Available online freely at www.isisn.org

Bioscience Research

Print ISSN: 1811-9506 Online ISSN: 2218-3973

Journal by Innovative Scientific Information & Services Network

RESEARCH ARTICLE BIOSCIENCE RESEARCH, 2019 16(1):573-595 **OPEN ACCESS**

Novel hybrid nanocomposite containing natural clay (*montmorillonite*) and indigo blue Vat dye for textile materials

A. A. Hebeish[1], A. A. Shahin,A. A. Ragheb, I. Abd El-Thalouth, E. E. Allam[2] and H. A. Shaban

[1]National Research Centre (Scopus affiliation ID 60014618), Textile Industries Research Division, Dyeing, Printing and Textile Auxiliaries Department, 33El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, **Egypt**
[2]Faculty of Applied Arts, Helwan University, Cairo, **Egypt**

***Correspondence:** hanona-shaban@yahoo.com **Accepted: 18** Sep 2018 **Published online: 28 Feb**. 2019

The present work is undertaken with a view to establish the best practice (formulation/conditions) for processing of new hybrid nano-composite as new colorant. .Synthesis of the new colorants is based on intercalation of Indigo Blue Vat dye with the silicate-layered nano-composite (SLNC) which is a natural clay known as montmorillonite (MMT). Current study addresses the ultrafine nanoparticles formed under the effect of ultrasound technology (i.e. sonication) on Indigo Blue Vat dye in admixture with the clay. The formation of Indigo Blue Vat dye /clay hybrid nano-composite under different formulations and conditions are 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 nano-composite. New colorants obtained by such synthesis are characterized, analysed and tested using state of the art tools. Ability of these ultrafine colorants to produce prints on Cotton textiles is also studied.

Keywords: New hybrid nano-composite, Indigo Blue Vat dye, montmorillonite (MMT), Cotton textiles

INTRODUCTION

Nanotechnology refers to the science and technology of designing, constructing and creating of novel nano scale structure, 1 to 100 nm in size, with huger quality, novel performance properties, along with fewer defects compared with those of the bulk material. It is an emerging technology which finds many fields of applications, for example, the textiles. The nanotechnology wave has shown a huge potential in areas of application in textile sector to improve properties of existing materials and/or to impact new and novel extraordinary functions to textile materials. R and D activities on application of nanotechnology in textile industry focus on including nano-size entities into or creating nano - size entities on textile fibres and fibrous materials during manufacturing and finishing processes. (Yuen C W M, et al., 2005)and Chattopadhyay D P and Patel B H (2010)

Known advantages of utilizing nanotechnology in textile sector can be discussed in terms of: (a) more effective, i.e. more active and large surface areas per unit weight, (b) minimal impacts on physical and mechanical properties, i.e. hand, strength and air permeability, (c) minimal use of chemicals (d) low energy consumption and costs and (e) lower environmental impact. Elhady H S A, (2010), Asmah et al., (2015)

The textile industry accounts for the largest consumption of dyestuffs at nearly 70 percent. Reactive Dyes, Vat Dyes & Azo Dyes are mainly required for dyeing and printing of cotton fibres.

Jäger et al.,(2004)

Vat dyes are insoluble in water. The dyes contain at least two conjugated carbonyl groups which, during their conventional application to cellulosic fibres, are converted by reduction under alkaline conditions to the corresponding, water soluble, 'alkali leuco' form which is applied to the substrate. Thetford D and Chorlton A P(2004) and She F Y, et al.,(2012) At this end, the alkali leuco form is oxidised, so as to regenerate the insoluble, parent vat dye in situ within the fibre.

In literature, the potential of vat dyes as organic pigments have been investigated. Polycyclic, perylenes and perinonones vat dyes, have the physical properties required to convert them into high performance pigments. Indanthrone (Pigment Blue 60), dibromoanthanthrone (Pigment Red 168), and anthrapyrimidine (Pigment Yellow 108), were all used as vat dyes, being Vat Blue 4, Vat Orange 3 and Vat Yellow 20 respectively, before they were used as pigments. However, organic pigments are difficult to be wetted and dispersed in aqueous media due to their low polarity and easy aggregation. She F Y, et al.,(2012)

Indigo has been used for thousands of years, and it's one of the oldest dyes used by mankind. There is evidence of indigo being used already in mummy clothe in ancient Egypt. Božič M and Kokol V(2008), Before the synthetic dyes were developed in the 19th century indigo as well as other dyes were produced from plants. Roessler A,(2003)

Indigo is one of the oldest dyes used by mankind. Today, it is considered as one of the world's most important industrial chemicals, with the current annual world consumption of indigo and other vat dyes being over 33 million kilogrammes. (Roessler A and Jin X,2003) Indigo –as a vat dye- needs to be reduced to its water soluble leuco-form before dying. Roessler A and Crettenand D,(2004) So far, most of the industrial reduction has been performed chemically by a continuous process using sodium dithionite as a reducing agent. Božič M and Kokol V(2008) This process has two major limitations: the choice of the reducing agent and the method of application. Indeed, using sodium dithionite is the cause of certain engineering problems, such as instability, storage, corrosivity, etc. and ecological problems because of the production of large amounts of sodium sulphate and sulphite, Božič M and Kokol V(2008) known to increase the cost of wastewater treatment. Roessler A and Jin X, (2003)

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Clay materials possess structures that are organized in layers and they are categorized by those different layered structures. Hou D W, et al., (2016).

Nowadays nanostructured materials is being introduced in structural applications, e.g. gas barrier, flame retardant products and other load bearing applications; a point which reflects the potential impact of this class of materials on the growth of every level of world economy in the 21stcountry. Sin S L, et al.,,(2003) A. V R and R. K,(2002)

Polymer/layered silicates nano-composites (PLSNCs)have shown an outstanding improvement in material properties comparing with origin polymer or conventional composite. Of this improvement mention is made of enhanced mechanical properties, Kornmann X ET AL.,(2001), Fu X and Qutubuddin S, (2001).Hult E L, et al., (2001),Yano K, et al., (1993) ,Nam P H, et al., (2001) Maiti P, et al., (2002)

increased thermal stability, Kato M, Usuki A, and Okada A, (1997) ,Chen T K, et al.,(2000) ,Wang Z and Pinnavaia T J, (1998) ,Joo S-H and Jin J-I (2004),Song L, et al., (2003) gas barrier properties, LeBaron et al.,(1999) ,Giannelis et al.,1999,Jeon H G, et al., (1998),LeBaron et al.,(1999) ,Sinha Ray S and Okamoto M, (2003))and inflammability Alexandre M and Dubois P, (2000).Waly A, et al.. (2006). Waly A, et al., (2008) Waly A I, et al., (2012) ,Hassabo A G, et al., (2015) ,Hebeish A, et al., (2016). Fornes et al., (2004).Lee D C and Jang L W, (1996).Noh M W and Lee D C, (1999).Usuki A, et al., (1995).Stretz H A, et al., (2005) Kojima Y, et al., (1995). Kojima Y, et al., (1994). Varlot K, et al., (2001).

with low filler loading . Such improved properties are a manifestation of the homogeneous dispersion of nanoclay as filler and even with fewer demerits vis a/ visconventional particulates filled composites (Varlot K, et al., 2001) .In addition ,a considerable progress in theory and simulations were occurred concerning the preparation and properties of these materials, (Yoon et al., 2002) and Masenelli-Varlot K, et al., (2002)) they are also regarded to be unique model systems in order to study the structure and dynamics of polymers in confined environments.

(Becker et al., 2002).
Wang K, et al., Langmuir, 21 (2005) 3613.
50. Sheng N, et al., Polymer, 45 (2004) 487.

There are two classes of hybrids between a polymer and nano-scopically dispersed layered silicates: (1)Intercalated hybrids and (2) exfoliated (delaminated) hybrids. In an intercalated hybrid, the polymer chains are interacted between swollen silicate layers with their regular alteration or galleries and lamina. The distance between the layers, that is, the space occupied by the polymers is typically of the order of a few nano-meters. The second class of silicate is totally delaminated and dispersed in the polymer matrix .Its ordered structure is lost and the distance between the layers is the order of radius of gyration of the polymer. It is also logical to say that the intercalated hybrid displays limited miscibility and that of delaminated hybrid is totally miscible. Both of these hybrid structures can coexist in the polymer matrix.

Apart from this, the intercalation of small molecules into silicate galleries have been found by researchers when studying Mayanarchaeological sites. (17) Maya blue was used in Mesoamerica and colonial Mexico as late as the 20th century.

Maya blue colour is resistant to diluted mineral acids, alkalis, moderate heat and even biocorrosion. This blue colour contains clay (mainly montmorillonite, MMT clay, and polygorskite [$Mg_5(Si,Al)_8O_{20}(OH)_2 8H_2O$] and indigo molecules ($C_{16}H_{10}N_2O_2$).

Interaction of Indigo molecules and MMT galleries and/or encapsulation in the pores of polygorskite might explain the resistance of the extreme conditions of the rain forest. Up to now Maya blue paint have been understood as an origin of the intercalation, and recognized as an ancient nano structured materials.

In the first progress report of current project, we have presented preliminary study that targeted towards innovation of new colorant nano hybrid composite for printing various textiles of different sources and origins. The new colorant was fabricated through intercalation of Indigo Blue Vat dye with a natural clay called montmorillonite. The latter is a nanostructured materials based essentially on silicate layered nano-composite.

In this work, we have presented preliminary with a view to establish the best practice (formulation/conditions) for processing of new hybrid nano-composite as new colorants. The latter could be achieved by mixing the dye and the clay followed by subjecting the mix to sonication. Such a processing is carried out under a variety of conditions including concentration 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. Considering the results obtained by each of the variables, optimal processing conditions for fabrication of the new colorant could be arrived at.

New colorants obtained by such synthesis are characterized, analysed and tested using state of the art facilities worldwide. Ability of these ultrafine colorants to produce prints on cotton textiles is inevitably studied.

MATERIALS AND METHODS

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

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

Two different kinds Montmorillonite (MMT)namely KSF and K-10 manufactured by ACROS Organics were used. Montmorillonite (K10;$H_2Al_2(SiO_3)_4$-nH_2O;274-324 g/mol),Montmorillonite (KSF; $Al_2O_9(SiO_3)$; 282 g/mol).

Redoxal Z kindly supplied by Chemicals Industry S.A.E., Dico Egypt. Potassium carbonate, sodium hydroxide, sodium chloride, L.histidine monohydrochloride mono hydrate, sodium dihydrogen orthophosphate, and disodiumhydrogen orthophosphate were of laboratory grade chemicals.

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 ± 100 HZ).

Preparation of Nanoparticles of Indigo Vat dye by Ultrasonic Processor

100 ml aqueous dispersion containing 3 g of Indigo Vat Dye (Blue) aggregates was vigorously shaken to ensure good mixing for 30 min at ca 80°C in the Ultrasonic Processor (The Probe is turned to resonate at a specific frequency , 20 KHZ ± 100 HZ).

Preparation of Nanoparticles of Indigo Vat dye in presence of Montmorillonite (MMT)K10 or KSF

Indigo Vat dye was converted to nano-sized Indigo Vat dye particles in presence of montmorillonite (KSF or K10) by making use of the Ultrasonic Processor described above. Thus 3 g of the Indigo Vat dyeaggregates were mixed with 1, 2 ,3, 5 ,7 ,9 g Montmorillonite (MMT)KSF or K10in 100 ml water. The so obtained well-mixed Indigo Vat dye/MMT KSF or K10dispersion was set to motion in the Ultrasonic Processor. The Ultrasonic radiation was operated for 30 min at ca 80°C.

Concentration of Indigo Vat dye

The optimum conditions of MMT K10 (i.e. 5 g/100 ml water) was mixed with1, 3, 5, 7 g Indigo Vat dye in 100 ml water. The dye/MMT mix was submitted to ultrasonic radiation for 30 min at ca 80°C.

Time of ultrasonic radiation

5 g of the Indigo Vat dye aggregates were mixed with 5 g MMT in 100 ml water. The so obtained well-mixed Indigo Vat dye/MMT dispersion was set to motion under the effect of Ultrasonic radiation for different periods of time (15, 30, 45, 60 min) at ca 80°C.

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:

Colorant *	**20g**
Urea	**2.5g**
Thickener(Soduim 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 or nanosized vat in presence or absence of MMT (KSF)or MMT (K10) hybrid before and after miniaturization.

Thickener was used at a concentration of 2.5%

Binder was used at a concentration of 1,2,3,4 or 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 (Soduim 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 fabric were rinsed and oxidized using 2g/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 (1g/l), then washed with cold water.

Printing of Cotton Fabrics with commercial Vat dye alone or in combination withMMT before and after being subjected to miniaturization 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 by steaming at 120ºC 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 95ºC 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 nanocolorant was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs.(36, 51, 52)

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.

Energy dispersive X-Ray analysis (EDX)

The elements analysis was performed using EDX, which is an attachment to the scanning electron microscopy. The spectra obtained during EDX studies were used for carrying out the quantitative analysis.

Colour measurements (33-35, 51-56)

The colour strength and whiteness degrees of the printed samples were evaluated by Hunter Lab Ultra Scan PRO.

Fastness properties (34-36, 52, 57-60)

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 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 95ºC. The test was run for 45 minutes at 42 rpm. The samples were then removed, rinsed twice in 100 ml bath of water at 40ºC for one minute with occasional stirring or hand squeezing ,souring in 100 ml of 0.014% solution of acetic acid for one minute at 27ºC, rinsing again for one minute in 100 ml water at 27ºC followed by drying.(54)

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. (58)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(59)

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 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 a 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 37ºC 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

Tentative Mechanism for the formation of New Colorant

As already emphasized, one of the objectives of current work is to establish the best practice (formulation/conditions) for synthesis of Indigo Blue clay hybrid nano composite new colorants. To achieve the goal, dispersion of the Indigo Blue Vat dye was prepared then added to a dispersion of montmorillonite (K10) which is a natural clay consists of layered silicates .The as prepared dispersion mix was submitted to sonication to effect (a) miniaturization of both the clay and Indigo Blue particles and,(b) compatibility and interaction of the Indigo Blue nano dispersion with the clay nanodispersion.The ultimate result of this is the formation of only one entity of the new nanocolorant as will be shown later on from TEM studies.

In another approach, Indigo blue/Clay mix together with Rongalite C (reducing agent for Indigo Blue) were subjected to sonication. Following this, the dispersion so obtained was filtered. It was observed that the material deposited on the filter acquired a deep blue solid colour while the filtrate wasabsolutely colourless.Subjecting this colourless filtrate to oxidation for a couple of days by occluded and atmospheric oxygen or by addition of sodium perborate oxidant left the filtrate colourless. Thus this filtrate is by no means the leuco form of the Indigo Blue Vat dye. It is understandable that reduction by Rongalite C is anticipated to convert the insoluble Indigo Blue vat dye to its soluble leuco form which is presented here by filtrate. Resistance of the filtrate to oxidation with no colour formation indicated that the filtrate does not contain the soluble dye and, indeed, the filtrate is no more belonging to the Indigo Blue Vat dye.

Based on the above , mixing the Indigo Blue Vat dye with the clay in aqueous dispersion allows the clay to intercalate/exfoliate into the dispersed Indigo Blue Vat dye and , in so doing , becomes no longer responding to reduction with Rongalite C. Indeed, such intercalation / exfoliation of the clay into the dye dispersion results in intercalated /exfoliated nano dispersion which remain as deep blue hybrid nano-composite on the filter. It is the base of our new colorants.

Factors Affecting Synthesis of Indigo Blue Vat Dye/ClayHybrid Nanocomposite New Colorants

Herein we present a study which addresses the ultrafine nanoparticles formed under the effect of ultrasound technology on Indigo blue Vat dye in admixture with the clay. The formation of Indigo blue Vat dye/clay hybrid nano composites under different formulations and conditions are 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. Factors studied and their effect on the new colorant nano composites may be realized from the following paragraphs.

Effect of clay concentration on new colorant size

The effect of the clay (Montmorillonite K10) concentration on the particle size of the new colorant as well as on the colour strength (K/S) of cotton fabrics printed thereof before and after sonication of the Indigo Blue Vat dye/clay mix was investigated.

Thus the Indigo Blue vat dye was mixed with different amounts of the clay (1, 3, 5 ,7 and 9 g/3g dye) suspended in 100 ml water and subjected for 30 min to Ultrasonic processors at 80°C . Different printing pastes were prepared containing the Indigo blue Vat dye and the clay before and after sonication, the pastes were thickened with sodium alginate. Samples of cotton fabrics were printed using the prepared pastes. After printing,the goods were subjected to drying and steaming(120°C for 15 min).Finally, the samples were washed, air dried and assessed for K/S and overall colour fastness properties .Furthermore, the particle size of the indigo blue vat dye before and after mixing with the clay were measured before and after miniaturization by making use of

Transmission Electron Microscopy.

Table 1 shows the particle sizes of the Indigo Blue Vat dye (3g dye /100 ml distilled water) without mixing with the clay and after mixing with the clay (3g dye +5 g clay/100 ml distilled water) before and after miniaturization by sonication as well as those of pure clay (5 g MMT/100 ml distilled water). It is clear that the particle size of the Indigo Blue Vat dye decreases from 127 to 27.9 nm under the effect of sonication. Similar situation is encountered with the particle size of the Indigo Blue Vat dye /the clay hybrid. However the value of the particle size of the latter decreases from 134.9 to 21.6 nm.As clarified in the foregoing paragraph, the Indigo blue Vat dye reacts chemically with the clay to form a new colorant. It is logical, therefore, to assume that this new colorant acquires larger surface area in addition to its larger susceptibility to miniaturization under the influence of the sonication action. Indeed, the chemical reaction occurring between the Indigo Vat dye and MMT(K10) seems to yield radically new compound with different behaviour vis -`a- vis the Indigo Blue Vat dye and MMT taken individually.

Particularly notable (Table 1) are the results of the particle size of the clay. Before miniaturization, the particle size is as high as 271.5 µm. The polymeric nature of the clay MMT(K10) accounts for this. When the clay (MMT K10) was submitted to the stirring action of Ultrasonic Processors the particle size of the clay fall down dramatically to attain a value of 605 nm, indicating the great susceptibility of the clay to miniaturization under the sonication. More interesting characteristic of the clay in question is its reaction with the Indigo Blue Vat dye to bring into Focus a new nanohybrid composite with a particle size of 134.9 and 21.6 nm before and after miniaturization respectively. The particle size of MMT(K10) clay was 271 µm and 605 nm before and after sonication.

Figure 1 shows TEM micrograph of Indigo Blue Vat dye before (a) and after sonication (b),Figure 1a shows that the average size for the Indigo Blue Vat particle ranges from 54.94 nm to 181.39 nm with significant aggregation/agglomeration. As is evident in Figure 1b, the Indigo Blue nanoparticles assume a size range between 10.06 to 50.9 nm. These Indigo Blue nanoparticles exhibit rod shape with uniform distribution of the nanoscale Indigo Blue particles which display an average size value of ca 27.9 nm and appearing as rods.

Figure 2shows TEM micrograph of clay MMT(K10) before (a) and after sonication (b). From Figure 2a,it is clear that, the clay displays range from 130.63 µm to 386.85 µm with an average particle size of 271.5 µm. The particles of the clay MMT (K10) appears like layers. Figure 2bobviously that, the MMT(K10)depicts a particle size range between 200 to 975 nm. Meanwhile, the majority of the particles have a uniform size with an average value of 605 nm.

Figure 3illustrate the TEM micrographs for different clay concentration. Figure 3a-bshows the range of particle sizes of the Indigo Blue Vat dye mixed with clay MMT(K10)before and after miniaturization under the effect of sonication respectively. It is clear that, before sonication (miniaturization)the Indigo Blue Vat dye and clay MMT (K10) appear as a mixture where the indigo Blue Vat dye is nicely accommodating the clay MMT (K10).The particle size for instance ranges from 9.81 to 214.66 nm which is rather a very wide range indicating the inconsistency of the two components in the mix(Figure 3a). In contrast, the particle size of the mix after miniaturization by sonication is different than before sonication. The 30 min time of sonication allows for chemical reaction between the Indigo Blue vat dye and clay MMT(K10) meanwhile the new colorant (product) brought about by such chemical reaction displays much lower particle sizes within the range 9.18 to 22.76 nm. Accordingly, the clay MMT K10 most probably intercalate/exfoliate into the dispersed Indigo Blue Vat dye and this intercalation/exfoliation is followed by chemical reaction of the dye and MMT(K10) to produce a homogenous colorant product of an average particle size of 11.82 nm (Figure 3b).

Table 1: The particle size of Indigo Blue Vat dye, the clay and the mix of dye and clay before and after sonication at 80°C for 30 min

Particle size(nm)					
Clay, (MMT-K10) 5g/100ml water		Indigo Blue Vat dyalone 3g/100ml water		Indigo/ clay mix 3g Indigo +5g Clay/100 ml water	
before	After	Before	After	Before	After
271.5µm	605nm	127nm	27.9nm	134.9 nm	21.6nm

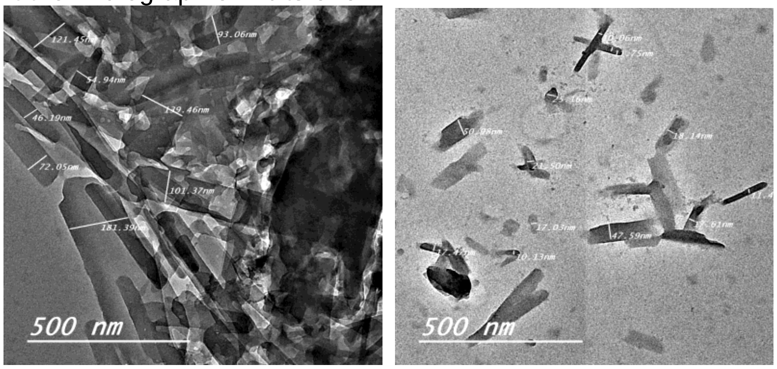
In conformation with above the new colorant (product) is characterized by rod shape similar to that of Indigo Blue Vat dye alone after being submitted to miniaturization for 30 min under the influence of sonication.

Figure 3c shows the TEM micrograph of Indigo Blue Vat dye mixed with clay MMT(K10) for 60 min then Rongalite C(a reducing agent) was added during 15 min sonication at 100°C. The TEM micrograph of the mix in question was not affected by addition of Rongalite C and indeed, the TEM micrograph obtained in absence of Rongalite C, that is Figure 3b,is a typical version of Figure 3c.This is very logical because presence of Rongalite C as a reducing agent for conventional Indigo Vat dye printing is essential to convert the dye to the leuco soluble from which is oxidized after printing to the insoluble form. Different situation is encountered here because the new nano colorant is brought about through interactions that most probably involve chemical reaction of the Indigo Blue Vat dye with the clay MMT(K10).The new colorant is no more an Indigo Vat dye. That is why this colorant is not affected by the Rongalite C reducing agent which is commonly used in printing with normal Vat dyes. This again confirms that formation of Indigo Blue Vat dye nanoparticles concomitantly with MMT(K10) nanoparticles results in a new nano sized colorant. The latter is brought into focus through chemical attachment of the two types of nanoparticles by chemical bonding as well as through intimate association (interaction) of the nano dispersed clay within the nano dispersed Indigo Blue Vat dye.

Figure 3dillustrates TEM micrograph of a mixture of 3 g indigo blue vat dye and 1 g clay MMT (K10)/100 ml water after 30 min sonication at 80°C. As is evident the micrograph exhibits one type of nanoparticles the size of which ranges from 21.75 to 78.14 nm with an average value of about 55.5nm .These nanoparticles are a manifestation of compatibility and intercalation of the indigo blue nano-dispersion with the clay MMT(K10) nano dispersion. The nanoparticles assume a rod shape which aggregates at certain positions on the rod shaped particle to give differently shaped aggregates.

Figure 3eillustrates TEM micrograph of a mixture of 3 g indigo blue vat dye and 3 g clay MMT (K10)/100 ml water after 30 min sonication at 80°C. The size of the particles ranges from 15.86 to 51.40 nm with an average value of 33.4 nm.

Figure 3f-hshows similar TEM image but when the clay MMT(K10) at a concentration of 5, 7 and 9 g with 3g Indigo blue vat dye/100ml water were used, and the dispersion so obtained was submitted to Ultrasound Technology for 30 min at 80°C. The image indicates that the sizes of the nano scale particles exhibit values ranging from 9.18to 35.12, 8.18 to 112.11 and 13.51 to 173.14 nm for 5, 7 and 9 g clay MMT(K10) respectively, with an average value of 21.6, 71.8 and 118.4 nm for 5, 7 and 9 g clay MMT(K10) respectively. This reflects the favourable effect of higher concentration of MMT (K10) on reducing the size of the new colorant nano particles. In addition, this reflects that increasing of the MMT more than 5 g may mask the dye particles through encapsulation. Figure 3hshows also that, with the indigo blue vat dye/MMT(K10),the interaction leads to nanoparticle size the shape of which is rod in addition to flatted rod or undergoes connection at certain parts with similar rods having similar size of the particles.



a b

Figure 1: TEM micrograph of Indigo Blue Vat dye particles before (a) and after (b) being subjected to sonication using the Indigo Blue (3 g/100 ml H_2O) at 80°C

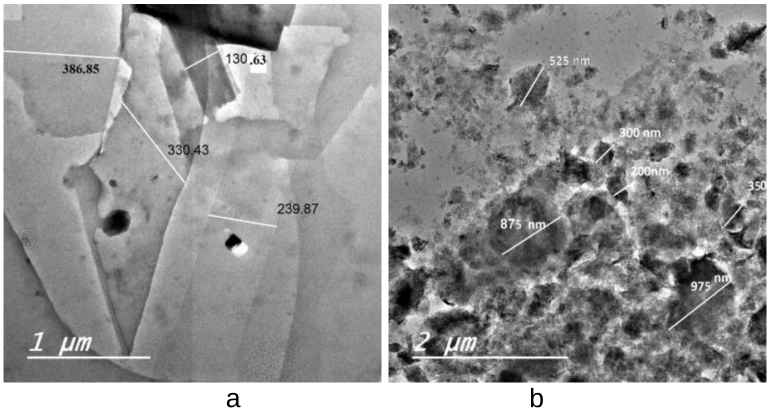


Figure 2: TEM micrograph of clay (MMT; K10) before (a) and after (b) being subjected to sonication using clay(g/100 ml H_2O) at 80°C for 30 min.

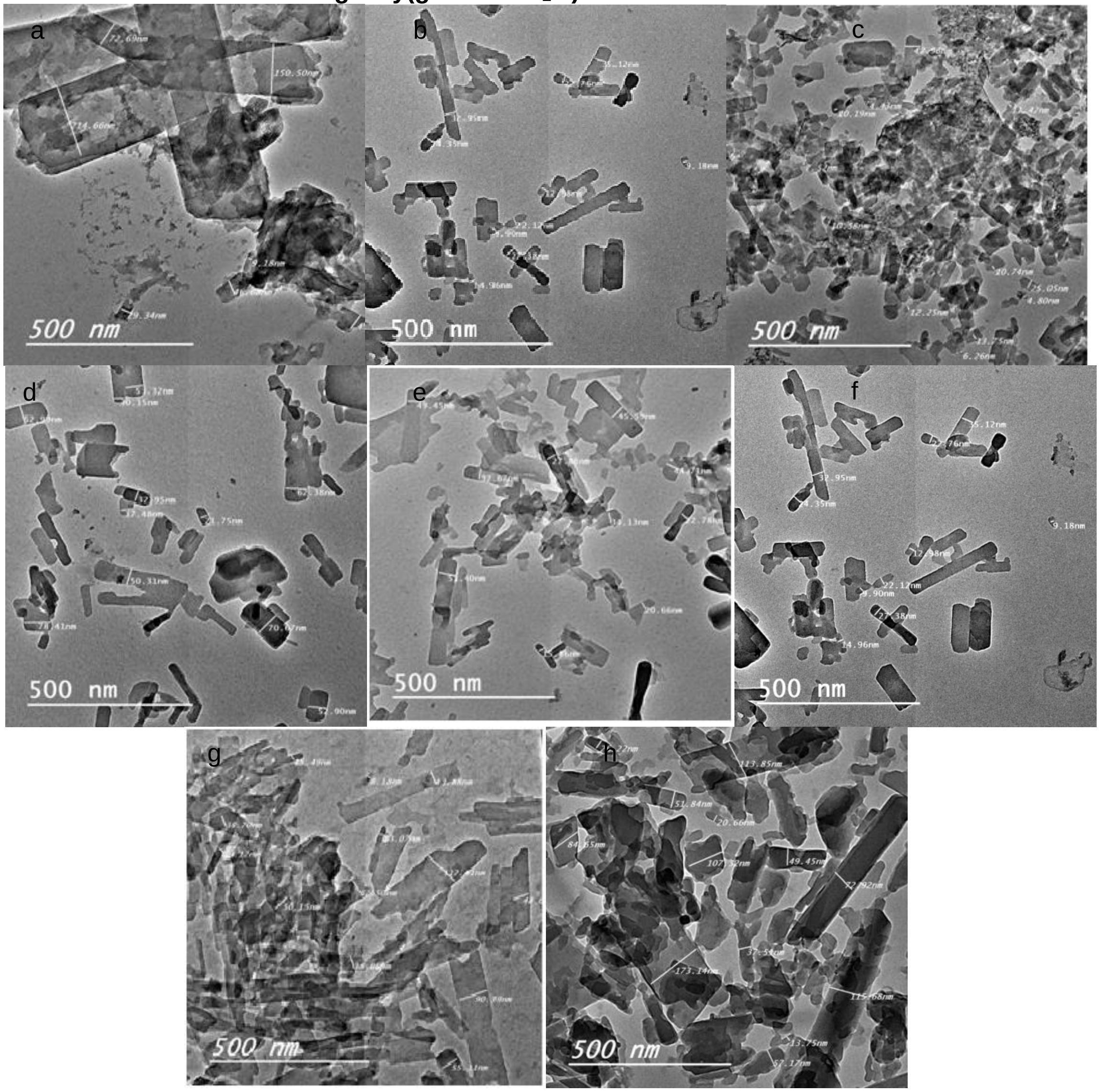


Figure 3: TEM micrograph of different clay concentration

a) 3 g Indigo Blue Vat dye and 5 g MMT (K10)/100 ml H_2O before sonication
b) 3 g Indigo Blue Vat dye and 5 g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 30 min
c) 3 g Indigo Blue Vat dye and 5 g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 60 min, then Rongalite C was added at 100°C for 15 min during sonication
d) 3 g Indigo Blue Vat dye and 1g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 30 min
e) 3 g Indigo Blue Vat dye and 3 g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 30 min
f) 3 g Indigo Blue Vat dye and 5 g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 30 min
g) 3 g Indigo Blue Vat dye and 7 g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 30 min
h) 3 g Indigo Blue Vat dye and 9 g MMT (K10)/100 ml H_2O after being subjected to sonication at 80°C for 30 min

Effectof Clay Concentration on K/S of Prints using New Colorant

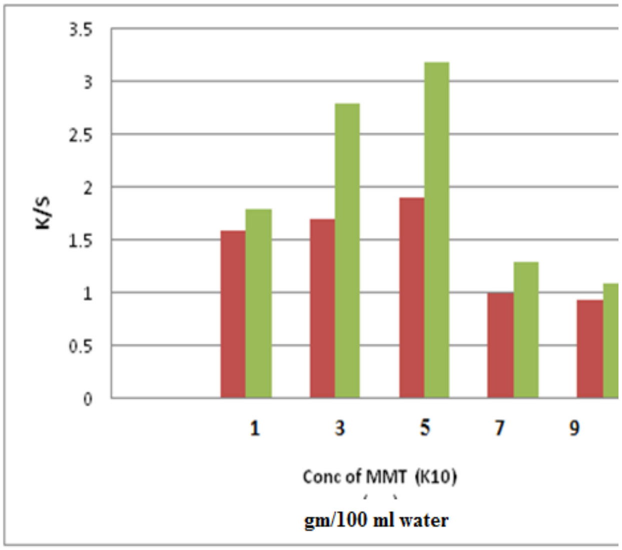


Figure 4depicts that K/S increases significantly to attain highest value when the new colorant was prepared using 5 g clay and Indigo Blue Vat dye (3g)dispersed in 100 ml distilled water. Further increase in this concentration brings about outstanding decrement in K/S values the same holds true for the particle size of the new colorant. But such increment in the particle size of new colorant diminishes its dye ability. Formation of higher amounts of the colorant aggregates due to the presence of higher concentration of MMT(K10) would account for this. It is logical that the ability of the Indigo Blue Vat dye for the interactions involving chemical reaction of the dye with MMT(K10)is augmented at higher concentrations of MMT (K10). In addition, the ability of these aggregates to disintegrate are difficult even under the influence of sonication. It is, therefore, concluded that no more than 5 g MMT(K10) per 3 g Indigo Blue Vat dye suspended in 100 ml distilled water should be exercised. It is also possible that the Indigo Blue Vat dye under investigation is sharing with lower ratios in the interactions occurring during mixing and sonication of the Indigo Blue Vat dye and MMT(K10).This would lead to clay rich hybrid nano-composite most probably with properties different than hybrid nano composites prepared using lower clay concentration as predicted within current lines for explanation. It is rather possible that MMT(K10) at its own higher concentrations would contribute in the formation of the hybrid nano composite through encapsulation of the Indigo Blue Vat dye particle and, in so doing, it masks the dye particles and, in turn, decreases the colour strength. It is,therefore, a must to build up a good understanding about mechanisms entailed in intercalation of the dye with the clay layers. Current work reveals that there is a maximum concentration of the MMT (K10) which should be exercised. In addition, K/S of the control sample attains values of 1.99 before miniaturization and 2.70 after miniaturization upon printing with Indigo Blue Vat dye alone at a concentration of 3 g/100 ml distilled water.

Nature of the clay

In the present work two types of the natural clay montmorillonite namely montmorillonite K10 (MMT- K10) and montmorillonite KSF (MMT- KSF) were used in admixture with Indigo Blue Vatdye. This was done to find out the effect of nature of the clay on (a) particle size of the Indigo Blue Vat dye clay hybrid nano composite which is indeed a new colorant and (b) the colour strength (K/S) of cotton fabric printed using the new colorants.

Investigation presented in the forgoing section cover the just stated two effects with respect to montmorillonite K10 (MMT - K10). Results given under are obtained upon replacing MMT - K10 with Montmorillonite KSF (MMT - KSF).Some of these results are compared whenever required with those of montmorillonite K10.

Thus MMT - KSF (5 g) was added to 100 ml water containing Indigo Blue Vat dye (3 g) and the obtained mixture was submitted to sonication for 30 min at ca 80°C. The Indigo Blue Vat dye was individually subjected to the sonication. The sizes of the miniaturized particles brought almost by sonication were examined and the results obtained are set out in Table 2.

Results of Table 2 make it evident that sonication under the conditions employed decreases the size particle of the individual indigo blue vat dye from 127 to 27.9 nm. Meanwhile the montmorillonite (KSF)/indigo blue vat dye mixture brings into focus hybrid nano composite new colorant with particle size of 22.2 and 218 nm after and before sonication respectively. On the other hand , the particle size of MMT KSF was found to amount to 463.38 µm and 341.07 nm before and after sonication respectively as clearly shown in c **d**
Figure 6a-b.

Figure **5**a-bshows the effect of concentration of MMT - KSF on the particle size of indigo blue vat dye MMT - KSF hybrid nano composite new colorant and colour strength of prints obtained thereof .It is clear that raising the concentration of MMT- KSF from 1 to 5 g/100 ml water increases the colour strength from 0.97 to 1.34 and from 1.37 to 1.60 before and after sonication respectively. On the contrary the particle size of the new colorant decreases from 60.76 to 22.2 nm after sonication. The colour strength decreases upon using MMT-KSF concentration of 7 or 9 g /3 g indigo blue vat dye in 100 ml water , opposite to the particle size which acquire higher values when MMT- KSF was used in the dye mixture at concentration of 7 and 9 g/100 ml water containing 3 g indigo blue vat dye.

c **d**

Figure 6ashows TEM micrograph for the clay MMT (KSF) using 5 gm/ 100 ml water before sonication.It is clear that the clay displays an average particle size of 463.38 µm. The particles of the clay MMT (K10) appears like layers. The nanoscale particles range from 159.21 to 877.65 µm.

c **d**

Figure 6bshows TEM micrograph for the clay MMT(KSF) using 5 g/100 ml water of MMT - KSF after sonication. The MMT (KSF) depicts a particle size range between 198.12 to 535.22 nm. Meanwhile, the majority of the particles have a uniform size with an average value of ca 341.07 nm.

c **d**

Figure 6c-d illustrate the TEM micrographs in which the range of particle sizes of the Indigo Blue Vat dye mixed with MMT(KSF) clay are shown before and after miniaturization under the effect of sonication respectively. It is clear that before sonication (miniaturization)the Indigo Blue Vat dye and MMT(KSF) depict a particle size for instance ranges from 115.17 to 325.51 nm with an average 218 nm.In contrast, the particle size of the mix after miniaturization by sonication is different than before sonication. The 30 min time allowed for sonication induce chemical reaction between the Indigo Blue vat dye and MMT(KSF)(clay) meanwhile the new colorant (product) brought about by such chemical reaction displays much lower particle sizes within the range 8.66 to 45.33 nm with an average 22.2 nm.

As a matter of fact, description of the results relating the concentration of the clay MMT KSF with the size of the new colorant created through intercalation/ exfoliation of the clay nano dispersion into the nano dispersed indigo blue vat dye , bring into focus a trend which is similar to that obtained with the clay MMT - K10(c
d
Figure 6a-d). Similar situation isen countered with K/S. Hence results of the clay MMT K10 can be interpreted on similar basis.

Table 2: The particle size of Indigo Blue Vat dye, individually and in admixture with MMT- KSF before and after Sonication

Indigo Blue Vat Dye (3 gm /100ml water)	MMT KSF(5 gm) + Indigo Blue Vat Dye(3 gm) in 100ml water	Clay KSF alone (5 gm /100ml water)

Particle size nm		Particle size nm		Particle size nm	
Before	After	Before	After	Before	After
127	27.9	218	22.2	463.38 µm	341.07 nm

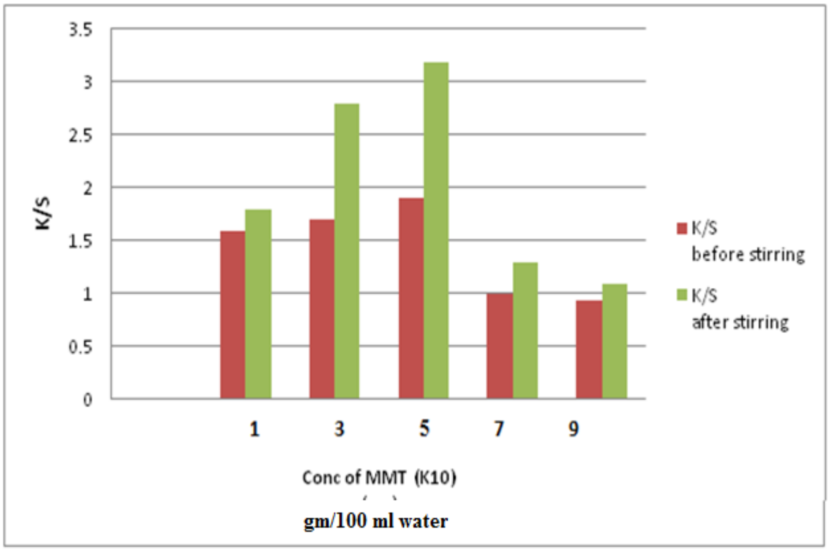


Figure 4: Effect of Montmorillonite clay (MMT)K10 concentration on K/S of fabric printed using new colorantsa

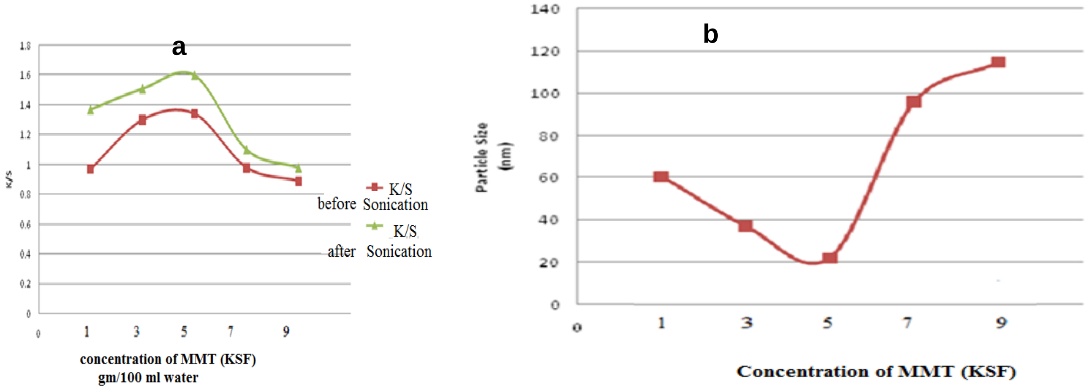


Figure 5: **Effect of MMT (KSF) concentration on (a) K/S and (b)particle size**

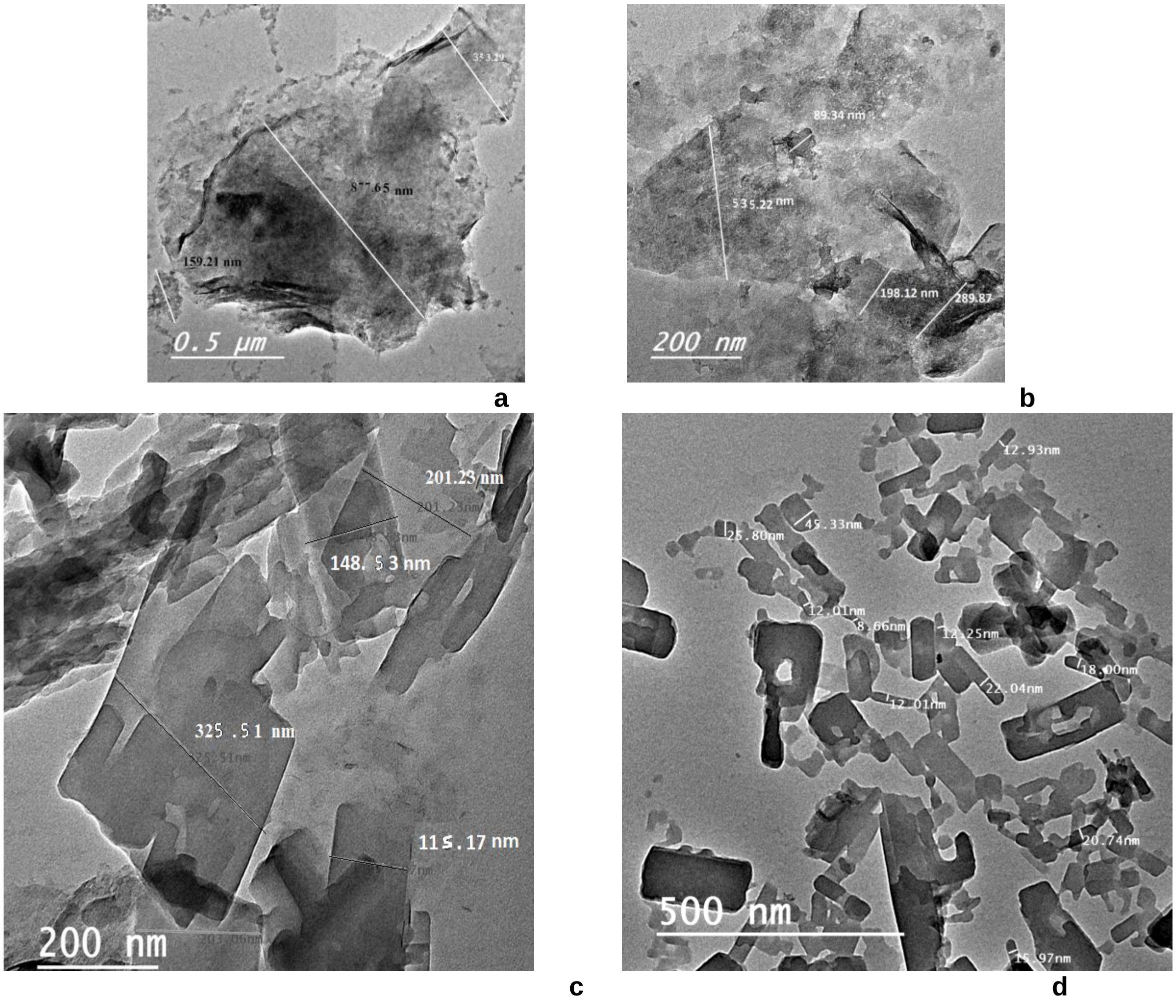


Figure 6: TEM micrograph MMT(KSF) with and without sonication in presence and absence of Indigo Blue Vat dye

a) MMT(KSF) at a concentration of 5 g/100 ml H_2O without sonication
b) MMT(KSF) at a concentration of 5 g/100 ml H_2O with sonication
c) 3 g Indigo Blue Vat dye + 5 g MMT (KSF)/100 ml H_2O without sonication
d) 3 g Indigo Blue Vat dye + 5 g MMT (KSF)/100 ml H_2O with sonication

A comparison between the K/S results of MMT- KSF (Table 2) with those of MMT - K10 (Table 1) would reveal that prints using the new colorants synthesized via intercalation of the MMT- K10 into the indigo vat dye dispersion acquire much higher K/S values than did the MMT- KSF new colorants. The percent increase in K/S at optimum conditions for formation of the new colorants amount to 67.8 and 19.40 for fabrics printed using the new colorants of MMT- K10 and of MMT- KSF respectively. This indeed could be interpreted in terms of differences in nature of the two types of the clays studied .Considering the advantage of the clay MMT K10 in producing more effective colorant, this kind of clay will be the choice for the work presented in next sections. K/S of printed fabric (control sample) using Indigo Blue Vat dye (3 g)alone was 1.99 and 2.70 before and after sonication.

Figure 7ashows the TEM image of the new colorant prepared using Indigo Blue Vat dye (3g) and MMT (KSF) (1g)/100ml water, and the dispersion so obtained was stirred for 30 min at 80°C. obviously, the size of the particles ranges from 30.26to 107.11 nm with an average value of 60.76 nm.

Figure 7cshows similar TEM image but when MMT(KSF) at a concentration of 5gm together with 3g Indigo Blue Vat dye/100ml water were used. The image indicates that the sizes of the nano-scale particles exhibit values ranging from

12.01to 45.33 nm. Nevertheless with the exception of one category of sizes which displays nano- sized particle of 22.2 nm for the new colorant, the majority of the particles possess a value of 12 nm. This reflects the favourable effect of higher concentration of MMT (KSF) on reducing the size of the nanoparticles of the new colorant for reasons cited earlier.

Figure 7eshows the TEM image of the nano-sized particles achieved using the Indigo Blue Vat dye (3g) along with MMT(KSF) (9g)/100ml water , and the dispersion so obtained was stirred for 30 min at ca 80°C. Obviously the size of the particles ranges from 22.99 to 190.88 nm with an average value of ca 114.4 nm.

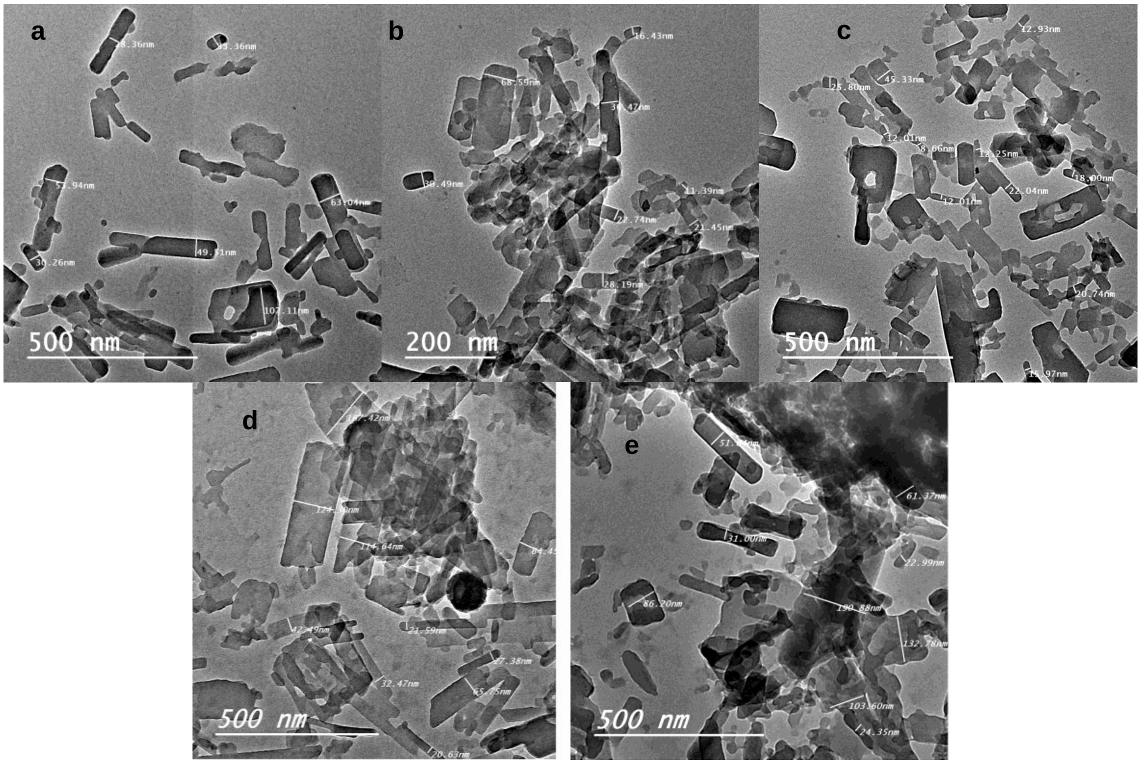


Figure 7: TEM micrograph of different concentration of MMT(KSF) with sonication in presence of Indigo Blue Vat dye

a) 3 g Indigo Blue Vat dye + 1 g MMT (KSF)/100 ml H_2O with sonicationafter30 min
b) 3 g Indigo Blue Vat dye + 3 g MMT (KSF)/100 ml H_2O with sonicationafter30 min
c) 3 g Indigo Blue Vat dye + 5 g MMT (KSF)/100 ml H_2O with sonicationafter30 min
d) 3 g Indigo Blue Vat dye + 7 g MMT (KSF)/100 ml H_2O with sonication after30 min
e) 3 g Indigo Blue Vat dye + 9 g MMT (KSF)/100 ml H_2O with sonication after30 min

Table 3: Effect of particle size of the new nano-colorant on colour strength and fastness properties of printed cotton fabric

Fastness properties											
Optimum conditions for fabrication of new colorant	**Particle size (nm)**	**K/S of printed fabric**	**Washing a60°C Cotton /wool**		**Rubbing Cotton /wool**		**Perspiration fastness**				**Light fastness**
							Acidic		**Alkali**		
			St.	**Alt.**	**Wet**	**Dry**	**St.**	**Alt.**	**St.**	**Alt.**	
Control sample[a]	127	2.10	4	4-5	3	3	4	4-5	4	4-5	6-7
I [b]	22.2	1. 60	4- 5	4- 5	3 -4	4	4- 5	4- 5	4- 5	4- 5	6-7
II [c]	21.6	3.19	4- 5	4- 5	3- 4	4	4- 5	4- 5	4- 5	4- 5	6-7
III [d]	24.47	5.03	4- 5	4- 5	4	4- 5	4- 5	4- 5	4- 5	4- 5	6-7
IV [e]	15.51	7.03	4- 5	4- 5	4	4- 5	4- 5	4- 5	4- 5	4- 5	6-7

[a] Control sample printed with Indigo Blue vat dye alone at concentration (5g/100ml H2O), without sonication

[b] 5g/l MMT (KSF)+ 3 g Indigo vat dye, sonication (80°C/30 min)

[c] 5g/l MMT (K10)+ 3 g Indigo vat dye, sonication (80°C/30 min)

[d] 5g/l MMT (K10)+ 5 g Indigo vat dye, sonication (80°C/30 min)
[e] 5g/l MMT (K10)+ 5 g Indigo vat dye, sonication (80°C/60 min)

Indigo Blue Vat dye concentration

Different amounts of the dye viz. 1, 3, 5 and 7 g/100 ml water containing MMT K10(5 g) were subjected to sonication at 80°C for 30 min under the same frequency of 20 KHZ+ 100 HZ. This experiments were performed in order to clarify the effect of the indigo Blue Vat dye concentration on the particle size of the new colorant formed through intercalation of the clay nano-dispersion into the dye nano dispersion , especially under the action of sonication. Results obtained along with color strength of cotton fabrics printed with the new colorants are given in (Figure 8).

It is clear that, increasing the concentration of the dye is accompanied by increment in both the particle size of the new colorants and color strength (K/S) of cotton fabric printed using these new colorants. This is observed before and after sonication of the dye/clay mixture but with the certainty that more effective colorants are obtained after sonication. Further the particle size of the nanocolorants as well as their K/S on cotton prints attain a maximum value at a dye concentration of 5 g along with 5 g MMT (K10)/100 ml water. The maximum is solicited despite the fact that both the K/S and particle size of the new colorant increases by increasing dye concentration within the range studied for the sake of dye conservation.

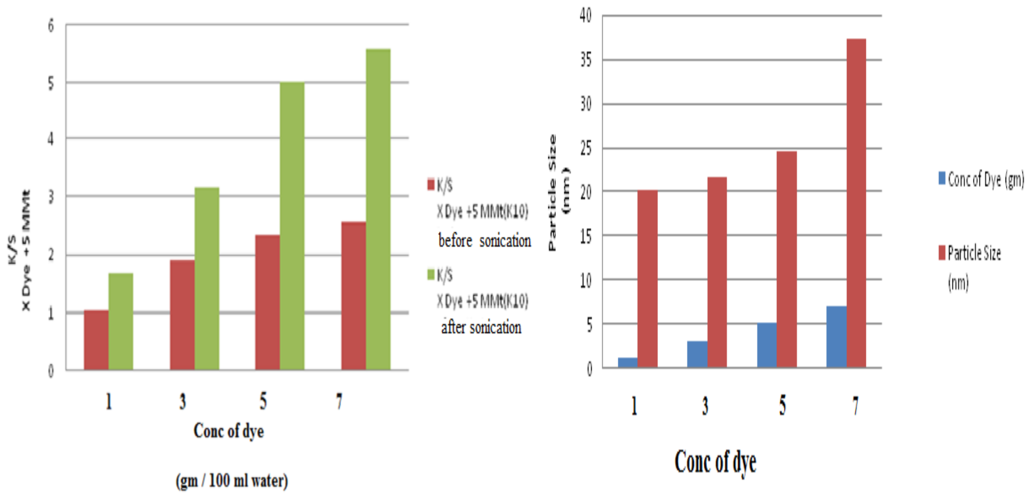
K/S of the control sample displays values of 2.10 before miniaturization and 2.90 after miniaturization upon printing with Indigo Blue Vat dye alone at a concentration of 5 g/100 mldistilled water.Control sample which is printed as per the traditional printing of vat dye, that is, the paste contains Rongalite as a reducing agent in addition to other components of the printing paste.

Figure 9a shows the TEM image of nano-sized new colorant obtained by sonication of Indigo Blue Vat dye (1gm) along with MMT(K10) (5gm) in 100ml water . Sonication was conducted at 80°C for 30 min. Obviously the size of the particles ranges from 11.75 to 62. 57 nm with an average value of 18.2 nm. There is also a tendency to aggregate (agglomerate).

Figure 9bshows the TEM image of nano-sized new colorant obtained by sonication of Indigo Blue Vat dye (3g) along with MMT(K10) (5g) in 100ml water . Sonication was conducted at 80°C for 30 min. As is evident the size of the particles ranges from 9.18 to 35.12 nm with an average value of ca 21.6 nm.

Figure 9cshows the TEM image of nano-sized new colorant obtained using the Indigo Blue Vat dye(5g) together with MMT(K10) (5g)/100ml water, and the dispersion so obtained was stirred for 30 min at 80°C. As is evident the size of the particles ranges from 19 to 39 nm with a mean value of 24.47 nm. The rod like shape of the new-colorant tends to associate to form aggregates and agglomerates with long diameter in the vertical.

Figure 9dshows the TEM image of the nano-sized new colorant direction brought about by using Indigo Blue Vat dye (7g) and MMT(K10) (5g)/100ml water, and the dispersion so obtained was stirred for 30 min at 80°C. The size of the particles ranges from 13 to 125 nm with an average value of 37.2 nm. It is also noted that the new nano-colorant acquires a great tendency to form aggregates and agglomerates through their strong interaction.



a b

Figure 8: Effect of indigo dye concentration on (a) K/S and (b) particle size with constant concentration of MMT (K10)

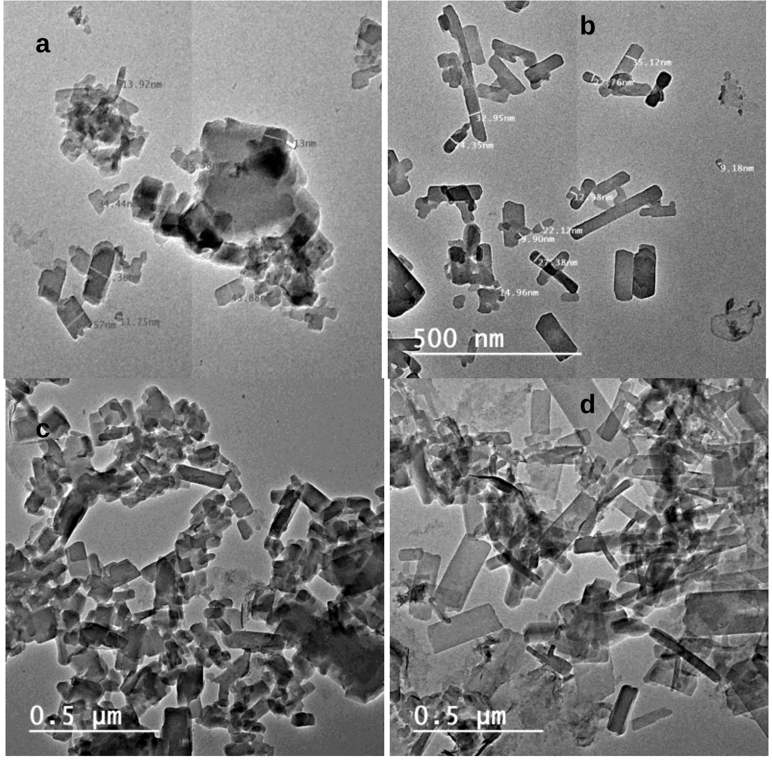


Figure 9: TEM micrograph of different concentration of Indigo Blue Vat dye with sonication in presence of MMT(K10)

a) 1 g Indigo Blue Vat dye + 5 g MMT (K10)/100 ml H_2O with sonicationafter30 min
b) 3 g Indigo Blue Vat dye + 5 g MMT (K10)/100 ml H_2O with sonicationafter30 min
c) 5 g Indigo Blue Vat dye + 5 g MMT (K10)/100 ml H_2O with sonicationafter30 min
d) 7 g Indigo Blue Vat dye + 5 g MMT (K10)/100 ml H_2O with sonication after30 min

Effect of sonication time

A perusal at the outcomes of the preceding sections would signify that indigo blue vat dye (5 g) dispersed in 100ml water containing 5 g of the clay MMT K10 constitutes optimal for fabrication of the new nano-colorant. That is why this condition was used to investigate the effect of sonication time 15, 30, 45and 60 min on the particle size and colour ability of the new nano-colorant. Figure 10show the effect of time of sonication on the particle size of the nano-colorant and its ability to colour - via printing - cotton fabric. It is clear that, the time of sonication has a remarkable effect on the particle size. The latter decreases from 73.4, 24.47, 19, 15.51 nm by increasing the time of sonication from 15, 30, 45 and 60 min respectively.

The increase in the K/S by increasing the time of sonication could be ascribed to larger numbers of new colorant nanoparticles which, in turn, provides larger surface area under longer duration of sonication. These ultrafine colorant would also exercise ease of penetration into and trigger exceedingly high colour uniformity on the prints. As a consequence the K/S displays increased values by prolonging duration of sonication.

K/S of the control sample attains value of 2.35 before sonication upon printing using a mixture of Indigo Blue Vat dye at a concentration of 5 g/100 ml and MMT(K10) at a concentration of 5 g/100 ml distilled water.

Effect of particle size of the new nanocoloranton color strength and fastness properties of its cotton prints

A close examination of the research output of the foregoing sections reveals that the optimum conditions to obtain the smallest particle size and the highest K/S are by adding the same weight of the Vat dye (5 g) to the same weight of the clay MMT(K10) (5 g) in 100 ml water followed by sonication at 80°C for 60 min under 20 KHZ 100HZ.

.

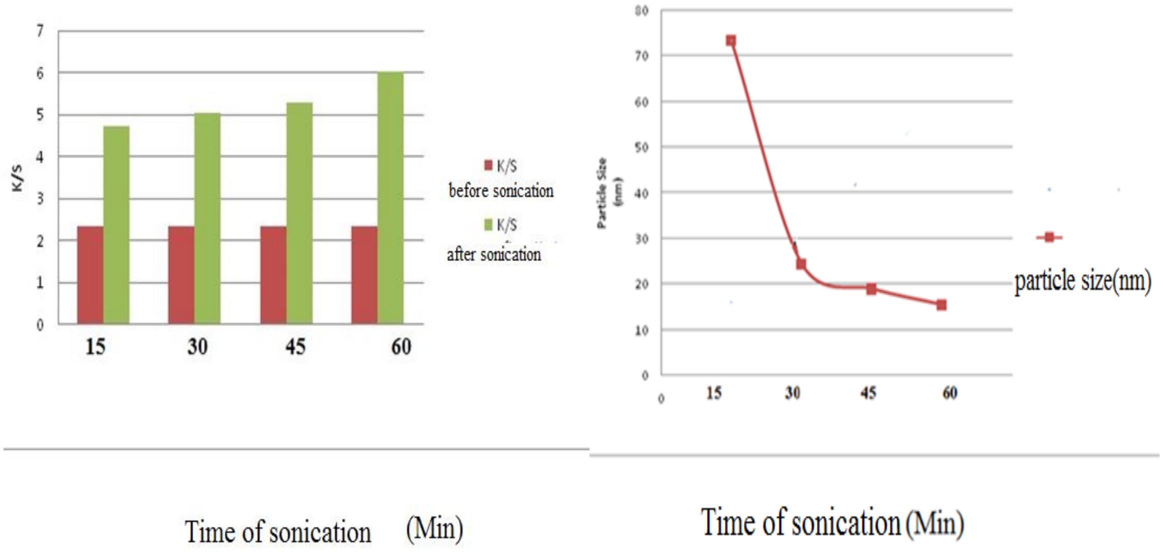


Figure 10: Effect of sonication time on (a) K/S and (b) particle size with constant concentration of MMT (K10)

Colourfastness properties of the cotton samples printed using the new nano-colorant synthesized under the optimum conditions were measured and set out in Table 3. K/S and colour fastness properties of cotton samples printed using the Indigo Blue Vat dye alone (g/100 mlH_2O), i.e. without adding the clay and without sonication, are also cited in the same table.

It is clear (Table 3) that addition of MMT K10 to the Indigo Blue Vat dye then subjecting the mixture to sonication for 1 hour exert great influence on both the particle size and K/S; the particle size decreases from 127 to 15.51nm while the K/S increases from 2.10 to 7.03 i.e. increases by 234.7 %.It is also clear that while the colour fastness properties namely, washing, perspiration and light. Remain intact, the rubbing colour fastness for both dry and wet are improved.

Evaluation of New Nano-colorant as a pigmentcolorant

The Indigo Blue Vat dye under investigation was evaluated as a pigment colorant and as nano - pigment colorant for cotton textile printing. Hence, two different printing pastes were prepared, the first paste contained the original

Indigo blue vat dye (control sample) before sonication along with Rongalite C, and the other required components for Indigo blue vat dye printing .Meanwhile same paste was also prepared and subjected to sonication to achieve Indigo blue vat nanoparticles. On the other hand, the second paste contained a mixture of the dye and MMT (K10) before and after being sonicated (new colorant). In all cases the paste consisted of the dye(colorant) ,urea , thickener, sodium dihydrogen phosphate along with different amounts of binder(0, 1, 2, 3 , 4 , 5 g %). After printing and drying, the samples were subjected to thermo fixation at 160°C for 3 minutes in case of the new colorant and steaming at 120°C for 15 min in case of original Indigo blue vat dye (control sample).At this end the samples were washed, dried and measured for K/S. The results obtained are given in

Table **4**.

The data (

Table **4**) make it evident that as the amount of binder in the printing paste increases from 0 to 5 g/100g printing paste, the K/S increases regularly, the % increase in K/S is raised from 18.90 to 29.83 as the amount of binder increases from 1 to 5 % respectively.

Previous data already presented in preceding paragraphs as well as current data (

Table **4**) indicate that Indigo Blue Vat dye can be used as Indigo blue vat dye or pigment colorant provided that it is miniaturized as per the experimental conditions used in this research. Nevertheless K/S is higher when used as a nano pigment (new colorant) than the nanoscale Indigo blue vat dye (the dye after being miniaturized).

At any event, the use of the Indigo blue vat dye as a pigment new colorant based on (Indigo vat + MMT K10) and as Indigo vat dye according to the traditional method before miniaturization display values of 0.89 and 2.10 respectively. This is against K/S values of 7.92 and 2.90 respectively upon using the Indigo blue as a nano pigment colorant and as nano vat dye respectively after miniaturization.

Of particular interest are the results obtained with Indigo Blue vat dye/MMT(K10) mix when used as pigment colorant before miniaturization, the K/S is almost double that of being used as vat dye (traditional method). Different situation is encountered after miniaturization. The K/S displays values of 7.92 and 2.90 upon using the Indigo blue vat dye as nano pigment colorant and as a nano Indigo blue vat dye(traditional method) respectively.

Miniaturization lessens greatly the difference in functioning of the Indigo blue vat dye as a pigment colorant and as vat dye under the printing conditions employed. However, miniaturization is a must in both cases as is evident from the K/S values after miniaturization. This can be attributed to the large surface area created upon miniaturization of the original dye particles (127 nm) to the nano sized colorant particles value of 15. 51 nm under the effect of sonication.

Mixing the Indigo blue vat dye with (K10) enhances the ability of the colorant produced to accommodate more colorant molecules due to larger surface area which, in turn, undergoes in combination with the polyhydroxylic groups of cotton strong interactions and which ultimately lead to strong interaction with the cotton cellulose layers in the fabric and the colorant whether considered as a pigment or a vat dye.

K/S of the control sample attains values of 2.10 before miniaturization and 2.90 after miniaturization upon printing with Indigo Blue Vat dye alone at a concentration of 5 g/100 ml distilled water. Control sample was printed as per the traditional printing of vat dye, that is, the paste contains Rongalite C as a reducing agent in addition to other components in the printing paste.

Table 5 shows the colour strength (K/S) and the fastness properties of cotton fabrics printed using the new colorant nanoparticles in presence of different concentrations of binder. Obviously, the K/S of the prints display exceedingly higher values after sonication of the newly processed colorant. For example, the prints exhibit K/S values of 0.89 and 3.27 before and after sonication, respectively, in absence of binder. In presence of the latter along with the new colorant accentuate the K/S which, indeed, display higher augmentation at higher binder's concentration within the range studied.

The fastness properties of the prints under investigation encompass fastness to washing, to rubbing, to perspiration and to light. These properties exhibit fastness values which can easily promote current prints to a highly acceptable category among international printing catalogues.

Table 4: Colour strength (K/S) of cotton fabrics printed using the new nano-colorant as a Pigment using different concentrations of binder

Binder concentration (g/100 g paste)	K/S of printed fabric	Increase in K/S %
Before sonication	**0.89**	
0	3.27	4.47
1	3.90	18.90
2	4.86	15.43
3	5. 58	17.22
4	6.33	18.31
5	7.92	29.83

Colorant processed using 5 g Vat dye+5 g MMT(K10)

Table 5: Fastness properties of cotton fabrics printed using the new colorant nanoparticlesin presence of different concentrations of binder

Fastness properties										
Concentration of binder gm/100gm paste	**K/S of printed fabric**	**Washing at 60°C Cotton /wool**		**Rubbing Fastness**		**Perspiration fastness Cotton /wool**				**Light fastness**
		St.	**Alt.**	**Wet**	**dry**	**Acidic**		**Alkali**		
						St.	**Alt.**	**St.**	**Alt.**	
0 MMT +dye before sonication	0.89	4- 5	4- 5	2	2- 3	4- 5	4- 5	4- 5	4- 5	6-7
0 MMT + dye after sonication	3.27	4- 5	4- 5	3 -4	4	4- 5	4- 5	4- 5	4- 5	6-7
1	3.90	4- 5	4- 5	4	4	4- 5	4- 5	4- 5	4- 5	6-7
2	4.86	4- 5	4- 5	4	4- 5	4- 5	4- 5	4- 5	4- 5	6-7
3	5. 58	4- 5	4- 5	4	4- 5	4- 5	4- 5	4- 5	4- 5	6-7
4	6.33	4- 5	4- 5	4	4- 5	4- 5	4- 5	4- 5	4- 5	6-7
5	7.92	4- 5	4- 5	4	4- 5	4- 5	4- 5	4- 5	4- 5	6-7

Fourier Infrared Spectral Analysis

The FT- IR spectra were recorded using an S -100 FT- IR spectrometer (Perkin Elmer) and scanned from 4000 to 400 cm^{-1} in ATR mode and using KBr as supporting material. Characterization of samples using FT- IR technique was carried out to follow the change in the functionality of CNW.

The FT- IR spectra of Indigo blue vat dye shows a broad NH band in the region 3421 cm^{-1} and broad band for C=O group in the region 1617 cm^{-1}(Figure 11a). Similarly the FT- IR spectra of clay MMT (K10) shows a broad OH band in the region 3435 cm^{-1} (Figure 11b).The infrared spectra of new colorant showed –C=O, NH and -OH group bands at 1624, 3272,3433 cm^{-1}, respectively(Figure 11c).

Elemental Analysis

Table 6contain various elementary analysis pertaining to carbon, hydrogen, nitrogen and sulphur for the new colorant, Indigo blue vat dye and MMT (K10). As is evident the natural clay MMT (K10) displays very low values of the said elements. This is rather expected since MMT(K10) consist essentially of silicon. In contract, the indigo blue vat dye exhibit very high values of carbon, nitrogen and hydrogen by virtue of the chemical structure of the dye, Analytical results of the new colorant disclose elements with values which lie in between those of the dye and the clay. They are also in full conformation with our assumption that the two components of the new colorant are combined together via chemical bonding. It is believed that chemical bonding occurs during MMT clay intercalating into the dispersed dye.

Morphology of Printed Fabrics (SEM and EDX)

SEM micrographs of MMT (K10) and the Indigo Blue Vat dye mix before sonication (Figure 12a,d) and after sonication(Figure 12b,e) indicate that surface morphology of the MMT(K10) appears as layers while those of the Indigo Blue Vat dye assume a tube- like surface which appears as rods. Meanwhile the new colorant is different and characterized by being more smooth and homogenous(Figure 12c, f).

Energy-Dispersion X-rays pectroscopy(EDS) technique was used for determination of essential elements in the clay (MMT-K10), Indigo Blue vat dye and the new colorant formed upon intercalating the clay into the dispersed dye.

Figure 12g, h and I shows SEM-EDS spectral analysis of the clay, the dye and the new colorant respectively.

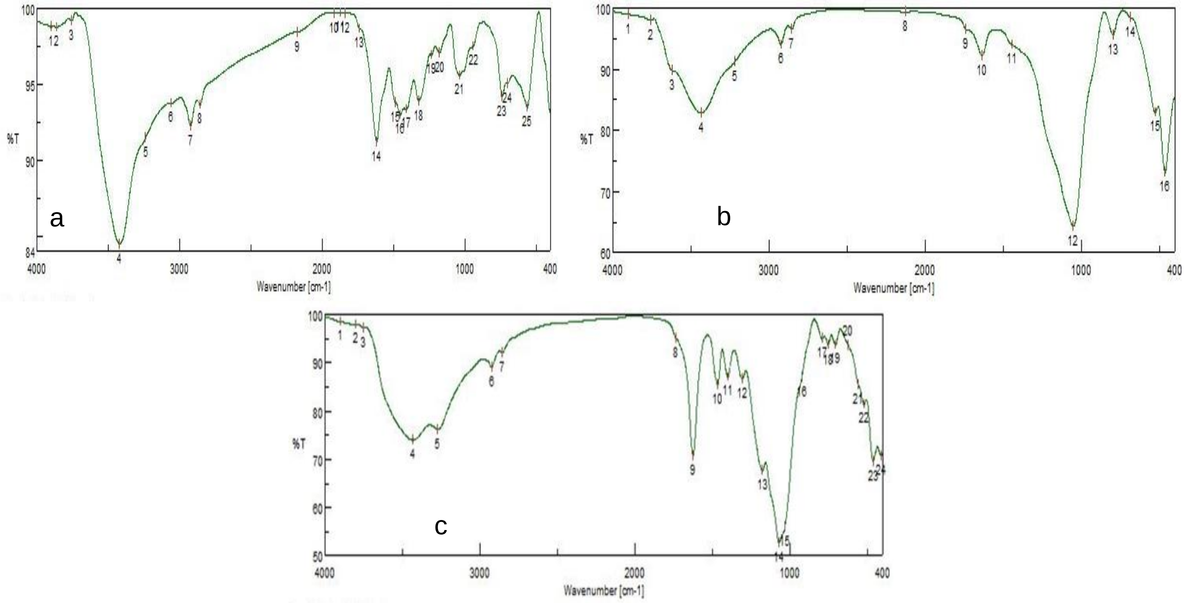
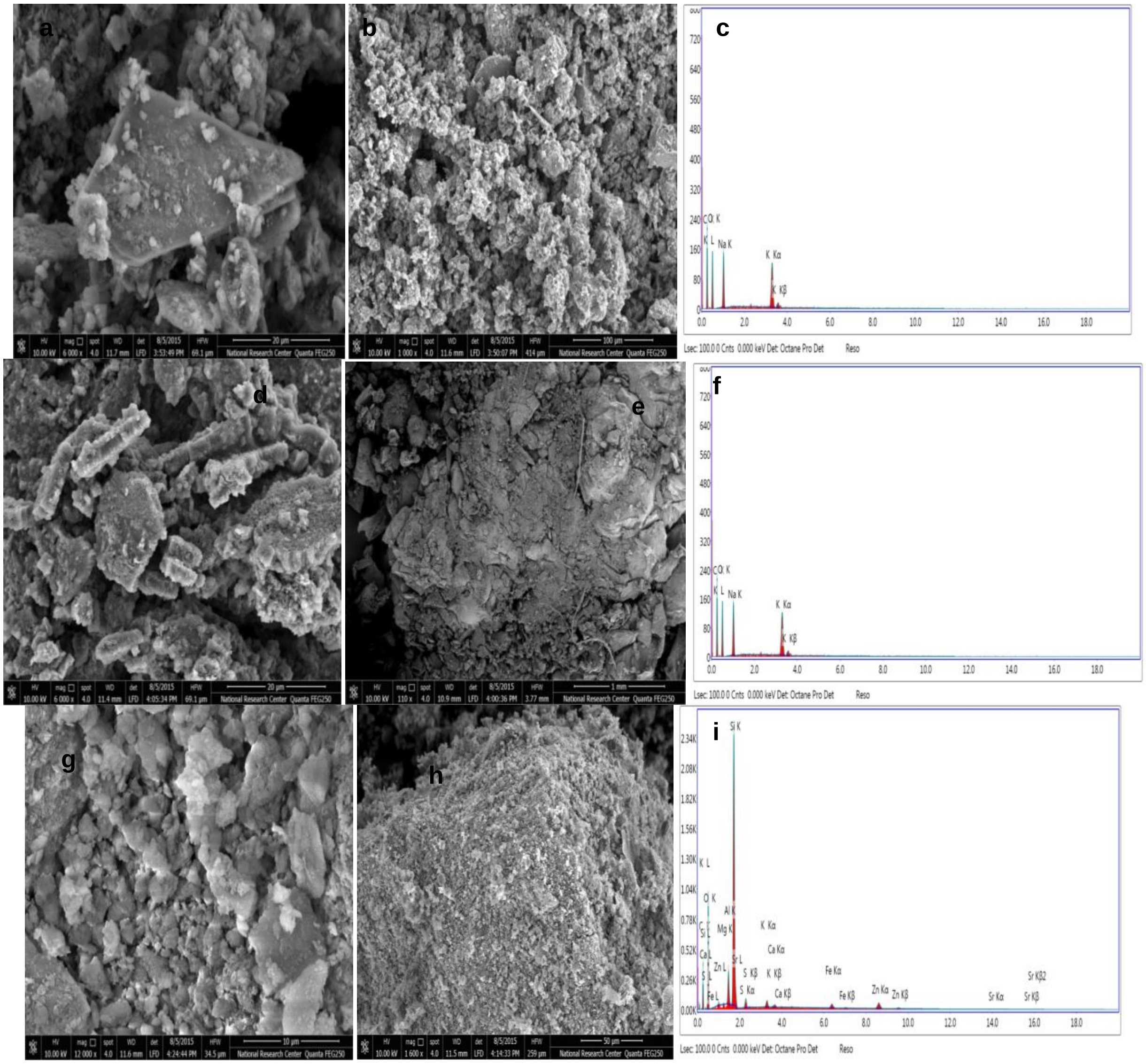


Figure 11: FT- IR spectra of (a) pure Indigo blue vat dye (b) clay MMT (K10) and (c) new colorant

Table 6:Analysis of new colorant,indigo blue vat dye and MMT (K10) samples on Vario El Elementary for measurement C, H,Nand S

Sample	N%	C%	S%	H%
Pure MMT(K10)	0.22	0.22	0.12	0. 56
Pure indigo blue vat dye	6.07	45.05	0.24	2. 64
New colorant(vat dye + MMT)	1.89	12.94	2.08	0.72



Element	clay (MMT- K10)		Indigo Blue Vat dye		new colorant	
	Atomic %	Net Int.	Atomic %	Net Int.	Atomic %	Net Int.
C			52.81	6.86	41.54	11.92
O	76.19	162.52	34.83	6.33	44.36	42.08
Na			10.31	8.33	0.27	4.31
K	0.31	7.31	2.05	11.74	0.21	4.65
Mg	1.34	10.5			0.14	1.05
Al	4.66	58.49			1.66	19.92
Kr	0.12	2.43			0.29	8.21
Si	17.11	261.05			10.93	174.53
Fe	0.13	3.99			0.25	4.86
Ca	0.13	0.63			0.08	1.61
S	0.01	0.31			0.27	4.36

Figure 12: Scanning electron microscopy (SEM) and Energy dispersive x - ray spectroscopy (EDS)
a, b and c) pure MMT (K10) (a and b) SEM before and after sonication and (c) EDX
d, e and f) pure Indigo blue vat dye (d and e) SEM before and after sonication and (f) EDX
g, h and i) new colorant (g and h) SEM before and after sonication and (i) EDX

Figure 12gmakes it evident that the clay is characterized by high Intensity due to the presence of Si, Al , O_2 and Mg which represent the combination silicate structure (Al SiO_2) according to figure 46 (e.g. O=76.19,Si =17.11 and Al=4.66 %) with the certainty that Si combined with (O) display the highest Intensity . Specifically, therefore, the clay major constituents are Si, Al and $O_2$and, the clay is constituted mainly of Si, Al and (O) along with other minor elements.

Figure 12hdepicts SEM–EDS spectra of Indigo Blue Vat dye. The latter display low Intensity which have not inorganic elements, the silicate structure does not present in Indigo Blue Vat dye. It seems possible that the dye is only contaminated with trace amounts of hydrocarbon structure (organic materials)(C)=52.81and (O)=34.38 meanwhile consist of salts(K)=2.05% and (Na)= 10.31%.

Figure 12iexhibits the SEM-EDS of the new colorant. Major elements shown by the new colorant as per its own spectral Intensity are those of: salts according to (Mg, Na, K) Aluminium silicate structure ($AlSiO_2$) and hydrocarbon material of Indigo blue vat dye (O,C). Also appeared are spectral intensity of those correspond to C-Si combination.

CONCLUSION

Research performed in this chapter lead to development of new hybrid nano-composite colorants through interaction of Indigo vat dye with the layered silicate of a natural clay known as montmorillonite. These new colorants could be arrived at by mixing the dye and the clay followed by subjecting the mix to sonication. Such a processing was carried out under a variety of conditions including concentration 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 nanosize of the new colorant and its printability. Considering the results obtained by each of these variables, optimal processing conditions for fabrication of the new colorant could be outlined as follows:

The as fabricated new colorant acquired a particle size of 15.51 nm, increase in colour strength of the prints by 2.7 % and fastness properties are improved compared with the original Indigo vat dye for washing, perspiration, rubbing and light respectively. Mechanism of formation of the new colorant is also reported. Furthermore, the SEM – EDS spectral constitution of the clay (MMT K10) and Indigo Blue Vat dye independently as well as in an intercalated two in one (new colorant) are made.

CONFLICT OF INTEREST

There is no conflict of interest here

ACKNOWLEGEMENT

Authors are gratefully grateful acknowledge to National Research Centre (NRC) for facilities provided.

REFERENCES

A. V R and R. K, Polymer Nanocomposites: Synthesis,Characterization,andModeling, in ACS Symposium Series 804, K. R. and V.R. A., Editors. 2002, American Chemical Society: Washington, DC, USA.

AATCC Test Method (15-2002), Colour Fastness to Perspiration, in Technical Manual Method 1993, American Association of Textile Chemists and Colorists. p. 30.

AATCC Test Method (61-1993), Colour Fastness to Washing: Characterization of Textile Colorants, in American Association of Textile Chemists and Colorists, Technical Manual Method 1993, American Association of Textile Chemists and Colorists. p. 89.

AATCC Test Method (8-1993), Colour Fastness to Crocking, in Technical Manual Method 1993, American Association of Textile Chemists and Colorists. p. 23.

AATCC, Colour Fastness to Light: Carbon – Arc Lamb, Continuous Light, in Technical Manual Method 1993, American Association of Textile Chemists and Colorists. p. 33.

Abo-Shosha M H, et al., Research Journal of Textile and Apparel, 13 (2009) 65.

Alexandre M and Dubois P, Materials Science and Engineering: R: Reports, 28 (2000) 1.

Asmah A E, Okpattah V, and Frimpong C, International Journal of Arts and Humanities, 4 (2015) 41.

Becker O, Varley R, and Simon G, Polymer, 43 (2002) 4365.

Božič M and Kokol V, Dyes Pigm, 76 (2008) 299.

Chattopadhyay D P and Patel B H, J Eng Fiber Fabr, 5 (2010) 1.

Chen T K, Tien Y I, and Wei K H, Polymer, 41 (2000) 1345.

Elhady H S A, Technological Innovations based on Advanced Sciences For Development of Textile Printing, in Faculty of Applied Arts. 2012, Helwan University, Egypt.

Fornes T D, Hunter D L, and Paul D R, Macromolecules, 37 (2004) 1793.

Fu X and Qutubuddin S, Polymer, 42 (2001) 807.

Giannelis E P, Krishnamoorti R, and Manias E, Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes, in Polymers in confined environments. 1999, Springer Berlin Heidelberg. p. 107.

Hassabo A G, et al., Research & Reviews in Polymer, 6 (2015) 118.

Hassabo A G, et al., Research Journal of Textile and Apparel, 18 (2014) 36.

Hassabo A G, Preparation, Characterisation and utilization of some textile auxiliaries. 2005, El-Azhar University: Cairo, Egypt.

Hassabo A G, Synthesis and Deposition of Functional Nano-Materials on Natural Fibres 2011, RWTH Aachen University. p. 154.

Hebeish A, et al., Der Pharma Chemica, 8 (2016) 259.

Hou D W, et al., Nanomaterials, 6 (2016).

Hult E L, Larsson P T, and Iversen T, Polymer, 42 (2001) 3309.

Jäger I, Hafner C, and Schneider K, Mutation Research/Genetic Toxicology and Environmental Mutagenesis, 561 (2004) 35.

Jeon H G, et al., Polymer Bulletin, 41 (1998) 107.

Joo S-H and Jin J-I, Journal of Polymer Science Part A: Polymer Chemistry, 42 (2004) 1335.

Kato M, Usuki A, and Okada A, Journal of Applied Polymer Science, 66 (1997) 1781.

Kojima Y, et al., Journal of Polymer Science Part B: Polymer Physics, 33 (1995) 1039.

Kojima Y, et al., Journal of Polymer Science Part B: Polymer Physics, 32 (1994) 625.

Kornmann X, Lindberg H, and Berglund L A, Polymer, 42 (2001) 1303.

Kubelka P and Munk F, Z. Tech. Phys., 12 (1931) 593.

LeBaron P C, Wang Z, and Pinnavaia T J, Appl Clay Sci, 15 (1999) 11.

LeBaron P C, Wang Z, and Pinnavaia T J, Appl Clay Sci, 15 (1999) 11.

Lee D C and Jang L W, Journal of Applied Polymer Science, 61 (1996) 1117.

Maiti P, et al., Macromolecules, 35 (2002) 2042.

Masenelli-Varlot K, et al., Journal of Polymer Science Part B: Polymer Physics, 40 (2002) 272.

Mehta K T, et al., Dyes Pigm, 5 (1984) 329.

Nam P H, et al., Polymer, 42 (2001) 9633.

Noh M W and Lee D C, Polymer Bulletin, 42 (1999) 619.

Roessler A and Crettenand D, Dyes Pigm, 63 (2004) 29.

Roessler A and Jin X, Dyes Pigm, 59 (2003) 223.

Roessler A, New electrochemical methods for the reduction of vat dyes. 2003, Swiss Federal Institute of Technology (ETH): Zurich.

Sawhney A P S, et al., Text Res J, 78 (2008) 731.

She F Y, et al., Advanced Materials Research, 441 (2012) 145.

Sheng N, et al., Polymer, 45 (2004) 487.

Sin S L, Polymer-based and Polymer-filled Nanocomposites, in Nanocomposite Science and Technology, P.M. Ajayan, L.S. Schadler, and P.V. Braun, Editors. 2003, Wiley-VCB Verlag GmbH & Co. KGaA: Weinheim.

Sinha Ray S and Okamoto M, Progress in Polymer Science, 28 (2003) 1539.

Song L, et al., Int J Polym Anal Charact, 8 (2003) 317.

Stretz H A, et al., Polymer, 46 (2005) 2621.

Thetford D and Chorlton A P, Dyes Pigm, 61 (2004) 49.

Usuki A, et al., Journal of Applied Polymer Science, 55 (1995) 119.

Varlot K, et al., Journal of Polymer Science Part B: Polymer Physics, 39 (2001) 1360.

Waly A I, et al., Research Journal of Textile and Apparel, 16 (2012) 66

Waly A, et al., Egyptian Journal of Textile Polymer Science and Technology, 12 (2008) 101.

Waly A, et al., Process of Single – Bath Dyeing, Finishing and Flam – Retarding of Cellulosic Textiles in Presence of Reactive Tertiary Amines. in 3rd International Conference of Textile Research Division, NRC; Textile Processing: State of the Art & Future Developments. 2006. Cairo, Egypt.

Wang K, et al., Langmuir, 21 (2005) 3613.

Wang Z and Pinnavaia T J, Chem Mater, 10 (1998) 3769.

Yano K, et al., Journal of Polymer Science Part A: Polymer Chemistry, 31 (1993) 2493.

Yoon P J, Fornes T D, and Paul D R, Polymer, 43 (2002) 6727.

Yuen C W M, et al., AATCC Review, 5 (2005) 41.