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Multifunctional Smart Nanocolorants for Simultaneous Printing and Antibacterial Finishing of Cotton Fabrics

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THE presented work studied the synthesis of a new multifunctional smart nanocolorant based on natural clay (montmorillonite K10), chitosan and metal nanoparticles (CuO, ZnO, TiO_2 or Ag) using ultrasonic technology. The prepared nanocolorants were characterized for their particle size and properties. These nanocolrants were used in printing paste for application to cotton fabric before and after sonication. Surface morphology antibacterial activity and fastness properties were evaluated for treated fabrics. It is observed that fabrics printed with prepared materials after sonication acquire much smoother surface than those printed with prepared materials before sonication. The new hybrid particles are small enough to diffuse into fibers and they create high fastness properties. In addition, printed fabrics with hybrids particles are highly fixed on the fabric surface.

Keywords: Montmorillonite K10, Chitosan, Ultrasonication, Nanocolorants printing and Antibacterial fabrics.

Introduction

Synthesis and properties of new nanocolorants through intercalation /exfoliation of natural clay (known as montmorillonite MMT) into aqueous dispersion of Indigo Blue vat dye have an excellent vision for their good properties. 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 [1, 2]. The formation of Indigo Blue Vat dye/Clay hybrid nanocomposite under different formulations and conditions were studied in order to achieve the best practice for optimization of the synthesis of the new colorant based on Indigo Blue Vat dye / clay hybrid nanocomposite. In addition, our research confirms the interaction of the Indigo Blue vat dye with the natural clay MMT under the influence of sonication to yield nanocolorants which were successfully used in printing of various fabrics irrespective of their origin: whether belonging to animal, vegetable, synthetic or natural fibers.

As a continuity of the foregoing, fabrication of radically new colorants based on Indigo Blue Vat dye/polymer/layered silicate intercalated nanocomposites [3-5], 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) [6-8] which is a natural clay known as montmorillonite (MMT/K10) in Indigo Blue vat dye dispersion [9]. Further development of the new colorant through

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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 [2, 10]. Citric acid was used in the fabrication formulation of the new hybrid nanocomposite colorants in 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). 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. Furthermore fastness properties of the printed fabrics obtained thereof are examined [11-14].

Several researches are interested in producing multifunctional surfaces using inorganic nanoparticles due to their ability to developing several properties such as stability, less energy consumption and eco-friendly consideration. Inorganic metal oxides nanoparticles such as zinc oxide, copper oxide and titanium dioxide have a great effect in different applications due to their ability to transporting charges, which make them able to oxidize organic substrates [15-19]. Therefore, impregnation of these metal oxides nanoparticles into hybrid materials have been studied for their applications in different field such as textiles [17-20].

The present work is undertaken with a view to fabricate multifunctional smart nanocolorants for simultaneous printing and antibacterial finishing of cotton fabrics. Based on our research and experience in the field concerned, these smart nanocolorants are established by sonication of quaternary mixtures consisting of Indigo Blue Vat dye/natural clay: MMT- K10/chitosan/ nano metallic particles. Suggested nanometallic particles include ZnO, CuO, TiO_2 and Ag. 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 nanocolorants.

Experimental

Materials

Mill desized, Scoured, bleached and mercerized cotton fabrics (100 g/m^2), were supplied by Misr Company for Spinning and Weaving, Mehalla El - Kubra. Chitosan of low molecular weight, manufactured by ACROS Organics was used.

High viscosity sodium alginate from brown algae, manufactured by Fluka Chemical Company was used as a thickening agent for printing. Commercial Indigo Blue Vat dye was kindly supplied by Dystar under the commercial name: Vat blue 40 % solution under trade name INDIGO(ACua, Fran, ICI), Montmorillonite (MMT - K10; $H_2Al_2(SiO_3)_4{-}n\,H_2O$) manufactured by ACROS Organics was used.

Potassium carbonate, sodium hydroxide, sodium chloride, L.histidine monohydrochloride mono hydrate, sodium di-hydrogen orthophosphate, sodium chloride and disodium hydrogen orthophosphate were of laboratory grade chemicals.

Zinc, Copper and Titanium oxide (ZnO, CuO and TiO_2) nano-powders were manufactured by SIGMA ALDRISH with an average particle size of 67, less than 50 and 21 nm respectively was used.

The most of 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), Pseudomonas aeruginosa (27853), Aspergillus niger (6275) and Bacillus cereus.

Synthesis

Ultrasound Technology Induced Miniaturization Of Indigo Vat Dye/Montmorillonite Mix

Ultrasonic Processor provides a mechanical process to reduce small particles in a liquid so that they become more uniformly small and evenly distributed. Ultrasonic processors are used as homogenizers, to reduce small particles in a liquid to improve uniformity and stability. These particles (disperse phase) can be either solids or liquids. Ultrasonic homogenizing is very efficient for the reduction of soft and hard particles.

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

Nano Silver particles

Silver nanoparticles (AgNPS) was prepared in the laboratory according to a reported method [1]. The citrate reduction is one of the simplest and most common method to synthesize noble metal nanoparticles. The Citrate plays several roles in the generation of AgNPs as reducing and stabilizing agent. The Citrate acts as strongly co-ordinate with Ag+ to form white complex Ag+ - citrate. At high temperature, the citrate complex acts as a reducing agent to generate Ag NPs. The mechanism of the reaction could be expressed as follows; the oxidation reaction of trisodium citrate, the hydroxyl group attached to the center carbon that has adjacent carbons with carboxylate groups attached respectively, is oxidized and protons and electrons are liberated. The electrons then facilitate the reduction of Ag+ to Ag0. The adjacent carboxylate groups in the structure are important in effecting this oxidation. The redox reaction for the formation of nanosilver using trisodium citrate is given below. The excess trisodium citrate controls the particle growth of the Ag particles and produces a stable nanosilver colloid.

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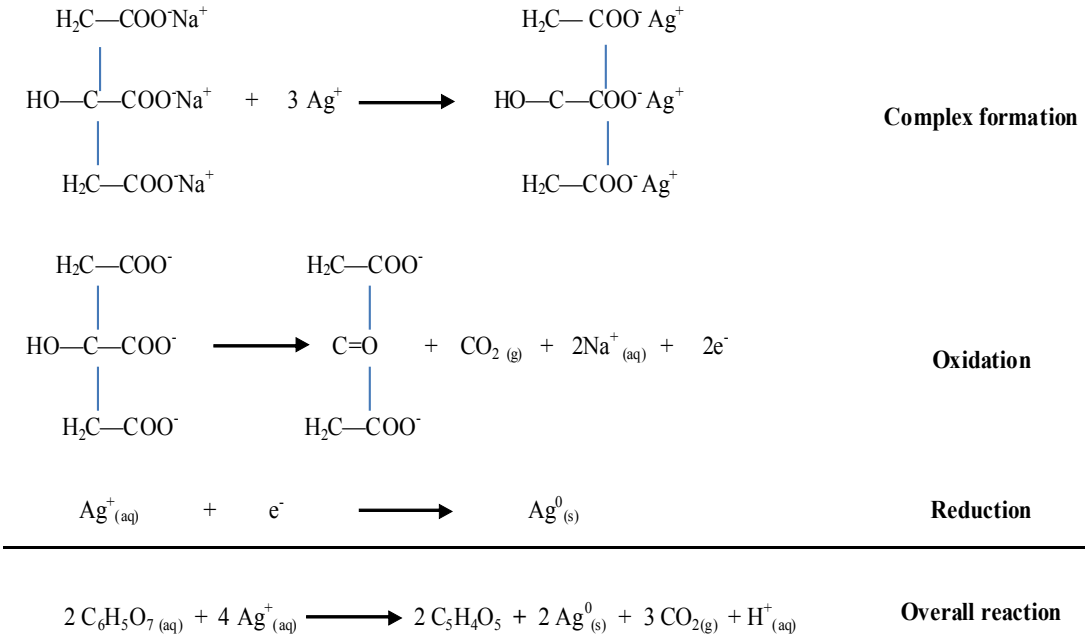

Immediately following the reduction, additional negatively charged due to the carboxylate groups from residual citrate were adsorbed onto the AgNPs, introducing a surface charge that essentially forms an electrical double layer which, they can repel one another and prevent particle aggregation. Therefore, the particles in the solution remain in a stable state without using other stabilizing agents.

TSC 1, %10 ml/100ml, Ag 200 ppm, Temp. 90°C, Reaction time 45 min., PVP (Poly Vinyl Prilidone) 0.1 %20 ml of the nano silver particle prepared were used.

Preparation of the Innovative nanocolorant based on Indigo Blue Vat dye in admixture with MMT (K10) and chitosan along with nano metal-licmaterials (Zinc, copper, titanium oxide or silver)

Indigo Blue Vat dye in admixture with MMT(K10), chitosan and nano-metal materials were subjected to miniaturization through sonication using Ultrasonic Processor. Hence, 5gm of Indigo Blue Vat dye was mixed with 5 gm chitosan (low molecular weight), 5 g MMT(K10) and 2 g of either (ZnO, CuO, TiO_2) or 20 ml of the prepared nano silver dispersion. As already stated, this mixture was subjected to sonication via stirring in Ultrasonic Processor for 60 min at 80°C. The prepared mixtures were used in preparation of the printing pastes.

Preparation of printing paste

The first component of the printing paste

refers to the commercial Indigo Blue Vat dye, which was suspended in100 ml distilled water after and before miniaturization, whereas the second component contains Indigo Blue Vat dye together with MMT (KSF and K10).

The printing pastes were prepared according to the following recipe[21]:

Colorant *	20g
Urea	2.5g
Thickener (Sodium alginate) **	50 g
Binder ***	5 g
Sodium dihydrogen phosphate dehydrate	0.5g
Distilled water	Y
Total	100g

* 20 g was taken from each colorant in 100 ml water.

* Colorants used to represent those hybrid nanocomposite innovative colorants which were fabricated according to the following formulations: (5g Indigo Blue Vat dye/5 g MMT-K10/5 g chitosan/2 g ZnO-NPS in 100 ml water from the first formula. When ZnO-NPs are replaced by either TiO_2-NPs or CuO-NPs three other formula were obtained. This formula before and after being subjected to miniaturization via stirring in ultrasonic processor for 60 min at 80°C were used in the preparation of the printing paste.

** Thickener was used at a concentration of 2.5%

*** Binder was used at a concentration of 5 g/100 g of the printing pastes.

Control sample, which is printed as per the traditional printing of vat dye, that is, the paste, contains Rongalite as a reducing agent in addition to other components in the printing paste as follow:

Colorant *	20 g
Glycerine	6 g
Thickener (Sodium alginate) **	50 g
Potassium carbonate	16 g
Rongalite C	2.5 g
Distilled water	Y
Total	100g

* 20 g was taken from colorant in 100 ml water.

Colorant represents commercial vat dye before and after miniaturization.

**Thickener was used at a concentration of 2.5%

The printed fabrics were rinsed and oxidized using 2 g/l sodium perborate and 10 g/l acetic acid (30 %), after oxidation the fabrics were boiled for 5 min in an aqueous solution of sodium carbonate (1 g/l), then washed with cold water.

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 160°C for 3 min.

Washing

Washing of the printed goods was carried out through five steps:

- Rinsing thoroughly with cold water.
- Rinsing with hot water.
- Soaping at a temperature of ca 95°C with a solution containing 2 g/l non-ionic detergent.
- Washing with hot water.
- Rinsing with cold water.

Finally, the samples were dried and assessed for colour strength (K/S) and overall colour fastness properties

Analysis and Measurements

Transmission electronic microscopy (TEM)

Particle shape, size and size distribution of materials under investigation were monitored using Transmission Electron Microscopy (JEOLJEM 1200. [22-24]

Scanning Electron Microscope(SEM)

SEM was studied using a scanning electron - JSM 5400 instrument (Joal, Japan). The specimens in the form of fabrics were mounted on the specimen stabs and coated with thin film of gold by the sputtering method.

Microbiological tests

All types of samples under evaluation were cut into square pieces of about 1 cm^2 and classified into 5 tested groups due to research authors. 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 on 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 pieces imbedded on the inoculated agar surface at 30 ^{0}C to the nearest mm. [25, 26]

Colour measurements [22, 23, 27-33]

Measurements of the colour strength of the dyed fabrics (expressed as K/S) have been done using the Hunter Lab Ultra-Scan Pro, at the National Research Center, Egypt. K/S value of the fabrics were evaluated by reflectance technique according to the Kubalka–Munk equation **[34]** given below:

$$K/S = \frac{\left(1 - R_{k_{max}}\right)^2}{2R_{k_{max}}}$$

where K is the coefficient of absorption; S is the coefficient of scattering; R_{kmax} is the reflectance value of the fabric at peak wavelength. The colour fastness to washing and light were for the dyed fabrics have been assessed according to a standard method [23, 31, 32].

Fastness properties [23, 24, 30, 31, 35-38]

Colourfastness to washing

The colourfastness to washing was determined according to the AATCC Test method 61- 1975 using Launder-Ometer. The specimens (5 x 10 cm) were sewed between two similar pieces of bleached cotton fabric and wool fabric. The composite specimen was immersed into an aqueous solution containing 5 g/1 soap and 2 g/l sodium carbonate using a material to liquor ratio 1:50. The bath was thermostatically adjusted to 95^{o}C. The test was run for 45 minutes at 42 rpm. The samples were then removed, rinsed twice in 100 ml bath of water at 40^{o}C for one minute with occasional stirring or hand squeezing, souring in 100 ml of 0.014% solution of acetic acid for one minute at 27^{o}C, rinsing again for one minute in 100 ml water at 27^{o}C followed by drying [28]. Evaluation of the wash fastness was established using the Gray Scale reference for colour change.

Colour fastness to rubbing (crocking)

The colour fastness to crocking was determined according to the AATCC test method 8 - 1977 [36]. This test is designated for determining the degree of colour, which may be transferred from the surface of the coloured fabric to other surface by rubbing.

A coloured test specimen fastened to the base of a Crock Meter was rubbed with white crock test cloth under controlled conditions.

- Dry Rubbing Test: The test specimen was placed flat on the base of the Crock Meter. A white testing cloth was mounted on the finger of the crock meter. The covered finger was lowered onto the test specimen and caused to slide back and forth 20 times by making ten complete turns at a rate of one turn/second.
- Wet Rubbing test: The white test sample was thoroughly wetted out in distilled water to a 65% wet pick up. The procedure was run as before. The white test samples were then air dried before evaluation.
- The evaluation was done using the Gray Scale for staining.

Colour fastness to perspiration [37]

Two artificial perspiration solutions were prepared as follows:

Acidic solution: L. Histidine monohy drochloride monohydrate0.5 g, sodium chloride 5.0 g, sodium di-hydrogen orthophosphate 2.2 g, were dissolved in one liter distilled water. Finally, the pH was adjusted to pH 5.5 by NaOH solution 0.1 N.

Alkaline solution: L. Histidine mono-hydrochloride monohydrate 0.5 g, sodium chloride 5.0 g di-sodium hydrogen orthophosphate 2.5 g, were dissolved in one liter distilled water. Finally, the pH was adjusted to pH 8 by NaOH solution 0.1 N.

The coloured specimen 5 x 4 cm was sewed between two pieces of uncoloured specimens, (so that an area of 5x1 cm of the coloured cloth is not in contact with the specimen) to form composite specimens. The composite sample was then immersed (for 15 - 30 minutes) in each of the above solutions with occasional agitation and squeezing to insure complete wetting. The test specimen was placed between two glass plates under a force of about 4.5 Kg. The plates containing the composite specimens were then held vertical in the oven at 37^{o}C for 4 hours.

The effect on the colour of the test specimens was expressed and defined by reference to the Gray scale for colour change.

Results and Discussion

Synthesis and application of the new nanocolorant in concomitant with printing were exercised as per three approaches. The first approach involves mixing the Indigo Blue Vat dye, MMT –K10, chitosan and metallic nanoparticles. This was followed by sonication then incorporating the as prepared new colorant in the printing paste. The second approach involved sonication of the dye, the MMT –K10 and chitosan mixture to yield nanocomposite to which the metallic nanoparticles was added. The as prepared new colorant was included in the printing paste. The third 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 colorant compound, 3) Printing the padded cotton fabric with the so obtained colorant, Only the first approach will be tacked in current study whereas the other two approaches will be the subject of forth coming studies.

New Hybrid Nanocomposite Colorants Fabricated through Interactions of Blue vat, MMT, Chitosan and Metal Nanoparticles

Research in our previous progress report leads to development of new hybrid nanocomposite colorants through intercalation of the layered silicate of a natural clay known as montmorillonite MMT(K10) in the dispersion of Indigo vat dye. Different polymeric components contributing in the formation of new colorants in the nano form could be achieved by incorporating two types of polymers in the nanocomposite formulation. The first is chitosan as a natural polymer having high and low molecular weight. The second type refers to in situ formed polyacylamide. Furthermore, addition of citric acid to the nanocomposite formulation is made.

Herein synthesis of the new colorants is based on intercalation of silicate layered nanocomposite (SLNC) in the dispersion of Blue vat/chitosan mix. SLNC is a natural clay known as montmorillonite (MMT- K10). Further development of the new colorant could be achieved via incorporation of nano metal oxides, viz. ZnO, CuO, TiO_2or nanosilver metal in the mix of the newly synthesized colorants.

Quaternary mixture was prepared by mixing in 100 ml distilled water. Indigo Blue Vat Dye (5 g), chitosan (5 g), MMT K10 (5 g) and nano metallic oxides of Zn, Cu,Ti (2g) or 20 ml of Silver suspension. It was then subjected to miniaturization via vigorous stirring using ultrasonic processor for 60 minutes at about 80°C. The particle sizes of new colorants resulting from mixing and miniaturization of the four components of the mix were measured and are shown in Table 1 and Fig. 1.

Particle size of the Quaternary Mix Based new colorants

Table 1 and Fig. 1 show that the particle size of the hybrid nanocomposite colorant obtained with the quaternary mixture is much higher before than after subjecting the mixture to sonication through ultrasound technology. It is logical that aggregates and/or agglomerates formed through mixing of the four components are disintegrated and brought down to the nanometers scale under the influence of the ultrasound technology. However, the magnitude of the fall in the particle size by sonication is a manifestation of the nature of the nanoparticles used. The largest difference in decrement in the particle size after sonication is observed with colorant containing nanocopper oxide and the least decrement is observed after sonication with colorant containing nano titanium oxide. Colorants containing either nano silver or nano Zinc oxide stand in mid-way position but with the certainty that the magnitude of decrement in the colorant containing nano Zn oxide due to sonication is lower than that of colorant containing nano silver. Particle sizes after sonication attain values of 15.10, 15.93, 11.9 and 5.8 nm for nano colorants containing TiO_2, Ag^0, ZnO and CuO nm respectively. Before sonication these colorants display values of 106.42, 217.17, 130.13, 318 nm.

The highest value of particle size recorded for colorant containing nano CuO before sonication could be ascribed to the presence of the colorant particles in the form of agglomerates where clusters of colorant particles are gathered to form larger agglomerates. During sonication these aggregate are exposed to the ultrasonic action resulting in breaking down these agglomerates, which, in turn, are dispersed as stable tiny particles in a colloidal solution. It is believed that the agglomerates of nano clusters are characterized by ease of formation of layer

TABLE 1. Dependence of particle size of new hybrid nanocomposite colorant brought about by mixing Indigo vat dye, MMT(K10), chitosan and either of nano metal on mode of interactions of the formulation components before and after miniaturization

Formulation components of new hybrid nanocomposite colorant	Particle size(nm)	
	Before miniaturization	After miniaturization
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 2 g **Nano titanium oxide**	106.42 nm	15.10
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 20 ml **Nano silver metal**	217.17 nm	14.93
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 2g **Nano zinc oxide**	130.13 nm	11.9
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 2g **Nano copper oxide**	318 nm	5.81

The four components of the formulation were dispersed in 100 ml distilled water.

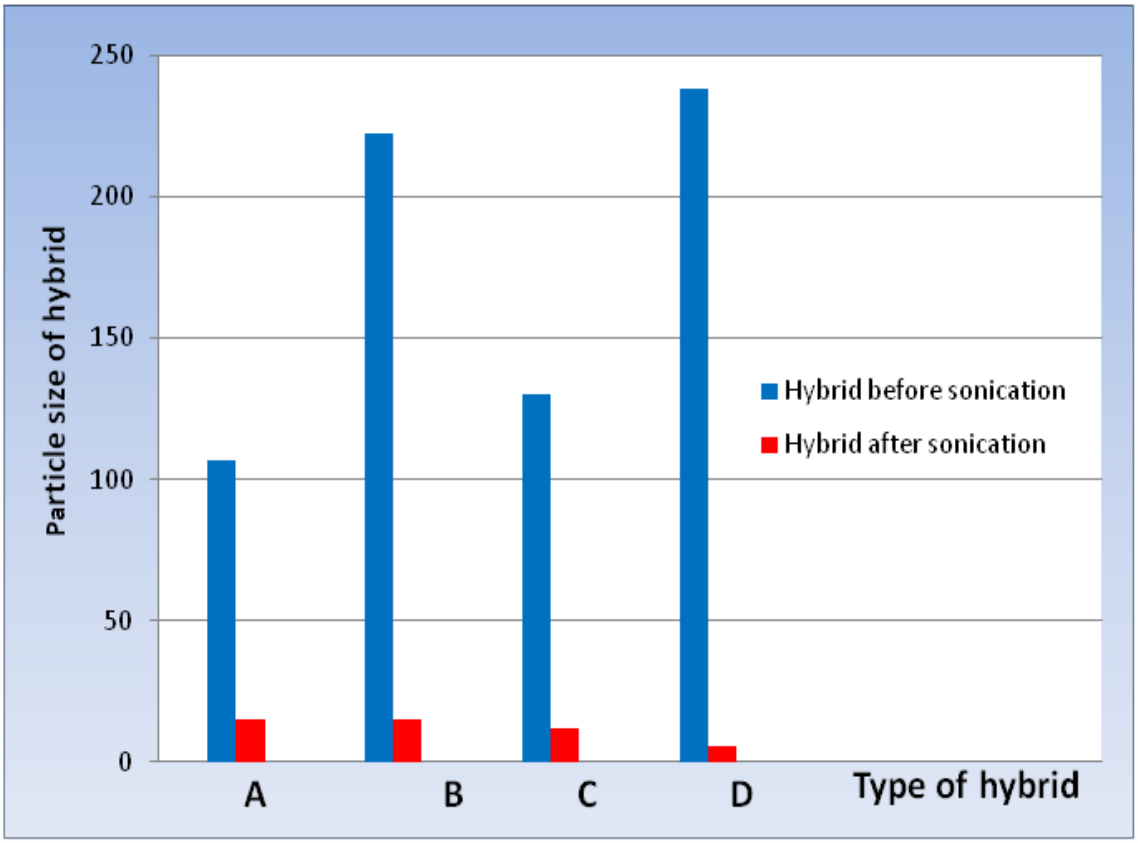

Fig. 1. Effect of using a mixture of chitosan + Indigo Blue vat dye + MMT(K10)+ either of nano metal as a new colorant on particle size of colorant before and after miniaturization through sonication

A) hybrid mixture of Indigo blue vat dye + MMT(K10) + chitosan (low molecular weight) +TiO_2NPs

B) hybrid mixture of Indigo blue vat dye + MMT(K10) + chitosan (low molecular weight) +AgNPs

C) hybrid mixture of Indigo blue vat dye + MMT(K10) + chitosan (low molecular weight) +ZnNPs

D) hybrid mixture of Indigo blue vat dye + MMT(K10) + chitosan (low molecular weight) +CuNPs

size and, liability to break down and disintegrate as compared with their aggregates mates. Such characteristic differences between agglomerates and aggregates are, indeed, responsible for the differences in the particles size observed among colorants fabricated using the quaternary mix under investigation.

Figure 2a shows the TEM image of the quaternary mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and TiO_2NPs(2g) before sonication. It is observed that the new hybrid quaternary mixture based colorant exhibits a wide scope of differences among the values of the particle size, which ranges from 7 to 173.4 nm with an average value of 106.42 nm. The particles display also different shapes indicating that the mixture still maintains its physical nature, i.e. very little or no chemical reaction occurred by mere mixing without sonication.

On the other hand, (Fig. 2b), discloses the particle size of colorant based on mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and TiO_2NPs (2g) after sonication. Evidently, the TEM micrograph is a manifestation of homogenous shape and small particle sizes as compared with its TEM micrograph before sonication. In addition, values of the particle sizes show no large differences as they only lie between 7.6 and 20.29 nm with an average value of 15.10 nm.

Figure 2c depicts the particle size of colorant based on a (mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and dispersion of AgNPs 20 ml) before sonication. It is clear that the particle sizes range from 10.20 to 594.82 nm, making an average particle size of 217.17 nm. It is also clear that the view of the TEM micrograph of these particles is not homogenous indicating lack of intimate association and interactions among the components of the quaternary mixture under investigation.

Figure 2d depicts the particle size of the colorant based on mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and dispersion of AgNPs (20 ml) after sonication, Obviously the particle sizes ranges from 10.65 nm to 26.62 nm with evidence of aggregation/ agglomeration, which in turn, implies that the nanoparticles sizes enjoy uniformity making an average particle size of 14.93 nm. Indeed majority of the particles acquire a uniform size.

Figure 2e shows TEM micrograph of colorant based on a mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and ZnONPs(2g) before sonication. The micrograph displays undefined view and the particles appear like aggregated layers and the particle sizes ranging between 5.57 nm to 218 nm with an average value of 130.13 nm.

Figure 2f illustrates the TEM micrograph of the particle sizes of colorant based on quaternary mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and ZnONPs(2g) but after being sonicated. Obviously, the particle size range between 3 to 40.91 nm with an average particle size of 11.9 nm. Figure 2f provides defined particles with much lower sizes than those observed before sonication. This reflects the influence of sonication on homogenizing while disintegrating the particles of the new colorant. The latter is formed as a result of interactions of the quaternary mixture components under the effect of sonication at the condition used.

Figure 2g shows TEM micrograph of the colorant based on a mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5 g) and CuONPs (2g) before sonication. The micrograph of this quaternary mixture appears non-homogeneous before sonication. The colorant particle size acquires a very wide range indicating the inconsistency of the four components in the mixture. Furthermore, the particle size ranges from 20 to 750 nm with an average particle size of 318 nm.

Figure 2h illustrates the TEM micrograph of colorant based on a mixture of Indigo blue vat dye (5 g), chitosan (5 g), MMT K10 (5g) and CuONPs(2g) after sonication. Uniform and beautiful distribution of the nanoparticles could be achieved. Indeed this average covers a wide distribution of size particles ranging from 5.2 to 9.2 nm. It is further noted that the nanoparticles exhibit a uniform spherical shape with a very broad particle size distribution and with little or no evidence of aggregation/agglomeration making an average particle size of 5.81nm. This small average particle size of the nanohybrid colorant is formed most probably due to interactions or intercalation between the quaternary mixtures components under the effect of sonication at the condition used.

Color Strength and Fastness of Cotton Fabrics Printed Using the New Nanocolorants

The aforementioned four quaternary hybrids before and after sonication were used in preparing 8 different printing pastes. Cotton fabrics were

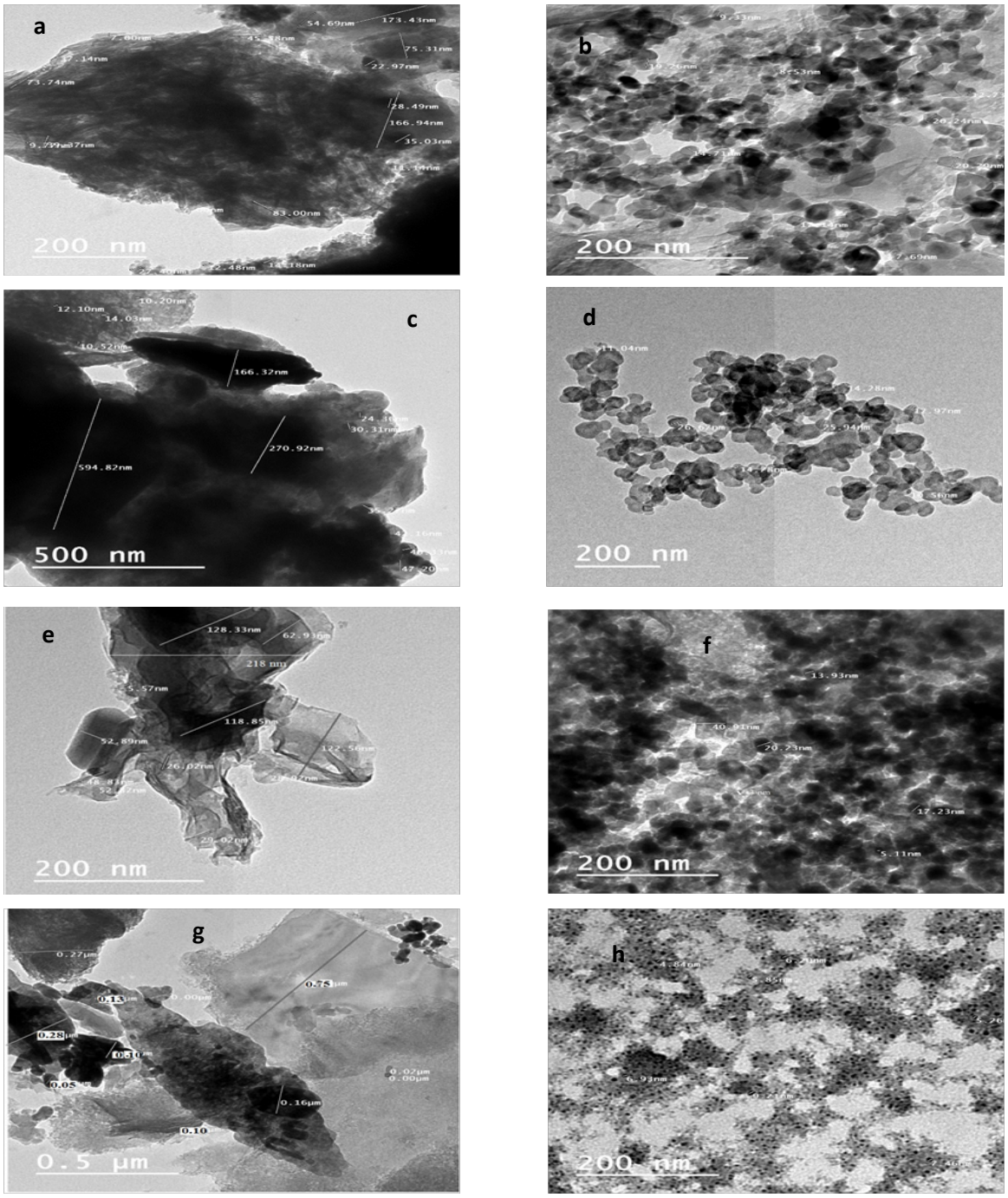

Fig. 2. TEM micrograph of different composite mixtures with different nanometal.

a) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (low molecular weight) / 2 g TiO_2NPs in100 ml H_2O before sonication

b) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (low molecular weight) / 2 g TiO_2NPs in100 ml H_2O after 60 min sonication at ca 80°C

c) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (high molecular weight) / 20 ml AgNPs in100 ml H_2O before sonication

d) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (high molecular weight) / 20 ml AgNPs in100 ml H_2O after 60 min sonication at ca 80°C

e) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (high molecular weight) / 2 g ZnONPsin100 ml H_2O before sonication

f) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (high molecular weight) / 2 g ZnONPs in100 ml H_2O after 60 min sonication at ca 80°C

g) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (high molecular weight) / 2 g CuONPs in100 ml H_2O before sonication

h) 5 g Indigo Blue Vat dye / 5 g MMT(K10) / 5 g chitosan (high molecular weight) / 2 g CuONPs in100 ml H_2O after 60 min sonication at ca 80°C

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 color fastness properties. The results obtained are given in Table 2.

It is clear (Table 2) that the K/S of the printed goods depends essentially on :(a) the composition of the quaternary hybrid (nanometals, in particular) (b) the particle size of the new hybrid colorant and (c) exposure to sonication.

Table 2 and Fig. 3 depict the effect of nature of the nanometals used in the mixture on the color strength (K/S) produced by the quaternary components mix of the new colorant before and after sonication on cotton fabrics. A perusal at the results would indicate that the increase in color strength (K/S) is very remarkable when the mixture was subjected to sonication in order to induce miniaturization of the particle size of the new colorant.

The lowest sonication effect on color strength (K/S) is observed when nano titanium oxide is present in the mixture; K/S attains values of 1.05 and 4.21 before and after sonication respectively with an increase in color strength of 300.9 %, meanwhile the size of the latter new hybrid is equal to 15.10 nm. The maximum decrease in particle size of the new hybrid composite nanocolorant containing nanocopper oxide attains a value as low as 5.81 nm. K/S displays value of 1.40 and 8.11 before and after sonication respectively with an increase in color strength of 479.28 %.

It is as well to report that cotton fabrics printed using a quaternary hybrid containing the nanoparticles follow the order: CuO>ZnO>Ag>TiO_2 with corresponding K/S values of 8.11, 5.32, 4. 61,

TABLE 2. Printing of cotton fabrics using new hybrid nanocomposite colorants based on mixture of chitosan + Indigo Blue vat dye + MMT(K10)+ along with either ZnO, CuO, Ag or TiO_2 nanomaterial before and after sonication.

Formulation components of new hybrid nanocomposite colorant	K/S		K/S Increase%
	Before sonication	After Sonication	
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 2 g **TiO_2NPs**	1.0**5**	4.21	300.95
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 20 ml **AgNPs dispersion**	0.71	4. 61	549.29
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 2g **ZnONPs**	1.19	5.32	347.05
Mixture of 5 g MMT (K10) +5 g Indigo blue vat dye +5 g chitosan (low molecular weight) + 2g **CuONPs**	1.40	8.11	479.28

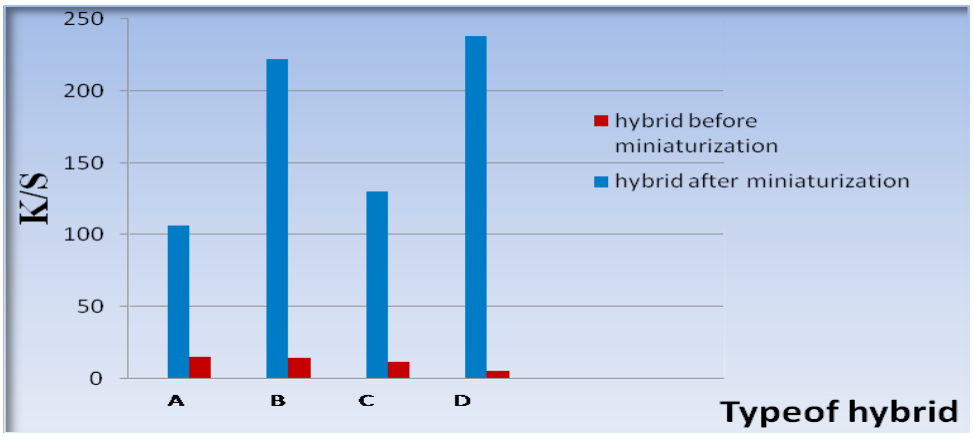

Fig. 3. Utilization of the new hybrid nanocomposite colorants based on a mixture of chitosan + Indigo Blue vat dye + MMT(K10) along with either the ZnONPs, CuONPs, AgNPs or TiO_2NPsin printing cotton fabric before and after their sonication.

Blank printed fabric with (Indigo blue vat dye +MMT(K10)+Chitosan low molecular weight)
A) hybrid mixture of Indigo blue vat dye + MMT (K10) + chitosan (low molecular weight) +TiO_2NPs
B) hybrid mixture of Indigo blue vat dye + MMT (K10) + chitosan (low molecular weight) +AgNPs dispersion
C) hybrid mixture of Indigo blue vat dye + MMT (K10) + chitosan (low molecular weight) +ZnONPs
D) hybrid mixture of Indigo blue vat dye + MMT (K10) + chitosan (low molecular weight) +CuONPs

4.21 as shown in Table 2 and Fig. 3.

The influence of sonication on the K/S is clear from Fig. 3 and Table 2 where it causes a remarkable effect on K/S. The percent increase in K/S after sonication attains values of 549.29, 479.28, 347.05 and 300.95 for the nanoparticles of Ag, CuO, ZnO and TiO_2 respectively.

Antimicrobial Activity

Antimicrobial Activity of Cotton Fabrics Printed Using the New Colorants

Table 3 summarizes the antimicrobial activity of cotton fabrics printed using new hybrids based on quaternary mixtures of Indigo blue vat dye, MMT(K10), chitosan and different nano metallic particles sonication.

The results shown in Table 3 reveal that, the most potent antimicrobial effect is viewed by sample containing AgNPsagainst B. cereus by 14.6 mm followed by sample containing ZnONPs by 14.2 mm as axial zone of inhibition respectively, followed by samples contain CuONPsand ZnONPsthat showed inhibition against E. coli 14.2 mm as axial zone of inhibition. Whereas, sample treated with the new colorant containing ZnONPsexhibits antibacterial effects towards Salmonella by 14.1 mm as axial zone of inhibition. The most effects observed in Table 3 is sample treated with ZnO that affected Salmonella, B. cereus and E. coli.

Antimicrobial activity of fabric printed using new hybrid composite nanocolorant based on the quaternary mixture after sonication

Table 4 summarizes the antimicrobial activity of cotton fabrics printed using new hybrids based on quaternary mixtures of Indigo blue vat dye, MMT(K10), chitosan along with different nano metallic materials after sonication.

Results in Table 4 depict that the most potent antimicrobial effect is dispersed by sample containing AgNPs.This particular sample reveals antifungal effect against A. niger by 14.5mm as axial zone of inhibition. Whereas, sample containing ZnONPs causes weariness to E. coli growth by 14.1 mm as axial zone of inhibition.

On comparing Table 3 and 4 is clear that sonication has a remarkable effect on the behavior of the fabrics printed with printing pastes containing different nano metallic materials. The activity towards antimicrobial decreases by sonication. Antibacterial activity could only be observed with the mixture containing nano silver upon using A.Niger and a mixture containing nano Zn upon using E.coli; the antimicrobial effect speaks of values of 14.5and 14.1 respectively. The decrease in the antimicrobial effect after sonication is also observed in case of mixing MMT(K10) / indigo Blue vat dye / Chitosan (low or high molecular weight) after sonication.

It is understandable that the antibacterial activity conferred on the printed fabrics using the new colorant based on mixture of Blue vat /MMT- K10/chitosan/nano metallic materials like (Ag, ZnO, CuO or TiO_2) is mainly due to these nanomaterials and chitosan to

TABLE 3. Antimicrobial activity of fabric printed using new hybrid prepared using before sonication .

Samples	A. Niger	Salmonella	B. cereus	E. coli	P.aeruginosa
1	-	-	-	14.2	-
2	-	14.1	14.2	14.2	-
3	-	-	-	-	-
4	-	-	14.6	-	-
5	-	-	-	-	-

1) Fabric printed using new colorant based onhybrid mixture of Indigo blue vat dye / MMT(K10) / chitosan (low molecular weight) / CuONPs
2) Fabric printed using new colorant based on hybrid mixture of Indigo blue vat dye / MMT(K10) / chitosan (low molecular weight) / ZnONPs
3)Fabric printed using new colorant based on hybrid mixture of Indigo blue vat dye / MMT (K10) / chitosan (low molecular weight) /TiO_2NPs
4)Fabric printed using new colorant based on hybrid mixture of Indigo blue vat dye / MMT (K10) / chitosan (low molecular weight) / AgNPs
5)Blank printed fabric printed using a mixture containing Indigo blue vat dye / MMT(K10) / Chitosan low molecular weight

TABLE 4. Antimicrobial activity of fabric printed using hybrid composite new nanocolorant after being sonicated.

Samples Printed fabric	A. Niger	Salmonella	B. cereus	E. coli	P.aeruginosa
1	-	-	-	-	-
2	-	-	-	14.1	-
3	-	-	-	-	-
4	14.5	-	-	-	-
5	-	-	-	-	-

Fabric printed with colorant prepared using
1) hybrid composite based on a mixture of Indigo blue vat dye / MMT (K10) / chitosan (low molecular weight) / CuONPs
2) hybrid composite based on a mixture of Indigo blue vat dye / MMT (K10) / chitosan (low molecular weight) / ZnONPs
3) hybrid composite based on a mixture of Indigo blue vat dye / MMT (K10) / chitosan (low molecular weight) / TiO_2NPs
4) hybrid composite based on a mixture of Indigo blue vat dye / MMT (K10) / chitosan (low molecular weight) /AgNPs
5) Blank: cotton fabric printed using a mixture of MMT +Vat dye / Chitosan (low molecular weight)

some extent. It is very likely that sonication enhances the magnitudes of interactions of the components of the new colorant including the nanometallic particles with each other. Involvement of the nano metals and chitosan in such interactions would detract from their effect as antimicrobial agent. Consequently, the antimicrobial activity of the printed fabric decreases by sonication.

Morphology of Fabrics Printed using the New Nano Colorants

SEM micrographs of cotton fabrics printed using quaternary mixture (the Indigo blue vat dye/MMT(K10)/chitosan of low molecular weight) and nano (Ti,Zn, Cu)oxide and nano silver suspension before miniaturization through sonication are shown in Fig. 4 (b, d, f and h). On the other, the corresponding SEM micrographs for cotton fabrics printed using these mixtures after sonication are illustrated in Fig. 4 (a, c, e and g). It is observed that fabrics printed using the quaternary mixture nanoparticles after sonication acquire 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.

Color fastness properties

The overall color fastness properties, i.e. fastness to washing, to 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 5. It is clear that color fastness to washing and perspiration (acidic and alkaline) are not affected by using hybrids before and after sonication. Different situation is encountered with respect to fastness to rubbing. The prints of the new hybrid after sonication display much better rubbing fastness properties than those before sonication. By virtue of their nano sized structure the new hybrid particles are small enough to diffuse into fibers and, in so doing, they create high fastness properties, in particular, to opposite to hybrids particles before sonication which are highly fixed on the fiber surface by the binder.

Conclusion

New multifunctional smart nano colorant were synthesized through intercalation/exfoliation of natural clay known as montmorillonite K10 into aqueous dispersion of the Indigo vat dye and chitosan and metallic nanoparticles of either CuO, ZnO, TiO_2 or silver. Thus we were dealing with aqueous dispersion based on quaternary mixtures each of which comprised the Dye/MMT K10/ chitosan/Nanometal system. This system was subjected to ultrasound technology (i.e. sonication) to give rise to ultrafine nanoparticles through interactions among the system components aided by intercalation /exfoliation of the silicate layered nanocomposite (SLNC) in the dye/chitosan/nano metal aqueous dispersion. Dependence of the particle size of the nanocolorant and the color strength of prints obtained thereof as ultimate product (i.e. new colorant) of such interactions was verified. The new nanocolorant depends also on the nature of the metal nanoparticles and so does their ability to effect antibacterial finishing. Morphology of the nanocolorants was also examined before and after sonication using SEM. Results obtained clarified that the particle sizes of the hybrid composites new colorants are

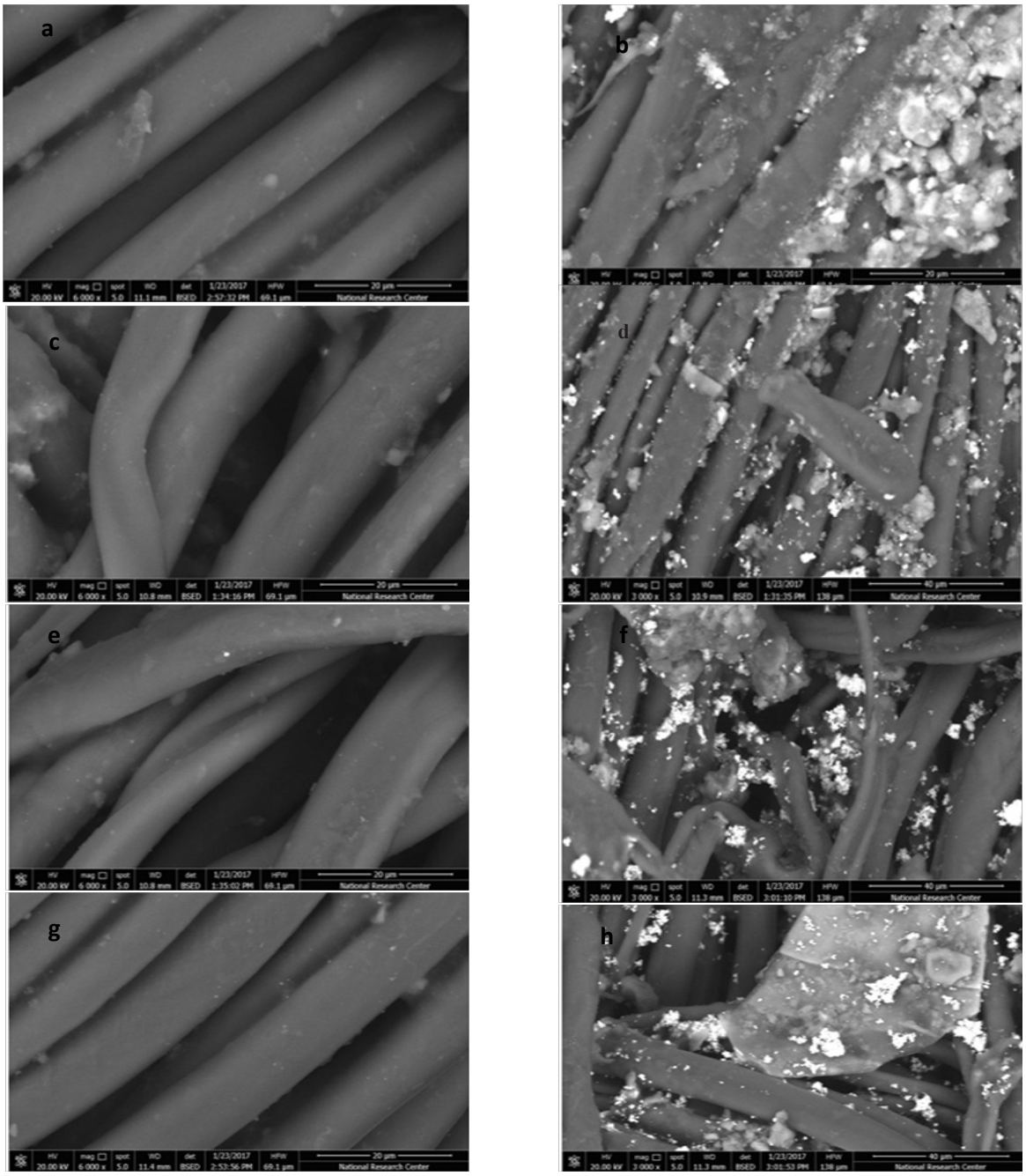

Fig. 4. SEM micrograph of the treated Fabric with different formulation.

a) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / TiO2NPs (2 g) / 100 ml H2O after being sonicated for 60 min at ca 80ºC

b) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / TiO2NPs (2 g) / 100 ml H2O before sonication

c) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / 20 ml AgNPs / 100 ml H2O after being sonicated for 60 min at ca 80ºC

d) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / 20 ml AgNPs / 100 ml H2O before sonication

e) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / ZnONPs (2 g) / 100 ml H2O after being sonicated for 60 min at ca 80ºC

f) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / TiO2NPs (2 g) / 100 ml H2O before sonication

g) new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / CuONPs (2 g) / 100 ml H2O after being sonicated for 60 min at ca 80ºC

h)new nanocolorant synthesized using a mixture of Indigo Blue Vat dye (5 g) / MMT(K10) (5 g) / chitosan (low molecular weight) (5 g) / CuONPs (2 g) / 100 ml H2O before sonication

TABLE 5. Color strength K/S and fastness properties of cotton fabric printed using the new nanocolorants.

Formulation components of new hybrid colorant	Fastness properties									
	Effect of sonication	Color Strength (K/S)	Washing fastness at 60°C		Rubbing fastness		Perspiration fastness			
							Acidic		Alkali	
			St.	Alt.	Wet	dry	St.	Alt.	St.	Alt.
Colorant I Basedon Indigo blue vat dye+ MMT(K10)+chitosan (low molecular weight) +2 g TiO_2-NPs	Before Sonication	1.05	4 5	4 5	2 3	3	4 5	4 5	4 5	4 5
	After Sonication	4.21	4 5	4 5	34	4 5	4 5	4 5	4 5	4 5
Colorant II Basedon Indigo blue vat dye+ MMT(K10)+chitosan (low molecular weight)+AgNPs	Before Sonication	0.71	4 5	4 5	2 3	3	4 5	4 5	4 5	4 5
	After Sonication	4. 61	4 5	4 5	4	4 5	4 5	4 5	4 5	4 5
Colorant III Basedon Indigo blue vat dye + MMT(K10)+chitosan (low molecular weight)+ ZnONPs	Before Sonication	1.19	4 5	4 5	2	2 3	4 5	4 5	4 5	4 5
	After Sonication	5.32	4 5	4 5	3	4 5	4 5	4 5	4 5	4 5
Colorant IV Basedon Indigo blue vat dye+ MMT(K10)+chitosan (low molecular weight)+CuONPs	Before Sonication	1.40	4 5	4 5	2	2	4 5	4 5	4 5	4 5
	After Sonication	8.11	4 5	4 5	4	4 5	4 5	4 5	4 5	4 5

where Alt. is Alternation and St. is Staining;

exceedingly higher before than after sonication. In contrast, color strength of cotton prints of the new colorants are far higher after than submitting the new colorants to sonication. Color fastness of the prints to rubbing are lower when printing was carried out using new nanocolorants 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.

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ابتكار ألوان مطورة لاكساب أقمشة القطن خواص وظيفية متعددة مثل الطباعة والتجهيز ضد البكتريا في مرحلة واحدة

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تناول البحث الحالي اجراء دراسة علمية/معملية /منظمة، استهدفت تحضير ألوان نانومترية زكية مطورة من خلال التداخل التفاعلي للطمي الطبيعي المعروف باسم (مونتمورالونيت) مع المستحلب المائي المحتوي على صبغة الانديجو الزرقاء والكيتوزان والمواد غير العضوية النانومترية الممثلة في جسيمات أكاسيد النحاس والتيتانيوم والزنك وعنصر الفضة تحت تأثير الموجات فوق الصوتية. بمعني أننا نتعامل مع مستحلبات مائية تقوم على مخاليط رباعية، يحتوي كل من هذا المخاليط على الصبغة والطمي والكيتوزان وأحد المواد غير العضوية النانومترية المذكورة

تم تعريض تلك المخاليط الي تكنولوجيا الموجات فوق الصوتية، كما سبق التنويه، لتعطي في النهاية جسيمات نانومترية غاية في الدقة من خلال التداخل التفاعلي والتفاعلات الأخرى فيما بين مكونات الخليط ومدعمة بتجاوب وتجانس الطمي الطبيعي- كما ثبت في دراسات سابقة لهذه الدراسة – فمثلا في التداخل التفاعلي لكومبوزيت السيلكا(المكون الأساسي للطمي الطبيعي) مع الصبغة في المستحلب المائي إضافة الي تفاعلات فيما بين كومبوزيت السيلكا والكيتوزان وجسيمات المادة العضوية النانومترية.

تم تعيين حجم جسيمات اللون الناونومتري وشدة اللون للمطبوعات التي استخدم في طباعتها، كما نم التأكيد علي أن اللون النانومتري الجديد يعتمد علي تفاعلات الصبغة والطمي والكيتوزان والمادة غيرالعضوية النانومترية علي النحوالمذكور عاليه.

تعتمد خواص اللون الجديد علي طبيعة المواد غير العضوية النانومترية وكذ لك الحال بالنسبة لتأثير تلك المواد علي أحدث التجهيز المضاد للميكروبات.

تم فحص المورفولوجي للألوان النانومترية قبل وبعد التعريض للموجات فوق الصوتية باستخدام) توضح النتائج أن حجم الجسيمات لكومبوزيت الألوان الجديدة أكبر بكثير قبل التعريض للموجات الصوتية عن بعدها. وعلي النقيض فإن شدة اللون لأقمشة القطن المطبوعة باستخدام الألوان الجديدة أكثر بكثير بعد التعريض للموجات فوق الصوتية.

ثبات عينات أقمشة القطن المطبوعة للاحتكاك أقل قبل تعريض اللون للموجات فوق الصوتية.

كما أوضحت النتائج أن مشاركة المواد غير العضوية النانومترية في تفاعلات مع المكونات الأخري للخليط الرباعي (موضوع الدراسة) أثناء التعريض للموجات فوق الصوتية تقلل من قدرتهم علي إحداث النشاط الحيوي ضد الميكروبات لأقمشة القطن المطبوعة بالألوان الجديدة.