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## Green and Eco-Friendly Indigo Printing using New Smart Nano-Colorants and Their Application in Combined Printing and Antibacterial Finishing

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**Abstract**

Traditional indigo dyeing processes use various chemicals. Due to the increased awareness of environmental aspects, the interest in eco-friendly processing has become a priority. Regarding the indigo dyeing process, in this study, the traditional reduction process will be carried out without the environmentally unfavorable sodium dithionite which will be replaced with the determinant role of ultra-sonication in the miniaturization of indigo dye particle size. The research presented herein is a continuity of our interest to adopt synthesis, characterization, and applications of radically new nano-colorants. The synthesis involves nano-processing of a quaternary mixture consisting of Indigo Blue Vat dye/Natural clay (Montmorillonite MMT(K10)/Chitosan/Metal or Metal oxide Nanoparticles. Nano-colorants obtained acquire unique properties and sound performance. Further information concerning the contribution of other factors on properties, performance, and sustainability is the major target of current work. Role of sonication during nano-processing of the composite of the nano-colorant components, the importance of the number of nanometal particles in the synthesis, and sequence of addition of the nanometal particles. This and another potential of the research create the hope for inner nano-pigment.

Keywords: new hybrid nanocomposite, indigo blue vat dye, montmorillonite (MMT), pigment, binder, and various fabrics

### 1. Introduction

In the textile industry, nanotechnology has brought a revolution as it plays an important role in the garment production process such as water repellent, [1-4] flame retardant, [5-9] insect and animal repellent, [10-12] antibacterial, [8, 13-17] pH-temperature thermosensitive [13, 18, 19] thermoregulating textile, [20-22] self cleainning fabrics, [23] ultravielot protection, [24, 25] and improving dyeing properties. [26-30]

Much effort towards processing and properties of new nano-colorants through intercalation /exfoliation of natural clay (known as montmorillonite MMT) into an aqueous dispersion of Indigo Blue vat dye was recently devoted. [31-33] Emphasis was placed on ultrafine nanoparticles formed under the effect of ultrasound technology (i.e. sonication) on Indigo Blue Vat dye in admixture with the clay. The formation of Indigo Blue Vat dye/ Clay hybrid nanocomposite under different formulations and conditions were studied to achieve the best practice for optimization of the synthesis of the new colorant based on Indigo Blue Vat dye/clay hybrid nanocomposite. Also, our previous research confirms the interaction of the Indigo Blue vat dye with the natural clay MMT under the influence of sonication to yield nano-colorants which were successfully used in the printing of various fabrics irrespective of their origin: whether belonging to an animal, vegetable, other natural fibers or synthetic fibers.

As a continuity, fabrication of radically new colorants based on Indigo Blue Vat dye/polymer/layered

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silicate intercalated nanocomposites induced cotton prints with Batik and denim effects were thoroughly investigated. Best practice (formulation/conditions) for processing of new hybrid nanocomposite as new colorant was established. Synthesis of the new colorants is based on intercalation of the silicate layered nanocomposite (SLNC) which is a natural clay known as montmorillonite (MMT-K10) in Indigo Blue vat dye dispersion. Further development of the new colorant through the involvement of polymeric materials in the Indigo Vat dye /MMT (K10) formulation was also performed. Polymers used included low and high molecular weight chitosan, and in situ formed polyacrylamide. Citric acid was used in the fabrication formulation of the new hybrid nanocomposite colorants in the presence and absence of chitosan.

The prepared new colorants were applied in cotton printing. New colorants obtained by such synthesis were characterized and analyzed using Transmission Electron Microscope (TEM) and Scannibig Electron Micrscope (SEM). The antibacterial activity of cotton fabrics printed using the newly synthesized nanocolorants was reported. Also reported was the antibacterial ability of these ultrafine colorants to produce prints on cotton textiles. These prints were uniquely characterized by Batik and Denim effects. Reasons for the formation of these effects were reported. Furthermore, the fastness properties of the printed fabrics obtained thereof were examined. [31-33]

The present work is undertaken to fabricating multifunctional smart nano-pigments for simultaneous printing and antibacterial finishing of cotton fabrics. Based on our research and experience in the field concerned, these smart nano-pigments are established by sonication of quaternary mixtures consisting of Indigo Blue Vat dye/natural clay: MMT-K10/chitosan /nano metallic particles.

Synthesis and application of the new nanocolorant in concomitant with printing are exercised as per two approaches. The first approach involves sonication of the dye, the MMT –K10, and chitosan mixture to yield nanocomposite to which the nanometals are added. The as-a prepared new colorant is included in the printing paste. The second approach comprises the following steps :1) padding the cotton fabrics with the suspension (dispersion) of the metal nanoparticles, 2) submitting the dye/MMT-K10/chitosan mixture to sonication to yield the new colorant, and 3) printing the padded cotton fabric with the so obtained colorant.

Testing, analysis, characterization, and applications of the mixtures before and after sonication are examined. Also examined are the properties of cotton fabrics before and after being submitted to treatments with the smart nano-pigments.

Then, the utmost concern of current work to synthesize multifunctional smart nano pigment from simultaneous printing and antibacterial finishing of cotton textiles. [11, 18, 34-39] The work stems from our research and, indeed, is based strongly on previous research and practices published elsewhere. [40] The aforementioned background, which, indeed, refers strongly to emerging smart and sustainable nano pigments. These nano-pigments attain final formation by sonication of quaternary mixtures consisting of Indigo Blue vat dye/natural clay (MMT K10)/chitosan /Nanometallic particles. [41] Needless to say, that the new colorant still needs to be understood through investigation targets such as sonication of various particle size, shape, and other characteristics and addition of nano metallic oxides as well as the sequence of addition of these nano metallic particles. It is anticipated that the results of the present work will add to our understanding concerning these new colorants.

## 2. Experimental

### *2.1. Materials and reagents*

Mill desized, scoured, bleached, and mercerized cotton fabrics (100 g/m2), were supplied by Misr Company for Spinning and Weaving, Mahalla El – Kubra, Egypt.

High viscosity sodium alginate from brown algae, manufactured by Fluka Chemical Company, was used as a thickening agent, for printing. Chitosan of low molecular weight (100000 – 300000), manufactured by ACROS Organics was used. Commercial Indigo Blue Vat dye was kindly supplied by Dystar under the commercial name: Vat Blue 40 % solution and trade name INDIGO (ACua, Fran, ICI). Montmorillonite (MMT - K10, Molecular Formula: $H_2Al_2(SiO_3)_4.n\ H_2O$) manufactured by ACROS Organics was used. Commercial Binder, namely, EBCA PRINT TB manufactured by Egyptian British Company was used.

Potassium carbonate, sodium hydroxide, sodium chloride, L. Histidine monohydrochloride monohydrate, sodium dihydrogen orthophosphate, and disodium hydrogen orthophosphate were laboratory-grade chemicals.

Zinc oxide (ZnONPs), Copper oxide (CuONPs), and Titanium dioxide (TiO2NPs) nano-powders were manufactured by SIGMA ALDRICH with an average particle size of 67, < 50, and 21 nm respectively. Silver nanoparticles (AgNPs) were prepared in the laboratory according to a reported method. [32]

## 2.2. Methods

### *2.2.1. Synthesis of silver nanoparticles*

The citrate reduction is one of the simplest and most common methods to synthesize noble metal nanoparticles. The Citrate plays several roles in the generation of AgNPs as a reducing and stabilizing agent. The Citrate acts as strongly co-ordinate with $Ag^+$ to form white complex $Ag^+$ - citrate. At high temperatures, the citrate complex acts as a reducing agent to generate AgNPs. Therefore, the synthesis of AgNPs occurred as follow: 10 ml of trisodium citrate (1%) was equipped in a conical flask then, 100 ml silver nitrate (AgNO3) with 200 ppm Ag and 10 ml polyvinylpyrrolidone (0.1 %) was stirred together for 45 min at 90°C. Then AgNPs were prepared for use.

### *2.2.2. Preparation of Innovative Nanocolorant Based on Indigo Blue Vat - MMT K10 - Chitosan using Ultrasonic Processor*

Indigo blue Vat dye together with MMT K10 was converted to nano-sized particles by making use of the Ultrasonic stirrer as follows. 5 g of the Indigo blue Vat dye aggregates were mixed with 5 g MMT K10 and 5 g chitosan (low molecular weight) in 100 ml water. The so obtained well-mixed Indigo Vat dye - MMT K10 dispersion was set to a motion under the effect of Ultrasonic radiation for (60 min.) at 80□C. fabrics sample was submitted to printing using the prepared printing pastes. After printing and drying the samples were subjected to thermo-fixation at 160□C for 3 min. At this end, the samples were thoroughly washed, dried, and monitored for further analysis.

The Ultrasonic Processor used in this work is (SONICS&MATERIALS, INC), Model: VCX750, Volts: 230VAC 50/60 HZNOM, U.S.A), (The Probe is tuned to resonate at a specific frequency, 20 kHz + 100 HZ).

### *2.2.3. Ultrasound Technology Induced Miniaturization of Indigo Vat Dye/Montmorillonite*

Synthesis and application of the new nanocolorant in concomitant with printing were exercised as per two approaches.

Mixing the Indigo Blue Vat dye, MMT –K10, chitosan, and nanoparticles. This was followed by sonication then incorporating the as-prepared new colorant in the printing paste. [33]

The first approach involves sonication of the dye, the MMT–K10, and chitosan mixture to yield nanocomposite to which the nanometals were added. The as-prepared new colorant was included in the printing paste. The second approach comprises the following steps: 1) padding the cotton fabrics with the suspension (dispersion) of the metal nanoparticles, 2) submitting the dye/MMT-K10/chitosan mixture to sonication to yield the colorant, and 3) printing the padded cotton fabric with the so obtained colorant.

### *2.2.4. Preparation of Innovative nano colorant based on Indigo Blue Vat - MMT K10 - chitosan using Ultrasonic Processor and adding either of the nanoparticles in the printing paste*

5 g of Vat dye, 5 g MMT(K10) were mixed well with 5 g chitosan (low molecular weight) then added to 100 ml distilled water. Thus, the obtained mixture was miniaturized using the Ultrasonic Processor for 60 minutes at 80□C. then 2 g of either nano metal oxides (ZnONPs, CuONPs, or TiO2NPs) or 20 ml of AgNPs was added to the printing paste (the metal oxides did not subject to sonication).

### *2.2.5. Printing of nanoparticles pretreated fabrics with new colorant after being subjected to miniaturization through sonication*

Cotton samples were subjected to padding in solutions containing 2 g of either nanometals oxides (ZnO, CuO, or TiO2) or 20 ml AgNPs and a 5g binder in 100 ml water. The padded samples were printed with printing pastes containing MMT-K10 (5 g/100 ml water) mixed with 5 g Indigo Vat dye and 5 g chitosan (low molecular weight) in 100 ml water. The dye /MMT-K10/chitosan was submitted to an ultrasonic Processor for 60 min at ca 80□C.

### *2.2.6. Preparation of printing paste*

Printing pastes were prepared to contain the recipe tabulated below:

| | |
|---|---|
| Colorant * | 20g |
| Urea | 2.5g |
| Thickener (sodium alginate; 2.5 %) | 50 g |
| Binder (EBCA Print TB; 5 g/100 ml water) | 5 g |
| Sodium dihydrogen phosphate dehydrates | 0.5g |
| Distilled water | X |
| Total | 100g |

* Colorants used to represent those hybrid nano-

composite innovative pigments which were fabricated according to the following formulations: 5 g Indigo Blue Vat dye/5 g MMT-K10/5 g chitosan in 100 ml water, before and after being subjected to miniaturization via stirring in the ultrasonic processor for 60 min. at 80°C was used in the preparation of the printing paste. Therefore, 20 gm were taken from each of the prepared colorants in 100 ml of water. ZnONPs, TiO2NPs, or CuONPs were added in the first approach.

*2.2.7. Printing technique*

All the printing pastes were applied to cotton fabric according to the conventional screen-printing method. Prints were then subjected to thermofixation at 160oC for 3 minutes.

*2.2.8. Washing*

Washing of the printed samples was carried out as per five steps: i) rinsing thoroughly with cold water, ii) rinsing with hot water, iii) soaping at a temperature of 95□C with a solution containing 2 g/l nonionic detergents, iv) washing with hot water, and v) rinsing with cold water. Finally, the samples were dried and assessed for color strength (K/S) and overall colorfastness properties.

***2.3. Analysis***

*2.3.1. Scanning electron microscopy.*

The morphology was observed by use the scanning electron microscope (SEM) type Quanta 200.

*2.3.2. Transmission Electronic Microscopy (TEM). (4)*

Specimens for TEM measurements were prepared by dissolving a drop of colloid solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in the air at room temperature. The average diameter of the new nano colorant was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs. Particle shape, size, and size distribution of material particles under investigation were monitored using a JEOLJEM 1200.

*2.3.3. Microbiological tests*

Most microorganisms used were ATCC registered strains except Bacillus cereus that was a local isolate obtained from Agricultural, Microbiology Department, National Research Centre; Egypt. The used microorganisms included test microorganisms: Streptococcus Pyogenes (19615), Escherichia Coli (25922), and Bacillus Cereus.

All sample pieces were sterilized by placing them under UV before the microbiological tests. The microbiological susceptibility tests were done by agar diffusion qualitative method using Mueller Hinton for testing bacteria and potatoes dextrose agar for testing fungi. The microbiological strains were grown in appropriate liquid media (up to count 106 CFU/ ml) then spread and on the last-mentioned solid media used. Susceptibility test microorganisms were determined after 24 h by measuring the axial (crude sample piece ax was about 13 mm) zone of inhibition around each sample piece embedded on the inoculated agar surface at 30 ºC to the nearest mm.

*2.3.4. Colour strength measurements*

The color strength and whiteness degrees of the printed samples were evaluated by Hunter Lab Ultra Scan PRO. [42-46]

*2.3.5. Fastness properties*

The colorfastness to washing was determined according to the AATCC Test method 61- 1993 using Laudner-Ometer. [47] Evaluation of the wash fastness was established using the Gray Scale reference for color change. The colorfastness to crocking (dry and wet) was determined according to the AATCC test method 8 - 1993. [48] This test is designated for determining the degree of color which may be transferred from the surface of the colored fabric to another surface by rubbing. The colorfastness to perspiration (acidic and alkaline) was determined according to the AATCC test method 15-2002. Two artificial perspiration solutions were prepared as follows: [49] The effect on the color of the test specimens was expressed and defined by reference to the Grayscale for color change. [44, 45, 47-52]

**3. Results and Discussion**

It was recently reported in detail the development of new hybrid nanocomposite colorants through intercalation of layered silicate of a natural clay known as montmorillonite-MMT(K10)- in the dispersion of Indigo Blue vat dye. [53] This occurs upon using Indigo Blue Vat dye /MMT/ Polymer tertiary system. Different polymeric components contributing to the formation of the new colorants in their nano - form could be achieved by incorporating two types of polymers in the nanocomposite formulation. The first is chitosan as a natural polymer having low molecular weight. The second type refers to in situ formed polyacrylamide. Our previous studies [33] emphasized also the addition of citric acid to the nanocomposite formulation.

The main concern of the current work is to insert metal or metal oxide nanoparticles among the constituents of the new nano-colorant composite to induce bioactivity to the new colorant.

It needs to study the impact of both nature and sequence of addition of nanometal or nano metal oxide particles on the size and morphology of the newly processed nano-colorants. Besides, the bioactivity of printed cotton using the new nano-colorant with/without metal or metal oxide nanoparticles. Further emphasis would certainly be considered regarding the color strength and the fastness properties along with their contribution and control of these properties.

### *3.1. Effect of addition of nanometal particles on new colorant size*

Particle sizes of new hybrid nanocomposite formulation (5 g Indigo Blue Vat dye, 5 g MMT (K10), and 5 g chitosan/100 ml H2O) were examined before and after sonication. Figure 1 depicts the TEM micrograph of the new colorant before and after sonication. As is evident the new colorant before sonication exhibits a particle size of 178 nm which changed 21 nm after sonication; indicating the vest difference in compactness, association, surface area, mode, and nature of interactions and intercalations of the microstructural entities.

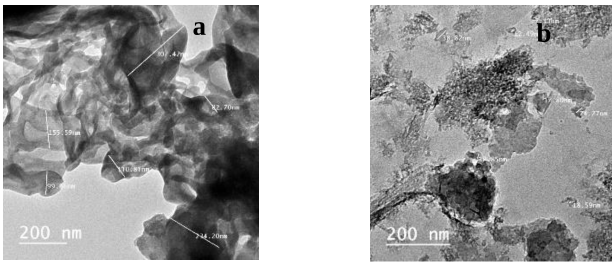


Figure 1: TEM micrograph of hybrid nanocomposite formulations with chitosan a) before and b) after sonication

### *3.2. Color strength and fastness properties of printed cotton fabrics using the new nano-colorants*

The aforementioned four quaternary hybrids before and after sonication were used in preparing 8 different printing pastes. Cotton fabrics were printed using pastes prepared as described in the experimental section using the screen-printing technique. After printing and drying, the printed fabrics were thermally fixed at 160°C for 3 minutes, followed by washing, drying, conditioning, and measuring the K/S and overall colorfastness properties. The results obtained are given in Table 1.

It is clear from Table 1 that, the highest value of color strength is obtained when the nanometal or nano metal oxide particles are applied to the fabric through padding with a solution containing these nanometal particles before printing. The lowest color value is obtained when the nanometal or nano metal oxide particles are added to the printing paste. In the first case, the nanometal particles are logically freer to get involved in interactions and intercalation within ultrafine entities and moieties of the new colorant. This leads to a more intimate association of the new colorant with the cotton fabrics.

A different situation is encountered with the second case where metal and metal oxide nanoparticles are restricted, difficult to move, and limited much in their contribution to enhancing high printing. In addition to these negative impacts, the total surface area available for interactions between the new colorant and cotton fabrics during printing is much smaller than the first case.

Table 1 signify that prints obtained as per the first case show much higher K/S values than those of the second case irrespective of the nanometal or metal oxide used. Nevertheless, higher K/S values are obtained with CuO in both cases but with the superiority of CuO in the first case.

**Table 1**: K/S of Printed cotton fabrics using new hybrid nanocomposite colorants based on the mixture of chitosan/Indigo Blue vat dye/MMT(K10) along with either ZnO, CuO, Ag, or $TiO_2$ nanomaterial after sonication

| **Formulation** | **Nano metals in the printing paste** | **Pre-treated fabric with the nano metals before printing** |
|---|---|---|
| A | 3.28 | 8.82 |
| B | 3.26 | 8.97 |
| C | 3.23 | 7.74 |
| D | 4.89 | 9.92 |
| E | 8.91 | |

A = 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g **Nano$TiO_2$**
B = 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 20 ml **Nano Ag dispersion**
C = 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2g **Nano ZnO**
D = 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2g **Nano CuO**
E = Blank printed fabric without nanometal, K/S of blank 8.91

### *3.3. Morphology of fabrics printed using the new nano-colorants*

SEM micrographs of cotton fabrics printed using the new nano-colorant are illustrated in Figure 2. The new nano-colorant was prepared using a quaternary mixture (the Indigo blue vat dye + MMT(K10) + chitosan) and nano metal oxide (TiO2, ZnO and CuO) or nanosilver suspension before sonication are shown in Figure 2(B, E, H, and K). On the other hand, the corresponding SEM micrographs for cotton fabrics printed using these mixtures after sonication in the three approaches involved in the intimate association of the hybrid composite nano-pigment colorant are illustrated in Figure 2(C, D, F, G, I, J, L, and M). It is observed that fabrics printed using the quaternary mixture nanoparticles after sonication acquire a much smoother surface than those printed using these mixtures before sonication. This reflects the importance of sonication in producing homogeneous prints with clear and smooth surfaces and sustainability. No strong colorant forces are readily generated in absence of sonication is, therefore, a must to promote new smart printing using currently new basics and practices. The SEM micrographs are following this. They are self-explanatory.

### *3.4. Antimicrobial Activity*

Antimicrobial Activity of Printed Cotton Fabrics Using the New Colorants and added nano metals in the printing paste. According to data in Table 2 and Figure 3, there is no effects are shown by the tested textile samples against the tested microorganisms before sonication. Table 2 reveals that the most potent microbial weariness viewed by sample blank that shows no antimicrobial effects against the tested microorganisms.

According to the results of Table 2 and Figure 3, the most potent antimicrobial effect is shown against E. coli which provides an excellent inhibition zone with all printed fabrics with nanoparticles. While B. cereus bacteria provide good inhibition zone by sample printed in presence of with AgNPs and ZnONPs giving 15.4 and 10.2 mm as an axial zone of inhibition respectively. Whereas, Streptococcus Pyogenes show weariness against samples printed in the presence or absence of nanometals. The followed antimicrobial potent is shown by sample treated after sonication with silver that reveals antibacterial effects against E. coli by 16.0 mm as an axial zone of inhibition. It is as a wall to reported that a sample treated with TiO2NPs exhibits antimicrobial effects against E. coli by 12.3 mm as an axial zone of inhibition. The sample can be used by people working in polluted zones where the polluted water is mixed with sewage such as (Sinai city).

### *3.5. Colorfastness properties*

The overall colorfastness properties, i.e., fastness to washing, perspiration, to rubbing of cotton fabrics printed using the hybrids containing different nano metals before and after sonication were measured. Results obtained are set out in Table 3.

## 4. Conclusion

It is ecologically and economically acceptable to use miniaturized indigo blue vat particles in textile printing which impacts well on the environmental aspect that inquires to decrease the use of environmentally unfavorable reducing agents by printing enhancement with nano indigo vat dyes.

New multifunctional smart nano colorant was synthesized through intercalation/ exfoliation of natural clay known as montmorillonite K10 into an aqueous dispersion of the Indigo vat dye and chitosan and metallic nanoparticles of either CuO, ZnO, TiO2, or silver. Special emphasis is placed on ZnO, CuO, TiO2, and metallic silver nanoparticles concerning their nature and sequence of addition during a single-stage process for coloration (printing) and antimicrobial finishing.

Testing, analysis, characterization, and application of the mixtures under investigation are examined. Dependence of the particle size of the nano colorant and the color strength of prints obtained thereof as an ultimate product (i.e. new colorant) of such interactions was verified. The new nano colorant depends also on the nature of the metal nanoparticles and so does their ability to affect antibacterial finishing. The morphology of the nano colorants was also examined before and after sonication using SEM.

Having obtained the results of each variable, optimal processing conditions for the fabrication of the new nano-colorant could be achieved. Nano-colorants synthesized as per the optimal processing conditions exhibit better performance properties as compared with the conventional indigo blue vat dye printing.

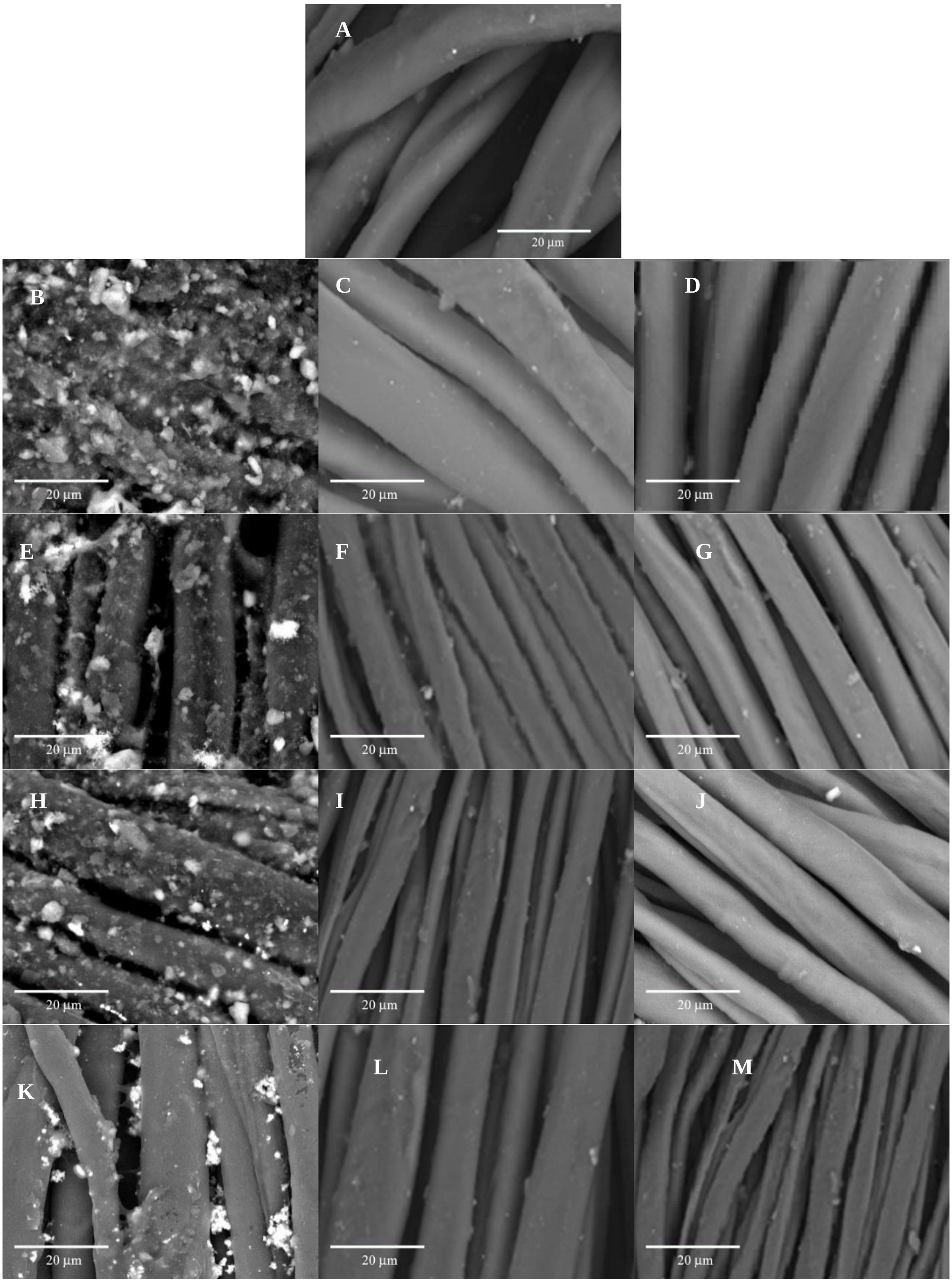


**Figure 2**: SEM micrograph of printed cotton fabrics with Indigo Blue Vat dye / MMT(K10) / chitosan with and without metal nanoparticles before and after sonication

**A**) without nano metals, after composite being sonicated for 60 min at 80°C , **B**) with $TiO_2$NPs, before sonication, **C)** $TiO_2$NPs were added directly to the printing pastes, after composite being sonicated for 60 min at 80°C, **D)** Cotton fabric was pre-treated with $TiO_2$NPs, after composite being sonicated for 60 min at 80°C, **E)** with AgNPs, before sonication, **F)** AgNPs were added directly to the printing pastes, after composite being sonicated for 60 min at 80°C, **G)** Cotton fabric was pre-treated with AgNPs, after composite being sonicated for 60 min at 80°C, **H)** with ZnONPs, before sonication, **I)** ZnONPs were added directly to the printing pastes, after composite being sonicated for 60 min at 80°C, **J)** Cotton fabric was pre-treated with ZnONPs, after composite being sonicated for 60 min at 80°C, **K)** with CuONPs, before sonication, **L)**CuONPs were added directly to the printing pastes, after composite being sonicated for 60 min at 80°C, **M)** Cotton fabric was pre-treated with CuONPs, after composite being sonicated for 60 min at 80°C

**Table 2**: Antimicrobial activity of cotton fabric printed using the new colorant with nano metal after sonication

| Printed fabric | Sonication | | E. Coli | *Streptococcus Pyogenes* | B. Cereus |
|---|---|---|---|---|---|
| Sample 1 | 1` | before | 0 | 0 | 0 |
| | 1 | after | 16.0 | 0 | 15.4 |
| Sample 2 | 2` | before | 0 | 0 | 0 |
| | 2 | after | 11.2 | 0 | 0 |
| Sample 3 | 3` | before | 0 | 0 | 0 |
| | 3 | after | 15.4 | 0 | 10.2 |
| Sample 4 | 4` | before | 0 | 0 | 0 |
| | 4 | after | 12.3 | 0 | 0 |
| Sample 5 | 5 | before | 0 | 0 | 0 |
| | 5 | after | 0 | 0 | 0 |

Sample 1 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 20 ml **AgNPs**
Sample 2 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g**CuONPs**
Sample 3 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g **ZnONPs**
Sample 4 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g **$TiO_2$NPs**
Sample 5 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan without nano metal

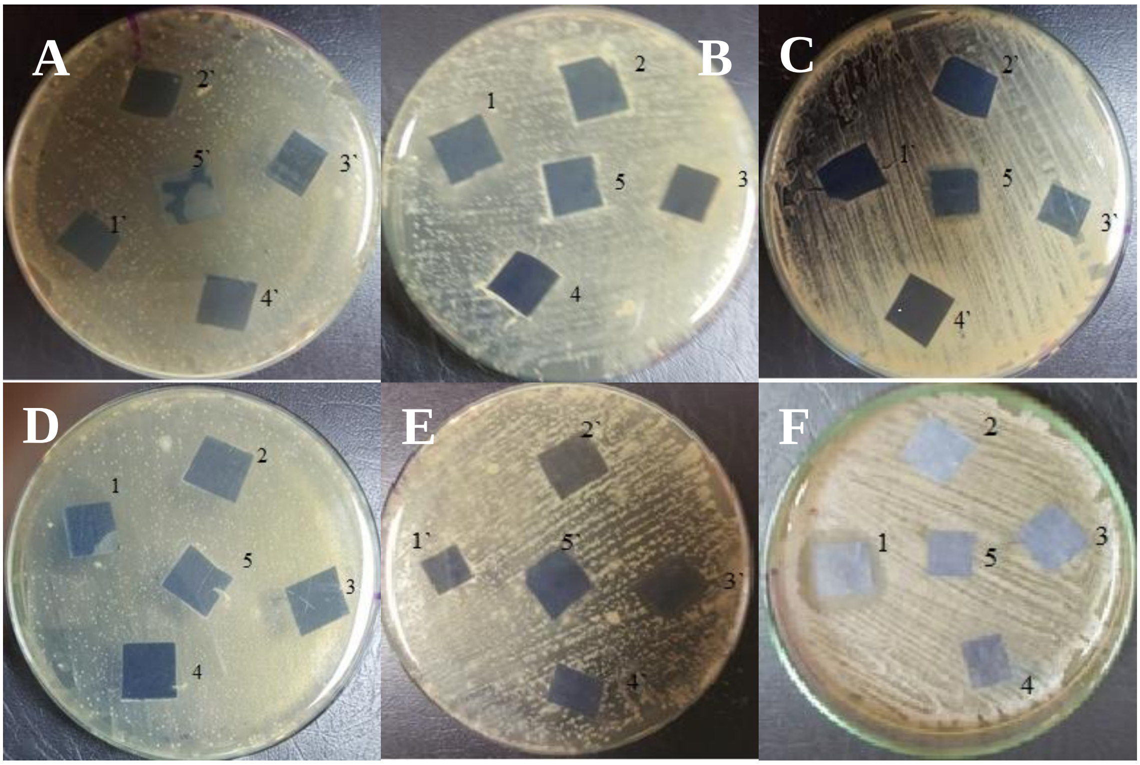


**Figure 3**: Antimicrobial activity of printed cotton fabric using the new colorant with nano metal before and after sonication

A) against E. Coli before sonication B) against E. Coli after sonication
C) against Streptococcus Pyogenes before sonication D) against Streptococcus Pyogenes after sonication
E) against Bacillus Cereus before sonication F) against Bacillus Cereus after sonication

**Table 3**: Colour strength K/S and fastness properties of cotton fabric printed using the new nano-colorants after sonication

| Formulation | Effect of adding nanometal | Color Strength (K/S) | Fastness properties | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Washing fastness at 60°C | | Rubbing Fastness | | Perspiration fastness | | | |
| | | | | | | | Acidic | | Alkali | |
| | | | St. | Alt. | Wet | Dry | St. | Alt. | St. | Alt. |
| Formulation 1 | AgNPs in the formulation | 3.26 | 4- 5 | 4- 5 | 4 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| | Pretreated fabric with AgNPs | 8.97 | 4- 5 | 4- 5 | 3-4 | **4** | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| Formulation 2 | CuONPs in the formulation | 4.89 | 4- 5 | 4- 5 | 4 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| | Pretreated fabric with CuONPs | 9.92 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| Formulation 3 | ZnONPs in the formulation | 3.23 | 4- 5 | 4- 5 | 3- 4 | 4 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| | Pretreated fabric with ZnONPs | 7.74 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| Formulation 4 | $TiO_2$NPs in the formulation | 3.28 | 4- 5 | 4- 5 | 3- 4 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| | Pretreated fabric with $TiO_2$NPs | 8.82 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 | 4- 5 |
| Formulation 5 | | 8.91 | 4- 5 | 4- 5 | 3-4 | **4** | 4- 5 | 4- 5 | 4- 5 | 4- 5 |

Formulation 1 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 20 ml **AgNPs**
Formulation 2 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g**CuONPs**
Formulation 3 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g **ZnONPs**
Formulation 4 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan + 2 g **$TiO_2$NPs**
Formulation 5 = printing paste containing 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan without nano metal

Colour strength of cotton prints exhibited exceedingly higher values by pretreatment of cotton fabric wish nanometal particles before printing than through the addition of the latter in the printing paste. The colorfastness of the prints to rubbing is lower when printing was carried out using the new nano-colorants before sonication. Involvement of the metal nanoparticles in reactions with the other components of the quaternary mixtures during sonication detracts from their ability to induce antibacterial activity to cotton fabrics.

The Case of padding the cotton fabric with nanometal particles before printing obtained the best results in K/S and scanning electron microscope and overall fastness compared with the other Approach, the nanometals were added in the printing paste.

## 5. References


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