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Functionalization of Natural Fibers Properties by using TiO_2Nanoparticles to Improve its Antimicrobial Activity

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Abstract: Natural dyes in textile coloration are earning popularity all over the world during the last decade. The current study deals with extracting dye from the alkanet plant as a natural dye by using the microwave to save energy and time. To obtain the color of aimed specific red hue, the influence of certain dyeing process conditions, namely, dyestuff concentrations, pH, temperature, and duration of the dyeing process, have been studied. This research presents the results of color strength (K/S) and CIEL (L* a*b*) color values. In addition, fastness tests of the dyed samples were assessed. Modifying natural fibers (silk and wool) are applied by using synthesized TiO_2 nanoparticles and the commercial one. The effect of treatment with TiO_2 NPs on the multifunctional properties of the silk and wool fibers, including coloration, antibacterial against *Escherichia coli* (G-), and *Staphylococcus aureus* (G+), and self-cleaning properties were evaluated. There were characterized by transmission electron microscopy (TEM). The obtained results indicated that the optimization of dyeing process parameters of pre-treatment and post-treatment of dyed silk and wool fibers with synthesized TiO_2 NPs has a significant influence on the obtained shades as well as the fastness properties. The post-treatment of silk and wool fibers with the synthesized TiO_2 NPs followed by dying displayed an excellent antimicrobial activity and self-cleaning properties.

Keywords: TiO_2 nanoparticles; natural dyes; alkanet; microwave irradiation; silk fibers; wool fibers.

1. Introduction

Synthetic dyes are harmful to health and result in a great deal of environmental pollution. Natural dyes can exhibit the best biodegradability and non-toxicity and generally have higher environmental compatibility [1-5]. Natural dyes have more attracting and more attention from both academics and industry due to their eco-friendly attributes [6, 7].

Manufacturing technologies are needed to meet the demands of consumers as the microwave. Microwave technologies facilitate that evaluation. It can enhance every sector of textile coloration [8-10]. It is one of the powerful techniques of non-contact heating and has been used for reaction, dye extraction, and dyeing of different types of fabrics. The classical processing of treatments and dyeing fibers consumed a large amount of energy. Many researchers studied some new techniques and methods for saving time, water, and energy [11-18]. Microwave heating has been proved to be more rapid, uniform, efficient, and it can be used as an alternative to conventional heating techniques.

Microwave irradiation can penetrate easily inside fiber particles, consequently reducing heat transfer problems. It has been supposed that microwave irradiation modification could effect on dyeability of textile fibers. However, the study on the effect of the different conditions of dye extraction and dyeing of wool and silk fibers coupled with microwave irradiation is scanty.

The high ability of TiO_2 nanoparticles for photocard catalytic leads to the degradation of organic and biological molecules into smaller and less harmful compounds [19, 20]. In addition, TiO_2 nanoparticles (TiO_2 NPs) have many advantages on the nanoscale, providing an increased surface area that may occur photocatalytic interactions [21,22]. This photocatalytic activity has a great interest in the application, including air purification, self-sterilization, water purification, and molecular hydrogen production [23]. Therefore, using different synthesized methods to produce TiO_2 is very useful to achieve maximum efficiency in applications of TiO_2.

The current work aimed to develop a new extraction technique using microwave irradiation to improve the extraction of natural dye from alkanet plants for the dyeing of silk and wool fibers. The influence of various factors, namely time, pH, dye concentration, as well as temperature of the dyeing bath, has been investigated. The synthesis of TiO_2 NPs coupled with microwave irradiation was described. The applicability of the prepared TiO_2 NPs to antimicrobial activity and self-cleaning properties were also evaluated.

2. Materials and Methods

2.1. Natural coloring matter.

The dyeing material used in this study was extracted from alkanet (*Alkannatinctoria* (*L.*), Plant Family*: Boraginaceae L.*) was peeling and crushed to the powder form.

2.2. Fibers.

Mill scoured 100% wool and silk fibers used for this study were supplied from Misr Co. (El Mahalla El-Kobra Egypt for spinning and weaving). The fibers were washed in a bath having 3g/l non-ionic detergent (Nonidet) at 30°C for 30min. to remove any impurities, thoroughly wash with water, then rinsed and dried by air at room temperature.

2.3. Chemicals.

Titanium tetrachloride $TiCl_4$ (Fluka), titanium dioxide nanoparticles (TiO_2NPS) were supplied from (Aldrich). All chemicals used in this study were of laboratory grade.

2.4. Equipment.

The microwave equipment used in this experiment was the Samsung M 245 with an output of 1,550 watts operating at 2450 MHz

2.5. Methods.

2.5.1. Extraction of natural coloring matter

The alkanet (*Alkannatinctoria* (*L.*), Plant Family: *Boraginaceae L.*) was peeling and grinded into a powder. Then the dying material was extracted using different concentrations

(1-4 g of powder / 1 dL water) and at different pH (3, 5, 7, 9) for different times (50-90 min) in a water bath by conventional method and (5-40 min) in microwave equipment. Finally, the solution was cooled down at ambient temperature.

2.5.2. Preparation of TiO_2NPS.

Synthesis of TiO_2NPS was done by Sol-Gel technique by following two different heating methods [24,25].

2.5.3. Conventional method.

Titanium tetrachloride ($TiCl_4$) of 3.5 ml was added to 50 ml deionized water in an ice bath. The process was done under a fume hood followed by adding 35 ml of ethanol with strong stirring for 30 min. at room temperature. Ammonium hydroxide was added drop into the titanium tetrachloride ($TiCl_4$) solution, ethanol and deionized water were added to neutralize it, and the precipitate was obtained. After stirring vigorously, the solution was left for twelve hours. The gained precipitate was washed with deionized water until the eliminations of chloride ion, centrifuged then filtrated. The precipitate was dried at 200°C to remove part of the absorbed water for 4 hours, and lastly, amorphous TiO_2 was obtained. The obtained amorphous TiO_2 was calcinated at 40°C for four hours step by step. Finally, the powder TiO_2 nanomaterial was obtained [26,27].

2.5.4. Microwave.

The same procedure was followed, but the precipitate was dried to remove part of the absorbed water. The obtained TiO_2 was calcinated at 90 watts for 8 min. Finally, the powder of TiO_2 NPs was obtained [28].

2.5.5. Treatment of silk and wool fibers using TiO_2 NPs.

Silk and wool fibers were treated with different concentrations (0.5-2% o.w.f) of prepared TiO_2 NPs using microwave irradiation equipment at 90 watts for 10 min. The commercial one was carried out by exhaustion method, L.R. 1:20 for 20 min at 800C in the presence of the wetting agent. The treated fibers were cured at 140 ºC for 10 min, washed at 600C for 20 min, followed by drying at room temperature.

2.5.6. Dyeing method.

Treated and untreated fibers (1g each) were colored with natural dyes extracted from alkanet, liquor ratio 1:50, pH 3 for 10 min at 80 Watt using microwave irradiation. After dyeing, the samples were washed in a bath containing 3g/L of non-ionic detergent at 30°C for 30 min. Finally, the fibers were washed with cold water and dried at ambient temperature [29].

2.6. Evaluation of dyed fibers.

2.6.1. Color measurements.

The color strength of the dyed fibers (printed fabric) was assessed by reflectance method[28], which was performed on Ultra-scan PRO spectrophotometer (Hunter Lab, USA)

under illuminant D65, 10° standard observer. The color strength (K/S) in the visible region of the spectrum (400–700) nm was calculated based on Kubelkae–Munk equation [30,31].

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

where, (K) is the adsorption coefficient, (S) is the scattering coefficient.

2.6.2. Color data CIELAB space.

The total difference CIE (*L**, *a**, *b**) was measured using the Hunter-Lab spectrophotometer (model: Hunter Lab DP-9000). CIE (*L**, *a**, *b**) between two colors each given in terms of *L**, *a**, *b**was calculated from:

(*L**) value: indicates lightness, (+) if the sample is lighter than standard, (-) if darker.

(*a**&*b**) values: indicate the relative positions in CIE Lab space of the sample and the standard, from which some indication of the nature of the difference can be seen.

2.6.3. Fastness properties.

Colorfastness to washing, rubbing, and perspiration was evaluated by using the standard method. Dyed fabrics were tested by standard ISO methods [31]. Wash fastness (ISO 105-C02 (1989)) and crock fastness (ISO 105-X12 (1987)) were evaluated using the visual ISO Gray Scale for both color change (AATCC Evaluation Procedure (EP 1- similar to ISO 105-A02) and color staining (AATCC EP 2- same as ISO 105-A03). Lightfastness (Xenon arc) was evaluated using ISO 105-B02 [32].

2.6.4. Antibacterial assay

Antimicrobial action was measured by the filter paper disc diffusion technique [33]. SMA and Mueller Hinton agar (Difco) containing 100 ppm of 2,3,5-triphenyltetrazolium chloride was used for the antibacterial test. 2,3,5-triphenyltetrazolium chloride was added to culture media to differentiate bacterial colonies and to clarify the inhibition zone [34,35]. Each plate was inoculated with bacteria, *Escherichia coli (G-), Staphylococcus aureus (G+)* (0.1 ml) directly from the broth. All plates were incubated at 32°C for 4 days, after which the inhibition zones were recorded in millimeters (mm). The measurement scale 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 [6]. Control plates were prepared by placing antibiotics to evaluate culture for antibiotic resistance patterns that might affect the assay's sensitivity. The antibiotic used was penicillin 10 IU.

2.6.5. Self-clean measurement.

The self-cleaning action of TiO_2 NPs treated wool and silk was investigated by exposing the samples with adsorbed coffee stains to visible radiation. The measured quantity of 6% coffee solution was introduced on both fibers and was allowed to spread. One-half of each stain on the fibers was exposed to sunlight for 12-48 h, while the other half was covered with black paper to avoid its radiation from sunlight. The exposed part of the stain was compared with that of the covered part for self-cleaning action. Premier color scan SS 5100A Spectrophotometer was used to measure the photodegradation of coffee stain [36].

2.6.6. Photo-Induced Discoloration on wool and silk fibers.

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

3. Results and Discussion

As an industry, we consume more textiles and create more products than ever before, and looking forward, future growth is predicted as global affluence increases. However, our industry is now driven by customization and personalization. Manufacturing more products, saving water, time, and energy. To facilitate fiber coloring, both extraction and coloring must adapt utilizing automation wherever possible from creation through the coloring process. Let us explore innovation alongside 'eco-friendly dye' and how the new coloring technique has been released to save energy, time as well as water.

3.1. Effect of some parameters on dye extraction.

3.1.1. Effect of extracted pH medium.

Figure 1 illustrated the results of color efficiency presented as K/S coefficient values are given graphically, with respect to four various dye bath pH mediums: 3, 5, 7, and 9. Dyestuff concentration was 2 % (O.W.F) to ensure satisfactory dye adsorption on the textile material at 90 watts for 10 min. From Figure 1, we can observe that the maximum K/S value was obtained at pH 3. Due to the results obtained, further research continued in acidic conditions.

The main color compound is alkanet, ranging from red to violet depending on the coloring pH medium. Adding acid gradually reduces the negatively charged ion (anion) of the dye molecule solubility, predominating the energy barricade versus ve- of the protein fiber. It is substantial to consider the coloring process takes place in 3 steps: 1st step, dye atoms are adsorbed on the fiber surface, 2nd step the dye distribute inside the fiber molecules, and finally, the 3rd step, formed the bonds among the dye molecules and the fibers. The leverage of the coloring process is based on the adsorption process (1st step), is occurred quietly. In the quick adsorption case, the dyes remain conglomerate on the fiber surface. Thus, it can't diffuse into the fiber atom, and it cannot form bonds. In the end, this results in unequal coloration and bad adsorption. This is because the color molecule is holding on the fiber surface, so the color fastness will be poor. The whole showed results emphasize the necessity for an acid medium for silk and wool fibers coloring with alkanet dye.

Figure 2 showed the situation of dyed samples in (a^*/b^*) color space, while table 1 illustrated the data values of essential color parameters L^* (lightness), C^* (chroma), and h (hue), all the results approve that the acid increment has a significantly affect the change of (h) parameter which corset in the area of the red shade, but it leads to definite changes in L^* and C^* parameters. From the data tabulated in table 1, It can be said that the increment of acid gives rise to the decrement of (L^*) value, as well as C^* values, The decrement of C^* parameter is due to the lower dye absorption affected by acid increment, and it is instantly associated with

lower K/S values, meaning lower color strength obtained. Due to the results obtained, further research was continued under acidic conditions.

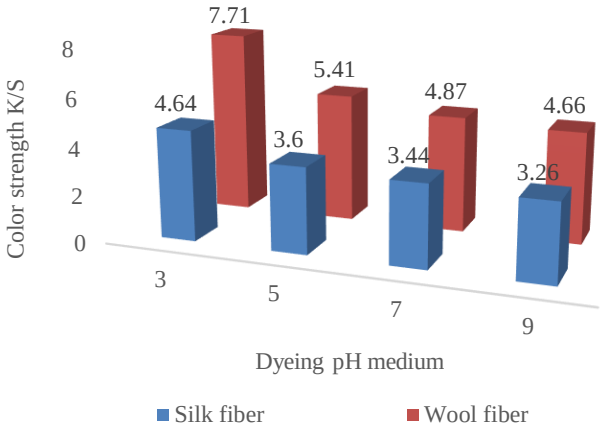

Figure1.The influence of dye pH medium on the color strength (*K/S)* value of colored silk and wool fibers simultaneously.

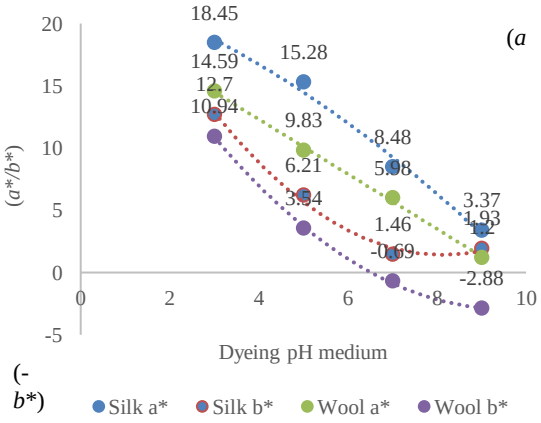

Figure 2. The influence of coloring pH medium on the color coordinates of colored silk and wool fibers simultaneously.

Table 1. The influence of coloring pH medium on the *L**, *C** and *h* values.

PH	Silk			Wool		
	*L**	*C**	*h*	*L**	*C**	*h*
3	46.95	34.61	241.26	36.42	24.54	251.39
5	46.38	30.74	241.53	36.33	23.20	250.78
7	44.95	24.51	242.39	35.53	19.09	249.33
9	39.75	16.85	247.83	33.56	19.00	248.81

Dyeing condition: Dye conc. 2% at 90 Watt for 10 min.

3.1.2. Effect of dye amounts.

The affinity of alkanet natural dye into silk and wool fibers in the acid medium was determined in the dye amount ranging from 1 to 6 % (O.W.F). The obtained results expressed to color strength (K/S) values (Figure 3) conformity with results obtained in a*/b* Fig. 4 (color space) and table 2, and are corroborative the increment of color strength with the increment of coloring amount, but only at the borderline amount where the maximum relation of L* and C* was completed(3-4 %). The maximum color strength (K/S) value was achieved at 4% (5.93) and 5% (11.24) for silk and wool, respectively. On higher amounts, the predictable decrease in color strength occurs. For dyestuff amount, 1% of the obtained K/S value was 4.98, while for maximum coloring amount of 6 % got K/S value was 3.64for silk, while it was7.71at 1% for wool at the higher amount, 6% the obtained K/S value was 6.11 (Figure 3). However, from the

data tabulated in Table 2, we can observe that for silk fiber colored with 4 % of coloring C* is 36.85 and L* is 44.92, while for wool fiber colored with 5% C* is 32.43 and L* is 36.09, while for 6 % C* decreases to 34.61, 23.54 and L* increases to 46.95, 36.42 for silk and wool fiber respectively. However, there is no significant change in color hue with the increase of dye amount, but the observed change of color C* placement the color of the colored sample values in a*/b* color space (Figure 4).

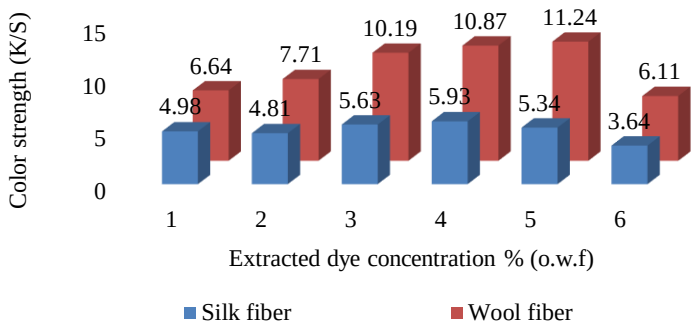

Figure 3. The influence of alkanet color amount on the *K/S* value of dyed silk and wool fiber simultaneous.

The results data listed in table 2 emphasize the relation of L* and C* as it was predictable: the decrease of L* value and increase of C* value with the increase of dye amount. The relationship of L* and C*is critical for a visible experiment of whole color appearance. It will define the density of color and the psychophysical influence on the superintendent. Thus, defining the border of the dye amount of alkanet color is important to realize the higher intensity, i.e., the hights C* on the specific level of L*. From the obtained data could be approved dye amount of 4, 5 % is a maximum to achieve favorable red shade with pursuing intensity and strength for silk and wool fiber, respectively.

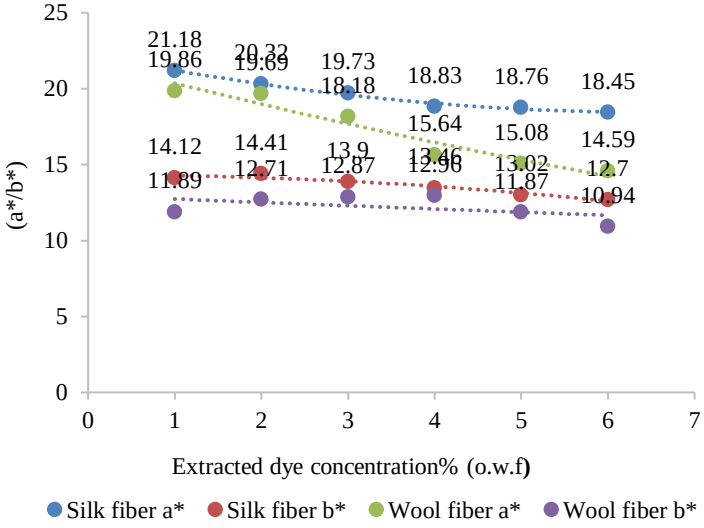

Figure4. The influence of extract dye concentration on the color coordinates of dyed silk and wool fibers simultaneously.

Table 2. The influence of dye concentration medium on the*L*, C**,and *h* value of dyed silk and wool fibers simultaneously.

Dye	Silk			Wool		
conc.%	*L**	*C**	*h*	*L**	*C**	*h*
1	57.57	35.61	231.26	40.35	26.20	241.39
2	57.12	35.91	231.53	39.56	29.00	245.73
3	51.76	36.09	232.39	38.28	29.09	248.81

Dye conc.%	Silk			Wool		
	*L**	*C**	*h*	*L**	*C**	*h*
4	44.92	36.85	237.83	37.48	30.54	249.33
5	44.42	36.74	240.45	36.09	32.43	250.78
6	46.95	34.61	241.26	36.42	24.54	251.39

Dyeing condition: pH.3, 60ºC for 5 min.

3.1.3. Influence of various coloring times on color strength of dyed silk and wool fibers.

The coloring time is essential in characterizing the adsorbate–absorbent interactions. Fabrics colored with 4, 5% for silk and wool fibers respectively at pH 3 and 60ºC were characterized with various coloring times (5-40 min). To define the relations among microwave irradiation time of the dye dispersal and penetration rate, the color strength of the colored fiber was characterized.

Figure 5 describes various coloring time influences on the K/S of colored silk and wool fiber with alkanet natural dye. The figure confirms the expected positive effect of coloring time, with increase coloring time, the color efficiency increases 52.11%, 7051%, and 42.79% for dyed samples for 10, 20, and 30 min respectively, then it remains constant due to the equilibrium state. The increase of K/S value may be due to unforeseen circumstances of microwave irradiation effect, which is transmitted directly to the molecular structure of both (dye molecules and fibers) with an electromagnetic field. Considering these phenomena, the majority of microwave heating of the material where the latte absorbs microwave irradiation from inside to the outside of the material and changes it into heat, which leads to quick, controlled, specific, and uniform heating in a short time.

The placement of all colored samples in (*a**/*b**) color space as well as the data values of color parameters *L**, *C** and *h* (table 3) confirms that various coloring times have a significant influence on the change of h parameter which lies in the range of red to violet shade which leads to certain changes in *L** and *C**parameters. It can be seen (Table 3) that the increases in coloring time cause a decrease of *L** value as well as *C** values.

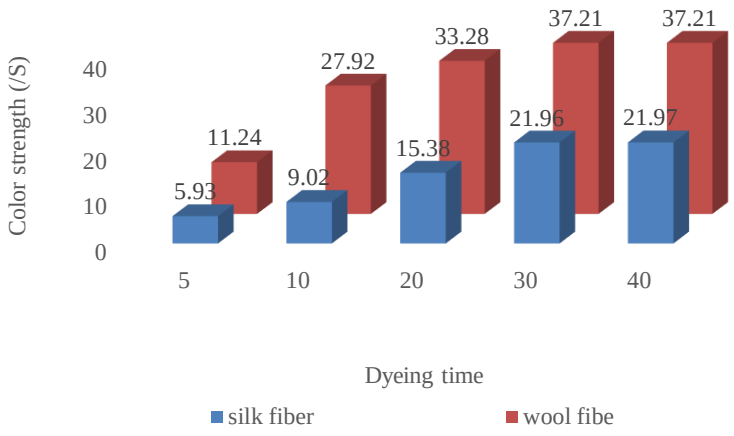

Figure 5. The influence of various coloring times on the *K/S* value of colored silk and wool fiber simultaneously.

Table 3. The influence of various coloring time on the color coordinates of dyed silk and wool fiber.

Time/ min	*L**	*a**	*b**	*C**	*h*
	Silk				
5	44.92	18.83	13.46	36.85	237.83
10	33.32	8.14	10.81	36.17	252.33
20	21.79	6.68	8.92	30.91	262.06

Time/ min	*L**	*a**	*b**	*C**	*h*
	Silk				
30	17.46	4.57	7.99	22.48	266.39
40	17.46	4.57	7.90	21.09	266.39
Wool					
5	40.35	15.08	11.87	32.43	250.78
10	16.47	5.50	2.64	33.09	269.93
20	20.57	2.64	1.30	32.16	266.50
30	12.05	2.69	0.28	27.80	274.50
40	12.09	2.69	0.28	24.00	274.50

Dyeing condition: Dye conc. 4% for silk and 5% for wool, pH 3, at 60ºC.

3.1.4. Effect of coloring bath temperature on K/S of dyed silk and wool fibers.

Results presented in Figure 6 approve the expected positive effect of coloring bath temperature. From the figure, we can conclude the following: a) with increasing dye bath temperature (4%, 5% of dyestuff (O.W.F.) for silk and wool fiber at pH 3 for 30 min), color efficiency (K/S) increases for all dyed samples (Figure 6) The highest K/S value was obtained at dye bath temperature 60ºC and at the increase of bath temperature the color efficiency (K/S) is dramatically decreased. The obtained results can be interpreted based on the protein coloring theory.

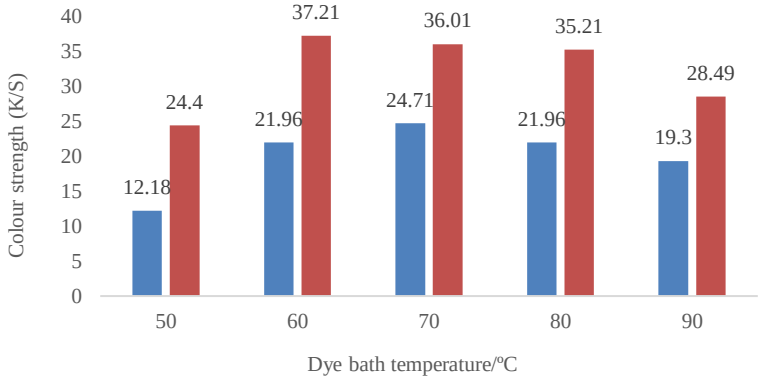

Figure 6. The influence of dye bath temperature on the *K/S* value of dyed silk and wool fiber simultaneous.

Table 4 indicates the color coordinates data of dyed silk and wool fiber simultaneously under the effect of microwave irradiation. The data confirm that microwave heating has a significant effect on all color coordinate parameters.

Table 4. Effect of dyebath temperature on the color coordinates of dyed silk and wool fibers.

Dyeing temp/º.C	*L**	*a**	*b**	*C**	*h*
	Silk				
50	11.39	4.27	11.07	21.85	244.08
60	17.46	4.57	7.99	22.48	266.39
70	22.79	9.54	5.22	20.91	258.83
80	18.46	7.57	2.99	19.48	269.39
90	14.98	6.98	1.83	11.09	264.23
Wool					
50	13.70	18.25	1.94	34.45	260.78
60	12.05	12.69	0.28	33.09	274.50
70	31.43	17.04	5.14	30.16	260.50
80	22.05	12.69	1.28	28.00	232.50
90	33.91	13.15	3.48	14.00	211.06

Dyeing condition: Dye conc. 4% for silk and 5% for wool, pH 3, for 30 min.

3.2. Treatment with TiO_2 NPs.

3.2.1. Effect of synthesized TiO_2 NPs.

In the last decades, we have been seen exponential growth in nanoscience and nanotechnology. When the size of the material becomes smaller to the nanometer scale, new physical and chemical properties come out. Properties differ in terms of the shapes, and the motion of the electrons in semiconductor nanomaterials is controlled by the mutual quantum retention and the transfer properties connected with phonons and photons are largely influenced by the size and geometry of the wrinkle by a considerable amount with the drop in the material size. The surface area of small particle size is helpful to many properties which are based on TiO_2, such as making easy interaction between the dyes and the textiles, which principally happen on the surface or at the interfaces and depends on the material surface. Therefore, TiO_2 is considered one of the most communal commercially available nano-size materials that have been applied in different fields due to its wide availability, non-toxicity, low cost and biocompatibility, and high chemical stability.

Figure 7 shows the TEM images of nano TiO_2 synthesized by two different heating methods (Traditional heating and microwave irradiation). In the first method, TiO_2 powder appears aggregated and having an elliptical shape, and the range of the particle size is between 40-60nm (Figure 7a), while in the microwave irradiation method, the powder appears as clear and having an octahedral structure and range of the particle size is between 10.6-18.38 (Figure 7b). However, it has been noticed that the particle size of synthesized TiO_2 by using microwave irradiation as a heating source is smaller than the commercial (range of the particle size is between 14.53-19.76) (Figure 7c) as well as the synthesized one by traditional heating. This may be attributed to the microwave irradiation effect, which prompts points of interest, such as quick, controlled, specific, and uniform heating in a short time.

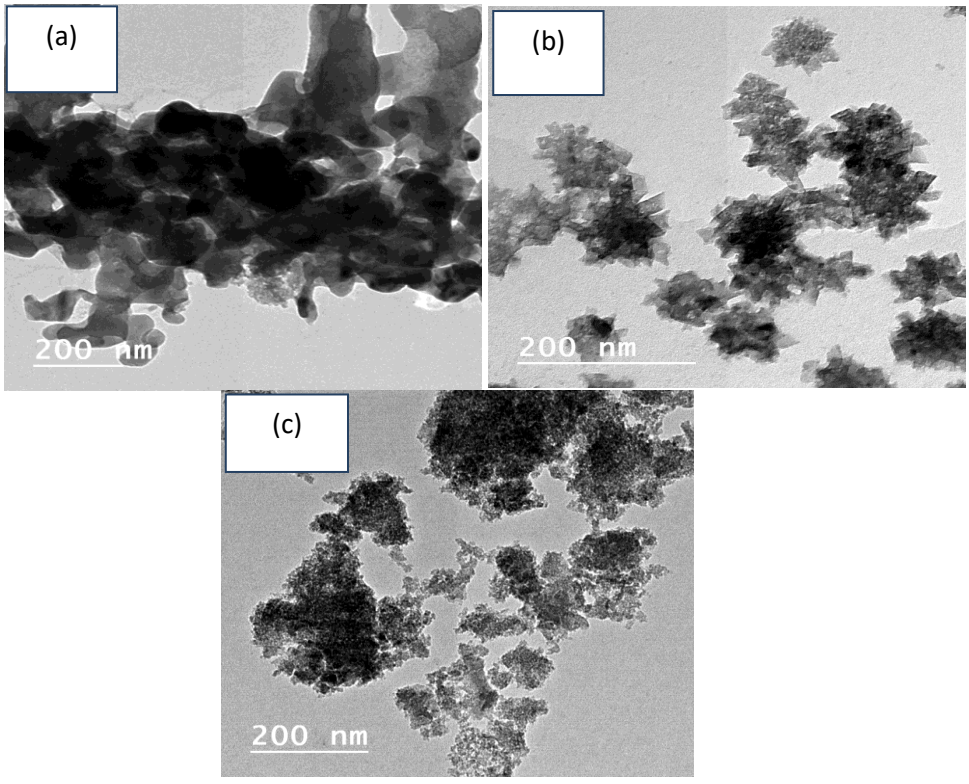

Figure 7. Transmission Electron Microscope (TEM) images TiO_2NPs: (**a**) traditional heating;(**b**) microwave irradiation;(**c**) commercial.

3.2.2.Treatment of wool and silk fiber with synthesized TiO_2NPs.

To determine the effect of treatment of wool and silk fiber with synthesized TiO_2 NPs by using microwave irradiation on K/S values and the commercial one to comparison, wool and silk samples are treated before and after coloring processes (2% shade, pH:3.5, L.R.1:40, at 100°C for 60min. the concentration of TiO_2 NPs was 2% W.O.F). The samples were dyed simultaneously by alkanet as natural dyes, using the exhaustion coloring method.

The results data listed in Table 5 can be concluded in the following findings (i) high K/S value was obtained for a treated sample before the coloring process, (ii) wool fiber gave a higher K/S value than Silk fiber, (iii) synthesized TiO_2 gives higher K/S vale than the obtained by using the commercial one, (iv) the treated fiber before dyed shifted toward the red color.

Table 5. Effect of treated fabric by using synthesized TiO_2 as well as the commercial one on K/S of wool and silk fibers.

Treated Fiber	K/S	*a**	*L**	*b**
Silk				
a	31.87	13.03	2.90	-1.70
b	15.86	24.52	7.42	4.30
c	28.09	22.94	5.76	4.43
d	14.04	25.16	3.07	0.61
Wool				
e	54.48	11.33	2.93	1.15
f	41.52	12.74	1.52	-0.27
g	31.60	13.60	4.11	0.73
h	16.04	13.60	4.11	0.73

a) Treated then dyed, b) Dyed then treated (synthesized TiO_2NPs), c) treated then dyed, and d) dyed then treated commercial TiO_2NPs of silk fiber. e) Treated then dyed, f) Dyed then treated (synthesized TiO_2NPs), g) treated then dyed, and h) dyed then treated (commercial TiO_2 NPs) of wool fiber

The durability of colors on the treated of silk and wool fiber samples before and after coloring by synthesized TiO_2 NPs using microwave irradiation as a heating source as well as the commercial one was evaluated in terms of fastness towards rubbing, washing, perspiration, and light fastness using the greyscale (Table 6). From data listed in Table 6, we can conclude the following findings: (i) the fastness properties of treated silk and wool fiber before coloring process are more resistant against washing and perspiration than those treated after coloring, (ii) the pre-treated of silk, as well as wool fiber by synthesized TiO_2 NPs by using microwave irradiation, displayed higher colorfastness than those pre-treated with the commercial one, (iii) the fastness of pre-treated both samples dyed samples with TiO_2 NPs by using microwave ranged from very good to excellent, while the samples treated with the commercial one were ranged from good to very good, (iv) the light fastness is excellent in all samples. The high color resistance of pre-treated dyed samples by synthesized TiO_2 NPs 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.

Table 6. Fastness properties of the untreated andTiO_2NPs-treated dyed silk and wool fibers.

Treated fibers	**Washing Fastness**		**Perspiration fastness**				**Lightfastness**
			Acidic		**Alkaline**		
	Alt	**Stain**	**Alt**	**Stain**	**Alt**	**Stain**	
Silk fiber							
BD (M)	4-5	4	4-5	4-5	4-5	4-5	6-7
AD (M)	4-5	4	4-5	4	3-4	4	6-7
BD (C)	4	4-5	4	4	4	4	6

Treated fibers	Washing Fastness		Perspiration fastness				Lightfastness
			Acidic		Alkaline		
	Alt	Stain	Alt	Stain	Alt	Stain	
AD (C)	4	4	2-3	2-3	2-3	2-3	5-6
Wool fiber							
BD (M)	4	4-5	4	4	4	4	6-7
AD (M)	4	4	4	4	4	4	6
BD (C)	4	4	4	4	3	3	6
AD (C)	4	4	3-4	3-4	2-3	3	5-6

M = synthesized $TiO_2$by microwave, C= commercial TiO_2, BD= treated before coloring, AD= treated after coloring.

3.3. Antibacterial activity of prepared TiO_2 NPs of treated silk and wool fibers.

The result given in Table 7 speaks of:

(i) Antibacterial activity of silk and wool fiber samples treated with the synthesized TiO_2 NPs are greater than the treated fiber with the commercial one,

(ii) The antibacterial activity of the treated samples against G+ bacteria was lower than the activity against G-,

(iii) The antibacterial activity of treated samples after dyes against G+ bacteria was less than the activity against G- in both fibers.

(iv) The antibacterial activity of wool fibers was greater than silk fibers.

Table 7. Antibacterial activity of TiO_2 NPs-treated wool fabrics.

Treatment Method	Silk fiber		Wool fiber	
	(G -)	(G+)	(G -)	(G+)
a	4.5	6.0	7.0	6.0
b	17.0	14.0	19	16.0
c	19.0	16.0	22	19.0
d	14.0	13.0	17	15.0
e	10.5	10.0	12.5	10.5
f	12.5	11.0	16.5	14.3
g	8.8	9.6	10.5	9.0

a-Dye only, b- synthesized TiO_2 NPs only, c- Dye/treatment, d- treatment/dye, e- Commercial TiO_2 NPs only, f- Dye/treatment, g- treatment/dye.

3.4. Self-Cleaning of TiO_2 NPs-Treated silk and wool fibers.

Photo-catalysis is the composing of photochemistry and catalysis with both light and a catalyst being desired to onset or precipitate a chemical conversion. In this study, TiO_2 NPs were synthesized by sol-gel process using Titanium Tetrachloride ($TiCl_4$) as a precursor, dried at 90 watts under microwave irradiation for 4 min, then calcined at 90 watts for 4 min. Self-cleaning properties were studied through a photocatalytic activity using potassium permanganate ($KMnO_4$) as a model organic pollutant. Table 8 shows the effect of synthesized TiO_2 NPs on untreated and treated silk and wool fibers after 24 h UV-lighting. From the obtained data, it was observed that there is a partial change in the color affected by UV-light for TiO_2 NPs striated samples. This is because the treatment sample led to form a thin layer from TiO_2 NPs, which led to increasing its hydrophilic and hydrophobic properties, both of them, fibers clean themselves through the work of water (formation by rolling droplets and increase the surface tension of the water, that carry out dirt away). Hydrophilic, hydrophobic coatings have an additional advantage: they can break down chemically adsorbed dirt in sunlight or UV light.

Table 8. Self-cleaning percentage of silk and wool fibers treated with synthesized TiO_2 NPs as well as the commercial one.

Treatment type	Dye removal %	
	Silk	Wool
Blank	-	-
Synthesized TiO_2NPs	85	88
Commercial TiO_2NPs	80	86

4. Conclusions

The present study focused on preparing multifunctional textiles based on natural dyes named alkanet and natural fiber. The multi-functionalization (dye extraction, color strength (K/S), colorfastness) of dyed fiber was successfully fabricated by assisting microwave heating as time, water, and energy-saving system during extraction processes. According to the colorimetric data, the microwave-assisted dye extraction imparted bright color with excellent all-over colorfastness properties related to the surface plasma resonance properties of the dye, fibers, and microwave irradiation.

The effect of treatment with TiO_2 NPs was characterized through transmission electron microscopy (TEM). The obtained results indicate that the optimization of coloring process parameters as well as optimized pre-treatment and treatment of dyed silk and wool fibers with synthesized TiO_2 NPs has a significant influence on the obtained shades and fastness properties.

The effect of treatment with TiO_2 NPs on the multifunctional properties of the silk and wool fibers, including coloration, antibacterial against *Escherichia coli* (G-) and *Staphylococcus aureus* (G+) species, and self-cleaning properties were evaluated. A high K/S value was obtained for a treated sample before the coloring process. Wool fiber exhibited a higher K/S value than silk fiber; synthesized TiO_2 gives a higher K/S vale than the commercial one obtained. Antibacterial activity of silk and wool fiber samples treated with the synthesized TiO_2 NPs is greater than the treated fiber with the commercial one. The antibacterial activity of the treated samples against G+ bacteria was lower than the activity against G-. The antibacterial activity of treated samples after dyes against G+ bacteria was less than the activity against G- in both fibers. The antibacterial activity of wool fibers was greater than silk fibers. The dyed silk and wool fibers followed by treatment with the synthesized and commercial TiO_2 nanoparticles (TiO2NPs) displayed an excellent antimicrobial activity as well as self-cleaning properties.

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