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## Fabrication of radically new colorants based on Indigo Blue Vat Dye/ polymer/layered Silicate intercalated nanocomposites induced cotton prints with Batik and Denim effects

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Our research outputs lead currently to a radically new base for innovation of a number of ultrafine colorants that are characterized by their involvement in the textile structure through mechanical trapping mechanism in addition to diffusion mechanism. These printing mechanisms are behind the high colour fastness and improved colour strength of the prints and also avoiding the lengthy steps involved in reduction and oxidation of the indigo vat dye associated with their harm effect on environment. The innovation comprises intercalation of indigo blue vat dye with the silicate layered nano-composite which is a natural clay known as Montmorillonite (MMT-K10). Four innovative hybrid nano-composites colorants are synthesized as per the following mixtures: (1) indigo vat dye/MMT-K10/chitosan mix; (2) Indigo vat dye/MMT- K10/in situ formed polyacrylamide mix; (3) Indigo blue vat dye/MMT-K10/citric acid mix and (4) Indigo blue vat dye/MMT- K10/chitosan/citric acid mix. The antibacterial ability of these ultrafine colorants to produce prints on cotton textiles as well as fastness properties and colour strength of these printed fabrics are reported.

**Keywords:** New colorant, Hybrid nano-composite, Mechanisms of printing, Batik like design, Jeans effect, MMT- K10 and Indigo Blue Vat dye.

### INTRODUCTION

In the preceding work, we have disclosed that hybrid nano-composite new colorant constitutes a new development in textile coloration and finishing. The new colorant is formed through intercalation of Indigo Blue Vat dye with the silicate layers of a clay known as montmorillonite under the miniaturization action of sonication. The term "nano-composite" is commonly used in two distinct areas of material science, namely,

ceramics and polymers. The typical nanomaterial is clay. AATCC Test Method (15-2013), (Aboelnaga et al.,2018) Other nano-materials such as graphite, single - wall and multi - wall carbon nanotubes, silica and titania are also available. (Morgan and Gilman ,2003)

(Hassabo et al., 2018), (Hassabo 2014), (Hassabo 2015), (Hassabo 2005).

Polymer - clay interactions or polymer layered silicates are the most common group of nano-

composites. They were extensively investigated during the sixties and the early seventies but the real exploitation of this technology started in 1990 when Toyota researchers (Hassabo 2011) and (Hebeish, et al.,2018) discovered the possibility to build a nanostructure from polymer and organophilic clay. Their new material based on polyamide 6 and organophilic montmorillonite exhibited at low clay content (4 wt. %) dramatic improvement in mechanical properties, barrier properties and thermal resistance as compared with pristine matrix. Since then, polymer - clay composites are divided into three general categories:

Conventional composite (immiscible or micro composites) in which the clay is not nano dispersed and essentially behaving as a micron sized filler( Hebeish, et al.,2017)

Intercalated nano-composite, in which the clay is completely nano-dispersed and the clay layers remain in registry.

Exfoliated nano-composite or delaminated nano-composite, which also display good nano dispersion but the registry between the clay layers is lost. This must induce dramatic changes in mechanical and physical properties(Waly, et al.,2012), (Mohamed, et al.,2016)

Another category can be defined which makes a distinction between fully exfoliated nano-composites and intercalated nano-dispersion. This category can be called the highly delaminated nano-composites. (Mohamed, et al.,2017)

In fully exfoliated nano-composites, clay layers are well dispersed as 1 nm thick no interacting clay layers. However, in highly delaminated nano-composites, stacks of about 2-20 nm layers of clay are well dispersed in the polymer matrix. In this type, the XRD Intensity of the ordered structure disappears despite the fact that stacked layers still exist. (Okada et al.,1990), (Waly et al.,2006)

The generic term "layered silicates" refers to natural clays but also to synthesize layered silicates such as magadite, (Waly et al.,2008) Mica, limonite (AATCC Test Method (16-2004),2005and fluorohectorite. AATCC Test Method (61-2007), Both natural clays and synthetic layered silicates are successfully employed in the synthesis of polymer nano-composites.

Layered silicate clays, because of their chemically stable siloxane surface, high surface areas, high aspect ratios and high strengths are most widely used for the formation of organic - inorganic nano-composites.( AATCC Test Method

2008)

Their high aspect ratios and high strengths make them reinforcing elements as well. Their two particular characteristics exploited for the formation of nano-composites are:

a-The rich intercalation chemistry used to facilitate exfoliation of silicate nano-layers into individual layers. As a result, an aspect ratio between 100- b-1000 can be obtained (compared to poorly dispersed particles). Layer exfoliation maximizes interfacial content between organic and inorganic phases. .( AATCC Test Method 2008)

The ability to modify finely their surface chemistries through ion exchange reactions with organic and inorganic cations.

Very recently, we have succeeded to establish novel technology for synthesis of radically new nano-colourants based on hybrid nano-composites. (Gürses et al.,2016)

The latter could be achieved through mixing indigo blue vat dye with natural clay known as montmorillonite K10 (MMT- K10) followed by submitting the mix to sonication. The hybrid nano-composites new colorants were applied as nano-pigment in printing on various textile fabrics including, interalia, cotton, wool, silk, polyester and nylon. The new colorants displayed better colour strength, fastness and performance than the indigo blue vat dye and commercial pigments. It is believed that the new nano colorants create positive colour attributes because diffusion mechanism for coloration is operated in addition to the mechanical trapping mechanism traditionally operated with the vat dye. ( Muzny et al.,1996)

As a continuity of the above, we have also studied the best practice (formulation/condition) for processing new hybrid nanocomposites as new colorants by mixing the dye and the clay followed by subjecting the mix to sonication. Such a processing was conducted under different concentrations of both the clay and the dye and their ratio in the mix, nature of the clay and sonication time and the onset of this on the nano-size of the new colorant and its printability. Having obtained the results of each variable, optimal processing conditions for fabrication of the new nano-colourant could be achieved. Nano-colourants synthesized as per the optimal processing conditions exhibit better performance properties as compared with the conventional pigment. Here again, it is logical to assume that creation of the colour and colour fastness are designed to a diffusion mechanism and a

mechanical trapping mechanism.

Current work is concerned with further development of the new colorants through involvement of polymeric materials in the indigo vat dye/MMT (K10) formulation. Polymers used encompass low and high molecular weight chitosan, and in situ polymerization of acrylamide. Citric acid is also used in the fabrication formulation of the new hybrid nano-composite colorants. Application of the latter in printing of cotton textiles is made. Testing, analysis and characterization of the new colorants are reported. Also reported are colour strength and overall fastness properties.

## MATERIALS AND METHODS

### Materials

Cotton fabrics (Mill desized, scoured, bleached and mercerized; 100 g/m<sup>2</sup>) were supplied by Misr Company for Spinning and Weaving, El-Mahalla El-Kubra, Egypt. High viscosity sodium alginate from brown algae, manufactured by Fluka Chemical Company, was used as a thickening agent, for printing.

Commercial Indigo Vat dye was kindly supplied by Dystar, under the commercial name: Vat blue 40 % solution under Trade name INDIGO (ACua, Fran, ICI).

Montmorillonite K10 (MMT-K10; H<sub>2</sub>Al<sub>2</sub>(SiO<sub>3</sub>)<sub>4</sub>-nH<sub>2</sub>O; 274-324 g/mol) and Chitosan, low and high molecular weight were manufactured by ACROS Organics were used.

Commercial Binder, namely, EBCA PRINT TB, manufactured by Egyptian British Company was used. Sodium hydroxide, sodium chloride, L-histidine monohydrochloride monohydrate, sodium di-hydrogen orthophosphate, di-sodium-hydrogen orthophosphate, acrylamide, potassium persulphate and citric acid were of laboratory grade chemicals.

### Synthesis

#### Preparation of Innovative Nanocolourant Based on Indigo Blue Vat - MMT K10 - Chitosan Mix using Ultrasonic Processor

MMT K10 (5 g) was mixed together with 5 g Indigo Vat dye and 5 g chitosan (either low or high molecular weight) in 100 ml water. The dye/MMT (K10)/chitosan mix was submitted to ultrasonic Processor for 60 min at ca 800°C.

#### Preparation of the Innovative Nanocolorant Based on Nano Indigo Vat colorant in admixture with MMT (K10) and insitu Formed Poly(acrylamide) using Potassium Persulphate as Initiator

Indigo Vat dye in admixture with MMT (K10) and acrylamide and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were subjected to miniaturization using Ultrasonic Processor followed by using the so prepared nanocomposite in printing of Cotton fabrics .Hence, 5gm of Indigo blue Vat dye was mixed with 5 g MMT (K10), 3 g acrylamide and 1 g per sulphate in 100 ml distilled water. This mixture was subjected to sonication via stirring in Ultrasonic Processor for 60 minutes at 80°C.

#### Mixing Indigo Blue Vat dye with MMT (K10) and citric acid

5 g of Vat dye, 5 g MMT (K10) and 3 g citric acid were mixed well then added to 100 ml distilled water. Thus obtained mixture was miniaturized using the Ultrasonic Processor for 60 min at 80°C.

#### Mixing Indigo Blue Vat dye with MMT (K10) and Citric Acid along with Chitosan (low molecular weight )

5 g of Vat dye, 5 g MMT (K10) and 3 g citric acid and 5 g chitosan (low molecular weight) were well mixed then added to 100 ml distilled water. The so obtained mixture was subjected to miniaturization by using Ultrasonic Processor for 60 minutes at 80°C.

#### Preparation of printing paste

The printing pastes were prepared according to the following recipe:

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. Colorant represents commercial vat dye (5 g) in admixture with one of the following mixture a) 5 g MMT (K10) together with 5 g chitosan (low and high molecular weight ), b) mixing 5 g MMT (K10) with 3 g acrylamide and 1 g potassium persulphate for in situ polymerization of

acrylamide, c) 5 g MMT (K10) and 3 g citric acid and d) 5 g MMT (K10), 3 g citric acid and 5 g chitosan (low molecular weight).

\*\* Thickener was used at a concentration of 2.5%

\*\*\* Binder was used at a concentration of 5 g/100 ml water

**Control sample, was 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 follows:**

<b>Colorant *</b>	20 g
<b>Glycerine</b>	6 g
<b>Thickener (Sodium alginate) **</b>	50 g
<b>Potassium carbonate</b>	16 g
<b>Rongalite C</b>	2.5 g
<b>Distilled water</b>	Y
<b>Total</b>	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% Printing of Cotton Fabrics with commercial Vat dye alone or in combination with MMT before and after being subjected to miniaturization via sonication were performed

### Printing technique

All the printing pastes were applied to cotton fabric according to the conventional screen printing method. Prints were then subjected to fixation at 160°C for 3 min except the (control sample) was subjected to fixation by steaming at 120°C for 15 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).

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 air at room temperature. The average diameter of new nano-colourant was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs. (Gilman et al.,2000). (Triantafillidis, et al.,2002) (Gilman et al.,2000)

### Scanning Electron Microscopy (SEM)

SEM studied were carried out 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.

### Ultrasonic Processor

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 in order 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 ± 100 HZ).

### Elemental Analysis

AXIOS advanced, Sequential WD-XRF Spectrometer, Panalytical, 2005 was used to estimate the elemental analysis. The Axios is a sequential instrument with a single goniometer based measuring channel, covering the complete measuring range. The instrument is microprocessor controlled from an external computer, running an analytical software package.

Colour measurements [(Triantafillidis, et al.,2002), (Gilman et al.,2000) ,(Kubelka and Munk,1931), ). (de Tacconi et al.,1998), (Yoonessi et al.,2004), (Abo-Shosha et al.,2009) (El-Naggar et al.,2017), (M. A. B., G. J. W., and J. C.L.,2000), (Mehta et al.,1984)

The colour strength and whiteness degrees of the printed samples were evaluated by Hunter Lab Ultra Scan PRO. (Hunter Lab Ultra Scan PRO (USA, 2007).

The colour intensity ( $\square E$ ) and the relative colour strength ( $K/S$ ) of the printed cotton fabrics was measured and assessed by applying the Kubelka–Munk equation as follow: (Wang et al.,2001)

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_o)^2}{2R_o}$$

where  $K$  is the absorption coefficient,  $S$  is the scattering coefficient,  $R_o$  is the reflectance of uncoloured (white) sample, and  $R$  is the reflectance of coloured sample.

Fastness properties (Gilman et al.,2000), (Gilman et al.,2000) (Yoonessi et al.,2004), (Abo-Shosha et al.,2009), (Lan and T. Pinnavaia1996) , (Kojima et al.,2011) (Cai et al.,1999)Wang and Pinnavaia (1998)

#### Colour fastness to washing

The colour fastness to washing was determined according to the AATCC Test method 61- 1975 using Launder-Ometer. The specimens (5 × 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/l soap and 2 g/l sodium carbonate using a material to liquor ratio 1:50 .The bath was thermostatically adjusted to 95°C. The test was run for 45 min at 42 rpm. The samples were then removed, rinsed twice in 100 ml bath of water at 40°C for one minute with occasional stirring or hand squeezing ,sourcing in 100 ml of 0.014% solution of acetic acid for one minute at 27°C, rinsing again for one minute in 100 ml water at 27°C followed by drying. [26]

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. [34] 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.

The evaluation was done using the Gray Scale for staining.

#### 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.

#### Colour fastness to perspiration (Kojima et al.,2011)

Two artificial perspiration solutions were prepared as follows:

**Acidic solution:** L. Histidine mono-hydrochloride mono hydrate 0.5 g, sodium chloride 5.0 g, sodium di-hydrogen orthophosphate 2.2 g, were dissolved in 1L 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 1L distilled water. Finally the pH was adjusted to pH 8 by NaOH solution 0.1 N.

The coloured specimen 5 × 4 cm was sewed between two pieces of uncoloured specimens, (so that an area of 5 × 1 cm of the coloured cloth is not in contact with the specimen) to form a composite specimens. The composite sample was then immersed (for 15 - 30 min) 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°C for 4 h.

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

#### Microbiological tests

All types of introduced samples (fabric printed with colorant prepared) were cut into square pieces of about 1 cm<sup>2</sup> and classified into 5 tested groups due to research authors. All sample pieces were sterilized by placing 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  $10^6$  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 was about 13 mm) zone of inhibition around each sample pieces imbedded on the inoculated agar surface at 30°C to the nearest mm.

The most of microorganisms used were ATCC registered strains except *Bacillus cereus* that was local isolate obtained from Agric. Microbiology Department, National Research Centre; Egypt. The used microorganisms were included Test microorganisms: *Streptococcus pyogenes* (19615), *Escherichia coli* (25922), *Pseudomonas aeruginosa* (27853), *Aspergillus niger* (6275) and *Bacillus cereus*.

## RESULTS

In our previous work, we have disclosed that the shape size and printability of the newly synthesized hybrid nanocomposite colorant depends upon the formulation and concentration of each component of this formulation as well as processing conditions. Components of the formulation were Indigo Blue vat dye and a natural clay called montmorillonite. Both the dye and the clay were mixed then miniaturized using ultrasound technology. Also studied were the effect of nature of clay, duration of the sonication and the dye/clay ratios on the size and printability of the as processed new colorant. Indeed the latter was created through intercalation of the dye with the silicate layers of the clay to yield nano-colored materials with unprecedented properties. (Wang and Pinnavaia 1996).

In the present work, experiments are designed to involve different polymeric components in the new colorant formulation with a view to solicit more advanced coloured hybrid nano-composites. These advanced colorants are anticipated to bring into focus cotton textiles having colour, thermal stability, dimensional stability, microbial activity, etc. Two types of polymeric components are incorporated in the nano-composite formulation; the first is Chitosan as a natural polymer having high molecular weight (HMwt) and low molecular weight (LMwt). The second type refers to in situ polymerization of acrylamide. Furthermore, addition of Citric acid to

the formulation components was also studied. Results obtained along with appropriate discussion are given below.

### Novel Colorants Nanocomposites Based on the Intercalation and the delamination of MMT (K10) in the Indigo Vat Dye/chitosan Dispersion

A tertiary mixture of Indigo blue vat dye (5 g), chitosan of low and high molecular weight (5 g each) and MMT K10 (5 g) was prepared in 100 ml of distilled water. It was then subjected to miniaturization via vigorous stirring using ultrasonic processor for 60 minute at about 80°C. The particle sizes of pure chitosan having high and low molecular weights before and after miniaturization are shown in Table 1.

Results of Table 1 show that the particle sizes of the hybrid nanocomposite colorant is much higher before than after being subjected to ultrasound technology; the latter disintegrates the colorant and brings them down to the nano-meter scale sizes. Similar situation is encountered with respect to the chitosan sizes before and after sonication irrespective of the molecular weight of chitosan. Nevertheless, the decrease in particle size is greater in case of low than higher molecular weight chitosan, indicating that the low molecular weight chitosan is more susceptible to miniaturization by sonication than dose chitosan of high molecular weight. As a matter of fact the tertiary mixture of the Indigo blue vat dye, MMT (K10) and chitosan of low molecular weight produces a new colorant the particle size of which attains a value equal to 21 nm. This is against a value of 55 nm obtained with the corresponding mixture containing high molecular weight chitosan. This could be interpreted in terms of greater ability of low molecular weight chitosan to enter in the layered silicate stack of MMT K10 and to diffuse therein, then intercalate through intimate association and interactions. In is likely that with such molecular interference, the resultant hybrid nano-composite colorant is more amenable to disintegration and miniaturization than those based on high molecular weight chitosan.

Figure 1-a illustrates TEM micrograph of the particle size of the tertiary mixture (the dye + MMT (K10) + chitosan of high molecular weight) before miniaturization through sonication. As is evident TEM micrograph exhibited different particle sizes ranging from 25.29 to 408.59 nm with an average value of 201.42 nm. The wide range of the particle sizes of the said mixture signify the non-uniformity, non-homogeneity and lacking factor

affecting or giving a tertiary structure for molecular arrangement of the mixture components. This indeed, could be achieved through submitting the mixture to miniaturization via sonication as shown under.

Figure 1-b shows the particle sizes of the tertiary mixture under investigation after being subjected to ultra-sonication processor. The latter exerts uniformity, homogeneity and miniaturization of the mixture which acquires a particle size

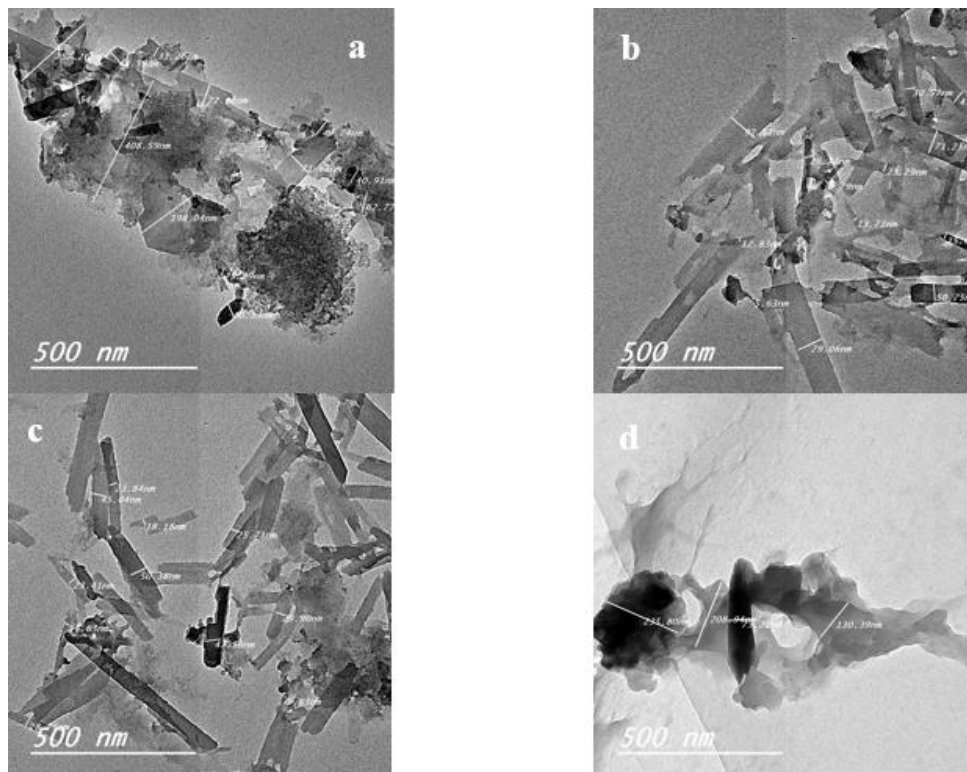
ranging from 5.36 to 92.51 nm with an average value of 9.5 nm. Narrowing the range of values of the particle sizes along with their reduced average values call for involvement of the three components of the mixture in chemical reactions within the intercalation of the finely dispersed dye and chitosan in the layered silicate of MMT (K10).

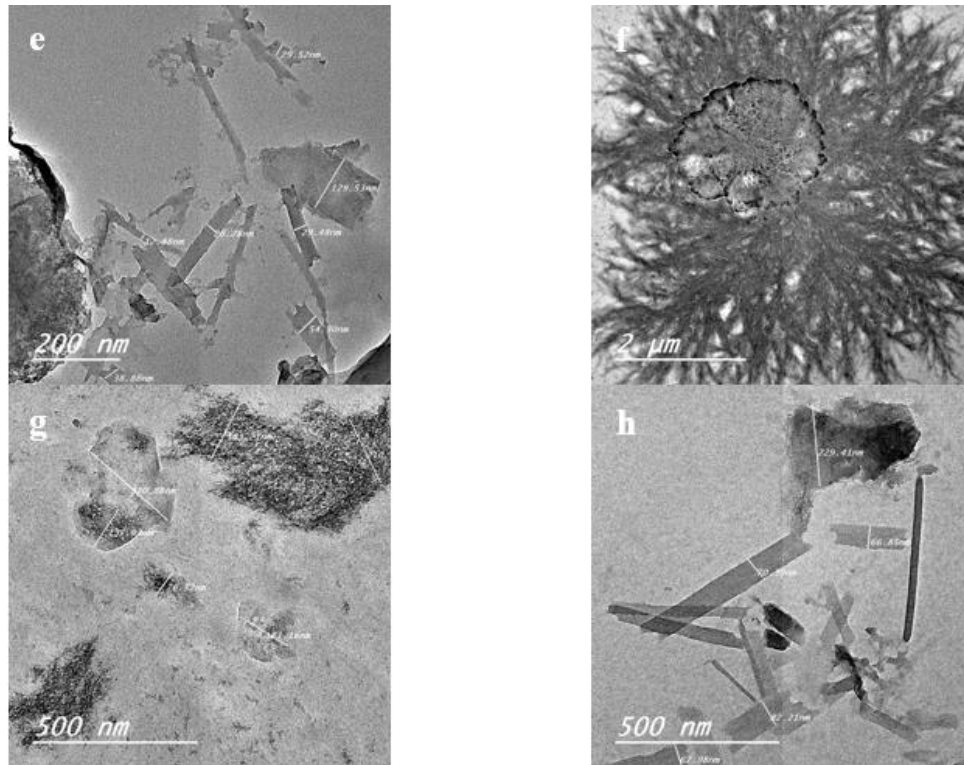
**Table 1: Particle size of new hybrid nano-composite formulation before and after miniaturization**

Formulation of new hybrid nano-composite colorant	Components				Particle size (nm)	
	chitosan		MMT (K10)	Indigo vat dye	Before miniaturization	After miniaturization
	H.Mwt	L.Mwt				
A	5 g	-	-	-	202	102
B	5 g	-	5 g	5 g	201	55
C	-	5 g	-	-	166	55
D	-	5 g	5 g	5 g	178	21

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

The three components of the formulation were dispersed in 100 ml distilled water. The same holds true for preparation of chitosan dispersion.





**Figure 1: TEM micrograph of different formulations before and after sonication**

- a) 5 g Indigo Blue Vat dye, 5 g MMT (K10) and 5 g H. Mwt chitosan/100 ml H<sub>2</sub>O before sonication
- b) 5 g Indigo Blue Vat dye, 5 g MMT (K10) and 5 g H. Mwt chitosan/100 ml H<sub>2</sub>O after sonication at 80°C
- c) 5 g Indigo Blue Vat dye, 5 g MMT (K10) and 5 g L. Mwt chitosan/100 ml H<sub>2</sub>O before sonication
- d) 5 g Indigo Blue Vat dye, 5 g MMT (K10) and 5 g L. Mwt chitosan/100 ml H<sub>2</sub>O after sonication at 80°C
- e) 5 g pure L. Mwt chitosan/100 ml H<sub>2</sub>O before sonication
- f) 5 g pure L. Mwt chitosan/100 ml H<sub>2</sub>O after sonication at 80°C
- g) 5 g pure H. Mwt chitosan/100 ml H<sub>2</sub>O before sonication
- h) 5 g pure H. Mwt chitosan/100 ml H<sub>2</sub>O after sonication at 80°C

A comparison between Figure 1-a and Figure 1-b would reveal that the micrographs of the particle size of the tertiary mixture in question change from undefined view (before miniaturization) to rod - like shape (after miniaturization). Similar situation is encountered with tertiary mixture consisting of Indigo Blue vat dye plus MMT (K10) plus chitosan of low molecular weight as demonstrated in Figure 1-c and Figure 1-d.

Figure 1-c shows TEM micrograph for the tertiary mixture with low molecular weight chitosan before miniaturization .The micrograph displays undefined view and the particle sizes ranging between 20 nm to 730 nm with an average value of 178 nm. While Figure 1-d shows the particle sizes of the same tertiary mixture but after

miniaturization. Here the particle sizes assume a rod-like and its particle sizes ranging between 5.63 and 50.38 nm with an average size of 21 nm.

It is as well to emphasize that the TEM micrograph of pure chitosan whether high or low molecular weight is nearly similar to those of the mixture. That is, it is undefined before miniaturization (Figure 1-e and Figure 1-g) and rod-like and more homogenous after miniaturization (Figure 1-f and Figure 1-h).

Back to Table 1, where the values of particle sizes of pure chitosan having high or low molecular weight before and after miniaturization are presented. It is clear that, the particle size of low molecular weight chitosan decreases from 166 to 55.2 nm (with a decrease percentage of 66.7 %). On the other hand, the particle size of high molecular weight chitosan decreases from



202.2 to 101.8 nm with a decrease percentage of 49.6%. These results are in conformation with the reasons given above to explain the high susceptibility of the low molecular weight chitosan to miniaturization under the effect of sonication.

Samples of cotton fabrics were printed using pastes prepared as described in the experimental section using the screen printing technique. After printing and drying, the printed goods were thermally fixed at 160°C for 3 min, followed by washing, drying, conditioning and measuring the K/S. 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 molecular weight of chitosan and (b) the particle size of the new colorant.

Involvement of low molecular weight chitosan in fabrication of the colorant makes the printability of this colorant higher than colorant fabricated using high molecular weight chitosan. Colorant based on low molecular weight chitosan produces printed samples with K/S values of 5.34 and 8.91 before and after miniaturization. This is against K/S values of 5.06 and 7.44 for samples printed using colorant based on high molecular weight chitosan. At any event, however, the particle size plays a dominant role on the values of K/S. This state of affairs holds true regardless of the nature of chitosan used.

#### **New Colorant Based on the In Situ Polymerization of Acrylamide in dispersion of Indigo Blue vat dye /MMT (K10)/Citric Acid**

This was done by mixing (5 g) Indigo blue vat dye with (5g) MMT (K10) in 100ml distilled water. Then (3 g) acrylamide and (1 g) potassium persulphate ( $K_2S_2O_8$ ) were added to the mixture. Conversion of acrylamide monomer to polyacrylamide is effected through initiation of polymerization of the acrylamide monomer under the influence of  $SO_4^-$  and /or  $HO^-$  free radicals. The latter are brought about by decomposition of ( $K_2S_2O_8$ ) initiator. Once polymerized, a tertiary mixture based on Indigo blue vat dye, MMT (K10)/polyacrylamide is formed. This tertiary mixture was subjected to miniaturization via stirring in Ultrasonic Processor for 60 min at 80°C. Measurement of the particle size of the as fabricated new colorant before and after miniaturization was performed. Two printing pastes containing the new colorant before and after miniaturization were prepared according to recipe previously described. Samples of cotton fabrics were printed using the two printing pastes. After printing and drying the printed samples were

subjected to fixation at 160°C for 3 min followed by washing, drying, conditioning and measuring the colour strength, expressed as K/S.

The particle size of the newly fabricated colorant which is based on the said tertiary mixture before and after miniaturization displays a value of 109.9 nm. This is rather the average value of particle sizes ranging from 21.7 to 276.8 nm as verified by Figure 2-a wherein the micrograph of the tertiary mixture appears inhomogeneous before miniaturization. After miniaturization, on the other hand, the average particle size amounts to 27.4 nm as shown in Figure 2-b which also exhibits a homogenous micrograph indicating the occurrence of a chemical reaction between the ingredients of the tertiary mixture during sonication. Furthermore the particle size ranges from 4.4 to 58.5 nm which is a narrow range when compared with the corresponding values before miniaturization.

The colour strength (K/S) increases by three fold after miniaturization which causes outstanding reduction in the particle size. Prints obtained using the new colorant exhibits K/S values of 2.91 and 9.35 before and after miniaturization respectively. The corresponding values for the particle sizes are 109.9 and 27.4 nm.

Printing pastes containing new colorant based on tertiary mixture (Indigo blue vat dye/MMT (K10)/polyacrylamide) before and after miniaturization (via sonication) of this mixture along with the binder, urea, sodium alginate thickener and sodium dihydrogen phosphate, were prepared. The as prepared pastes were used for printing cotton fabrics according to the screen printing technique. After printing and drying, the samples were washed, dried, conditioned and monitored for K/S.

Of particular interest is the surprising feature observed with the prints. After washing, the printed samples display no homogeneity. On the contrary, the prints assume a Batik design and denim (jeans) effects. Such printing is not reproducible. When we tried to repeat the printing under similar conditions, different results were obtained, i.e. same prints could not be obtained by conducting printing again and again. This is, indeed, the first time to achieve prints like Batik from screen printing technique and represents a phenomenon which is clearer with the miniaturized new colorant. Thus it may be concluded that in situ polymerization of acrylamide using  $K_2S_2O_8$  as initiator in a dispersion of Indigo Blue vat dye and MMT (K10)

followed by miniaturization brings about a new colorant which when printed on cotton fabric as per the screen printing technique produces prints that exactly like Batik design and jeans effects. (Figure 2-c and d).

In spite of the inhomogeneity of the printed fabrics, we have measured the K/S in several location. As already emphasized the K/S increases from 2.91 to 9.35, i.e. increasing by 221 % by decreasing the particle size from 109.9 to 27.4 nm.

Particularly notable is the production of Batik like design and jeans effects (appeals). Such phenomenon occurs only after the prints were thermally fixed at high temperature (160°C/min) followed by washing. This was not the case when the prints were submitted to drying and washing. To this end two essential reasons can logically be responsible for the Batik like design and jeans effects: 1) thermal instability of the new colorant based on, Indigo Blue vat dye/MMT (K10)/polyacrylamide and 2) decomposition of the new colorant and the release of SiO<sub>2</sub> molecules which were associated together to form SiO<sub>2</sub> nanoparticles.

In situ polymerization of acrylamide and diffusion of the polyacrylamide formed into the vicinity of the Indigo Blue vat dye/MMT (K10) dispersion seem to reduce the magnitude of interactions among the components of the tertiary mixture in question. As a result thermal stability, the decomposition temperature of the colorant obtained decrease. The new colorant decomposes to yield, inter alia, SiO<sub>2</sub> which form cluster of SiO<sub>2</sub> nanoparticles. It is understandable that SiO<sub>2</sub> is originated from silicate layers of MMT (K10). The SiO<sub>2</sub> nanoparticles are characterized by strong white colour. Diffusion of the SiO<sub>2</sub> nanoparticles in the printing paste and their distribution on the printed area on the cotton fabric during thermos-fixation of the prints would not lead to normal solid blue prints but rather disrupted prints due to the presence of SiO<sub>2</sub> nanoparticles.

With the above in mind, it can be concluded that the observed Batik like design and the jeans effects phenomenon is a manifestation of the haphazardly distributed SiO<sub>2</sub> cluster (small aggregates) in the prints.

#### **New Colorant Based on the Tertiary Mixture of Indigo Blue vat dye /MMT (K10)/Citric Acid**

To put into practice, 5 g of Indigo Blue Vat dye, 5 g MMT (K10) and 3 g citric acid were mixed well then subjected to miniaturization using

Ultrasonic processor for 60 min at about 80°C. Samples before and after sonication were monitored for their particle size.

Figure 4-a depicts the particle size of the mixture before sonication. It is clear that the particle sizes range from 12 to 451 nm, making an average particle size of 170 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 tertiary mixture under investigation.

Figure 4-b illustrates the TEM micrograph of the particle sizes of the same tertiary mixture but after being sonicated. Obviously, the particle size range between 10 to 40 nm with an average particle size of 22 nm. Figure 4-a shows also a defined micrograph containing defined particles with much lower sizes than those observed before sonication. This reflects the influence of sonication on homogenizing while miniaturizing the particles of the new colorant. The latter is formed as a result of interactions of the tertiary mixture components under the effect of sonication at the condition used.

Printing pastes were prepared containing colorants formed before and after sonication along with urea, thickener (sodium alginate), binder and sodium dihydrogen phosphate, according to the recipe described in the experimental section. After printing and drying, the prints were fixed thermally at 160°C for 3 min then washed, dried and conditioned at 25°C and 65% relative humidity. At this end the K/S was measured. K/S of the prints of the new colorant displays a value of 4.32 before miniaturization which increases to 10.65 after miniaturization. This is corresponding to particle sizes of this colorant of 170 and 22 nm respectively. Because of these results the K/S increases by 146.5 % when the new colorant was used after miniaturization.

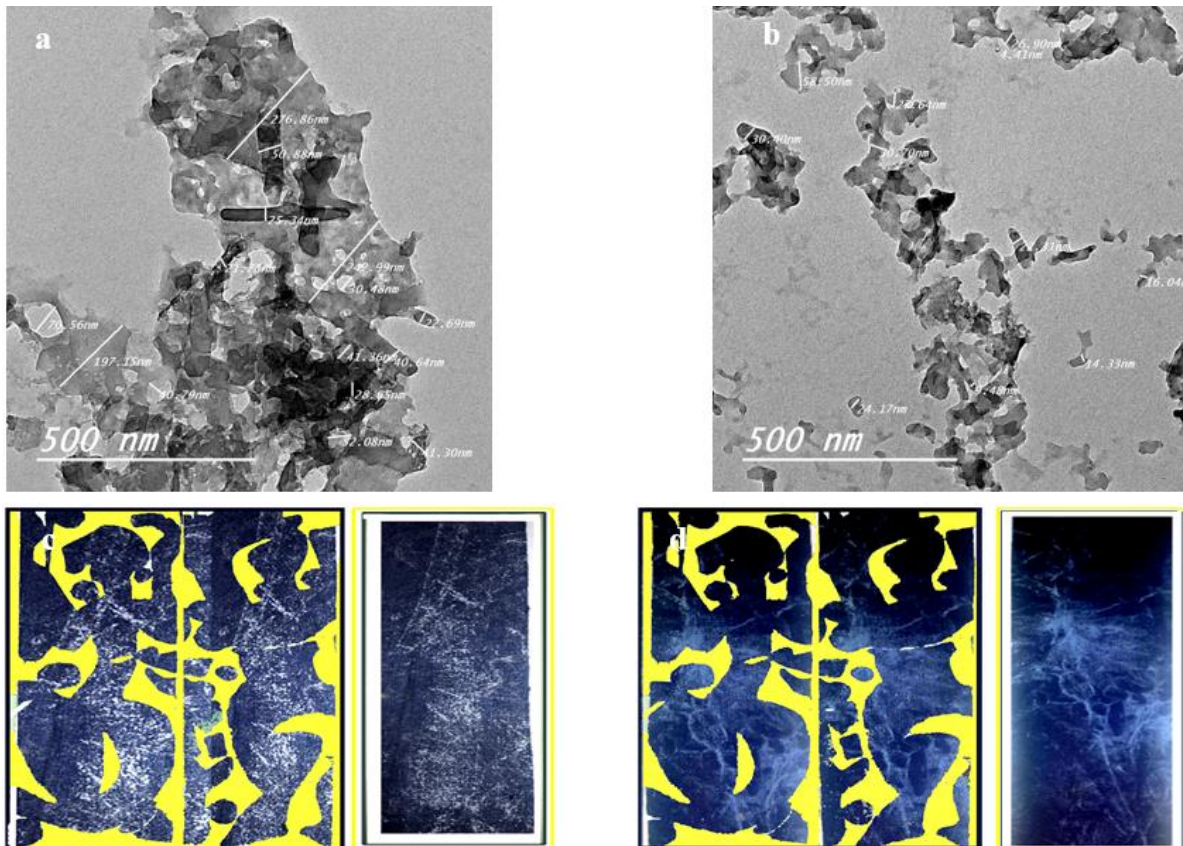
It is as well to designate that fabrics printed using new colorant based on the tertiary mixture of Indigo Blue vat dye/MMT (K10)/Citric acid is characterized by Batik - like design exactly the same as colorant containing polyacrylamide, and can be explained on similar lines. Citric acid seems to introduce crosslinks in the colorant nanostructure and, in so doing; it detracts from the thermal stability of the new colorant formed. In combination with this is the possible decomposition of this new colorant with the release of SiO<sub>2</sub> nanoparticles and their disrupting impact on the solid blue colour of the prints as

detailed above. (Figure 4-c-d)

**Table 2: K/S and particle sizes of new hybrid nanocomposite formulation before and after miniaturization**

Pastes Colorant with Chitosan	Components				Particle size (nm)	
	chitosan		MMT (K10)	Indigo vat dye	Before miniaturization	After miniaturization
	H.Mwt	L.Mwt				
I	5 g	-	5 g	5 g	5.06 (201 nm)	7.44 (55 nm)
II	-	5 g	5 g	5 g	5.34 (178 nm)	8.91 (21 nm)

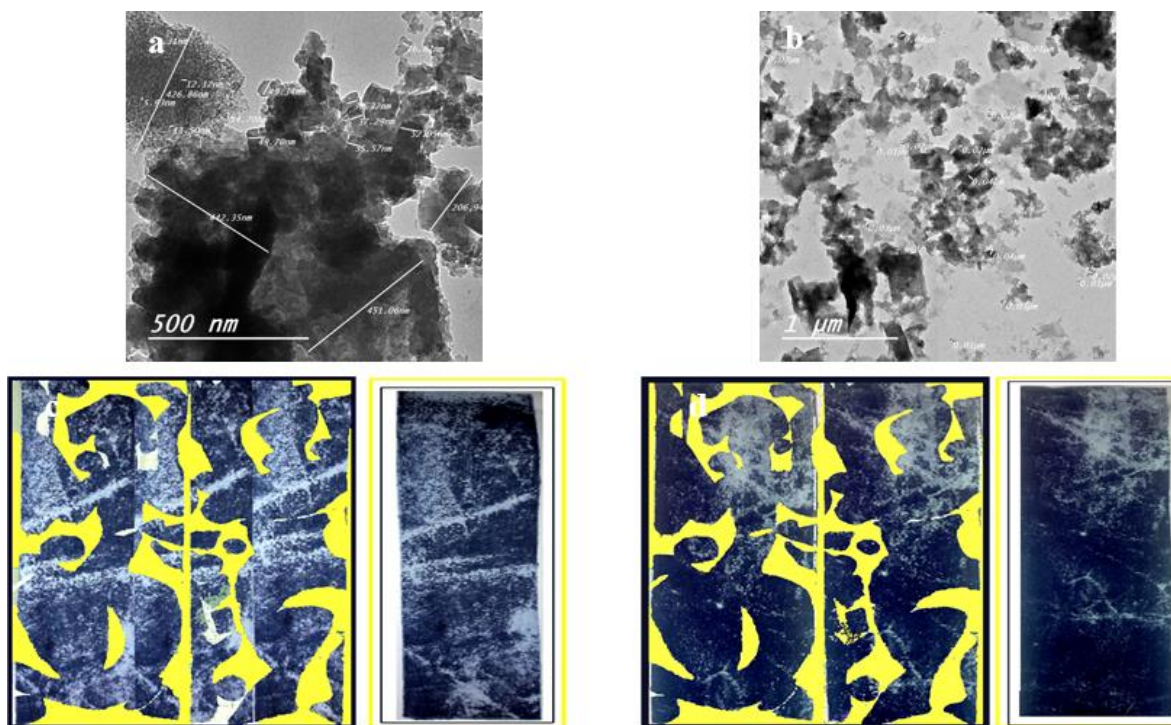
Values in brackets represent those of the particle sizes of the new hybrid nanocomposites



**Figure 2: TEM micrograph and photo of printed fabrics with different formulation before and after sonication**

a and c) 5 g Indigo Blue Vat dye, 5 g MMT (K10), 3 g acrylamide and 1 g persulphate/100 ml H<sub>2</sub>O before sonication

b and d) 5 g Indigo Blue Vat dye, 5 g MMT (K10), 3 g acrylamide and 1 g persulphate/100 ml H<sub>2</sub>O after sonication at 80°C



**Figure 3: TEM micrograph and photo of printed fabrics with different formulation before and after sonication**

a and c) 5 g Indigo Blue Vat dye, 5 g MMT (K10) and 3 g citric acid/100 ml H<sub>2</sub>O before sonication  
b and d) 5 g Indigo Blue Vat dye, 5 g MMT (K10) and 3 g citric acid/100 ml H<sub>2</sub>O after sonication at 80°C

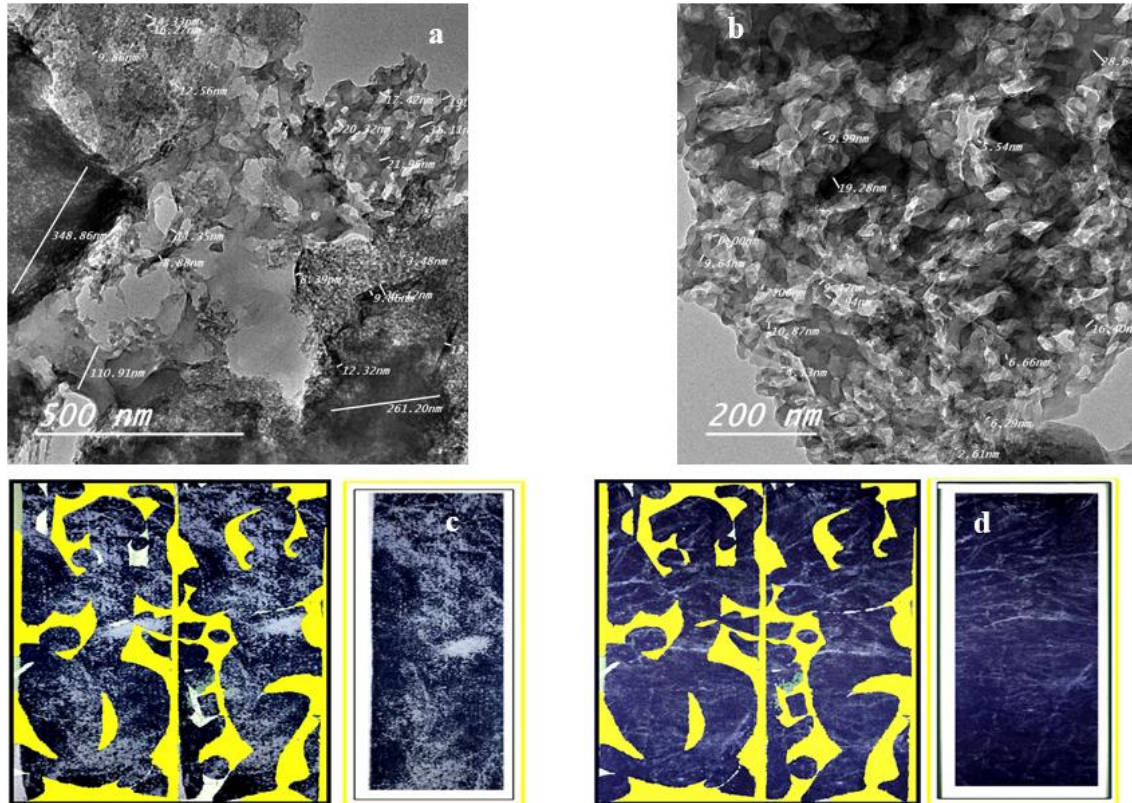


Figure 4: TEM micrograph and photo of printed fabrics with different formulation before and after sonication

a and c) 5 g Indigo Blue Vat dye, 5 g MMT (K10), 3 g citric acid and 5 g L.Mwt chitosan/100 ml H<sub>2</sub>O before sonication

b and d) 5 g Indigo Blue Vat dye, 5 g MMT (K10) , 3 g citric acid and 5 g L.Mwt chitosan /100 ml H<sub>2</sub>O after sonication at 80°C

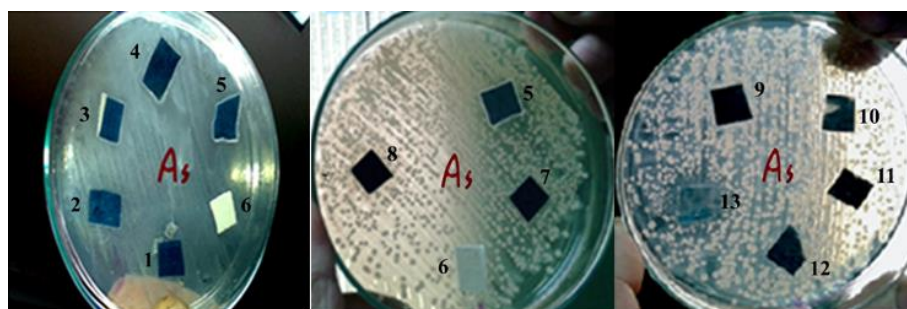
Table 3: Antimicrobial activity of fabric printed using new colorants

Sample	Inhibition zone (mm)				
	A.niger Fungi	St. Albus	Bacillus cereus	E.coli	Pseudomonas
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	-	-	-	-
5	17	16.8	16.8	16.7	-
6	-	25	-	17	-
7	-	-	-	-	-
8	-	-	-	-	-
9	-	-	-	-	-
10	-	-	-	-	-
11	-	-	-	-	-
12	-	-	-	-	-
13	-	-	-	-	-

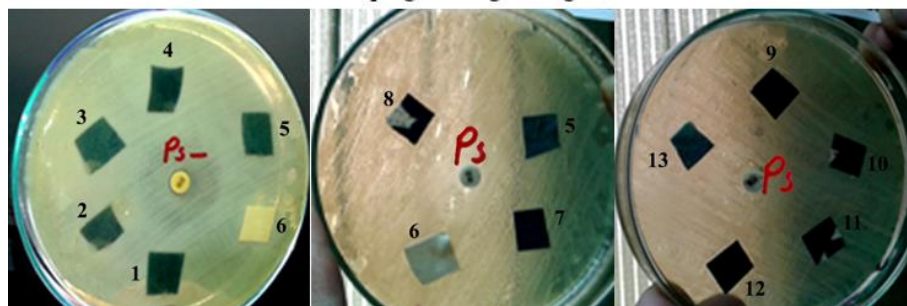
1) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 5 g L.Mwt. chitosan before miniaturization

2) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 5 g L.Mwt. chitosan after miniaturization

- 3) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 5 g H.Mwt. chitosan before miniaturization
- 4) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 5 g H.Mwt. chitosan after miniaturization
- 5) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10) after miniaturization
- 6) Fabric printed with 5 g MMT (K10) after miniaturization
- 7) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 3 g acrylamide and 1 g  $K_2S_2O_8$  before miniaturization
- 8) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 3 g acrylamide and 1 g  $K_2S_2O_8$  before miniaturization
- 9) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10) and 3 g citric acid before miniaturization
- 10) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10) and 3 g citric acid after miniaturization
- 11) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 3 g citric acid and 5 g L.Mwt. chitosan before miniaturization
- 12) Fabric printed with new colorant using 5 g Indigo Vat, 5 g MMT (K10), 3 g citric acid and 5 g L.Mwt. chitosan after miniaturization
- 13) Fabric printed with 5 g Indigo blue vat dye after miniaturization



*Aspergillus niger* fungi



*Pseudomonas aruginosa*

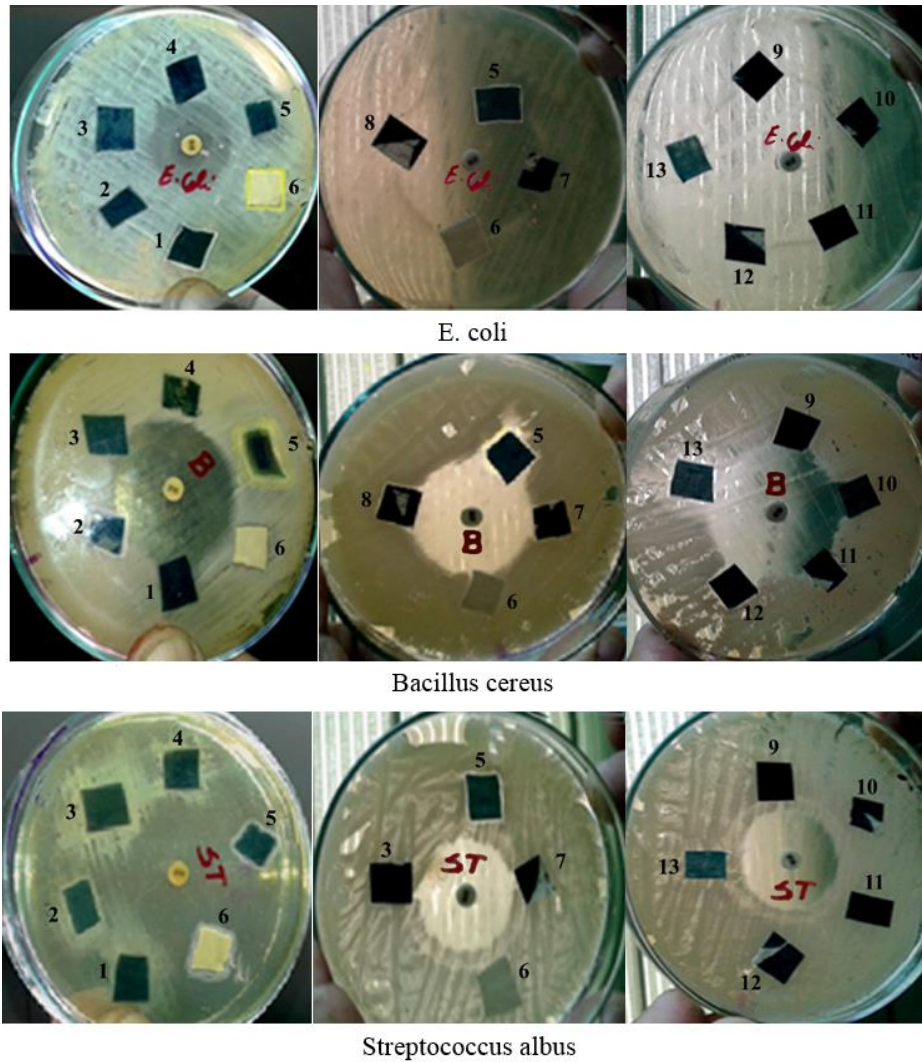


Figure 5: Antimicrobial activity of fabric printed using new colorants prepared using different formulations

Table 4: Effect of nanocolourant before and after sonication on colour strength K/S and fastness properties of printed cotton fabrics

Colorant Before and after miniaturization		K/S of Printed fabric	Fastness properties								
			Washing at 60°C Cotton /wool		Rubbing Fastness		Perspiration fastness Cotton /wool				Light fastness
			St.	Alt.	Wet	dry	Acidic		Alkali		
							St.	Alt.	St.	Alt.	
I	Before	2.35	4-5	4-5	3	3	4-5	4-5	4-5	4-5	
	After	7.03			4	4-5					
II	Before	5.34	4-5	4-5	2-3	3	4-5	4-5	4-5	4-5	6-7
	After	8.91			4	4					
III	Before	5.06	4-5	4-5	2-3	3	4-5	4-5	4-5	4-5	6-7
	After	7.44			3-4	4					
IV	Before	2.91	4-5	4-5	3	3	4-5	4-5	4-5	4-5	6-7
	After	9.35			4	4-5					
V	Before	4.32	4-5	4-5	3	3	4-5	4-5	4-5	4-5	6-7
	After	10.65			4	4-5					

Colorant I:	based on Indigo blue vat dye + MMT (K10)
Colorant II:	based on Indigo blue vat dye + MMT (K10) + chitosan (low molecular weight)
Colorant III:	based on Indigo blue vat dye + MMT (K10) + chitosan (high molecular weight)
Colorant IV:	based on Indigo blue vat dye + MMT (K10) + polyacrylamide
Colorant V:	based on Indigo blue vat dye + MMT (K10) + citric acid

### Antimicrobial Activity of Printed Cotton Fabrics Using New Colorants

Table 3 and Figure 5 summarizes the antimicrobial activity of cotton fabrics printed using new colorants based on binary and tertiary mixtures of Indigo blue vat dye, MMT (K10), chitosan and in situ polymerized acrylamide. Obviously, the highest antimicrobial activity is observed with colorant based on indigo blue vat dye/MMT (K10) binary mixture after miniaturization via sonication. This colorant displays antagonistic effects against *Aspergillus Niger*, *Streptococcus Albus*, *E. Coli* and *Basillus Cereus* by inhibition zone (textile cutting flat axis) of 20, 25 and 8 mm respectively (Sample 5). Following this are the antagonistic effects of fabric samples printed using MMT (K10) alone where inhibition zone of 25 and 17 mm are observed with *St. Albus* and *E. Coli* (sample No. 6). On the other hand, sample 1 and sample 2 acquire no antagonistic effects against all tested microorganisms.

Fabric samples printed using new colorants based on tertiary mixtures consisting of Indigo blue vat dye, MMT (K10) and chitosan of high molecular weight (Samples 3 and 4) acquire no antagonistic effects against all tested microorganisms. The same situation was encountered with colorant based on tertiary mixtures containing low molecular weight chitosan as shown by Samples 1 and 2 outlined above. High molecular weight chitosan seems to offset the antagonistic effect of colorant based on Indigo blue vat dye /MMT (K10) binary mixture. By virtue of its high or low molecular weight, chitosan seems to interact strongly with MMT (K10) and, in so doing; it destroys the antagonistic effect of MMT (K10). It is understandable that the release of metallic cations originated from MMT (K10) is the essential reason of its antagonistic effects; chitosan seems to interact with such cations thereby vitiating the antagonistic effects of MMT (K10). This is not the case in absence of chitosan.

Indigo blue vat dye/MMT (K10) binary mixture produces colorant with the highest antagonistic effects as described above. This indicates that this mixture after being miniaturized constitutes the base of the best new colorant with the

possibility that the Indigo blue vat dye help establishing the antagonistic effects in the new colorant.

On the other hand, Sample 13 is without any antimicrobial effects against all tested microorganisms indicating that the indigo dye alone has no antagonistic effects against the tested microorganisms. Other samples (Samples 7 – 12) display no antimicrobial effects against the tested microorganisms. Presence of polyacrylamide, chitosan and/or citric acid in printing paste along with Indigo blue vat dye/ MMT (K10) binary mixture would account for this. These polymeric ingredients with and without citric acid as crosslinking agent would certainly determine the ability of colorant based on this mixture to resist the attack of microorganisms.

### Fastness Properties of Printed Cotton Fabrics Using New Colorants

Colour fastness of fabric printed using new colorants prepared using (MMT (K10) + Indigo blue vat dye), binary mixture as well as using different colorants based on the vat dye and MMT (K10) along with either acrylamide or citric acid with or without chitosan (low molecular weight) before and after sonication of these mixtures were measured and the results are illustrated in Table 4. Table 4 shows that the colour fastness to washing and to perspiration (acidic and alkaline) as well as to light are not affected. Different situation is encountered with respect to fastness to rubbing. The prints of the new colorant after sonication display much better rubbing fastness properties than before sonication. By virtue of their nano - sized structure the new colorant particles are small enough to diffuse into fibres and, in so doing, they create high fastness properties, in particular, to rubbing.

### CONCLUSION

Research in this paper gives rise to development of new hybrid nano-composite colorants through intercalation of Indigo blue vat dye with the layered silicate of a natural clay known as montmorillonite MMT (K10). Different polymeric components as new colorants in the nano form could be achieved by incorporating two types of polymeric components in the nano-



composite formulation. The first is chitosan as a natural polymer having high and low molecular weight. The second type refers to in situ formed polyacrylamide. Furthermore addition of citric acid to the nano-composite formulation is made. The onset of this on the nano-size of the new colorant and its printability are examined. Considering the results obtained by each of these variables, optimal processing conditions for fabrication of the new colorant could be established.

A salient feature is that Batik like prints are obtained. This is rather encountered with colorants based on Indigo blue vat dye/MMT (K10)/polyacrylamide tertiary mixtures. Batik like prints could also be achieved upon using the quaternary mixture the vat dye/MMT (K10)/Polyacrylamide/Citric acid. Citric acid seems to weaken the interactions among the other components of the mixture and in so doing, it decreases the thermal stability and the decomposition temperature of the new colorant. As a consequence decomposition of the new colorant based on the current quaternary mixture occurs with the creation of SiO<sub>2</sub> molecules which are the essential reasons for the observed Batik like design and jeans effects.

#### CONFLICT OF INTEREST

The authors declared that present study was performed in absence of any conflict of interest.

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#### AUTHOR CONTRIBUTIONS

This article is a part from PhD thesis for HAS under supervision from the other authors, AAH and EEA were the main supervisors and they designed and performed the main idea of the thesis. AAR and IAE were observed and control the work and the results, the last author AAS was observed and control all the experiments performed the experiments and data analysis and wrote with HAS the manuscript. All authors read and approved the final version.

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