Innovative Multi-Protection Treatments and Free-Salt Dyeing of Cotton and Silk Fabrics

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ABSTRACT

In recent years, with the improvement of the living standard, people pay more attention to the health function of textiles that could be a shield or pathogen transmission medium. In the present work, surface cationization of cotton and silk fabrics was demonstrated by increasing the nitrogen content (N %) values. Different treatment techniques were successfully applied using chitosan, UV absorber, and reactive dye for producing multipurpose protective cotton and silk fabrics. Protective properties such as UV-blocking activity achieved a remarkable enhancement in UPF values (50+) and excellent protection. The anti-odor activity as measured by antibacterial reduction percentage was 98% for cotton and 99% for silk fabrics. Significant enhancement in dyeability values of cotton and silk fabrics are demonstrated. The durability of the treated fabrics was assessed after 30 repeated washing cycles and the treatment formulations showed sustainable UV blocking properties and anti-odor efficiency.

Keywords: UV protection, UV absorber, chitosan, anti-odor, no-salt dyeing, light fastness, treatment durability, cotton, silk

INTRODUCTION

With the dramatic rise in skin diseases, protecting human skin against harmful UV radiation is an acute problem. Due to the decreased thickness of the ozone layer, more UV light reaches the ground. Long-term exposure to UV light can result in a series of skin diseases such as acceleration of skin aging, photo dermatosis (acne) and even skin cancer, skin inflammation, and erythema (sunburn). UV radiation consists of three ranges: UV-A (315 - 400 nm), UV-B (290 - 315 nm) and UV-C (100 - 290 nm). UV-C radiation is absorbed by the ozone layer, but UV-A and UV-B reach the earth's surface and cause serious health problems [1]. Therefore, the main UV radiations that should be blocked by textiles are UV-A and UV-B [2]. Natural fibers, especially cotton and silk, have long been used in the textile industry because of properties such as good moisture absorption, dyeing affinity, thermal tolerance, perspiration management and comfort. Nevertheless, these natural fibers, especially silk, are susceptible to damage by UV rays. Ultraviolet radiation is capable of breaking molecular bonds when absorbed by the fibers, causing what is known as photolysis. If the molecules of the fibers contain covalent bonds, visible light may also cause photolysis. Photolysis begins when an atom is separated from a molecule, leaving a very active radical. This radical reacts with atmospheric oxygen, producing peroxide radicals. This process is called photo-oxidation [3].

Textile and clothing are the most suitable interface between environment and the human body. They can reflect, absorb and scatter solar wavelengths, but in most cases, they do not provide full sun screening properties. UV protection ability highly depends on a large number of factors such as the type of fiber, fabric surface and construction, type and concentration of dyestuff, fluorescent whitening agent (FWA), and UV absorbant protective finishing [4]. Moreover, the fading of colored textiles upon exposure to light is a well-known phenomenon, depending on the dye and fiber type. The ability of dyed fabrics to withstand prolonged sunlight exposure without fading or undergoing physical deterioration is largely determined by the photochemical characteristics of the absorbing dyestuff itself [5]. There are many different reaction pathways due to the light-excited dye molecule, such as ionization, dissociation into free radicals, oxidation, reduction, isomerization, etc. The light-induced fading of dyes in the presence of air usually entails oxidation, and such photo-oxidation reactions may involve oxygen free radicals, singlet oxygen or superoxide ions. The auto-oxidation reaction of dyes is generally considered to occur on exposure to UV radiation and is prevented by adding UV absorbers [5,6].

UV absorbers are organic or inorganic compounds that absorb UV radiation and protect human skin. The function of a UV absorber is to absorb UV radiation effectively throughout the UV region (280-400 nm). UV absorbers convert the electronic excitation energy into thermal energy through a fast reversible intramolecular proton transfer reaction. UV absorbers based on Oxalanilides are the most important groups of UV absorbing compounds as shown in *Figure 1* [6,7].

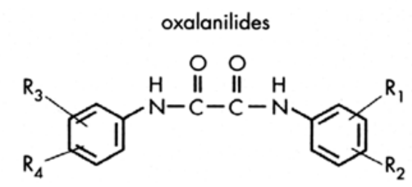


FIGURE 1. Structure of UV absorbers based on Oxalanilides.

Chemical modifications with compounds containing cationic groups have been carried out to attempt to reduce the use of salts as well as to introduce cationic sites in order to increase the absorption of reactive dyes into cotton and silk fabrics. However, the majority of chemicals used for cationization are not safe for the environment. Therefore, the use of chitosan, a polycationic biopolymer, is eco-friendlier for modification of cotton fabric [8,9,10]. There are certain advantages in salt-free dyeing over conventional dyeing techniques: elimination of salts; maximum fixation and minimum hydrolysis of dyes, the low volume of water required during the wash off process, i.e. significant savings in process costs [11]. Moreover, the application of chitosan to silk fabric increases dye exhaustion, which has a positive effect on textile wastewater. The application of chitosan in textiles can be divided into two main categories: the production of manufactured fibers and textile wet processing, which includes dyeing (improving the dyeability), finishing (antimicrobial properties), and printing (as a print paste thickener) [8]. The quaternary amino group of chitosan inhibits the growth of many bacteria, including gram-negative and gram-positive species [12].

Textiles act as carriers for microorganisms, especially in natural fibers such as cotton and silk because of their hydrophilic nature. Pathogenic bacteria such as mold and fungi affect both the fabric itself and the users. This results in unpleasing skin odor, damage to clothing, discoloration, stains, reduction in fabric mechanical strength, and even skin diseases [13]. Humid environment and suitable temperature provide a desirable living environment for the growth of microorganisms. Human sweat, dirt, dander, and spilled food on fabrics provide nutrition for the growth of bacteria and accelerate their reproduction. Antimicrobial finishes maintain hygiene and enable resistance to infection from pathogens, especially in hospitals, nursing homes, schools, hotels, and crowded public areas. They prevent unpleasant odor on intimate apparel, underwear, socks, athletic wear, and even daily use outfits [14,15]. Additionally, the unpleasant odor has a negative impact on textiles and their comfort properties and damages the aesthetic function of the fabric. Until recently, the use of bio-stats to inhibit the development of odor resulting from biological growth on textiles exposed to perspiration has not been considered a real need [16]. There are several bacteria found on the human skin such as *Enterobacter agglomerates* and *Staph epidermis;* that are capable of producing characteristic foul odors, especially on the foot and in the axillary regions [17].

The aim of this study is enhancing the UV blocking and anti-odor properties, as well as enhancement the dyeability and fastness properties of cotton and silk fabrics using a number of different treatments.

EXPERIMENTAL WORK

Materials

Fabrics

- ***Cotton fabric:*** scoured and half bleached (140 g/m^2) (1/1) plain weave, was purchased from Misr Company for spinning and weaving, Egypt.
- ***Silk fabric:*** scoured (93 g/m²) (1/1) plain weave, was purchased from Al-Gammal Company, Suhag, Upper Egypt.

Chemicals And Dyes

Chitosan (low molecular weight), glacial acetic acid, citric acid, sodium hypophosphite, peptone, beef extract, and agar were laboratory grade chemicals, UV-SUN® a reactive anionic UV absorber based on oxalanilides was kindly supplied by Huntsman, a nonionic detergent Hostpal® CVL-EL, and Cibacron® Red LS-B (C.I. Reactive Red 270) were kindly supplied by Ciba-Geigy.

Microorganisms

Staphylococcus Epidermis (*S. epidermis*) Gram-positive odor causing bacteria, was used for estimation of antibacterial imparting anti-odor activities.

Media

Nutrient broth/agar medium: contains beef extract (3 g/l), peptone (5 g/l), for a solid medium (15 g/l) agar was added. This medium was sterilized for 20 min at 121°C under pressure.

Methods

Fabrics Treatments

Before undergoing any treatments, cotton and silk samples were washed in a bath containing sodium carbonate (2 g/L) and Hostpal® CVL-EL a nonionic detergent (5 g/L) at 60 ºC for 30 minutes. The fabrics then thoroughly rinsed with water and finally dried at ambient temperature.

In order to determine a suitable method and the best results, chitosan and the UV absorber were applied independently, alternatively, and/or simultaneously to cotton and silk fabrics. Different options of treatment mixtures and applications were explored.

- ***Chitosan treatment:*** (1% w/v) chitosan was dissolved in 10% citric acid, sodium hypophosphite 7 g/l, and 0.5% glacial acetic acid and applied as pretreatment and/or simultaneously by the exhaustion method for 30 minutes at 60 °C and M: LR 1:40.

- ***UV absorber treatment:*** (3% owf) UV-SUN®, sodium sulfate 15 g/l, sodium carbonate 10 g/l was applied as pretreatment and/or simultaneously by the exhaustion method for 30 minutes at 70 °C and M: L.R 1:40, in presence of salt and salt-free.

Washing Procedures

All treated cotton and silk samples were washed repetitively for 10 washing cycles before any dyeing, testing, and evaluation. The treated fabrics were washed for 30 repeated washing cycles to evaluate the treatment durability according to AATCC test method (124-2006).

Dyeing With Reactive Dye

All untreated and treated cotton and silk fabrics were dyed with Cibacron® Red LS-B (C.I. Reactive Red 270) in the presence of salt and salt-free according to the following formulation: Cibacron® Red LS-B dye (1%) shade, (15) g/l sodium sulfate, (10) g/l sodium carbonate, M:LR 1:50. All dyed samples were washed with nonionic detergent (5 g/L) at 60 °C for 20 minutes, and M: LR (1:50) before testing and evaluation. The dyeing process was carried out as shown in *Figure 2*.

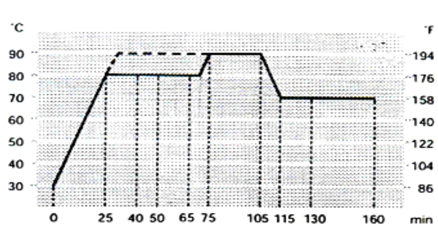


FIGURE 2. Dyeing process with Cibacron® Red LS-B dye.

Testing And Evaluation

Nitrogen Content (N %)

Nitrogen content was determined according to the Kjeldahl method [18].

UV Blocking Ability

The amount of ultraviolet protection provided by cotton and silk fabrics was evaluated by measuring ultraviolet (UVR) transmission using a UV-Shimadzu 3101-PC-Spectrophotometer. The ultraviolet protection factor (UPF) values were calculated according to the Australian/New Zealand Standard (AS/NZS-4399-1996). The following equation based on the percent ultraviolet radiation transmittance through the specimen was used to calculate the UPF:

$$UPF = \frac{\sum E\lambda \cdot S\lambda \cdot \Delta\lambda}{\sum E\lambda \cdot S\lambda \cdot T\lambda \cdot \Delta\lambda} \qquad (1)$$

Where $E\lambda$ is the relative erythema spectral effectiveness, $S\lambda$ is solar spectral irradiance in $W/cm^2/nm$, $T\lambda$ is the spectral transmittance of the fabric (measured), and $\Delta\lambda$ is the bandwidth in nm [19].

Antibacterial Causing Odor Efficiency

Staphylococcus Epidermis (*S. epidermis*) Gram-positive odor causing bacteria was used for estimation of antibacterial imparting anti-odor activity according to AATCC test method 100-1993. The reduction in number of bacteria was calculated using the following equation:

$$Reduction\ rate\ (\%) = (A-B)/A*100 \qquad (2)$$

Where: A = the number of bacterial colonies recovered from untreated fabrics. B = the number of bacterial colonies recovered from treated fabrics.

Color Strength (K/S)

Dyeing performance was characterized in terms of color strength (K/S) value (in the presence and/or absence of treatment) and was assessed using the Kubelka–Munk equation $K/S= (1-R)^2/2R$. Where, K, S, and R are the absorption coefficient, scattering coefficient, and reflectance respectively [13].

Fastness And light Fading Properties

Colorfastness to wash and light fading of the dyed cotton and silk fabric samples were evaluated according to ISO 105-C10:2006, and ISO 105-B02:1994 (Xenon Lamp) respectively.

FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) of the untreated, treated samples were recorded by using an FTIR spectrophotometer (JASCO 4700, Japan) in the region of 4000-400 cm^{-1} with a spectral resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Different treatments (individually and/or simultaneously) with chitosan, UV absorber, and dyed with reactive dye were carried out. Because of the differences in the nature and chemistry of cotton and silk, different combinations of treatments were required to achieve optimum performance in the two types of fabric.

Nitrogen Content (N %)

Nitrogen content (N %) values in cotton and silk fabrics structures are shown in *Table I*. It is obvious from the obtained results that cotton and silk fabrics independently treated with chitosan showed a significant increase in N percentage. That is evidence for cationization of both types of treated fabrics. Such interaction took place at a molecular level and involved hydrogen bonding of functional groups of chitosan such as the amino groups of the glucosamine units with hydroxyl groups of cotton fabric and with amino, hydroxyl, carbonyl groups of silk fabric [8,9,18]. Meanwhile, the N % content values were also increased to some extent when the UV absorber was individually applied to cotton and silk fabrics. This increase is due to the nature and molecular structure of the applied UV absorber, which is based on oxalanilides [7]. Mixing the chitosan with the UV absorber led to interaction between the two reagents and decreased the interaction between the UV absorber and fabrics. On the other hand, the data that there was a remarkable increase in N % of cotton and silk fabrics pre-treated with chitosan then salt-free post finished by UV absorber. These results suggest that pre-cationization of cotton and silk fabrics would impart better penetration, adsorption and interaction of the anionic UV absorber into the structure of the fabrics [18].

TABLE I. Nitrogen content (N %) of cotton and silk fabrics treated with different treatments.

Finishing Bath Formulations	Nitrogen Content (N %)	
	Cotton	Silk
Untreated	-	0.37
Chitosan	0.2	13.42
UV absorber	0.15	0.62
Pre-treatment with chitosan, post finished by UV absorber (No salt)	0.47	14.77

UV Blocking Properties And Durability

According to AS/NZS 4399:1996 the protection categories are non-ratable protection (UPF <15), good protection (UPF >15), very good protection (UPF >30) and excellent protection (UPF >40, 50, 50+). It is suggested that UPF values required for apparel and garment applications should be at least 40 to 50+ [19,20].

In order to optimize UPF values of treated fabrics, different treatment mixtures were prepared and applied to cotton and silk fabrics without adding salts. The rate of UV protection of cotton and silk fabrics was quantified and expressed via UPF values in *Figure 3*. It can be seen from the data that chitosan treatment had no positive impact on UPF values for both types of fabrics. The chitosan may have formed into a transparent film on the fabrics, allowing UV rays to transmit through their surface [20]. On the other hand, incorporating UV absorber in the finishing process significantly enhanced the UPF values according to the following order: chitosan and UV absorber mixture < UV absorber < pre-treatment with chitosan post finishing with UV absorber. The oxalanilide UV is functioning as a colorless dye. When it is incorporated into the fibers, electronic excitation energy is converted into thermal energy. Hence, it acted as a radical scavenger and singlet oxygen quencher. The high-energy, short-wavelength ultraviolet radiation excited the UV absorber to a higher energy state the energy is absorbed and then dissipated as longer-wavelength radiation [3,21]. Additionally, it blocks UV light before it reaches the fibers.

One bath treatment of cotton and silk fabrics with chitosan and UV absorber enhanced the UPF values and protection category (good and very good) for cotton and silk respectively. Pre-treatment with chitosan followed by post finishing with the UV absorber achieved the highest UPF values 50+ (68, 57), as well as protection categories (excellent protection) for both for cotton and silk. Moreover, application of chitosan as a pre-treatment step in presence of citric acid as a cross-linking agent increased the uptake of active moiety in the anionic UV absorber. That would be responsible for the significant enhancement of UPF and protection category. Therefore, it can be assumed that chitosan reacted with hydroxyl groups of cellulose and several functional groups such as amino, hydroxyl, carboxyl and carbonyl in silk proteins, creating cationic charges on the surface of the fabrics. As a result, cotton and silk acquired cationic active sites that are strongly bound to the polymer chains [1].

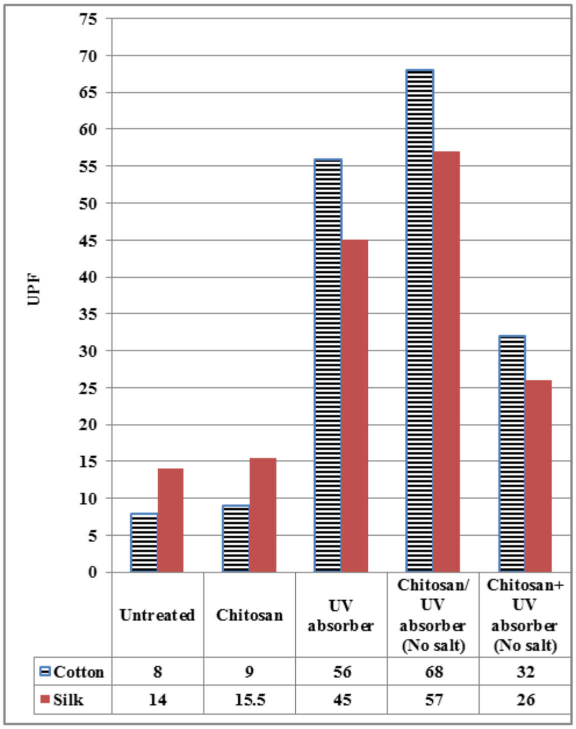


FIGURE 3. Effect of different treatments on UPF values of cotton and silk fabrics.

Effect of the Dyeing Process on UPF Values

Effective UV protection is extremely desirable in lightweight summer clothing. This would allow fashionable, comfortable to wear clothing to offer protection against UV rays [2]. The data represented in *Figure 4* showed the effect of the dyeing process by Cibacron® Red LS-B (C.I. Reactive Red 270) reactive dye applied using different treatment conditions on the UPF values of cotton and silk fabrics. It can be concluded from the figure that conventionally dyed samples had a significantly higher UPF values and protection category (very good for cotton and good for silk fabrics) than the non-ratable undyed reference samples. These obtained results may be attributed to the assumption that can have a considerable influence on the permeability of ultraviolet radiation in textile materials. Specific factors affecting this include the type of dye, chemical structure, absorptive groups present, dye uptake, depth after dyeing, uniformity and additives. It is known that the absorption band of many dyes extends into the ultraviolet spectral region. As a result, such dyes act as ultraviolet absorbers and can increase the UPF of the fabrics [3,19].

Additionally, no-salt post dyeing of pre-treated cotton and silk fabric samples with chitosan showed enhancement in UPF values and protection category as well (excellent for cotton and very good for silk fabrics). This is a result of cationization of cotton and silk fabrics prior to dyeing which increased dye uptake and color yield. UV absorber pre-treatment, simultaneously treatment, and post-treatment with dyeing process all resulted in a significant enhancement in UPF values (50+) and protection category (excellent) for both cotton and silk fabrics. These results may be due to the dual screening power of UV absorber and dye that limited UV radiation to transmission through the surface of the fabrics. The optimum UPF values (50+) were achieved in case of pre-treatment with chitosan followed by UV absorber finishing followed by the dyeing step without salt for cotton (82) and silk (71), and pre-treatment with chitosan followed by post UV absorber finishing and dyeing in one bath without salt for cotton (100) and silk (80). Consequently, the last treatment option produced the maximum UV blocking properties as well as permitting dyeing without the addition of electrolyte, which in turn saved chemicals.

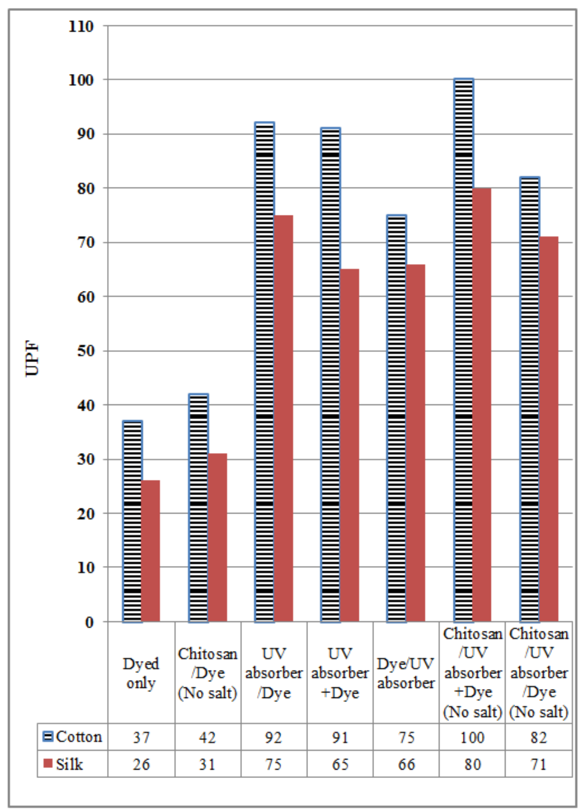


FIGURE 4. Effect of dyeing process on UPF values of cotton and silk fabrics.

Anti-Odor Efficiency

The evaluation of antibacterial properties as an indicator for the anti-odor activity of cotton and silk fabrics treated with different finishing techniques and dyed was carried out. The results are presented in *Table II*. Gram-positive bacteria *Staphylococcus Epidermis* (*S. epidermis*), an odor causing bacteria, was used to assess antibacterial conferred anti-odor activity of cotton and silk fabrics. It can be concluded from the obtained results that the untreated samples of both fabrics had no bacterial reduction activity. Cotton and silk fabrics treated with chitosan had significantly enhanced the bacterial reduction percentage, i.e. anti-odor activity. It is likely that the amino groups in chitosan interfered with the bacterial metabolism by stacking on the cell surface and binding with the DNA to inhibit the m-RNA synthesis [14,15,18]. Additionally, citric acid was used as a crosslinking agent to fix chitosan on cotton and silk fabrics. Citric acid acted as a polycarboxylic crosslinking agent, reacted with the hydroxyl groups of cellulose, and produced an ester bond between the cotton and citric acid. In addition, carboxylic acid groups in the citric acid reacted with hydroxyl or amino groups in the chitosan and produced an ester or amide bond. Therefore, citric acid was held in the chitosan by covalent bonds [22].

Treatment of cotton and silk fabrics with a UV absorber individually or before dyeing also imparted antibacterial properties. This may be attributed to the anionic nature of the oxalanilide UV absorber as well as the structure of applied bi-functional reactive dye. Simultaneous treatment with chitosan and the UV absorber in one bath significantly increased the anti-odor activity. Additionally, pre-treatment of cotton and silk fabrics with chitosan followed by salt-free finishing by UV absorber imparted excellent anti-odor properties (94% for cotton and 96% for silk).

Pre-treatment of cotton and silk fabrics with chitosan followed by salt-free post finishing with the UV absorber in the dye bath achieved the maximum anti-odor efficiency i.e. 98% and 99% bacterial reduction for cotton and silk fabrics, respectively. These findings prove that chitosan pre-treatment of cotton and silk fabrics improves the anti-odor efficiency of dyed samples when Cibacron® Red LS-B dye is applied to the treated fabrics.

TABLE II. Antibacterial causing odor properties of cotton and silk fabrics treated with different treatments.

Finishing Bath Formulations	*S. epidermis* bacteria causing odor reduction %	
	Cotton	Silk
Untreated	0	0
Chitosan	89	91
UV absorber	70	74
Pre-treatment with chitosan, post finished with UV absorber (No salt)	94	96
Chitosan and UV absorber in one bath (No salt)	78	82
Pre-treatment with UV absorber post-Dyed	77	80
Pre-treatment with chitosan, post-UV absorber finishing, and Dyed in one bath (No salt)	98	99

Color Strength (K/S)

In order to determine the effect of treatment types and application methods on the Cibacron® Red LS-B (C.I. Reactive Red 270) reactive dye uptake, cotton and silk fabrics before and after treatment with chitosan; in presence and absence of UV absorber; were subjected to salt and salt-free dyeing processes. The values obtained are shown in *Figure 5*. The dyed only samples had the lower K/S values even though they were dyed in presence of salt according to the manufacturer recommended dyeing instructions. Treatment with the UV absorber either before or after the dyeing process slightly enhanced the K/S values of both fabrics, indicating that the presence of UV absorber did not alter the shade of the dyed fabrics. Treatment with the UV absorber and reactive dye in in the presence of salt significantly increased the K/S values of cotton and silk fabrics. UV absorbers can be considered colorless dyes and are thus compatible with dyeing processes [21]. The K/S values of pre-treated cotton and silk fabrics with chitosan followed by salt-free reactive dyeing caused significant enhancement in K/S values over conventionally dyed fabric samples. The maximum dye uptake i.e., K/S values, are achieved in the case of pre-treatment with chitosan followed by salt-free UV absorber finishing and reactive dyeing in one bath for cotton and silk fabrics. This is likely a result of crosslinking by the chitosan in the presence of citric acid, which introduced positive dye sites on the fiber surface. The cationic nature of chitosan causes adsorption of anionic substances such as dyes and finishing agents by electrostatic attraction. The application of chitosan as a pre-treatment to cotton and silk fabrics increases the hydroxyl, carbonyl, and carboxyl groups and results in formation of covalent bonds with reactive dyes, resulting in the desired high level of exhaustion in salt-free finishing and dyeing techniques. [1,8, 9,10].

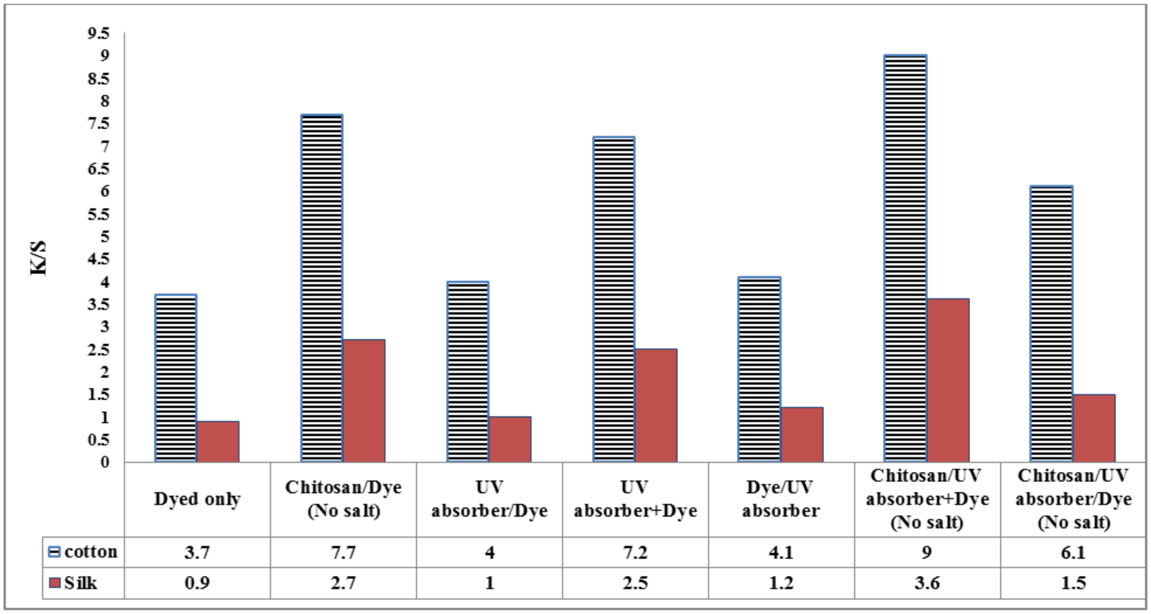


FIGURE 5. Effect of finishing bath formulations on K/S values of cotton and silk fabrics.

Washfastness and Lightfastness Properties

The relationship of dyeing process characteristics to photo fading of dyed cotton and silk fabrics was examined. It is also important to study the photo stabilization of dyed fabrics as a means of developing textiles that are protected against photo-fading as well as harmful UV radiation. The protection efficiency of different treatments and applications using chitosan and the UV absorber against photo fading were examined for the cotton and silk fabrics. The color fastness results for these optimally finished and/or dyed fabrics are shown in *Table III*.

In general, all color fastness of the treated fabrics results met the “acceptable” wash and color fastness standard rating regardless of the fabric type. However, the wash fastness of chitosan treated cotton fabric post finished with the UV absorber and dyed in one bath showed a slightly lower rating than conventional dyed fabric, while the silk fabrics showed similar wash fastness to conventionally dyed fabrics regardless of treatment. It can be assumed that chitosan sorption on cotton was a result of the ionic interaction between the negative charges of hydroxyl groups in the cellulose chains and the protonated amino groups of chitosan and the hydrogen bonding between hydroxyl groups of fibers and similar groups in chitosan, as well as van der Waals' forces. Therefore, a portion of reactive dyes absorbed by chitosan could be removed from treated cotton during the washing process and lead to significant decreases in washing fastness [23]. Simultaneous UV absorber finishing and dyeing in one bath enhanced the wash fastness rating of both cotton and silk fabrics.

Pre-treatment with chitosan prior to dyeing without application of the UV absorber slightly lowered the light fastness of both cotton silk fabrics. This may be attributed to formation of a chitosan film that allowed UV rays to transmit through fabric surfaces [20]. On the other hand, incorporating the UV absorber in the finishing process significantly enhanced the light fastness rating of for cotton and silk fabrics. Pre-treatment with chitosan followed by salt-free UV absorber finishing and reactive dyeing in one bath imparted the maximum light fastness properties for both cotton and silk fabrics. It could be assumed that the presence of cationic groups in the molecular structure of treated fabrics enhanced the interaction between fiber and dye, thus increasing the diffusion of dye molecules into the fiber increasing the lightfastness values [1].

TABLE III. Wash and lightfastness properties of cotton and silk fabrics treated with different treatments.

Finishing Bath Formulations	Wash Fastness*						Lightfastness	
	Cotton			Silk			Cotton	Silk
	A	*C*	*W*	*A*	*C*	*W*		
Conventional Dyeing	4	3-4	4-5	4	4	4-5	2	3
Pre-treatment with chitosan, post dyed (No salt)	4	3	4-5	4	4	4-5	2-3	4-5
UV absorber and dyed in one bath	4	4	4-5	4-5	4-5	4-5	4-5	5
Pre-treatment with chitosan, post-UV absorber finishing, and Dyed in one bath (No salt)	4	3	4-5	4	4	4	5-6	6

**A = alteration or change in color*
C = Staining on cotton
W = Staining on wool

FTIR Analysis

The FTIR spectra of both pristine and treated cotton are presented in *Figure 6*. The spectrum of the pristine cotton is characterized by a broad band assigned to hydrogen bonded hydroxyl groups around 3300 cm^{-1} *(Figure 6a)*. This broadness decreased due to the chemical reaction of the UV absorber and chitosan *(Figures 6b-d)*. Additionally, N-H bending appeared at 1717 cm^{-1} and 1800 cm^{-1}, as well as a peak at 1630 cm^{-1} assigned to C=O stretching. Treated cotton fabrics are characterized by a peak in the range of 3057 cm^{-1} to 3779 cm^{-1} assigned to OH stretching. New peaks appeared at 3708 cm^{-1} and 3783 cm^{-1} for N-H stretching (chitosan and/or UV absorber).

FTIR spectra of both pristine silk and treated fabrics are presented in *Figure 7*. The spectra of pristine silk in *Figure 7a* and those of the fabrics with the various treatments in *Figures 7b-d* show little difference save for a slight increase in the intensity of the C=O stretching peak in the range of 1600 cm^{-1}.

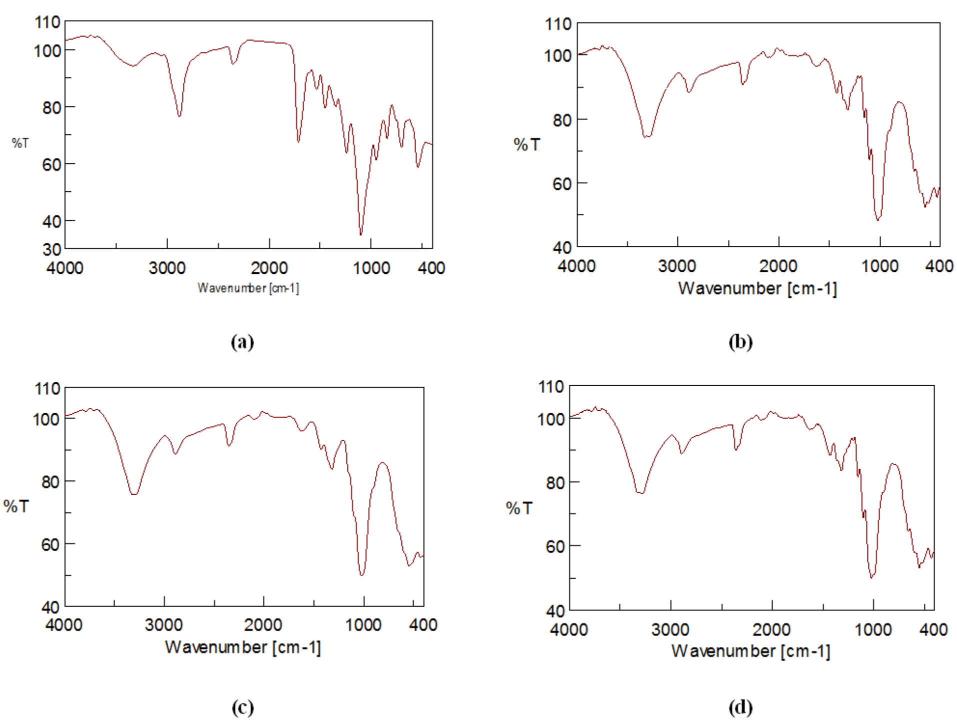


FIGURE 6. FTIR spectra of cotton fabrics: (a) untreated, (b) treated with UV absorber, (c) treated with chitosan, and (d) pretreated with chitosan post finished with UV absorber.

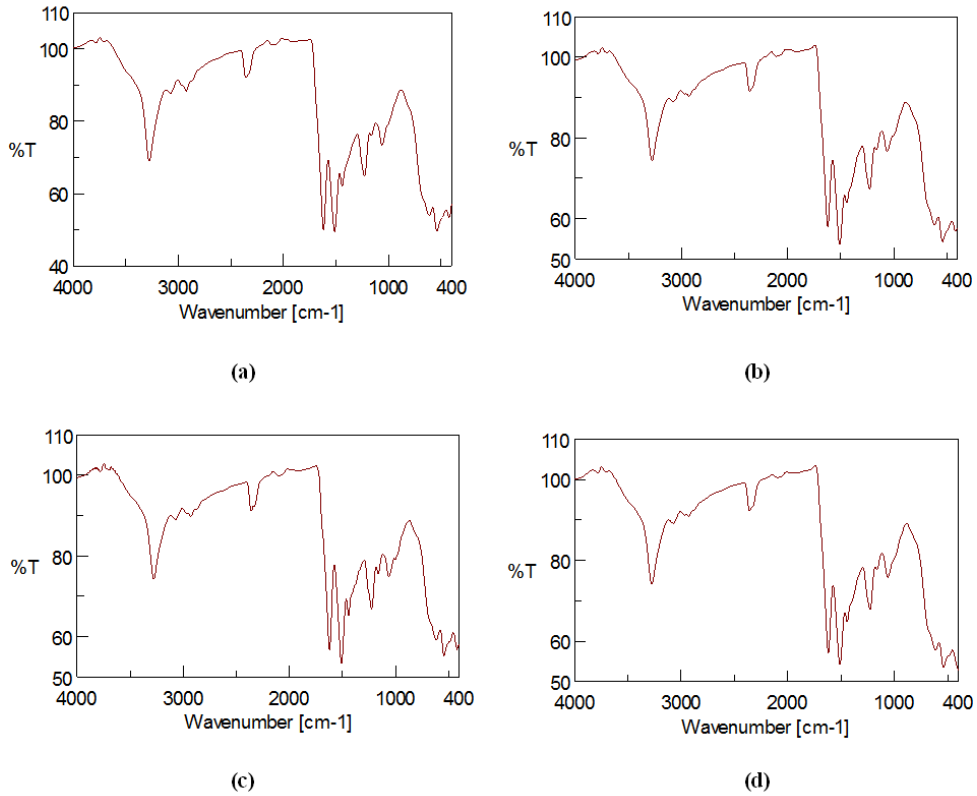
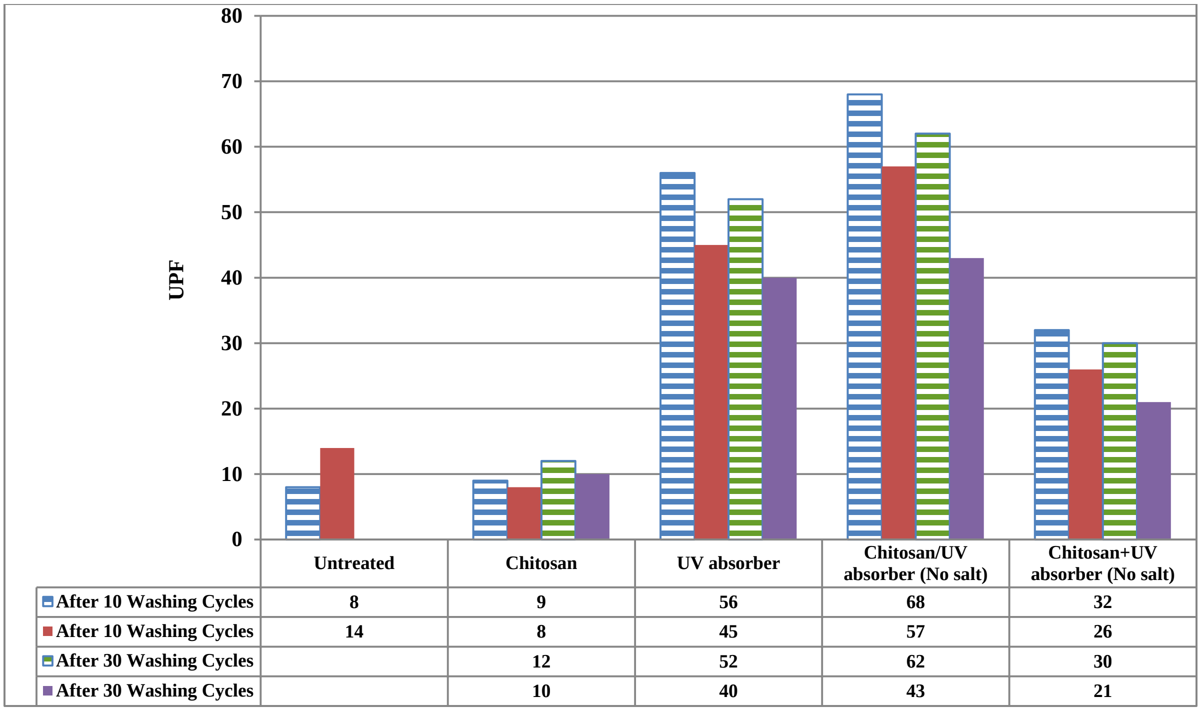


FIGURE 7. FTIR spectra of silk fabrics: (a) untreated, (b) treated with UV absorber, (c) treated with chitosan, and (d) pretreated with chitosan post finished with UV absorber.

Effect Of Repeated Washing Cycles On UV Blocking And Anti-Oder Properties Of Obtained Functional Fabrics

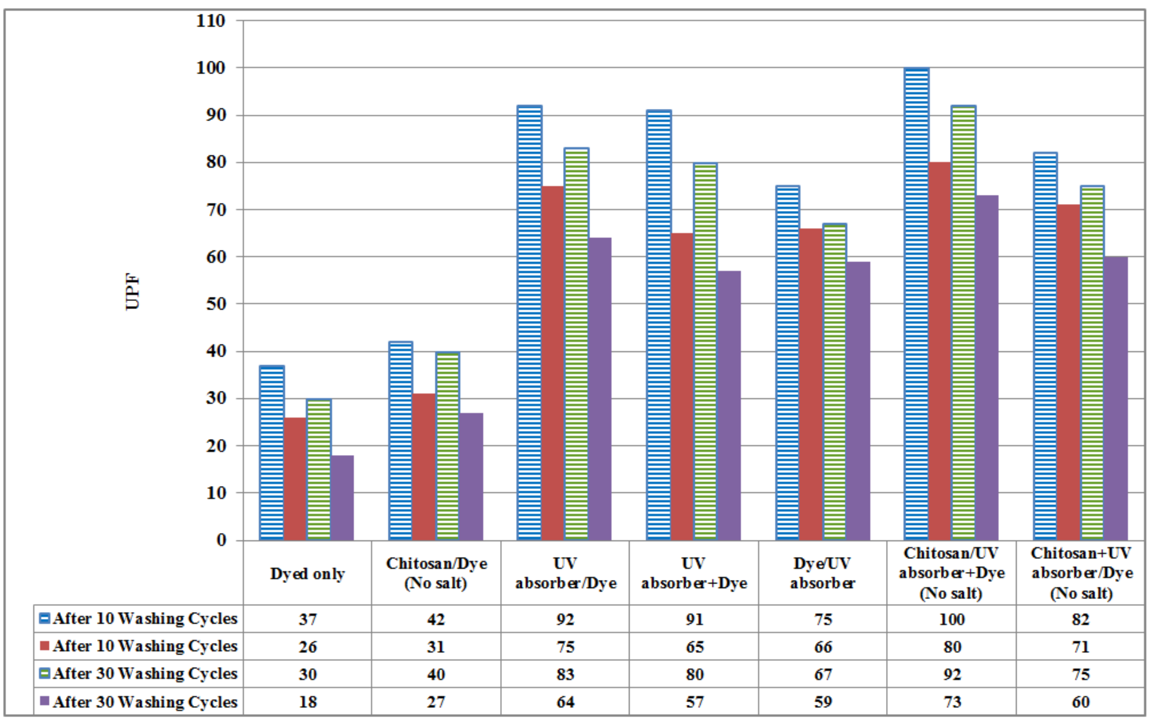
The silk and cotton textile materials finished with different treatment routes were subjected to repeated washing cycles and UPF values obtained after 10 and 30 washing cycles to assess the durability of the treatments. The UV blocking properties after repeated washing cycles are represented in *Figure 8* and *Figure 9*. The results show that the UPF values of the treated cotton and silk fabrics were decreased regardless of the treatment type and application of reactive dyeing. However, these decreases did not affect the protection category (excellent and very good protection) according to the standard test method.

The effect of repeated washing cycles on antibacterial activity as an indicator of the anti-odor properties of cotton and silk fabrics treated with different finishing techniques results were presented in *Table IV*. The results show that antibacterial activity decreased after 30 repeated washing cycles regardless of the treatment and fabric type, but still maintained their acquired functional property. The sustained durability after treatment with chitosan may be a result of it crosslinking to the fabrics. The hydroxyl groups of chitosan and fibers form covalent bonds with carboxyl groups of the polycarboxylic acid in an esterification reaction, which greatly improved durability and wash resistance [13].



	Untreated	Chitosan	UV absorber	Chitosan/UV absorber (No salt)	Chitosan+UV absorber (No salt)
After 10 Washing Cycles	8	9	56	68	32
After 10 Washing Cycles	14	8	45	57	26
After 30 Washing Cycles		12	52	62	30
After 30 Washing Cycles		10	40	43	21

FIGURE 8. Effect of repeated washing cycles of different treatments on UPF values of cotton and silk fabrics.



	Dyed only	Chitosan/Dye (No salt)	UV absorber/Dye	UV absorber+Dye	Dye/UV absorber	Chitosan/UV absorber+Dye (No salt)	Chitosan+UV absorber/Dye (No salt)
After 10 Washing Cycles	37	42	92	91	75	100	82
After 10 Washing Cycles	26	31	75	65	66	80	71
After 30 Washing Cycles	30	40	83	80	67	92	75
After 30 Washing Cycles	18	27	64	57	59	73	60

FIGURE 9. Effect of repeated washing cycles after application of dyeing process on UPF values of cotton and silk fabrics.

TABLE IV. Antibacterial causing odor properties of cotton and silk fabrics treated with different treatments after 10 and 30 repeated washing cycles.

Finishing Bath Formulations	*S. epidermis* bacteria causing odor reduction %			
	After 10 washing cycles		After 30 washing cycles	
	Cotton	Silk	Cotton	Silk
Untreated	0	0	0	0
Chitosan	89	91	82	81
UV absorber	70	74	67	60
Pre-treatment with chitosan, post finished with UV absorber (No salt)	94	96	89	81
Chitosan and UV absorber in one bath (No salt)	78	82	74	76
Pre-treatment with UV absorber post-Dyed	77	80	70	70
Pre-treatment with chitosan, post-UV absorber finishing, and Dyed in one bath (No salt)	98	99	93	90

CONCLUSION

A series of different treatments and application techniques of a reactive anionic UV absorber based on oxalanilides, chitosan, and/or reactive dyeing were carried out using both cotton and silk fabrics in an attempt to improve a number of different performance attributes. The test results indicate significant enhancement of UPF values ("excellent" protection category), excellent anti-odor efficiency, improved dyeability and potential for minimizing cost and pollution through salt-free finishing and dyeing techniques. The treatments applied also enhanced the light and wash fastness of dyed fabrics. FTIR characterization of both treated and untreated cotton and silk fabrics confirmed that chemical interaction occurred in both fabrics after treatment with chitosan and/or the UV absorber. The final modified cotton and silk fabrics obtained in this study could have potential as salt-free, durable apparel textiles offering protection against UV radiation and body odor.

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