Preparation of an Anti- microbial Cotton Fabric and enhance physical properties Using Synthesize Zinc Nano particles stabilizing by Citric Acid

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Abstract: *In order to enhanced the attached of nanoparticles to surface of fabric, in this work Zinc oxide (ZnO) nanoparticles were synthesized on the surface of cotton fabric via a sol-gel method, in presence of citric acid as natural crosslinking agents. In order to providing antimicrobial activity and enhancing physical properties. Surface morphology and chemical composition of finished and unfinished fabric have been examined by scanning electron microscopy (SEM), electron diffraction (EDs) and Fourier transfer infrared (FTIR). Antibacterial properties was evaluated against (Gram-negative) E.coli and (Gram-positive) Staphylococcus aureus bacteria. The results showed that ZnO nanoparticles was successfully synthesizes on fiber surface, in the present of Citric acid as crosslinking agent. And it's distributed non homogenies on fabric surface. Antibacterial tests showed that the ZnO-coated fabric with Citric crosslinking possesses good bacteriostatic activity against to staphylococcus and Physical properties shrinkage, crease recovery angle (CRA), abrasion and tensile test were investigated by using Shirley (CRA), crokmerter and belistone instruments, the results were showed excellent enhancement in physical properties.*

Keywords— Anti- microbial; Zinc Nano particles; Citric acid; Physical properties

1. INTRODUCTION

Conventional textiles lose between 5% and 20% of their weight during their use phase [1], e.g. through laundry, exposure to sunlight, or mechanical abrasion. Therefore, it can be assumed that nanomaterial's integrated into, or applied onto, textiles will enter the environment. Studies of the behavior of nanoparticles in textiles show that the released of nanoparticles from textiles during laundry, abrasion and thermal depending on the way they are integrated. Release during laundry [1]varies from almost zero to almost 100%. This make the finishing of textile valueless.
The nanoparticles assumed to be stably embedded to maintain the product quality and functionality of the textiles. This also prevents the release of nanomaterials with potential hazards to human health and the environment.
Zinc oxide due to the unique properties there possible wide range of application common in textile finishing .ZnO has three key advantages. First, it is a semiconductor with a direct wide band gap of 3.37 eV and a large excitation binding energy of 60 meV. It is an important functional oxide, exhibiting excellent photo-catalytic activity. Secondly, because of its non-central symmetry, ZnO is piezoelectric, which is a key property in building electromechanical coupled sensors and transducers. Finally, ZnO is bio-safe, biocompatible and can be used for biomedical applications without coating. With these three unique characteristics, ZnO could be one of the most important nanomaterial's in future research and applications.[1-3] although of these unique properties there is some dis advantages of ZnO one of these was a big concern to scientists it is agglomerations. they were try to solve these problem by using stabilizers agent chemicals and natural .hence focused of natural stabilizers due to availability , low cost and bio friendly . fruits acid(citric acid) [4] were commonly used as stabilizer to stop aggregate of nano particles and keep it in homogenous distribution these promote homogenous innovated properties in each point on surface area , also make across linker to enhance stability ,abrasion resistant and durability against wash.

2. MATERIALS AND METHODS

2.1 Materials

Plain weave (1/1) 100% cotton fabric with 150 GSM, 20 Ne warp and weft count, 75 ends/inch and 54 picks/inch was used in this research work.

2.2 Fabric modification with ZnO (F –ZnO)

Fabric-ZnO was prepared via a sol–gel process using zinc acetate anhydrite (Zn (Ac)2.2H2O) as a precursor material as follow: One gram (1 g) of fabric was immersed in 150 ml of deionized water and mixed with 0.5 g of Zn (Ac)2.2H2O pre-dissolved in 5 ml methanol (5% w/v). A concentrated sodium hydroxide solution (2 M) was added drop-wise to the mixture to keep the ph above 10 during the reaction. The mixture was heated to 70°C under vigorous stirring until a milky white solution was obtained. There after a milky solution was heated for a further (2 h) under the same temperature. Fabric was removed, and squeezed, washed by distilled water and dried at room temperature.

2.3 Fabric modification with citric acid and ZnO (F-CI-ZnO)

(2g) of citric acid dissolved in (100 ml) distilled water, and (1g) of fabric was immersed in solution for (30 min). Then, the fabric was removed, rinsed and dried at room temperature. The dried sample, was placed on oven at 120 C0 for (10min), to dehydration of citric acid. Then, sample was immersed in (150 ml) of deionized water and mixed with (0.5 g) of Zn $(Ac)_2.2H2O$, pre-dissolved in (5 ml) methanol, (5% w/v). Concentrated sodium hydroxide solution (2 M), was added drop-wise to the mixture to keep the PH above 10 during the reaction, then mixture was heated to (70°C) under vigorous stirring until a milky white solution was obtained. Then the solution was heated for (2 h) under the same temperature, Then fabric was taken out squeezed, rinsed , washed by distilled water, and dried at room temperature.

3. METHODS

3.1 **Characterization**:

3.1.1 FTIR

FT-IR stands for Fourier Transform Infra- Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Of this makes infrared spectroscopy useful for several types of analysis Results.

3.1.2 SEM

Scanning Electron Microscope – SEM – is based on the scanning of the specimen surface by an electron fascicle and the analysis of the signal (electromagnetic particles and waves) resulting from the interaction between the primary fascicle and the specimen The depth at which information on the specimen is obtained ranges between 1 nm (Auger electrons) and 5 µm (characteristic X radiation). With SEM the contrast may be of the following types: topographic contrast, atomic number contrast, magnetic contrast, etc.

3.1.3 EDS

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the lines in the spectrum and is straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition. By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can be produced. In addition, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images, but can also be used for element mapping, and even point analysis, if an X-ray spectrometer is added. There is thus a considerable overlap in the functions of this instrument.

Figure 1: SEM and EDS Instrument

3.1.4 Antimicrobial Test

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Antimicrobial activity of the ZnO-coated fabrics was studied with standard methods: AATC using tC 100-2004 (modified colony counting method). The former method shows bactericidal activity. (E.coli, ATCC 10031, Gram-negative bacterium) and Staphylococcus aureus (S. aureus, ATCC 25923, Gram-positive bacterium) were used as model challenge microorganisms. Nutran agar was prepared as a solid media, modified fabrics was fixed on surface of media at 37°C for 24 h. [5] Then, a single colony was moved with an inoculation loop from the culture media to the MH media and cultured at 37°C until the desired concentration was reached. The suspension of bacteria must be cultured to (0.5 Maxwell turbidity units).

3.1.5 Abrasion

The crock meter is a relatively simple rub tester commonly used to determine the amount of color transferred from textile materials to other surfaces by rubbing. This instrument has also been utilized to conduct smear or abrasion resistance tests on images produced by a printer or copier. For paints and coatings, the crock meter is useful when evaluating the change in gloss due to rubbing, scuffing or marring. A test sample is clamped to the instrument base and a square of standard crocking cloth is fixed to a 16mm diameter, acrylic-rubbing finger. The finger rests on the sample with a pressure of 900 grams force and traverses a straight path approximately 100mm long with each stroke of the arm.

Figure 2: Crock meter Instrument

3.1.6 Crease recovering

The ability of fabrics to resist the formation of crease or wrinkle when lightly squeezed is termed as crease resistance of the fabric is associated with the fabric stiffness[6] .Cotton though is comfortable to wear; it has very poor crease recovery angle (CRA). Cotton fabrics are most prone to crease formation, since their ability to recover from the applied deformation is poor and has been explained in the mechanism of crease formation. The crease recovery of the fabrics have been tested using the Shirley crease recovery tester as it shown in figure(3), and the value reported in this instrument was crease recovery angle (CRA) [7]

Figure 3: the' Shirley' crease recovery instrument (CRA)

3.1.7 Shrinkage test

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It is a necessarily required parameter of quality control, to ensure the sizes of the products to avoid any complaints regarding deformation or change in dimensions after domestic laundry [6]

3.1.8 Tensile test

Tensile test is most commonly applied test method for analyzing the mechanical properties of fabric materials. Although the direction of applied force is always in tension. BELLSTONE- HI-TECH INTERNATIOAL made in India, it is use to examine tensile force. Specimen with 30 cm long and 5 cm width is gripped in the tensile grip jaws of bellstone tensile test instrument ,during this test ,tensile force applied on the fabric specimen until it rupture ,the mechanical properties analyze include the force at rupture and the elongation .

Figure 4: Tensile test instrument

4. Result and Discussion

4.1 FTIR

FTIR spectrum. Analysis results was showed new peaks were found in treated samples (F-ZnO), and (F-CI-ZnO) when were compared with the control sample peaks, which its cellulose. FTIR transmission spectrum of cellulose showed OH stretching vibration regions between 3000 and 3500 cm-1, The OH stretching region always covers 3-4 sub-peaks and these sub-peaks cannot be determined in the original data set [8]. FTIR spectrum of sample (F-CI-ZnO), in addition to cellulose peaks, showed a new peaks between 1500 and1845 cm-1 and it related to C=O stretching vibration peak.[4] and it is probably a coalescence peak which is caused by the ester bond and carboxyl. The new observed peaks is resulted of treated sample with CI. This confirm that the modification was achieved successfully. The sample which treated by ZnO nanoparticles without using cross linking agent showed new peaks in modified fabric, to detect of this peaks farther more(SEM) had been used and it was definitely confirmed presence of ZnO nanoparticles in samples.

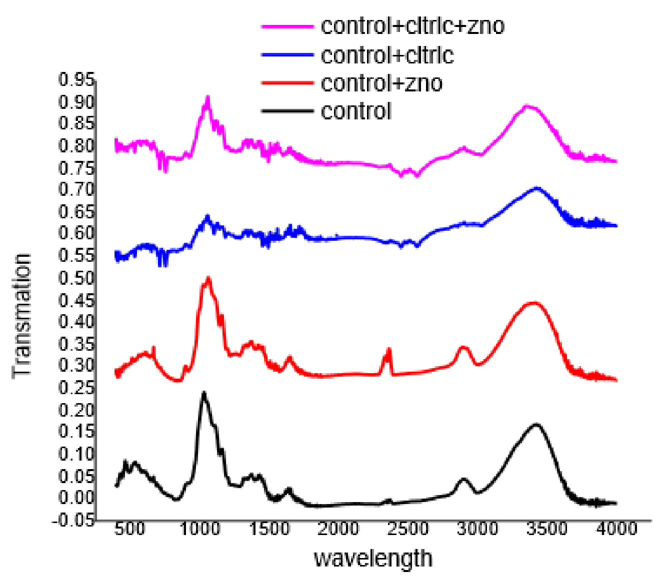


Figure 5: FTIR of (Control, Control + ZnO, Control +Citric acid and Control + ZnO +Citric acid)

4.2 SEM:

Morphological changes of the cotton fabric treated by solution of zinc acetate dehydrate can be clearly seen from the scanning electron microscopy (SEM) as shown in (Figure (6.1), (6.2), (6.3). The presence of ZnO nanoparticles on fibers' surface is clearly distinguished. As it can be seen homogenous and nonhomogeneous ZnO nanoparticles, were formed, and distributed on the fiber surface. In fig (6.1), (F-ZnO) observed amount of ZnO nanoparticles were synthesized on the surface of the fiber and this was approved by tested via (SEM), as was obvious in fig(6.1). This evidence to successfully synthesis ZnO nanoparticles on fiber by sol- gel methods which we used to synthesis ZnO nanoparticles, they were synthesized with average of diameters size (138.85 nm), this seen clearly in fig (6.2), which was tested under magnification of 500 ZnO nano particles clustering on the surface of fibers, like bundle, at different size with average diameters (70.6 nm) under magnification (2µm), as it is shown obvious in fig (6.3). ZnO nano particles were clustering but was distributed in homogeneous miner on the surface of the fibers which is refer to homogeneous distribution hydroxilic groups in citric acid structure, which has ability to catch amount of ZnO nanoparticles with homogeneous distribution.

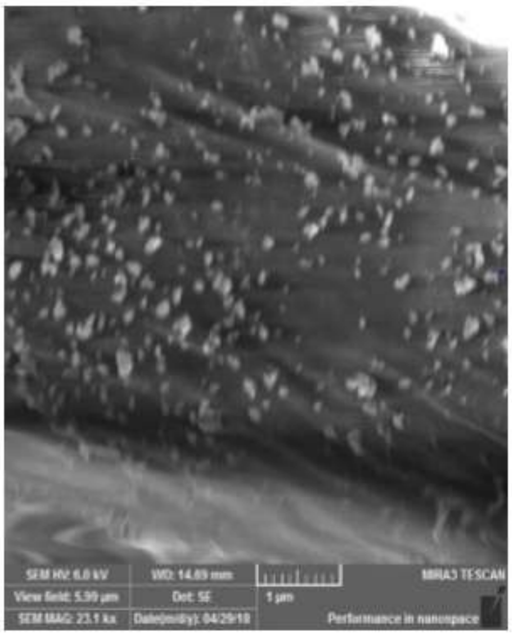


Fig (6.1): SEM of fabric modified with ZnO at magnification (1µm)

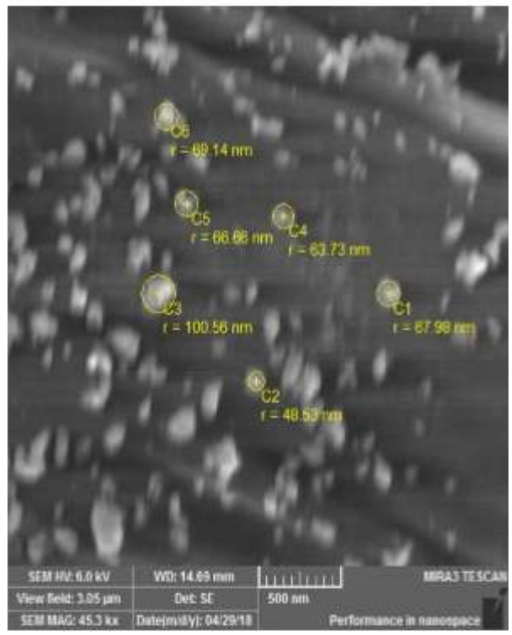
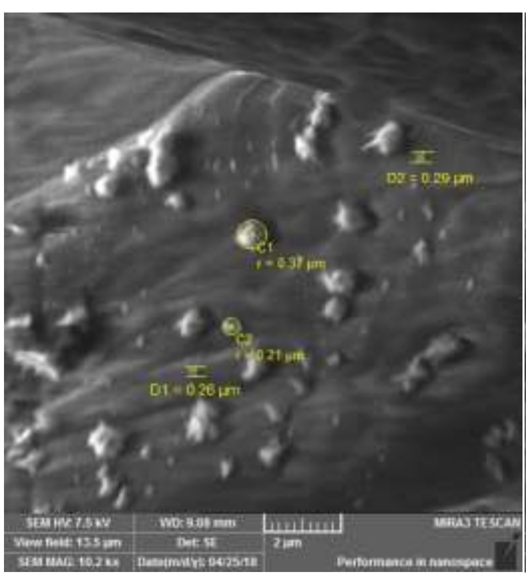


Fig (6.2): SEM of fabric modified with ZnO at magnification (1µm)



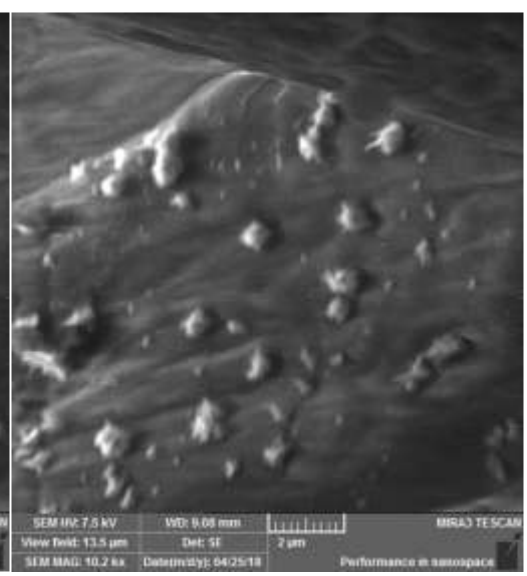


Fig (6.3): SEM of fabric modified with citric at magnification (2µm)

4.3 EDS

EDS measurements were carried out for element detection of the fabric surface. The representative EDS patterns are shown in Figure (7 and 8). Peaks at about 9.5 keV are characteristic for O, Na and Zn signals are located at about 0.4,1.0,1.0, 8.6, and 9.6 keV[5] . The peaks of Si and Ca were observed at about 1.8, 1.0 and 3.9 keV, which are from the lap environment. The EDS results reveal that the prepared nanostructures are certainly composed of Zn and O.

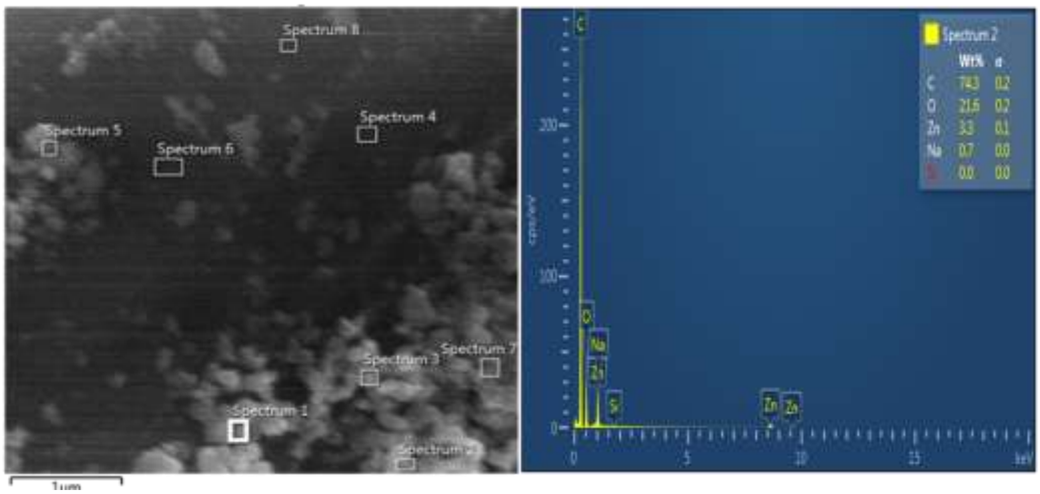


Figure 7: EDS of fabric modified with ZnO (F-ZnO)

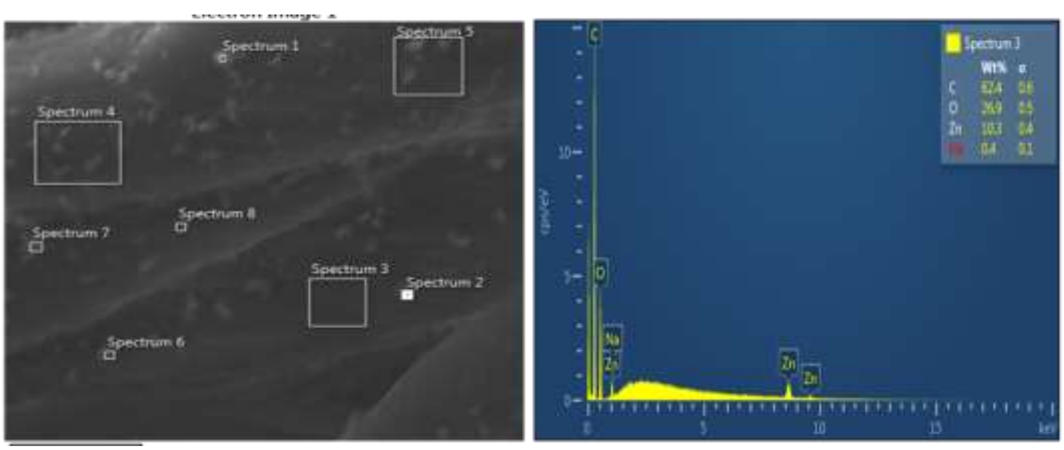


Figure 8: EDS of fabric modified with ZnO and citric (F-CI-ZnO)

4.4 Anti-bacterial

4.4.1 Fabric modified with ZnO (F–ZnO):-

To investigate the performance of antibacterial properties anti- microbial test was done before and after washing (5 cycles), the result showed anti-bacterial activity for ZnO nano particles on fabric which observed clearly from zoon which formative around the fabric in bacteria ambient, the activity of ZnO was observed before and after washing fabric. Which was indicator to durability of bactericidal activity even after washing large zoon formative around (F- ZnO) in staphylococcus ambient and it was seem organized in whole direction and stable before and after washed in distilled water for 5 cycle ,rinsed and dried. Verses in Ecoli ambient small zoon, non –organized and it seem stable before and after washing.

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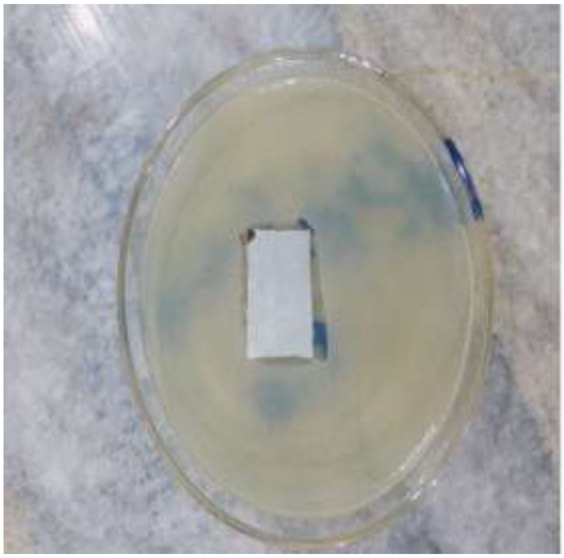

Fig (9.1): The treated fabric with ZnO (St- before washing)

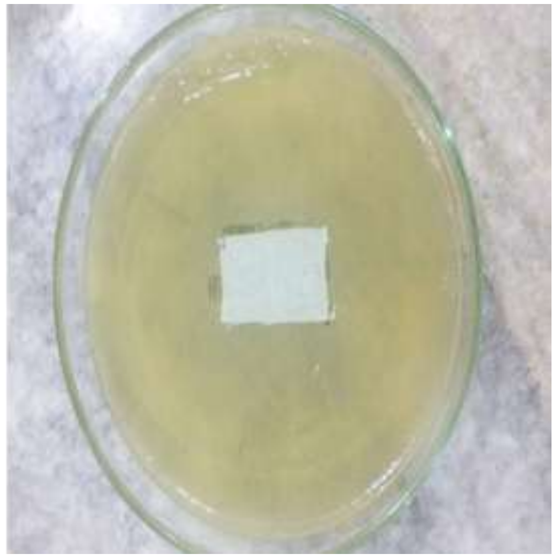

Fig (9.2): The treated fabric with ZnO (*Ecoli*-before washing)

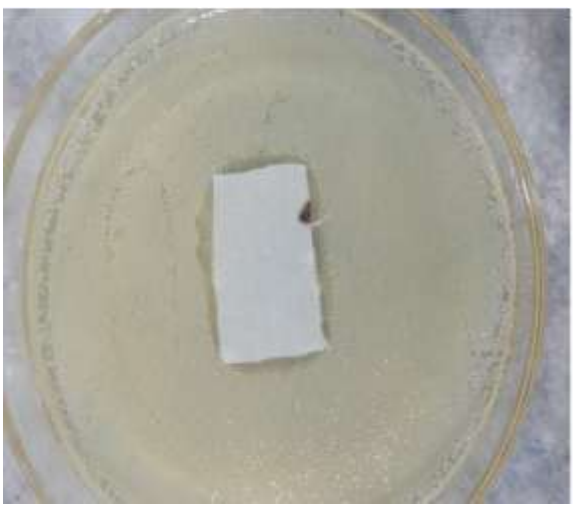

Fig (9.3): The treated fabric with ZnO (St-after washing)

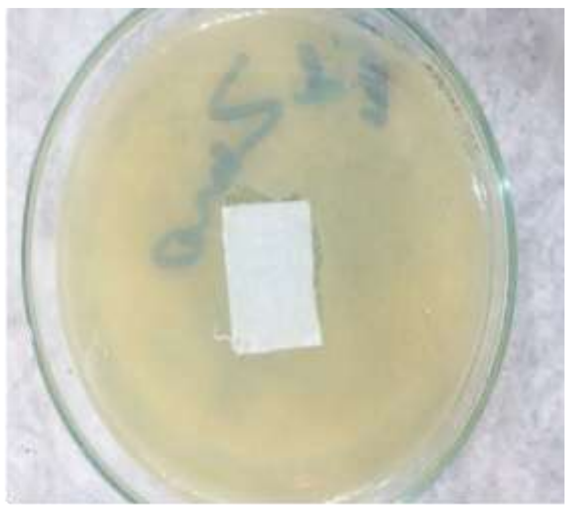

Fig (9.4): The treated fabric with ZnO (*Ecol*i-after washing)

4.4.2 Fabric modified with (citric acid) and ZnO (F- CI –ZnO) :

zoon with Small organized shape formative around (F- CI –ZnO) in staphylococcus culture .small and non- organized shape formative around (F- CI –ZnO) in E coli ambient .after washing 5 times small and non- organized shape of zoon formative around both and covered large area in staphylococcus ambient than Ecoli ambient.

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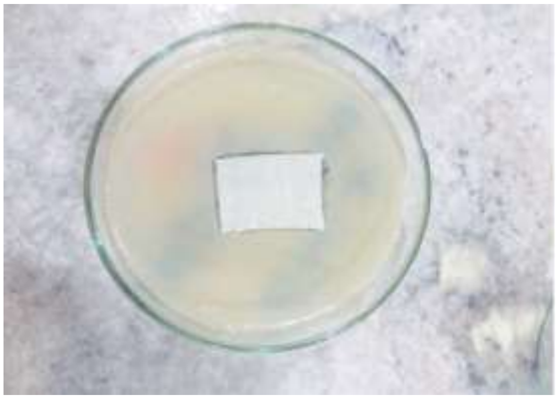

Fig (10.1):(CI-ZnO) treated fabric with St- before washing

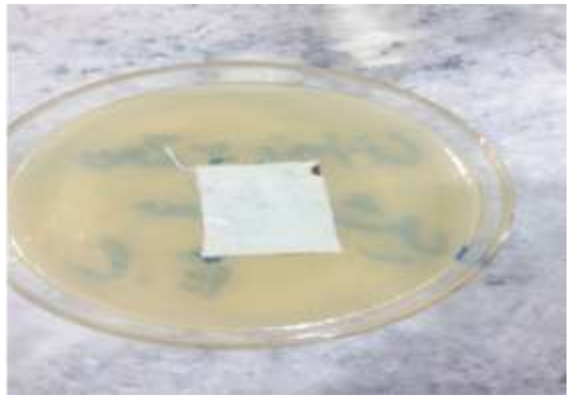

Fig (10.2): (CI-ZnO) treated fabric with *E.coli* before washing

Fig (10.3): (F-CI-ZnO) treated fabric with St- after washing

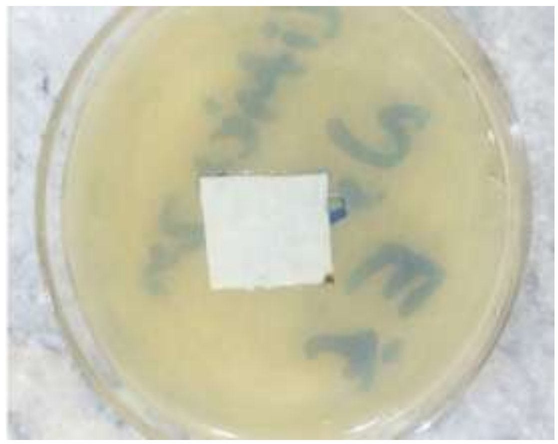

Fig (10.4): (CI-ZnO) treated fabric with *E.coli* after washing

4.5Physical test

4.5.1 Crease recovery:**-**

The cotton fiber is relatively inelastic due to it is crystalline polymer system so it is easily wrinkle and readily crease thus the blank sample shown the lowest crease recovery angle. After treatment, ZnO nanoparticles easily penetrate into the fabric pores and adhere tightly on the surface so it is not easily wrinkle or crease after treatment. On this basis cotton sample does not shrinkage when treated with ZnO nanoparticles[9]. From tables 1, 2, and 3, it could be observed that the crease recovery in modified fabric was increased by (1 degree) when compared to control fabric. This is mean a modified fabric will keep the good appearance for wearer to the long time (eliminated iron time). The warp CRA was greater than the weft CRA, this could be attributed to the higher number of ends than picks found in each of the case.

Table (1): CONTROL

Cotton fabric (control)	Sample number	Face side	Back side	Average face side	Average back side	Total average
warp	1	84° 85°	90° 95°	87°	94°	91°
	2	90° 90°	95° 94°			
weft	1	90° 80°	85° 85°	86°	90°	88°
	2	80° 95°	90° 100°			

Table (2): (F-ZnO)

F-ZnO	Sample number	Face side	Back side	Average face side	Average back side	Total average
Warp	1	95^0 105^0	80^0 100^0	95^0	89^0	92°
	2	80^0 100^0	85^0 90^0			
Weft	1	100^0 105^0	90^0 95^0	95^0	88^0	91^0
	2	85^0 90^0	80^0 85^0			

Table (3) :(F-CI-ZnO)

F – CI-ZnO	Sample number	Face side	Back side	Average face side	Average back side	Total average
Warp	1	100° 105°	80° 85°	96°	88°	92°
	2	85° 95°	85° 90°			
Weft	1	87° 100°	80° 85°	92°	86°	89°
	2	85° 95°	84° 95°			

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4.5.2 Shrinkage

The result of this test showed the dimension of warp and weft to modified fabric, still stable in the same positions before and after immersed in water, and this indicates to a good dimensions stability in modified fabrics than gray fabric.

Fig (11) number (1) present fabric without treated, (3) fabric modified with ZnO nanoparticles, (4) fabric modified with ZnO nanoparticle and citric.

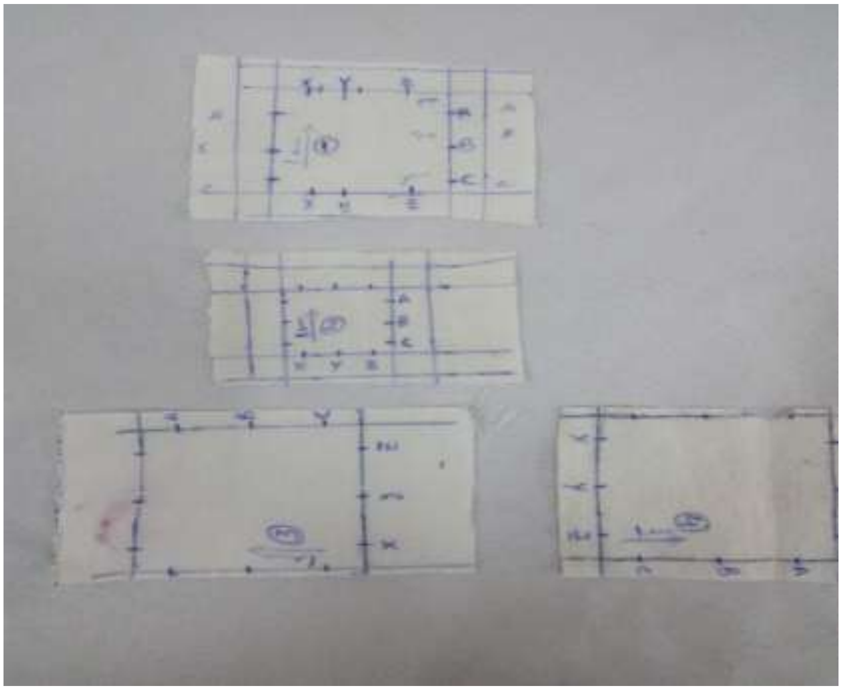

Figure (11): shrinkage test

4.5.3 Abrasion

Crokometer is used to investigate the abrasion of the treated fabric. The samples (F-ZnO), and(F-CI-ZnO) were rubbed for 15 second instead of 10 second (ISO and ASTM) to insure of stability limit of ZnO nanoparticles on surface of fabric. Two samples of fabric were tested via crokometer instrument to study abrasion behavior, one on top(treated sample) and second on the bottom (untreated sample) , After rubbing the sample at the bottom were checked under SEM and EDS to investigate if there is any nanoparticles were released of the top sample and stable on bottom fabric surface. The result showed there is no ZnO nanoparticles removed for treated samples. The result of EDS bellow showed that.

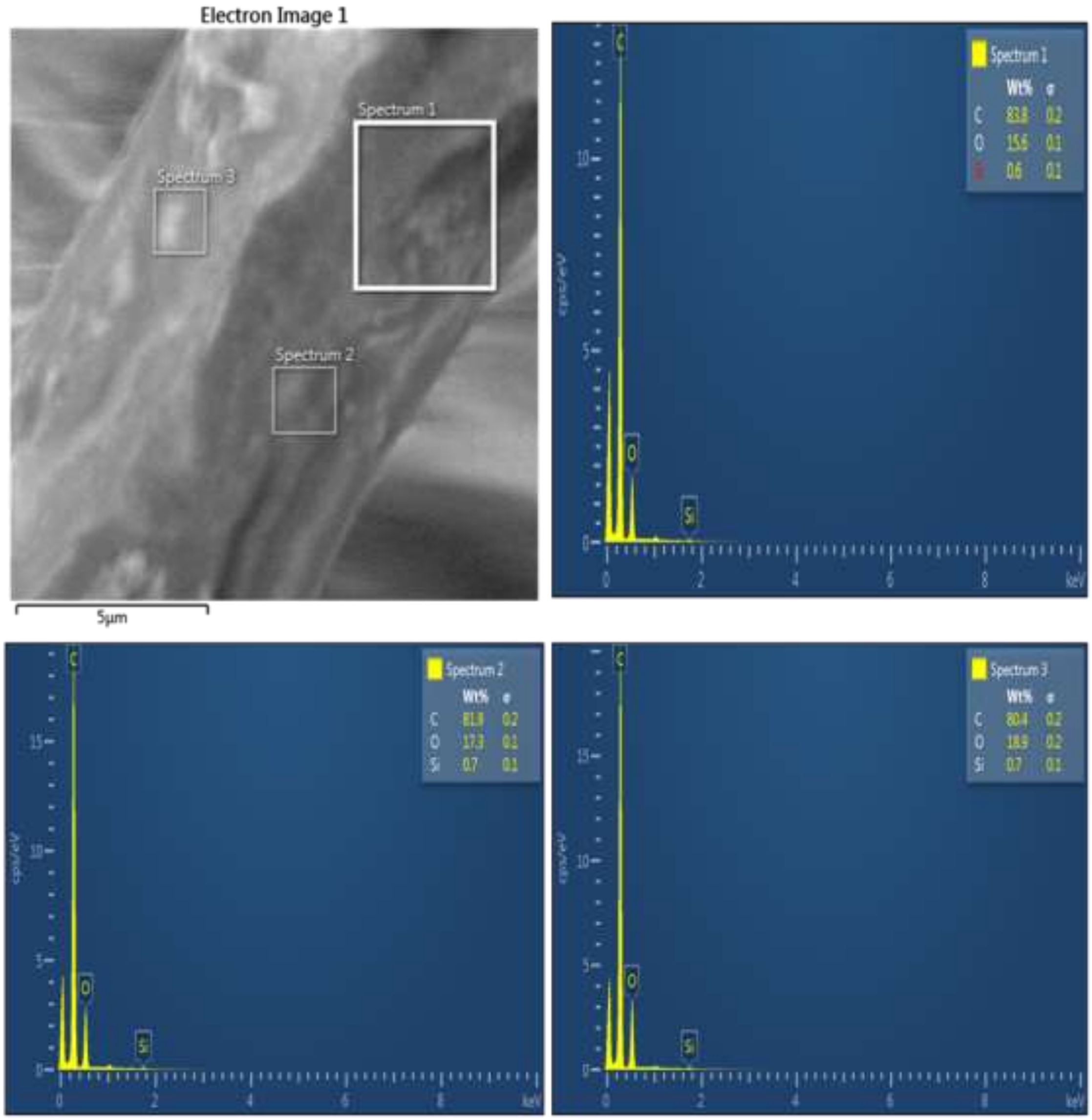

Figure (12): The treated fabric with ZnO after rubbing

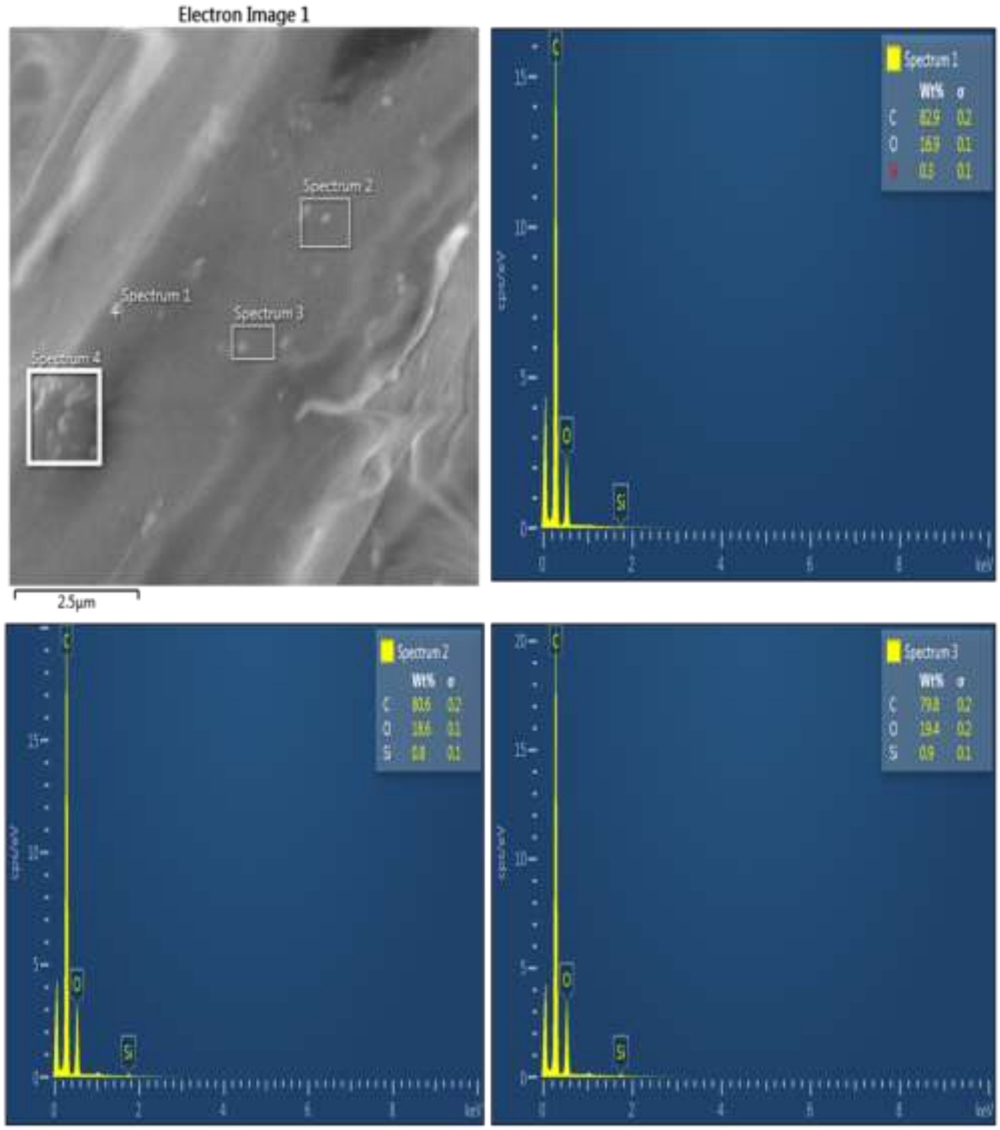

Figure (13): The treated fabric with ZnO and citric after rubbing

4.5.4 Tensile test

Belistone instrument was used to study tensile strength of modified and unmodified fabric, the data depicted in table (4.5.1) showed increase in force and decrease in elongation of modified fabric in case of ZnO and citric acid, comparing with untreated fabric. This indicate that the tensile properties of fabric has been enhanced after modification.

Table (4.5.1): tensile test result

samples	Elongation (mm)		Breaking Force(kg f)	
	warp	weft	warp	weft
Unmodified fabric	2.5 mm	3.7 mm	44 kg f	37.8 kg f
The modified fabric with ZnO nanoparticles	2.1 mm	3.5 mm	53.1 kg f	42.7 kg f
The modified fabric with citric acid	1.7 mm	3.1	50.3 kg f	39.4 kg f

5. CONCLUSION:

To increase the stability of nanoparticles and stop release of it of surface fabric natural crosslinking agents was used in this study, to synthesize ZnO nanoparticles by solution method. In this study the results showed good stability of ZnO Nanoparticles when citric acid was used as cross-linking agent (natural capping agent). From characterization of ZnO nanoparticle when was used citric acid as crosslinking agent the SEM, results showed homogeneous distribution of nanoparticles.
EDS results confirmed presence of ZnO nanoparticle in chemical composition of treated samples and this confirmed of successfully synthesis of nanoparticles. Also FTIR results verified the (EDS) results.
The physical tests showed the different properties of treated samples when compared with untreated sample. Crease recovery test (CRA) showed that the recovery increased in modified fabric by (1 degree) than gray fabric Shrinkage test indicated that a good dimensions stability in modified fabrics than gray one.
Finally, abrasion test was a doubted no ZnO Nano particles removed from treated samples. The innovation of this study natural extract as crosslinking agent it was showed good results for all tests, from this results natural extract preferable than chemicals crosslinking agent in textile finishing because it is more safety and low cost compared with chemical agents.

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