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Research Article

Efficient One Pot Synthesis of TiO_2-induced Nanoparticles via Microwave Irradiation and its Application in Cotton Dyeing with Some Acid Dyes

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ABSTRACT

In the current approach, microwave heating is applied to assist a rapid method for one pot synthesis of TiO_2 nanoparticles (NPs) within a few minutes. The effect of prepared TiO_2 NPs by using microwave irradiation as well as conventional method on dyeing of cotton fabric with acid dye was studied. TiO_2 NPs were examined through transmission electron microscopy (TEM). The effects of TiO_2 NPs on the multifunctional properties of the cotton fibers including coloration, antibacterial and anti UV were evaluated. The overall results point out that, the TiO_2 NPs is successfully prepared by using microwave heating by saving time and energy. The treatment of cotton fibers by prepared TiO_2 NPs exhibited excellent color fastness as well as good antibacterial and anti UV properties.

Keywords: Titanium di-oxide, Nanoparticles, Cotton treatment, Microwave heating, Antimicrobial, Self-cleaning.

INTRODUCTION

Lately, there are increasing interest in photograph catalysis stimulation using semiconductor materials as photograph catalysts for the removal of ambient concentrations of inorganic and organic species from the aqueous phase or gas in cleaning up the environment, drinking water treatment, industrial and health applications. This is due to the ability of TiO_2 to oxidize organic and inorganic materials in air and water through redox processes [1].

The high ability of TiO_2 for photo catalytic leads to retro gradation of organic and biological molecules into smaller and less harmful compound. In addition, TiO_2 nanoparticles have many advantages on the nano scale, providing increased the surface area that may occur photo catalytic interactions. This photo catalytic activity may be of interest in the application including air purification, self-sterilization, water purification and the production of molecular hydrogen. So the use of different synthesis methods to produce TiO_2 motif is very useful to achieve maximum efficiency in applications of TiO_2 [2].

The polymer is antibacterial, nontoxic, biodegradable and biocompatible. Researcher work has been done on the planning of chitosan/silver nano composites in the solid forms, such as fibers, powders and films [3]. The use of chitosan covers of fields, for example, pharmaceutical and therapeutic applications, paper production, textile, waste water treatment, biotechnology, cosmetic, sustenance preparing and horticulture [4-8].

Chitosan is the deacetylated derivative of chitin that is the second most numerous polysaccharides next to cellulose on the earth. Chitin is the main component in the shell of scavengers, for example, shrimp, crab, and other lobster, and also be found in exoskeletons of mollusks and insects walls of some Fungi [9-11]. Every year plenty of crabs and shrimp shells are abandoned as wastes by seafood companies worldwide, and considerable scientific and technology interest arouses in the attempt to utilize chitin and chitosan in these renewable wastes.

Microwave-assisted route is one of innovative methods and is a rapidly developing area of research. In contrast to conventional methods, microwave activity requires very short reaction time, and is able to produce small particles with a narrow molecule size distribution and high purity. Microwaves, as other radio waves, are a form of electromagnetic waves. Electromagnetic waves are wavelike amplitude of electric and permanent magnetic fields. Electrical fields are what makes electric charges attract or repel. (e^+) or (e^-) electric charges produce electric fields which in convert act on other charges. In a same way, magnetic fields cause permanent magnetic forces [12]. These types of fields are vertical to one another and constantly oscillate between maximum (e^+) and maximum (e^-) (pointing in the opposite way).

In the present work, a fast strategy for one pot amalgamation of TiO2 inside a couple of minutes was portrayed

The purpose of this research was to develop method suitable for prepared TiO_2 nanoparticles by using microwave heating. In comparison with routine heat preparation, microwave irradiation is a more efficient heating method due to its rapid heat and energy penetration, therefore decrease the reaction time. Currently, many microwave-based straightforward, quick and energy-efficient routes have been created to prepare the nano structured materials, including nanoparticles, nano wires, nano plates, nano rods, etc. [12-16]. In the present work, a fast method for one pot synthesis of TiO_2 within a couple of minutes was described. The effect of prepared TiO_2 by using microwave irradiation as well as conventional method on dyeing of cotton fabric with acid dye was studied. The applicable of the prepared TiO_2 as antimicrobial and anti UV was also evaluated.

EXPERMINTAL

Materials

Substrate - 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.

Chemicals and instrumentation

Chitosan (low molecular weight) (Aldrich), Titanium tetrachloride $TiCl_4$ (Fluka), acid dyes 1,2 which synthesized according to the published methods [17] and it's structure as shown in fig.1, Titanium dioxide TiO_2 nano particles were supplied from (Aldrich) . All chemicals used in this study were of laboratory grade.

UV spectra were recorded on a Perkin Elmer Lamb 15 UV/Vis spectrophotometer. Transmission electron microscope (TEM),

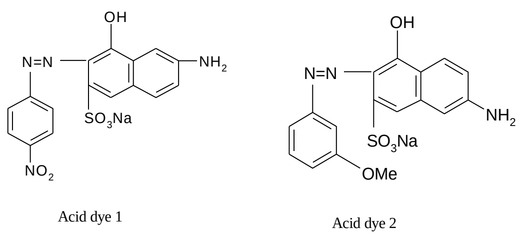


Figure 1: structure of acid dye according to the published

Preparation of TiO_2 Nano particles

Synthesis of TiO_2 nano particle was done by Sol-Gel technique by following two different heating methods.

Conventional method

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. The obtained precipitate was washed with deionized water until the removals of chloride ion, centrifuged then filtrated. 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 400°C for four hours step by step. Finally, the powder TiO_2 nano material was obtained [18-21].

Microwave irradiation

The same procedures were repeated as mentioned above until the ppt. was obtained. Then the ppt. was dried via microwave for 8 min. and then calcinated amorphous TiO_2 in microwave for 8 min. at 90% watt (total preparation time 16 min.). Instead of dried the ppt. at 200°C for 4 hours, then calcinated amorphous TiO_2 at 400°C for four hours (total preparation time 8 hours).

Treatment of cotton fabric with chitosan

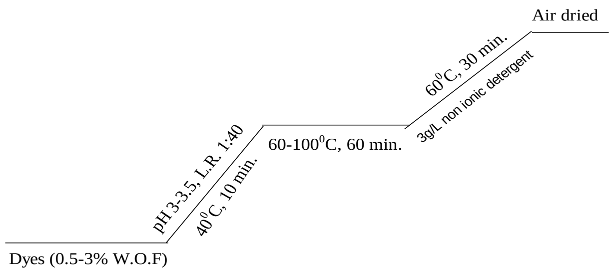
Treated cotton fabric by different concentration of Chitosan (1, 1.5, 2% W.O.F) dissolve in distilled water and 2% acetic acid for 60 minutes at 60^{0}C, squeezed, dried at ambient temperature then dyed with the tow acid dyes mentioned above [22].

Treatment of cotton fabric by TiO_2 nano particles[23]

Cotton fabrics were treated with different concentration (0.5-2% W.O.F) of prepared TiO_2 nanoparticles by using microwave irradiation, conventional heating and with commercial one via exhaustion method, for 20 min. at 80°C in the presence of wetting agent in dyeing machine. The liquor ratio of exhaustion bath was 1:10. Then the treated Cotton fabrics were cured at 140 ^{0}C for 10 min., washed at 60 ^{0}C for 20 min. followed by drying at room temperature.

Dyeing of cotton fabric

The cotton fabrics was dyed using exhaustion dyeing processes [24] according to the following diagram



Color Measurements of dyed samples.

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 [25].

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

Where,

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

K = absorption coefficient, and S = scattering coefficient

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.

Antimicrobial activity

The standardized disc–agar diffusion method was followed to determine the activity of the synthesized compounds against the tested microorganism[26]

Antibacterial assay

Antimicrobial activity was tested by the filter paper disc diffusion method [27]. SMA and Mueller Hinton agar (Difco) containing 100 ppm of 2,3,5-triphenyltetrazolium chloride were used for antibacterial assay. 2,3,5-triphenyltetrazolium chloride was added to culture media to differentiate bacterial colonies and to clarify the inhibition zone (28). Each plate was inoculated with bacterial, ***Escherichia coli (G-), Staphylococcus aurous (G+)*** (0.1 ml) directly from the broth. All plates were incubated at 32ºC for 4 days, after which the inhibition zones were measured and recorded in millimeters (mm). The scale of measurement was the following (disc diameter included):≥28 mm inhibition zone is strongly inhibitory ≤16 to 10 mm inhibition zone is moderately inhibitory; and ≤ 12 mm is no inhibitory [26-28]. Control plates were prepared by placing antibiotic to evaluate culture for antibiotic resistance patterns that might affect sensitivity of assay. The antibiotic used was penicillin 10 IU

Self-clean Action

The self-cleaning action of TiO_2 treated cotton fabric was investigated by exposing the samples with adsorbed coffee stain to visible radiation. Measured quantity of 6% coffee solution was introduced on the cotton fabric and was allowed to spread. One half of each stain on the fabric was exposed to sun light for 12-48 h, while the other half was covered with a black paper to prevent its radiation from sunlight. The exposed part of the stain was compared with that of the covered part for self-cleaning action. Premier colour scan SS 5100A Spectrophotometer was used to measure the photo degradation of coffee stain [29].

Photo-Induced Discoloration on Cotton Textile

This study aimed to the use of the stable and durable product of inorganic TiO_2 NPs with a focus on the photo catalytic properties of TiO_2 NPs as textile finishes. The influence of surface coating on the photo catalytic degradation of acid dye I and II was studied, since the photocatalytic activity of TiO_2 NPs in form of textile coating material was evaluated in normal laboratory environment and after UV irradiation. The samples were irradiated by UV lamp for 24 hr.

RESULTS AND DISCUSSION

Preparation of TiO_2 Nano particles

Fig.2 shows the TEM images of TiO_2 NPs prepared by traditional, microwave, and commercial one. In all samples TiO_2 NPs powder appears aggregated in all sample and particle size ranged from 9-16, 8-11, 9-18 nm, respectively.

From the fig. we can notice that the TiO_2 NPs size that prepared by using traditional method and/or microwave irradiation is smaller than the commercial one. We can also notice that the TiO_2 NPs that prepared by using microwave irradiation is smaller than that prepared by 43traditional one; this may be attributed to microwave irradiation. The predominance of microwave heating could be emerged from that, the materials can absorb microwave energy specifically and inside and change over it into heat. This prompts points of interest, for example, quick, controlled, specific and uniform heating in a short time.

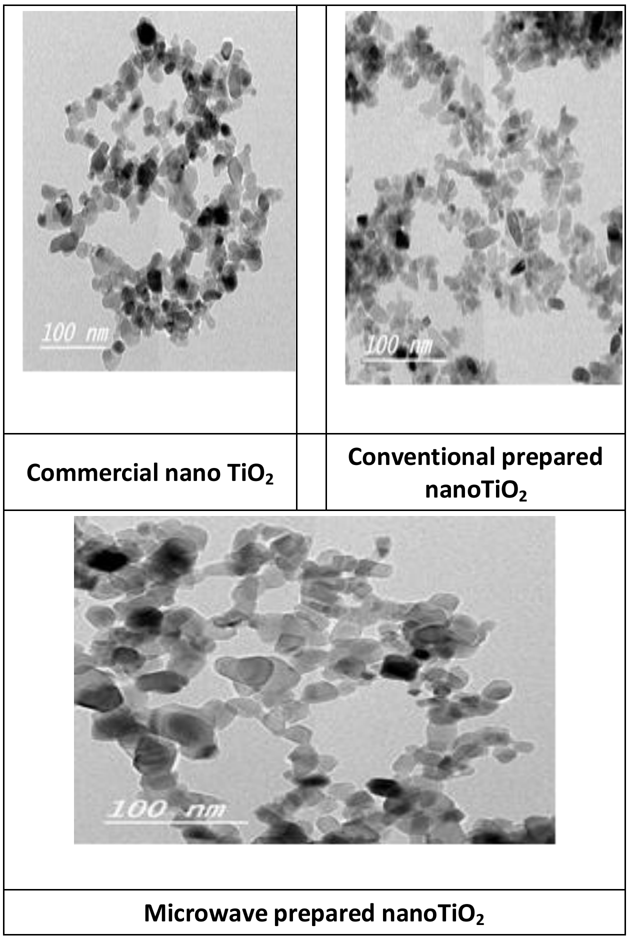


Figure 2: Transmission electron microscopy (TEM) image of TiO_2 nano particles

Treatment of cotton fabric with chitosan

To optimize the chitosan concentration in the treatment conditions, cotton fabric was pretreated at different concentrations of chitosan (0.5-2% w of) for 60 min. at60°C using thermal heating. The pretreated samples were then dyed by Acid dye 1, and Acid dye 2 using the conventional thermal dyeing method as described in the experimental section. The results are presented in table 1. The results clearly demonstrate that chitosan treatment enhances the color strength of both selective acid dyestuffs. The average increase in color strength increased as chitosan concentration increased until 1.5%. On the other hand, there is no any significant increase in color strength when using higher chitosan concentration. It is clear from table 1 that the K/S value increases when the chitosan concentration increases to 1.5%, irrespective of the type of dye.

Table 1: Effect of chitosan concentration on the color strength of the dyed cotton fabrics

Chitosan Conc. Dyes	λ	K /S			
		0.5%	1%	1.50%	2%
acid dye1	540 nm	1.24	1.63	1.63	1.56
acid dye2	380 nm	3.24	3.94	4.1	3.71

Dyeing condition: 2% shade, pH: 3.5, L.R.1:40, at 100°C for 60min

Treatment of cotton fabric by TiO_2 nano particles.

To determine the effect of treatment of cotton fabric on K/S values, cotton samples are pretreated before and after dyeing processes (2% shade, pH:3.5, L.R.1:40, at 100°C for 60min.) by different concentration of TiO_2 NPs (0.5-2% WOF) (Prepared by using microwave and conventional method as well as commercial one). The samples were dyed by tow selective acid dyes, using the exhaustion dyeing method. The results are given in figs. 3, 4. It is clear that the K/S of dyed cotton increase by increasing the concentration of TiO_2. It is worthy to mention that the high K/S value was obtained at 1.5% of TiO_2 when fabric was treated before dyeing while the high value was obtained at 1% when fabric treated after dyeing, then there is no affected for increase TiO_2 treatment concentration.

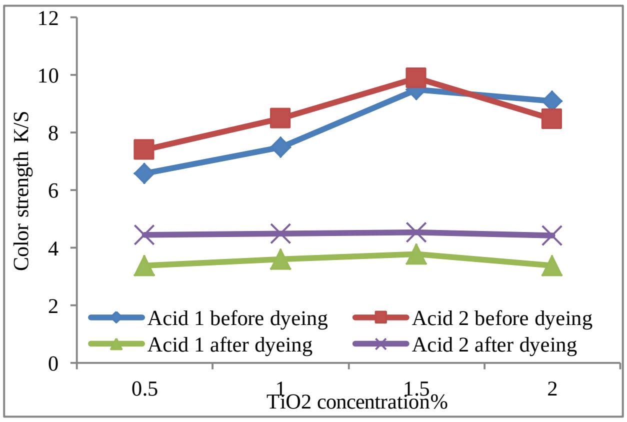


Figure 3: Effect of TiO_2 concentration synthesis by using microwave irradiation on color strength of treated before and after dyeing of cotton fabric

On other word, TiO_2 which prepared by using microwave irradiation processing can heat up in a very short time, and then achieve the effect of higher K/S value if compared to prepared by conventional heating. We can also notice that the acid dye 1 give high value of K/S in all cases than the acid dye 2. Accordingly, further studies of the pretreatment conditions were carried out at 1.5% for prepared TiO_2 NPs in microwave irradiation and 1% when using conventional methods. While when using commercial the highest K/S value was obtained at 2% concentration, fig.5.

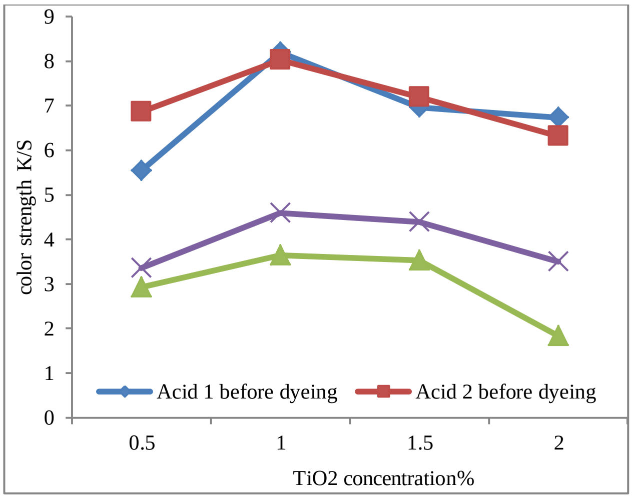


Figure 4: Effect of TiO_2 concentration synthesis by using traditional heating on color strength of treated before and after dyeing of cotton fabric

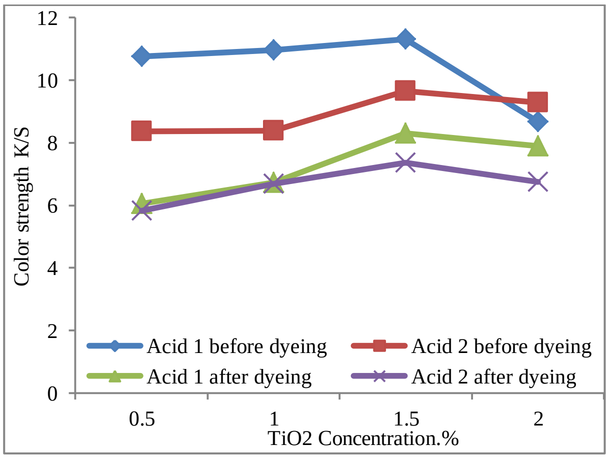


Figure5: Effect of commercial TiO_2 concentration on color strength of treated before and after dyeing of cotton fabric

Fastness Properties of NPs-treated cotton Fabrics

The durability of colors on the treated before and after dyeing of cotton fabrics by TiO_2 NPs prepared by using microwave and conventional heating method as well as the commercial one was evaluated in term of fastness towards rubbing, washing, perspiration and to light fastness using the gray scale as shown in Table 2. As shown in Table 2, the fastness properties of treated cotton fabrics before dyeing are more resistant against rubbing, washing and perspiration than those treated after dyeing, irrespective of mode and type of dye. Besides, the pretreated of cotton fabric by TiO_2 NPs which prepared by using microwave heating displayed higher color fastness than those pretreated with the same TiO_2 NPs prepared by thermal heating. It was also appeared that the fastness of pretreated cotton dyed samples with TiO_2 NPs by using microwave ranged from 4 to 5, while the prepared by conventional one ranged from 3 to 5. The high color resistance of pretreated dyed samples by TiO_2 NPs prepared by microwave may be attributed to the increase of dye penetration and its interaction with fibers, where the fixation rate of the colors is accelerated, We can also notice that the light fastness is ranged from good to excellent in all cases.

Table 2: Fastness properties of the untreated andTiO_2NPs-treated dyed cotton fabrics

Prepared TiO_2	Washing Fastness		Rubbing Fastness		Perspiration fastness				Light fastness
					Acidic		Alkaline		
	Alt	Stain	Dry	Wet	Alt	Stain	Alt	Stain	
Acid dye 1									
BD (M)	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	6-7
AD (M)	4-5	4	4-5	4-5	4-5	4	3-4	4	6-7
BD (T)	3	3	4	3-4	3	3	2-3	2-3	5
AD (T)	2-3	2-3	3	3	2-3	2-3	2	2	5
BD (C)	4	4-5	4	4	4	4	4	4	6
AD (C)	4	4	4	4	2-3	2-3	2-3	2-3	5-6
Acid dye 2									
BD (M)	4	4-5	4-5	4-5	4	4	4	4	6-7
AD (M)	4	4	4-5	4-5	4	4	4	4	6
BD (T)	2-3	2-3	3	3	2-3	2-3	2-3	2-3	5
AD (T)	2	2	2-3	2-3	2	2	2	2	4-5
BD (C)	4	4	4	4-5	4	4	3	3	6
AD (C)	4	4	4	4	3-4	3-4	2-3	3	5-6

M = TiO_2 prepare by microwave, T = TiO_2 prepare by conventional method, C= TiO_2 commercial, BD= Before Dyeing, AD= After Dyeing; Treatment condition: Dyeing condition: 2% shade, pH: 3.5, L.R.1:40, at 100°C for 60min

Antibacterial activity of NPs-treated cotton fabrics

The important characteristic of the material that is purposed for biomedical applications is the antibacterial property. TiO_2 atom and TiO_2 NPs are highly toxic to the microorganisms and they show strong antibacterial effects on the gram positive and gram negative bacteria. (*E.coli*) bacteria which responsible for urinary tract and wound contaminations is a well-known test organism. (*S. aureus*) bacteria are harmful bacteria responsible for a lot of infections like, toxic shock, fibrin coagulation, and endocarditic. Bacterial effects of unmodified and the NPs-modified cotton against both of *E. coli* and *S. aureus* microorganisms were computed, table (3).The photo catalytic effect of TiO_2 NPs, i.e. nano-metal oxides, is the basic reason for its antibacterial effect by the production of numbers of active oxygen species, e.g. super oxide anions, hydrogen peroxide, singlet oxygen, hydroxyl radicals that responsible for destroy of bacterial cell. The treated cotton fabric by TiO_2 NPs exhibit antibacterial effect on G+ve bacteria greater than on G −ve bacteria due to the existence of the external cell wall membrane in the G−ve bacteria thereby making as a bloke to the antibacterial effect.

In most cases we noticed that antibacterial activity of pre-treated fabric with TiO_2 NPs (before and after dyeing) that prepared by using microwave heating was greater than the prepared one by using traditional heating. Also, in most cases antibacterial activity of treated fabric against gram- positive bacteria was greater than the activity against gram- negative in both prepared TiO_2NPs.

As shown in table (3) antibacterial activity of undyed fabric show higher antibacterial efficacy compared to dyed fabric.

Self-Cleaning of TiO_2 Nano particles-Treated Cotton Fabrics

One of the susceptibility of TiO_2 nanoparticles treated fibers is converting the absorbed light into the self-cleaning materials to decompose its stain. Table 4 shows the effect of C I RO 14 on untreated and TiO_2NPs treated cotton fabric after 24 h UV- illumination.

Table 3: Antibacterial activity of TiO_2 NPs-treated cotton fabrics

Sample	Inhibition zone diameter (mm/ 1cm Sample)	
	***Escherichia coli* (G^-)**	***Staphylococcus aurous* (G^+)**
Comm. (control)	12	12
Microwave (control)	15	16
Traditional (control)	12	14
Before dyeing		
comm. acid (I)	12	13
comm. acid (2)	0.0	13
(T) acid (I)	16	17
(T) acid (2)	14	14
(m) acid (I)	24	24
(m) acid (2)	20	22
After dyeing		
comm. acid (I)	20	21
comm. acid (2)	20	21
(T) acid (I)	25	26
(T) acid (2)	24	25
(m) acid (I)	26	28
(m) acid (2)	26	27

Dyeing condition: 2% shade, pH: 3.5, L.R.1:40, at 100°

Table 4: Self-cleaning % of cotton fabrics treated with different prepared TiO_2 NPs

Cotton samples treated	Dye removal %
Blank	-
Commercial TiO_2 treated cotton	85%
CH prepared TiO_2 treated cotton	80%
MV prepared TiO_2 treated cotton	80%

A partial change of the color affected by UV-light was observed for TiO_2 NPs striated cotton fabric. The treatment of cotton led to the development of thin layer TiO_2 NPs that increases its hydrophilic properties. The high decay effect of TiO_2NPs has been appeared on the treated cotton fabric.

The two types of surfaces that result from treating of cotton with TiO_2 NPs may explain its self cleaning ability. Both hydrophilic and hydrophobic surfaces can remove the color from the cotton based on different mechanisms. The idea of producing hydrophobic surfaces has been developed based on Lotus effect [30] (Stamate and Lazar, 2007). A hydrophobic surface stop the adsorption of dirt, preserve the surface of cotton clean in all the time. On the other hand, on hydrophilic surfaces water droplets are dispersion and subsequently a flood of water existing on the surface of cotton expels the pollutants [31].

CONCLUSION

The multi-functionalization (coloration, antibacterial and photo catalytic properties) of TiO_2 NPs was successfully prepared by assisted microwave heating as a time and energy saving system. The transmission electron microscopy (TEM) proves the formation of TiO_2 nanoparticles in nanometer range. The effect of prepared TiO_2 NPs by using microwave irradiation as well as conventional heating on dyeing of cotton fabric with acid dye was studied. According to colorimetric data, the effects of TiO_2 NPs on the multifunctional properties of the cotton fibers coloration imparted bright colors with various shades. The treatment of cotton fabric by prepared TiO_2 NPs provides excellent antibacterial activity against ***Escherichia coli* (G-), and *Staphylococcus aurous* (G+)** antibacterial and anti UV. Treatment of cotton fibers by prepared TiO_2 NPs exhibited excellent color fastness to washing, rubbing and light fastness. It is worthy to say that it exhibited poor color fastness to respiration fastness.

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