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Imparting Multi-functional Performance on Cellulosic Fabrics via Nanotechnology

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ABSTRACT: Three different metal oxides namely TiO_2 , MgO and ZnO in the nano particle size (NPs)form were prepared through chemical methods and characterized by transmission electron microscope (TEM) to evaluate its particle size and size distribution. The cotton and viscose fabrics were first pre-treated separately with the NPs metal oxides and then printed with pastes containing reactive and/or natural dyes. The colour strength (K/S) of pre-treated fabrics with nanoparticles were measured and compared with the untreated one. The existence of NPs on the fabrics during printing process highly increase the K/S of the printed goods irrespective of the nature of the colour or the kind of fabrics to be print. However, the value of the K/S of the printed goods depends on: (a) the nature of the metal oxide, (2) its concentration, (c) the nature of the colour, and (d) the nature of the printed fabric. Besides the NPs-treatment leads to produce a coloured fabrics with excellent antibacterial and very good UV protection properties and very good fastness properties.

KEYWORDS: Cellulosic Fabrics, Nanotechnology, transmission electron microscope.

1 INTRODUCTION

Nanotechnology is considered to be one of the most important emerging technologies worldwide. It is an innovation driver for many sectors of industry [(1)].

Known advantages of utilizing nanotechnology in textile sector can be discussed in terms of: (1) more effective, i.e. more active and large surface areas per unit weight, (2) minimal impacts on physical and mechanical properties, i.e. hand, strength, and air permeability, (3) minimal use of chemicals, (4) low energy consumption and costs, and (5) lower environmental impacts[(2)].

In the last decades, several research and industrial efforts have been devoted to the development of new products for enhancing the quality of human life. The textile production, one of the most relevant and ever-advancing industrial field around the world, is not an exception. In particular, with a rising awareness in personal health and hygiene, the textiles with antimicrobial properties are becoming an appealing field for both manufacturers and researchers [(3-10)].

Human beings are often infected by microorganisms such as bacterium, mold, yeast, virus, etc., in living environment [(11)]. In recent years, antimicrobial agents that have been used industrially have included quaternary ammonium salts, metal salts solutions, and antibiotics. Unfortunately, some of these agents are toxic or poorly effective, which makes them not suitable for application in health foods, filters, and textiles, and for the exclusions of pollution. In contrast, silver is a non-toxic, non-tolerant disinfectant that can reduce many bacterial infections significantly [(12)].

Using nanotechnology in enhanced functionalization of textile to produce smart fabric with antibacterial, stain resistant, and UV protection properties has been increased dramatically [(13-17)]. The application of nanoparticles, especially metal oxides and nano-metals, to impart cellulosic fabric with multifunctional performances was the object of this study improving its hydrophilicity, antibacterial properties, and UV-resistance.

The present research article involves three major objectives: (1) the use of chemical methods to synthesis three metal oxide NPs (TiO_2, MgO and ZnO) under different conditions to reduce their particle size; (2) functionalization and modification of cotton and viscose fabrics by surface treatment with the prepared metal oxide NPs; (3) improvement of printing properties of NPs-treated cotton and viscose fabrics with reactive and natural dyes by increasing the dye affinity and (4) evaluation of the colour fastness, antibacterial properties, and UV protection of the NPs-treated fabrics.

2 EXPERIMENTAL

2.1 SUBSTRATE

2.1.1 COTTON FABRIC

Scoured cotton fabrics 140 g/m^2 were supplied from Misr for Spinning and Weaving Company, Mahalla El- Kobra., Egypt. Cotton fabric was further treated with a solution containing 2g/L nonionic detergent (Hostapal ® CV-Clariant), at 60 ^{0}C for 30 minutes, then the fabrics were thoroughly rinsed with water and air dried at room temperature.

2.1.2 VISCOSE FABRIC

Scoured viscose fabrics 110 g/m^2 were supplied from El- Shorpagy Company, Cairo ., Egypt. Viscose fabric was further treated with a solution containing 2g/L nonionic detergent (Hostapal ® CV-Clariant), at 50 ^{0}C for 30 minutes, then the fabrics were thoroughly rinsed with water and air dried at room temperature.

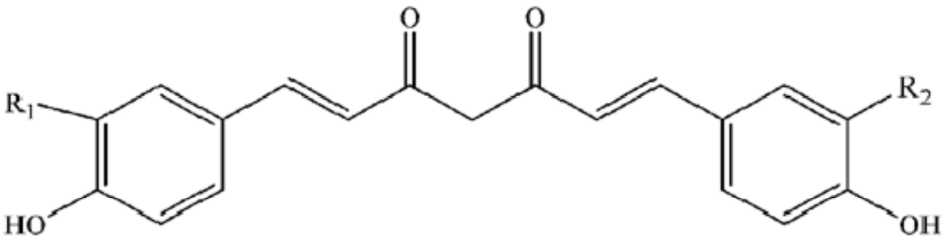
2.2 MATERIALS

2.2.1 DYESTUFFS

The following different two dyes were used:

2.2.1.1 NATURAL DYES

Curcuma Longo L, known as turmeric which are used as colouring agent and also medical properties[18]. Its major active matter is Curcumin, along with small amounts of demethoxy curcumin and bisdemethoxy Curcumin (Scheme 1) [19].



R1 = OCH_3, R2 = OCH_3 - curcumin
R1 = R2 = H - bisdemethoxycurcumin
R1 = OCH_3, R2 = H - demethoxycurcumin

Scheme 1: Structure of Curcumin and its analoge

2.2.1.2 REACTIVE DYE

Reactive dye namely Suncion Red P2B OH Young Industrial LTD.

2.2.2 THICKENER

Sodium alginate of medium viscosity under the commercial name Daico thickener RE was kindly supplied from Daico Chemica Industry S.A.E Cairo, Egypt.

2.3 METHODS

2.3.1 SYNTHESIS OF METAL OXIDES

2.3.1.1 SYNTHESIS OF ZNO NANO PARTICLES

Zinc oxide nano particles were synthesized [20,21]. Synthesis was carried out at a high degree of super saturation in order to achieve a nucleation rate much greater than the growth rate (5.5 g) $ZnCl_2$ (98%) was dissolved in 200 mL of water at 90ºC in an oil bath. Then 16 mL of 5 M NaOH (pellet min.99%) aqueous solution was added drop-wise to the zinc chloride solution with a gentle stirring over a period of 10 min at 90ºC. The particles were separated from the supernatant dispersion by sedimentation. The supernatant solution was discarded and the remaining suspension was washed five times with distilled water to lower the concentration of NaCl below 6-10M. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was checked using a solution of $AgNO_3$. The purified particles were then peptized with 2-propanol (98%) in an ultrasonic bath for 10 min at room temperature. The peptization process is necessary to disrupt the micro-agglomerates and to release the nano particles of zinc oxide.

The particles were then collected by centrifugation at 6,000 rpm for 15 min. The washing procedure was repeated three times. Thermal treatment of the particles at 250ºC for 5 h leads to the formation of ZnO[22].

TREATMENT OF COTTON AND VISCOSE FABRICS BY ZNO NANO PARTICLES

The samples were impregnated in ZnO treatment bath (conc. 0.5 % - 2 % wof), using liquor ratio of 1:30, in presence of dispersing agent in order to suspend the ZnO in water to obtain homogenous solution. After padding, the samples were squeezed to 80% pick up, then they were dried at 60^0C .The treated fabrics were cured at 140 ^{0}C for 10 min. Finally treated fabrics were washed at 60 ^{0}C for 20 min. followed by drying.

2.3.1.2 PREPARATION OF TiO_2 NANO PARTICLES

Titanium tetra chloride ($TiCl_4$) of 3.5 ml was added to 50 ml deionized water in ice bath and the process was done under fume hood followed by the addition of 35 ml of ethanol with vigorous stirring for 30 min at room temperature. Drops of ammonium hydroxide were added wisely into solution of the titanium tetra chloride ($TiCl_4$), ethanol and deionized water to neutralize it and precipitate was obtained. After stirring vigorously, the solution was made to settle for twelve hours. Then, precipitate was centrifuged. The obtained precipitate was washed with deionized water until the removals of chloride ion and was centrifugally separated. Then, using oven, the precipitate was dried at 200°C to remove part of the absorbed water for 4 hours and finally amorphous TiO_2 was obtained. The obtained amorphous TiO_2 was calcinated at the temperatures of 400°C for four hours step by step. Finally, the powder TiO_2 nanomaterial was obtained [23-26]

TREATMENT OF COTTON AND VISCOSE FABRICS BY TiO_2 NANO PARTICLES

The fabrics treated with TiO_2 nanoparticles via exhaustion method. the fabrics were treated with 4 different percentages of TiO_2 nanoparticles (0.5 % - 2 %wof) at 80 ^{0}C for 20 min. in the presence of wetting agent in dyeing machine. The liquor ratio of exhaustion bath was 1:10. After 20 min. The treated cotton and viscose fabrics were cured at 140 ^{0}C for 10 min. Finally treated cotton and viscose fabrics were washed at 60 ^{0}C for 20 min. followed by drying.

2.3.1.3 SYNTHESIS OF MGO NANOPARTICLES

MgO nano particlesare usually synthesized by hydrothermal or sol–gel techniques [27-30]. In this experiment, nano-MgO was synthesized by the sol–gel method. To prepare nanoparticles of MgO, 100 g of MgCl •6H 2O was first dissolved in 500 ml of distilled water in a 1L beaker, into which 50 ml of 1N NaOH solution was added. The solution was then rapidly stirred for 4 h to generate the magnesium hydroxide precipitates. The suspension was centrifuged at 3000rpm for 5 min to obtain the

$Mg(OH)_2$ gel, washed several times with distilled water and dried at 60 ^{0}C for 24h. The dried powder was finally calcinated in air under 450 ^{0}C for 2 hour and MgO nanoparticles were such made.

TREATMENT OF COTTON AND VISCOSE FABRICS BY MgO NANO PARTICLES

The fabrics treated with MgO nanoparticles via exhaustion method. The fabrics were treated with 4 different percentages of MgO nanoparticles (0.5 % - 2 % wof) for 20 min. in the presence of wetting agent in dyeing machine. The liquor ratio of exhaustion bath was 1:20. After 20 min. The treated fabrics were cured at 120 ^{0}C for 3 min. Finally treated fabrics were washed at 60 ^{0}C for 10 min. followed by drying.

2.3.2 PRINTING

Both cotton and viscose after pretreatment with MgO, TiO_2 and ZnO of different concentration was subjected to printing through screen printing technique. Followed by steaming at 100-103 ^{o}C for 15 minutes for the samples printed with reactive dye and at 120 ^{o}C for 20 minutes for the samples printed using natural dye[31] .

Preparation of reactive dye printing paste:

The printing paste of the reactive dye was prepared according to the following recipe:

Reactive dye	30 g
Thickener	40 g
Urea	100 g
Resist salt	10 g
Sodium bicarbonate	30 g
Water	X g
Total	1000 g

Preparation of natural dye printing paste:

Curcuma (natural colour)	100 g
Thickener (alginate)	40 g
Diamonium phosphate	12.5 g
Urea	40 g
Water	X g
Total	1000 g

2.4 MEASUREMENTS AND ANALYSES

2.4.1 METAL OXIDES PARTICLE SIZE

The synthesized powder was determined after appropriate sample dilution with distilled water and freshly prepared by transition electron microscope (TEM). One drop of each emulsion was mounted on a copper grid covered by a thin film of carbon and after drying, the samples were examined by TEM (Model EM-1230; Jeol, Germany) at high voltage (hV) 100 kV and with resolution ca. 10 A . The average vesicle size distribution was determined either by volume or number of the particles in the drop.

2.4.2 COLOR STRENGTH

The colorimetric analysis of the dyed samples was performed using a Hunter Lab ultra Scan® PRO spectrophotometer. The corresponding colour strength value (K/S) was assessed by applying the **Kubelka Munk** equation as follows.

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

Where,

R = decimal fraction of the reflection of the dyed fabric,

K = absorption coefficient, and S = scattering coefficient

2.4.3 FASTNESS TESTING

The dyed samples were subjected to rubbing, washing, perspiration and light according to standard ISO methods, ISO 105-X12 (1987), ISO 105-co4 (1989), ISO105-EO4 (1989), ISO 105-BO2 (1988) respectively.

2.4.4 ANTIBACTERIAL ACTIVITY

Biological activity of untreated and NPs-treated cotton was tested by Kirby-Bauer modified method [32-33].Plates were incubated with filamentous gram-positive bacteria as staphylococcus aureus (S.aureus) and gram-negative bacteria as Escherichia coli (E.coli) at 35-37 °C for 24-48 hours. For the disc diffusion, the zone diameters were measured with slipping calipers of the national committee for clinical laboratory standards.

2.4.5 THE TOTAL COLOUR DIFFERENCE (ΔE)

CIE Lab Difference:

Now, in a lot of dye houses, there is a datamatch system which helps colorist to obtain different shades and to judge about the acceptance of these shades against a particular standard. The most widely used equation is CIE lab difference equation.

($\Delta E = L^2 + \{(a^2 + b^2)\}^{1/2}$

a: represents the red – green axis

b: the yellow – blue axis

L: describes lightness

3 RESULTS AND DISCUSSION

The main aim of the present work is to investigate the effect of pretreatment with metal oxides in the nanoform particles in improving the printability of cellulosic fabrics and enhance their ultraviolet and microbial protection. To achieve this goal, TiO_2, ZnO and MgO in the nanoparticles form were prepared according to the procedure indicated in the experimental section. The particle size of the prepared metal oxides were monitored using transmission Electron Microscopy (TEM).

To start with TEM investigation of the particle size of the synthesized metal oxides. Figures 1,2 and 3 show the TEM micrographs of ZnO, TiO_2 and MgO respectively.

A close examination of the TEM micrographs signifies an average of 10:42, 9:94 and 17:37 nm for the synthesized ZnO, TiO_2 and MgO respectively.

Samples of cotton and viscose fabrics were treated with the prepared nanoparticle size of the aforementioned metal oxides at four different concentrations (0.5, 1, 1.5 and 2% wof) as indicate in the experimental section. The pretreated samples were subjected to printing with either reactive or natural dye, followed by fixation, washing and drying. The K/S as well as the colour fastness properties of the treated and printed samples, in addition to their antibacterial properties and UV protection of the NPs- treated fabrics were also investigated.

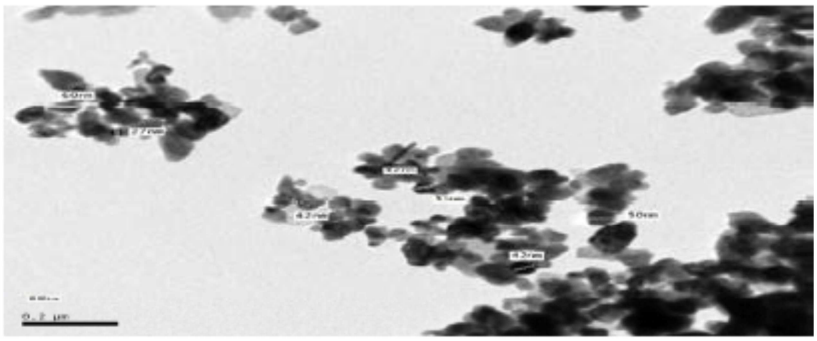


Figure 1: (TEM) of ZnO nano particles

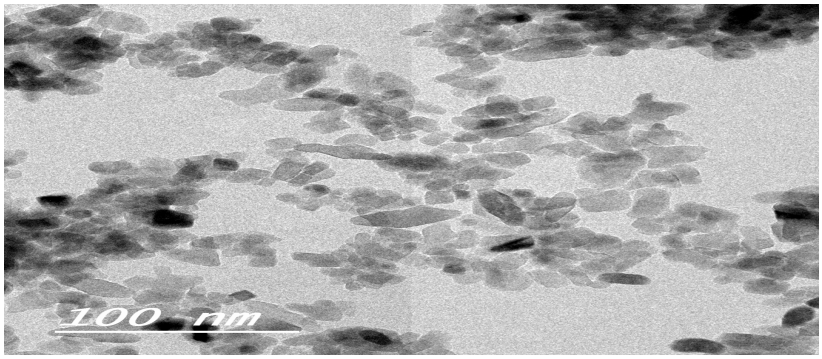


Figure 2: (TEM) of TiO_2 nano particles

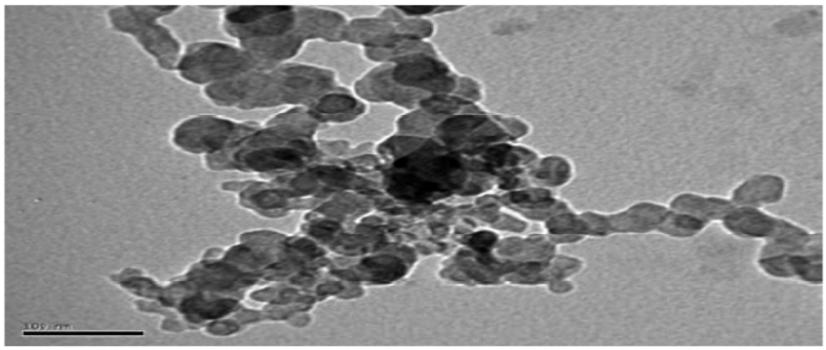


Figure 3: (TEM) of MgO nano particles

3.1 EFFECT OF TREATING WITH NANOPARTICLES ON COLOUR STRENGTH OF CELLULOSIC FABRICS

3.1.1 ON USING REACTIVE DYE

Nanotechnology is concerned with materials whose structures exhibit significantly novel and improved physical, chemical and biological properties, phenomena and functionality due to their nano scaled size [(34)].

To investigate this functionality, 12 samples were first treated with ZnO, MgO and TiO_2 nano respectively. For each type of oxide four concentrations were used to optimize the most proper concentration. The concentrations used were 0.5, 1, 1.5, and 2 % wof respectively.

The aforementioned concentration of oxides were applied to two kinds of cellulosic fabrics i.e. cotton and viscose. The pretreated samples were subjected to screen printing using a reactive dye namely Suncion red P2B (as detailed in the experimental section), steamed at the mentioned temperature, then washed and finely subjected to K/S measurement. The results of K/S were illustrated in table I.

Table I: Effect of pretreatment of cotton fabrics with different NPs metal oxides on the K/S of fabrics printed with reactive dye:

Nature of Nano particles	Concentration	K/S
Blank	-	13.04
ZnO	0.5	14.31
	1.0	14.61
	1.5	15.05
	2.0	14.69
MgO	0.5	14.17
	1.0	15.38
	1.5	15.15
	2.0	14.69
TiO_2	0.5	16.54
	1.0	15.68
	1.5	14.26
	2.0	14.08

The reactive dye used was Suncion Red P2B

It is clear from the data of table I, that the K/S value of cotton samples depends on:

(a) Nature of nano oxide used. (b) Its concentration. The K/S values were found to have the order of TiO_2 > MgO > ZnO nano particles respectively. However, there were found variations in the concentrations as will be discussed.

It is also clear from the data that the higher K/S value was achieved on using TiO_2 nano particles. It is obviously seen also that even at lower concentration at 0.5 % wof of TiO_2 nano particles, the K/S was increased from 13.04 to 16.54. i.e. by almost 26.04%, while increasing the concentration of TiO_2 nano particles more than 0.5% , i.e. 1, 1.5 and 2 % wof cause a slightly decrease, this means that treatment of cotton fabrics with lower concentration of TiO_2 0.5% is so sufficient to achieve a remarkable increase in the K/S values. The increase in K/S value at lower concentration of TiO_2, may be due to the rule of Ti^{+4} ions which causes an increase in the +ve charges i.e. more ionic attraction with the reactive anionic dyes, while increasing the concentration of TiO_2 nano particles more than 0.5% i.e. from 1, 1.5 and 2 % respectively causes a slightly increase in K/S when compared by the untreated samples. Hence optimum conditions for treatment with TiO_2 was found to be at a lower concentration as 0.5 % wof.

Furthermore, it is also clear from the data of table 1 that the K/S values were found to follow the order of TiO_2 > MgO > ZnO which means that modifying cotton fabrics with MgO nano particles were found to achieve higher K/S values when compared with that of ZnO.

We can obviously illustrated from the data of table I that the higher K/S values of the fabric treated with MgO nano particles was 1% while increasing the concentration the concentration of MgO nano particles more than 1% i.e. from 1.5 and 2 % wof causes a slightly decrease in K/S when compared with the optimum one (1% wof MgO), while when comparing these values with those of untreated samples, it is obviously illustrated that the incorporation of the MgO nano particles on the cotton fabrics have a significant effect on improving its printability, this phenomena may be due to the negative surface charge which was deduced for the ZnO NPs, and it was investigated that the illumination can increase the dye reaction with the fabrics, ended in an increase in the value of K/S values after washing.

Table I also comprises the data of treating cotton fabrics with four concentrations of ZnO NPs viz 0.5, 1, 1.5, 2 % wof. As it is clear from the data that as the concentration of ZnO NPs increase, the K/S increases too, i.e. increasing the concentration of ZnO from 0.5 to 1 to 1.5, was accompanied by an increase in the K/S values from 13.04 (blank sample), to 14.31, to 14.61, to 15.05 respectively. Which means that the highest K/S value for the ZnO NPs treatment was achieved at a concentration of 1.5 %. While increasing the concentration of ZnO NPs, more than 1.5 i.e. 2% causes a slightly decrease up to 14.69 which may be due to the un uniform distribution of the particles on the cotton fabrics at relatively high concentration and hence cause a slight decrease in K/S.

The K/S values of viscose fabrics treated with the aforementioned NPs and printed with the reactive dye were illustrated in table II.

Table II: Effect of pretreatment of viscose fabric with different NPs metal oxides on the K/S of fabrics printed with reactive dye:

Nature of Nano particles	Concentration	K/S
Blank	-	28.66
ZnO	0.5	29.34
	1.0	29.04
	1.5	29.51
	2.0	29.51
MgO	0.5	29.05
	1.0	29.46
	1.5	29.71
	2.0	29.65
TiO_2	0.5	30.36
	1.0	28.77
	1.5	28.15
	2.0	25.71

The reactive dye used was Suncion Red P2B

As it is clear from the data, that the K/S of the viscose treated fabrics was found to be depends on the nature of NPs used as well as the concentration of the NPs the same trend was also observed in case of cotton fabrics.

On comparing the data we can illustrated that the highest K/S was found to be at 0.5% for TiO_2 and 1.5 % for MgO and 1.5% for ZnO. Furthermore TiO_2 NPs achieved the higher K/S values with a concentration of 0.5 % wof which was 30.36 while. All the treated samples were found to achieve higher K/S values when compared to that of the untreated sample.

On comparing the data of Table I with that of Table II, it is clear that the K/S for viscose before and after treatment with the current 3 metal oxides at any specific concentration is much higher than that of cotton samples.

It is worthy to mention that viscose fabrics are cellulosic fabrics like cotton but it have much number of amorphous regions when compared to the latter. These amorphous regions found in viscose fabrics due to the influence of NaOH during its preparation, causes an opening up to the structure of cellulosic fabrics and hence, ended in a higher ability of viscose fabrics for dye uptake and even for further wet process.

From all previously mentioned discussion we can illustrate the higher ability of viscose fabric to dye uptake that, the K/S of the untreated viscose fabric was 28.66 in contrast to 13.04 for the cotton fabric, i.e. increase in the K/S by almost the double.

This ability of viscose fabrics wasn't only for dye molecule but also for all the particles in contact with it to treat with, i.e. facilitates its reaction with the metal oxide NPs particles irrespective of its kind and/or concentration and hence treated viscose fabrics were found to be more affected with this modification when compared to that of cotton at the same conditions.

As it is clear the table II that the TiO_2 NPs was found to achieve higher K/S values when used to treated viscose fabrics. This increase was found to be depending on the concentration of TiO_2NPs used. i.e. the higher K/S values (30.36) was achieved with 0.5%wof Tio_2 NPs while increasing the concentration of TiO_2NPs while increasing the concentration of TiO_2 NPs from 1, to 1.5, to 2 % was found to cause a slightly decrease in K/S values which were 28.77, 28.81, and 28.15 respectively. While on using MgO NPs , the order differs completely, the higher K/S was achieved when treated viscose fabrics with a concentration of 1.5% wof MgO NPs which was 29.71 while at lower concentration of MgO, there was found to cause a slightly decrease while achieve a higher values for K/S when compared to the blank sample.

In case of ZnO NPs which used to cause a slightly increase in K/S when compared to the other particles (TiO_2 NPs and MgO) the highest K/S value was achieved at a concentration of 1.5% wof ZnO NPs which was 25.51 while increasing the concentration up to 2 % wof ZnO have no influence on the values of K/S fabrics i.e. it reaches the optimum at such concentration.

From the previous study it can be concluded that treating of cellulosic fabrics with metal oxides i.e. TiO_2, ZnO and MgO in the nano from improves its printability with reactive dyes. However, the % increase in K/S depends on: a) the nature of the metal oxide used, b) its concentration, and c) the nature or the cellulosic fabric used, i.e. nature of regenerated fabrics.

3.1.2 ON USING NATURAL DYE

The word natural dye comprises all the dyes and pigment derived from the nature sources like plants, animal and minerals. Natural dyes can be used to dye different natural and man-made materials[35].

Curcuma longa L. known as turmeric, which used as a coloruring agent , and also has medicinal properties[36]. Curcuma Long L., which belongs to the Zingiberaceae family. The pigments in the colourant extracts obtained from Curcuma collectively known as Curcuminoids, the major constituent being Curcumin, along with small amounts of demethoxy curcumin and bisdemethoxy curcumin Scheme (1).

Cotton has no inherent affinity for most natural dyes. However the affinity of cotton can be modified to make it dyeable with natural dyes by the use of metallic salts mordants or the process of cationization which creates positively charged sites on Cotton or by addition of NaOH or enzymes[37].

From all above, and to achieve the goal of improving the printability of cotton fabrics with the natural dyes. Cotton samples were treated with the mentioned three kinds of NPs metal oxides viz TiO_2, ZnO, MgO at four concentration for each oxide . viz 0.5, 1, 1.5 and 2% wof. The treated samples were printed with Curcuma colour, dried, steamed, washed and finally assisedfor K/S measurements. The results were shown in table III.

On investigating the data of table III we can easily observed that regardless of the kind of NPs used in treating cotton fabrics and /or the concentration used. The K/S was found to be enhanced and improved by this modification. These improvements were found to be depends on the nature of NPs used and/or its concentration.

Table III: Effect of pretreatment of cotton fabric with different NPs metal oxides on the K/S of fabrics printed with natural dye:

Nature of Nano particles	Concentration	K/S
Blank	-	1.39
ZnO	0.5	1.80
	1.0	1.73
	1.5	1.58
	2.0	1.77
MgO	0.5	1.75
	1.0	1.66
	1.5	1.40
	2.0	1.72
TiO_2	0.5	1.84
	1.0	1.33
	1.5	1.44
	2.0	1.76

The Natural dye used was Curcuma longa L

The highest K/S values were achieved when treating cotton fabrics with TiO_2 NPs. As at a lower concentration of TiO_2 NPs (0.5 % wof) it achieves 1.84 values compared with 1.39 of the untreated sample. While increasing the concentration more than that have no remarkable effect.

According to previous reports [38-40]. Preparation of TiO_2-nanosol and the gel formation /fixation of titania cluster onto cotton fabric involve a number of interactions that may be categorized an represented as follow:

1) Preparation of TiO_2-nano sol

$\equiv Ti(OR) + H_2O \rightarrow \equiv TiOH + ROH$ Hydrolys≡ Tis (1)

$\equiv TiOH + \equiv TiOH \rightarrow \equiv Ti\text{-}O\text{-}Ti \equiv + H_2O$ Condensation and/or (2)

$\equiv TiOH + \equiv Ti(OR) \rightarrow \equiv Ti\text{-}O\text{-}Ti \equiv + ROH$ Condensation (3)

Where R: is an organic group, and, Ti-O-Ti is a colloidal oxide network in the sol form.

2) Gel formation/fixation of titania-cluster onto cotton fabric[40]

TiO_2 –nano sol network $\xrightarrow{heat}$ Gel formation (4)

Titania ——— OH + Cell.OH $\xrightarrow{heat}$ Nano-TiO_2- Loaded cotton fabric (5)

As it is obvious from the previous scheme that incorporation of Tio_2 NPs into the cotton fabrics enhance its surface as it causes an +ve charge surface which intern create host guest for the natural dye. By another meaning treating cotton fabrics with TiO_2 NPs can increase its affinity towards the natural curcuma dye.

The increase in K/S values was found to be also in case of MgO as well as ZnO NPs. Treating cotton fabrics with MgO NPs causes an increase in K/S values or an enhance in the cotton printability slightly more than that treated with ZnO NPs.

The metal oxides such as TiO_2, MgO and ZnO are of particular interest because of their stability under harsh process conditions and generally regarded as safe materials to human beings and animals [41,42].

So from all above we can easily illustrate the application of the bio nano composite to the textile cotton materials aimed at producing not only functional textiles but also for improving its printability with natural dye even without any need for mordant addition.

Table IV showed the data of K/S values for viscose fabrics treated with ZnO NPs, MgO, and TiO_2 NPs. All samples in question were found to have K/S values higher than that of the untreated blank sample. While the extent of improving varies, depends on the kind and/or the concentration of NPs oxide used.

Table IV: Effect of pretreatment of viscose fabric with different NPs metal oxides on the K/S of fabrics printed with natural dye:

Nature of Nano particles	Concentration	K/S
Blank	-	1.13
ZnO	0.5	1.34
	1.0	1.29
	1.5	1.12
	2.0	1.32
MgO	0.5	1.10
	1.0	1.20
	1.5	1.10
	2.0	0.88
TiO_2	0.5	1.23
	1.0	1.81
	1.5	1.87
	2.0	1.48

The Natural dye used was Curcuma longa L

As previously mentioned the highest K/S were achieved when treated with TiO_2 NPs followed by treating with ZnO NPs ended with MgO NPs. All previously oxides NPs can easily achieve an improvement into the cellulosic surface by introduce a +ve charged surface, which in terms create a similar case to protenic fabrics which ended in an increase in the printability of these fabrics.

However, the magnitude of improvement in K/S in case of viscose fabrics is less than that of cotton; also the K/S of untreated viscose is less than that of cotton. This may be due to the larger amount of amorphous regions in viscose compare with that of cotton. Hence viscose comprises high present of free OH- groups when compared to that of cotton. These free hydroxyl groups in terms causes an increase in its negatively charged surface, and hence caused a difficulty when printed with natural dye. That was obviously illustrated from the results of table IV, that regardless the kind and/or the concentration of NPs oxides used the K/S values were found to be less than that of cotton.

3.2 Effect of treatment of cellulosic fabrics with NP oxides on the fastness properties of reactive & natural prints

The samples pretreated with NPs of TiO_2 , ZnO or MgO and printed with either reactive or natural dye which acquire the highest K/S was chosen and subjected to overall colour fastness measurements. The printed untreated cotton and viscose fabrics were also measured under the same conditions for the sake of comparison. Table 5 represent the data of overall colour fastness properties, i.e. for washing, rubbing (wet and dry), and perspiration (acidic and alkaline).

It is clear from the data of Table V that the overall colour fastness properties ranges between good to very good depending on: (a) the nature of dye used, (b) the kind of fabric, (c) the nature of the nano-particles used in pretreatment and its concentration.

However, it is also clear from table V that in all cases the values of the overall colour fastness for the pretreated fabrics is nearly equal or slightly better than that of the untreated fabric.

Table V: Fastness properties of cotton and viscosic samples treated with NP metal oxideas and printed with reactive and natural dyes:

Kind of fabric	Sample	Dye	Rubbing		Washing		Perspiration			
			Wet	Dry	St.	Alt.	Acidic		Akaline	
							St.	Alt.	St.	Alt.
Cotton	Blank	Reactive dye	3	3-4	3-4	3-4	3	3-4	2-3	3
	ZnO 1.5%		4	4	3-4	4	3-4	4	4	4
	MgO 1.5%		3-4	4	4	4	3-4	4	3-4	4
	TiO_2 o.5%		3-4	3-4	4	4	3-4	4	4	4
Viscose	Blank		4	4	3	3-4	3-4	3-4	3	3-4
	ZnO 1.5%		3-4	3-4	4	4	3	4	4	4
	MgO 1.5%		4	4	4	4-5	3-4	4	3-4	4
	TiO_2 o.5%		3-4	3-4	4	4	4	4	3-4	4
Cotton	Blank	Natural dye	2-3	3	2-3	3	3-4	3-4	4	4
	ZnO 2%		4	4	5	3-4	3-4	4	4	4
	MgO 1.5%		4	4	4	4	3-4	4	4	4-5
	TiO_2 0.5%		4	4	3-4	4	3-4	4	4	4-5
Viscose	Blank		3-4	3-4	3	3	3-4	3-4	3-4	4
	ZnO 2%		4	4	3-4	4	3-4	4	4	4
	MgO 1.5%		4	4	4	4	4	4	4	4
	TiO_2 0.5%		4	4	4	4	4	4	4	4-5

St: staining Alt: Alteration

3.3 THE ANTIBACTERIAL ACTIVITY OF TREATED AND UNTREATED PRINTED CELLULOSIC FABRICS

The antibacterial properties can be imparted to the textile materials by chemically or physically incorporation functional agents onto the fibers or fabrics [43-45].

Table VI: Effect of antibacterial activity for treated cotton samples

Sample	Dye	Staph. G (+ve)	E.C.C. G (-ve)
Blank	Natural dye	0.0	0.5
ZnO 2%		10.0	6.5
MgO 1.5%		17	9.0
TiO_2 0.5%		10.5	13.5
Blank	Reactive dye	9.5	6.0
ZnO 1.5%		20.5	16.0
MgO 1.5%		17.0	12.0
TiO_2 0.5%		18.0	13.0

Table VI show the dependence of the antibacterial activity of the cotton reactive and natural prints, respective on the kind of NPs oxide used viz, ZnO (0%), MgO (1.5%) and TiO_2 (o.5%), for natural dyes, and Zn (1.5%), Mg 1.5% and TiO2 0.5 for reactive cotton prints.

When observing table 6, in case of natural cotton prints. The highest value of antibacterial was achieved on treating with TiO_2 NPs. These means that TiO2 is preferable to other inorganic forms of titanium because of its higher efficiency in preventing infection.

It is clear from table 6 that, the untreated cotton fabric sample has no reduction in the bacterial count against both staph. G(+ve) or E.C.C G(-ve). While in the nano- TiO_2 treated cotton sample has exhibited better reduction of bacterial count % and this is because nano-TiO_2 has photo catalytic effect and when exposed to light, photons with energy equal to or greater than the bond gap of the titanium dioxide excite electrons up to the conduction band. The excited electrons within the crystal structure react with oxygen atoms in the air, creating free-radical oxygen. These oxygen atoms are powerful oxidizing agents, which can break down the cell wall of microorganisms through oxidation- reduction reaction [46].

While in case of ZnO, it is clear from table 6 that it also characterized by antibacterial activity, this activity may be related to the induction of oxidative stress due to generation of reactive oxygen species, which may cause the degradation of the membrane structure of the cell.

This antibacterial modification was found to be not also in the case of TiO_2 NPs treated sample but also for the other oxides NP. i.e. for the case of ZnO as well as MgO regardless the day used. i.e. the ability of the fabric to overcome the action of growing the bacteria was found to be un affected by the nature of dye used.

3.4 THE UV PROTECTION FOR THE TREATED AND UNTREATED PRINTED CELLULOSIC FABRICS

Table VII represent the data of fading of viscose fabric samples pretreated with the aforementioned nano metal oxides followed by printing with either reactive or natural dye.

Table VII: The rate of fading of cotton fabrics dyed with reactive red and natural yellow dyes after irradiation time 0-105 hrs.

Time of Irradiation In hrs		Samples printed with Reactive red				Samples printed with Natural yellow			
	Sample tested	**L**	**A**	**B**	**ΔE**	**L**	**A**	**B**	**ΔE**
0h	**Blank**	43.20	55.73	8.04	68.90	77.01	3.29	32.50	31.58
	ZnO 2%	44.56	56.83	6.67	68,86	76.68	2.29	34.65	33.72
	MgO 1.5%	44.25	57.29	8.02	69.54	77.48	2.73	32.35	31.34
	TiO_2 0.5 %	42.97	57.29	9.44	70.90	77.62	2.83	23.13	34.11
35h	**Blank**	45.96	56.56	9.29	66.80	83.02	2.11	35.07	30.28
	ZnO 2%	47.23	56.07	7.51	67.33	83.77	1.12	26.44	32.72
	MgO 1.5%	46.22	57.26	9.03	68.01	83.01	1.85	25.21	32.14
	TiO_2 0.5 %	45	58.34	10.46	69.48	84.48	1.63	25.15	35.01
70h	**Blank**	46.96	55.31	9.39	69.80	87.02	2.11	10.39	32.58
	ZnO 2%	47.23	52.21	8.51	68.33	84.77	1.0	22.51	32.92
	MgO 1.5%	47.22	53.49	8.13	69.01	84.01	1.45	21.13	33.34
	TiO_2 0.5 %	48.51	52.34	8.17	70.48	83.48	1.53	21.17	35.61
105h	**Blank**	50.17	49.92	6.44	67.80	85.82	1.11	18.19	32.59
	ZnO 2%	49.79	49.35	7.38	68.83	85.37	1.0	18.12	34.73
	MgO 1.5%	47.89	51.45	7.94	69.71	85.31	1.05	18.65	32.84
	TiO_2 0.5 %	48.71	53.91	9.14	71.28	85.41	1.23	18.71	33.21

It is worthy to mention that, We have measured ΔE for all printed samples before irradiation and after irradiation from 0 to 105 hours according to CMC 2:1 equation which gives more accurate results, the results indicates that the color alteration ΔE between the treated samples with ZnO, MgO and TiO_2 nano particles and the untreated dyed are small but the alteration rate differ between the treated and the untreated fabrics with the different nano powder. i.e following the order o.5% wof of TiO_2 > 1.5% wof of MgO >and finally 2% wof of ZnO nano particles this holds true for all the pretreated viscose fabrics since the effect of using the nano particles as anti UV absorbent before printing give better results. This in case of the reactive dye as well as in case of natural dye, but with less effect.

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