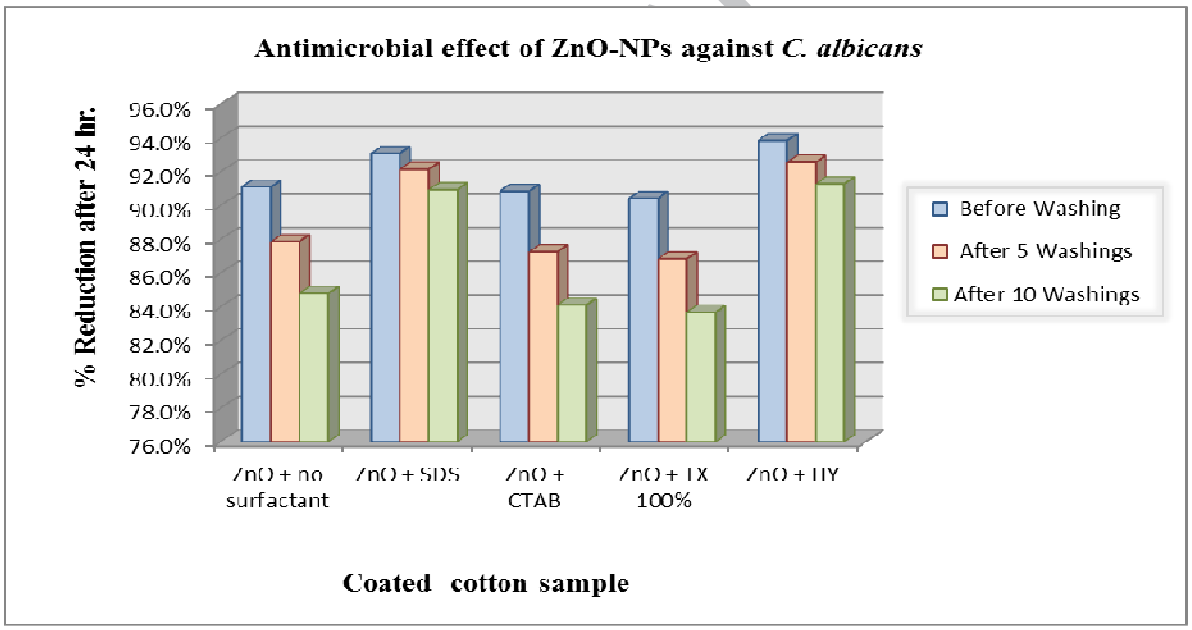


Fig. 12

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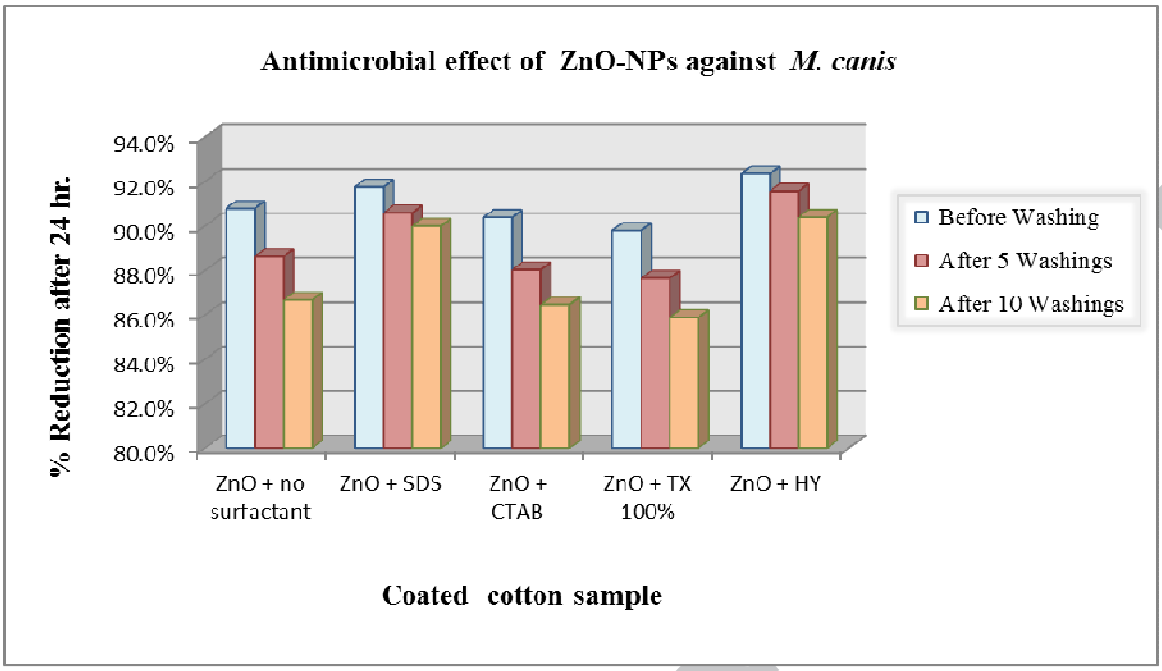


Fig. 13

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Highlights

a. ZnO-NPs were deposited onto cotton fibers via ultrasound irradiation.
b. Surfactants have stabilized the coated ZnO-NPs, controlling their shape and size as encapsulated species.
c. The use of surfactants has increased the durability of cotton coated ZnO-NPs and decreased its leaching.
d. ZnO-SDS and ZnO-HY was the most effective systems in reduction of the antimicrobial activities.
e. SEM and XRD analysis revealed that shape and size of the coated ZnO-nanopaticles.

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