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Eco-Friendly Surface Modification and Multifunctionalization of Cotton Denim Fabric

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Abstract

In this study, an eco-friendly strategy for the surface modification and multifunctionalization of denim fabric is successfully developed by N2 or air atmospheric plasma pretreatment followed by Post-treatment with environmentally sound active ingredients, namely aloe vera, neem, cinnamon, vanillin, ZnO nanoparticles, SiO2 nanoparticles, ascorbic acid, and salicylic acid, both individually and in combination. The change in surface morphology and the imparted antibacterial properties, UV resistance, hydrophobicity, and scent emission, along with coloration and durability to wash, are evaluated. A combination of plasma treatment and subsequent functional finishes result in a remarkable improvement in the imparted functional properties along with a variation in the color properties. The variations in the imparted functional and color properties are governed by the type of plasma gas and functional additive. The imparted functional properties are still high, even after 10 washing cycles. The mode of interaction between the modified substrate and the functional materials applied is also discussed.

Keywords: Denim fabric, Plasma, Surface modification, Functional finishing, Durability to wash, Multifunctional/Protective textiles.

1. Introduction

Recently, the adoption and implementation of environmentally sound emerging technologies to develop eco-friendly, comfortable, multifunctional, and durable denim fabric (DF) with high added value have received much attention [1-4]. The major focus of R&D activities to innovate and ensure the sustainable development of DFs and denim clothing is in i) using regenerated cellulosic substrates, such as viscose, tencel, modal, or bamboo, as weft yarns along with indigo-dyed cotton warp [5]; ii) using elastane fibers to develop stretch DFs to avoid deformation and dimensional changes, as well as to achieve garment resiliency [6]; and iii) potential applications of innovative technologies, such as biotechnology [7-12], nanotechnology [10, 13-15], plasma technology [16, 17], and/or biologically active natural products [18-21], to develop sustainable, high-quality, multifunctional DFs with remarkable durability, comfortability, and high added value in consideration of ever-growing customer needs, human health, and environmental concerns.

However, to our knowledge, there are limited R&D efforts exploring the synergetic effect of applying the most promising technologies, namely plasma, nanotechnology, and biotechnology, either alone or in combination, to develop sustainable, multifunctional DFs.

In this research, a facile and eco-friendly route has been adopted and developed to obtain durable, antibacterial, anti-UV, and hydrophobic indigo-dyed DF with a pleasant aroma.

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In the first step, N_2 plasma gas was used to preactivate the DF surface and create new functional groups. In the second step, the modified fabric samples were functionalized with numerous bioactive materials, namely aloe vera, neem, cinnamon, vanillin, and nanometal oxides (ZnO and SiO_2 nanoparticles [NPs]), or selected phenolic acids, namely ascorbic and salicylic acids. The impact of using air plasma as well as mixed active ingredients on the functional properties imparted upon the treated substrates was also investigated.

2. Experimental

2.1. Materials

Ocean Blue-indigo dyed denim fabric (100% cotton, twill 3/1 Z, 180 g/m^2) was supplied by EL-Robaea Co.Egypt. ZnONPs (50 wt% in water, 10-30 nm avg., Skyspring®, USA), SiO_2NPs (10-20 nm avg. Aldrich®, USA) and Vanillin R, (molecular weight 152.15, SDFCL®, India) were of commercial grade.

Aloe vera oil, neem oil, and cinnamon oil were purchased from the local market. Ascorbic acid and salicylic acid, (Sigma Aldrich), were of reagent grade.

2.2. Methods

2.2.1. Plasma pretreatment

DF samples were placed between two dielectric barrier discharge plasma electrodes with atmospheric-pressure plasma for 60 or 120 s for preactivation. The power supply had a frequency of 20,000 Hz, output power of 50 W, and output voltage of 5 kV. N_2 or air was used as the working gas at a fixed flow rate of 3 L/min [22].

2.2.2. Post-loading of the essential oils and vanillin

Immediately after N_2 plasma treatment, the preactivated fabric samples were post-treated using the exhaustion technique with essential oil dissolved in a 3:1 ethanol/water solution or in an aqueous solution of vanillin (5 or 10 g/L) with an LR of 1/20 at 30°C for 30 min in a 37-kHz sonicator bath at 50 W.

2.2.3. Post-treatment using salicylic or ascorbic acid

The N_2 plasma-pretreated DF samples were immediately post-treated with an aqueous solution (5 or 10 g/L) of salicylic or ascorbic acid, LR 1/20, at 30°C for 30 min using a sonicator bath (37 kHz, 50 W).

2.2.4. Post-immobilization of nanometal oxide (MO NPs)

The N_2 plasma premodified DF samples were post-treated with an aqueous solution of ZnO or SiO_2 NPs (5 or 10 g/L), LR 1/20, at 30°C for 30 min using a sonicator bath (37 kHz, 50 W), and then squeezed to a wet pickup of 85%.

2.2.5. Post-treatment with mixed active ingredients

After N_2 plasma premodification, the DF samples were immediately post-treated with vanillin/ZnO NPs, vanillin/salicylic acid, or ZnO NPs/salicylic acid solution (5/5 g/L), LR 1/20, at 30 °C for 30 min using a sonicator bath (37 kHz, 50 W).

The post-treated samples were then squeezed to a wet pickup of 85%, followed by microwave fixation at 450 W for 6 min, thoroughly washed to remove unfixed/unreacted active ingredients, and finally dried and conditioned before evaluation.

2.2.6. Surface modification using air plasma followed by postfinishing

Immediately after air plasma pre-activation, the DF samples were post-finished with an aqueous solution of vanillin, ZnO NPs, or salicylic acid (10 g/L), LR 1/20, at 30°C for 30 min using a sonicator bath (37 kHz, 50 W), and then squeezed to a wet pickup of 85% wet pickup, followed by microwave fixation at 450 W for 6 min. They were thoroughly washed to remove unfixed/unreacted active material and then dried and conditioned before analysis.

2.3. Testing and analysis

- The wettability of untreated and treated denim swatches was assessed according to the AATCC test method 39-1980. The shorter the wetting time, the better the water absorbency.
- The nitrogen content (N%) of the treated and untreated fabric samples was evaluated using the Kjeldahl method.
- The antimicrobial activity of the untreated and post-treated fabric samples was tested using the plate count agar method according to the AATCC test method 100-1999. The percent reduction in bacterial colonies was calculated using the following equation:

$$R\% = (B–A)/B \times 100,$$

  where R% is the percent reduction in bacterial colonies, and A and B are the numbers of bacterial colonies on the agar plates for treated and untreated fabric, respectively.
- The UV-protection factor (UPF) of the treated and untreated fabric samples was evaluated according to the Australian/New Zealand Standard Method AS/NZS 4399:1996 and classified as follows: good (UPF: 15–24), very good (UPF: 25–39), and excellent (UPF > 40). The higher the UPF value, the better the UV-protection ability.
- The color lightness (L*) of the treated and untreated DF samples were obtained using a Colour-Eye 3100 Spectrophotometer supplied by SDL Inter. England. The color strength (K/S)

values were determined using the Kubelka–Munk equation, $K/S = \frac{(I-R)^2}{2R}$, where K, S, and R are the absorption coefficient, scattering coefficient, and reflectance of the DF samples respectively.

- The water contact angle was measured using Contact Angle OCA 15EC (Company of Data Physics Instrument Gmbh) at ambient conditions.
- The metal content of the finished DF samples was assessed using a flame atomic absorption spectrophotometer (GBC-Avanta, Australia).
- The sensorial evaluation of the scent intensity of the post-treated DF samples was evaluated by a well-trained test panel at different intervals [23].
- The durability of the imparted functional properties after 10 washing cycles was assessed according to the AATCC Test Method 61 (2A)-1996.
- The surface morphology of the selected functionalized DF samples was observed via SEM (Guanta SEM 250 FEG field-emission gun) with an attached energy-dispersive X-ray analysis unit with an accelerating voltage of 30 kV (FEL Co., Netherlands).

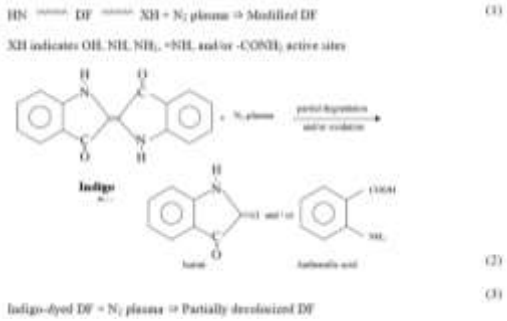
All the tests were performed in triplicate and the results are presented as mean values.

3. Results and discussion

To develop eco-friendly, sustainable, antibacterial, anti-UV, indigo-dyed cotton DF with a pleasant aroma, premodification of the cotton fabric surface with atmospheric plasma using N_2 or air as the working gas was performed to create new active sites. The fabric was subsequently treated with i) a natural bioactive ingredient, i.e., aloe vera, neem oil, cinnamon, or vanillin; ii) nanometal oxide, i.e., ZnO or SiO_2 NPs; iii) selected natural phenolic acid, i.e., ascorbic or salicylic acid; or vi) a functional mixture, i.e., vanillin/ZnO NPs or vanillin/salicylic acid.

3.1. Tentative mechanism (Scheme 1)

3.1.1. Premodification using N_2 plasma [16, 24]



3.1.2. Post-loading of bioactive material

Scheme 1. Surface premodification followed by fixation of the bioactive compounds

3.2. Post-treatment with natural bioactive additives

The data in Table 1 demonstrate that pretreatment of the indigo-dyed cotton DF with N_2 plasma for 120 s results in no change in wetting time (<1 s), increase in N% (from 0.254% to 0.456%), remarkable improvement in antibacterial efficacy against both Gram-positive bacteria (GPB; *Staphylococcus aureus*, up to 47.50%) and Gram-negative bacteria (GNB; *Escherichia coli*, up to 41.20%), marginal decrease in UPF (from 34 to 31), slight decrease in K/S value (10.74 to 10.22), and slight improvement in lightness (from 30.13 to 31.42).

The significant increase in N%, as well as in the imparted antibacterial activity against the tested pathogens, is a direct consequence of the creation of N_2-containing cationic active sites, e.g., $-NH_2$, as indicated in Eqs. 1 and 4, along with the generation of active species, such as ions and radical metastable neutrals, onto the preactivated fabric surface. These, in turn, negatively affect harmful bacteria's growth, cell wall structure, and/or cell membrane permeability [25]. However, the decrease in UPF and K/S values and increase in lightness compared with DF without plasma treatment is a direct consequence of the partial degradation, oxidation, and/or decolorization of the indigo dye molecules on the surface.

The data in Table 1 also show that the treatment of pristine DF with aloe vera (5 or 10 g/L) produces an increase in the wetting time and nitrogen content as a direct consequence of the deposition of aloe vera's hydrophobic and nitrogen-containing components, such as aloetic acid. In contrast, the loading of anthraquinones/anthrones from aloe vera, e.g., emodin, barbaloin, aloetic acid, isoaloeresin D, and lupeol [26, 27], during the microwave fixation step results in an increase in the antibacterial efficacy and UV-protection ability of the finished DF samples, reflecting the positive role of its bactericides and antiseptic components in killing *S. aureus* and *E. coli* pathogenic bacteria [27-29], along with the ability of its different constituents to absorb harmful UV radiation, regardless of the concentration used. The higher aloe vera concentration, 10 g/L, imparted better antibacterial/anti-UV functionalities and resulted in a darker hue.

Additionally, atmospheric N_2 plasma pretreatment followed by loading aloe vera constituents during the microwave fixation step prolongs the wetting time, increases N%, and remarkably improves both the

antibacterial and anti-UV-protection functionalities along with a reasonable increase in K/S and decrease in L* of the preactivated and post-treated fabric samples compared with the non-preactivated ones, irrespective of the aloe vera concentration. The remarkable improvement in the developed fabric functionalities reflects the positive role of plasma pretreatment and aloe vera Post-treatment, especially at the highest concentration (10 g/L), in enhancing the extent of loading and fixing of aloe vera's active ingredients, phytochemical components, and UV-absorbing ingredients onto the preactivated surface active sites (Eq. 1).

The imparted antibacterial activity against the tested pathogens was greater against *S. aureus* (GPB) than *E. coli* (GNB), which can be discussed in terms of their differences in cell wall structure, extent of cell wall damage and permeability, degree of inhibition of enzymatic activity, and subsequent destruction of the cell wall and death of the pathogenic microorganisms [30, 31].

Table 1 also reveals that Post-treatment of the preactivated DF samples with neem oil (10 g/L) results in a significant increase in wetting time (>180 s), noticeable increase in N%, significant increase in antibacterial activity against *S. aureus* (>91%) and *E. coli* (>79%), and sharp improvement in the UPF value (180). There was also a noticeable increase in K/S value and decrease in L* value of the attained products compared with the nonactivated fabric. The higher the neem concentration, the better the imparted antibacterial and anti-UV functionalities. The imparted antibacterial activity and UV absorption capability of neem-loaded substrates is attributed to its limonoids, azadirachtin, flavonoids, and tannins (bioactive constituents) and their ability to inhibit the microbial growth/disrupt cell wall membrane and interface with cell wall division and protein synthesis during the reproduction step, thereby leading to cell death [32-35], as well as the positive role of neem's active ingredients in absorbing harmful UV, especially UV-B, radiation [36, 37]. The imparted antibacterial activity of neem-loaded DF samples was more effective on GPB than GNB, keeping other parameters constant.

The data in Table 1 also demonstrate that the Post-loading of neem constituents onto N_2 plasma-treated samples results in an increase in N% and K/S, along with a decrease in the lightness of the preactivated/post-treated denim samples. This could be ascribed to the chemical composition and hydrophobic nature of neem's active ingredients, extent of their fixation and interaction with the indigo dye molecules, and modified fabric structure during the microwave fixation step.

Regarding the change in the physicochemical, functional, and coloration properties as a function of the Post-treatment of preactivated DF samples with cinnamon oil (5 or 10 g/L), the data in Table 1 clearly demonstrate that increasing the cinnamon concentration from 5 to 10 g/L in the finishing bath of the nonactivated denim samples is accompanied by a significant increase in wetting time (>180 s), slight increase in N%, improvement in antibacterial activity and UV-protection, increase in K/S value, and decrease in L* value compared with the untreated fabric.

Table 1. Effect of post-treatment with selected bioactive agents

Post-loaded functional agent	Conc. g/L	Plasma exposure time (s)	WT (s)	N (%)	Bacterial reduction (%)		UPF	Color properties	
					S. aureus	E. coli		K/S	L*
Untreated	0	None	<1	0.254	0.00	0.00	34	10.74	30.13
N2-Plasma treated	0	120	<1	0.456	47.54	41.20	31	10.22	31.42
Aloe vera	5	None	12	0.284	25.35	19.07	53	11.63	28.88
	10		15	0.325	30.05	25.08	75	11.79	28.68
	5	120	35	0.498	71.64	48.82	109	12.55	27.80
	10		50	0.523	82.22	65.89	120	13.82	26.39
Neem	5	None	>180	0.255	33.03	27.23	120	9.31	30.95
	10		>180	0.247	35.76	32.15	131	11.18	28.68
	5	120	>180	0.442	84.49	70.70	160	12.19	27.90
	10		>180	0.457	91.50	79.03	180	13.07	27.23
Cinnamon	5	None	>180	0.260	25.22	20.01	100	10.94	27.76
	10		>180	0.249	30.23	27.13	120	11.43	27.87
	5	120	>180	0.460	78.51	70.70	145	12.78	26.24
	10		>180	0.459	86.02	76.91	170	13.98	25.22
Vanillin	5	None	3	0.241	36.22	29.41	181	10.61	28.78
	10		4	0.236	41.73	34.12	239	10.24	29.71
	5	120	<1	0.445	85.19	79.33	313	10.65	30.38
	10		<1	0.451	96.97	91.41	377	9.48	32.12

Plasma-modification: N2-plasma exposure time (60, 120 s).
Post-loading of functional agents: solubilized ethanol/water (3:1) aqueous solutions of essential oils (5, 10 g/L), aqueous soluti on of vanillin (5,10 g/L), LR 1:20 at 30oC for 30 min. using a sonicator bath, microwave fixation at 450 w for 6 min.
%N: nitrogen content, WT: wetting time, UPF: UV-protection factor, K/S: color strength, L*: lightness

The extent of variation in the aforementioned properties is governed by the concentration of cinnamon oil. In contrast, N_2 plasma pretreatment of DF samples followed by loading with cinnamon oil produce a negligible effect on wetting time, increase in N%, significant improvement in antibacterial efficacy against the tested bacteria, noticeable improvement in UV-protection ability, and decrease in the lightness of the obtained products, regardless of the cinnamon concentration used in the postfinishing step. The remarkable increase in the imparted antibacterial and anti-UV functionalities is ascribed to bioactive phytochemicals, namely cinnamaldehyde and eugenol, as well as to polyphenolic compounds, such as vanillic, gallic, ferulic, caffeic, and p-coumaric acids [38, 39]. It is worth noting that the imparted antibacterial efficacy against the tested *S. aureus* was better than that against *E. coli*, regardless of the concentration, which is attributed to the differences in their cell wall thicknesses. The higher the cinnamon concentration during Post-treatment, the better the antibacterial activity and UV-protecting capability of the developed DF samples.

Additionally, the increase in wetting time of the cinnamon-loaded substrates can be attributed to the physical surface roughness of plasma-pretreated DF, along with the deposition of a hydrophobic film onto the fabric surface during the microwave fixation stage as a direct consequence of interactions among the hydrophobic constituents of cinnamon oil and the preactivated DF active sites.

Moreover, our experimental results (Table 1) indicate that Post-treatment with vanillin (5 or 10 g/L) increases hydrophilicity (<1 s), slightly increases N%, remarkably improves the antibacterial and UV-protection properties, decreases K/S value, and increases L* value. The higher the concentration of vanillin in the Post-treatment step, the greater the increases in hydrophilicity and chemical, functional, and lightness properties compared with those of the nonactivated/vanillin treated samples. The remarkable antibacterial and anti-UV functionalities of vanillin-loaded substrates (Eq. 4) reflect vanillin's ability as a phenolic/aromatic aldehyde compound to damage the bacterial cell wall, thus inhibiting cell membrane function, as well as to disrupt protein and/or nucleic acid synthesis, which in turn negatively impacts the bacteria's metabolic processes, growth, and survival [28, 40, 41]. Additionally, the remarkable improvement in the UPF value of vanillin-loaded substrates reflects vanillin's positive role in coating the preactivated fabric surface, thereby absorbing and blocking the transmission of harmful UV radiation within the fabric structure [42].

According to the experimental results, the physicochemical, functional, and coloration properties of the preactivated and post-finished DFs vary in the following orders as a function of the type of functional additive (10 g/L):

i) Antibacterial activity: vanillin > neem > cinnamon > aloe vera >> none
ii) Anti-UV functionality: vanillin > neem > cinnamon > aloe vera >> none
iii) Fabric hydrophilicity: N_2 plasma ≈ vanillin > aloe vera >> neem ≈ cinnamon
iv) Fabric darkness: cinnamon > aloe vera > neem > N_2 plasma > vanillin

The variation in the abovementioned properties reflects the differences among the functional additives' active ingredients, chemical constituents, extent of loading onto the N_2 plasma-preactivated substrate, location and extent of distribution onto/within the treated substrates, mode of interactions during the microwave fixation step, antimicrobial action, and anti-UV performance [43]

3.3. Post-treatment with ZnO and SiO_2 NPs individually

The data in Table 2 show the variation in some physicochemical, functional, and coloration properties of the untreated and N_2 plasma-preactivated DF samples as a function of type and concentration of MO NPs used in the finishing process. For a given treatment condition, it is clear that, compared with no treatment, treatment with ZnO NPs of N_2 plasma-untreated fabric samples results in a significant increase in wetting time (>180 s), slight decrease in nitrogen content, noticeable increase in antibacterial activity against *S. aureus* and *E. coli*, significant improvement in UV-protection ($>50^+$), slight decrease in K/S value, and improvement in L* value. The variation in these properties is governed by the concentration of ZnO NPs in the finishing bath and the degree of fixation, immobilization, and entrapment of NPs onto and/or within the indigo-dyed denim structure [10].

With all other parameters fixed, the Post-treatment of N_2 plasma-preactivated substrates with ZnO NPs brings about a reasonable improvement in wetting time of the treated fabric samples, slight decrease in N%, remarkable improvement in antibacterial efficacy against the tested pathogens, significant improvement in UV-protection ability, and slight increase in fabric lightness compared with N_2 plasma-treated samples without postfinishing with ZnO NPs. Moreover, increasing the ZnO NP concentration up to 10 g/L in the postfinishing step slightly increases the wetting time and N%, has a positive impact on the antibacterial and anti-UV functionalities, and has an insignificant effect on K/S and L* values.

The improved antibacterial and anti-UV functionalities after N_2 plasma pretreatment and post-finishing with ZnO NPs is attributed to the creation of new cationic active sites (-NH_2, etc.) by N_2 plasma pretreatment, photocatalytic activity of the ZnO NPs loaded onto the fabric surface, and generation of

numerous highly active oxygen species, such as $^{\bullet}OH$, $^{\bullet}O_2^-$, and H_2O_2, as described in the equations below [24, 44, 45].

$$ZnNPs + h_v \xrightarrow{UV/sun\ irradiation} ZnONPs + h^+ + e^- \quad (7)$$

$$h^+ + H_2O \rightarrow HO^{\bullet} + H^+ \quad (8)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (9)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \quad (10)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2^{\bigcirc} \quad (11)$$

These improvements can also be ascribed to the mechanical action of ZnO NPs and their negative impact on the bacterial cell membrane, thereby leading to inhibited cell manipulation and death of the bacteria [45]. Both the ability of the indigo-dyed DF to absorb harmful UV irradiation and the shielding and blocking capability of ZnO NP-loaded DFs significantly enhance the UV-protection functionality of the developed DF samples [10, 44].

The increase in wetting time, i.e., hydrophobicity, of N_2 plasma-untreated/ZnO NP-loaded substrates is likely due to the formation of a thin, hydrophobic layer onto the physically roughened fabric surface during the microwave fixation steps [46].

The results in Table 2 also reveal that post-finishing of plasma-untreated DF samples with SiO_2 NPs is accompanied by a reasonable decrease in hydrophilicity, expressed as wetting time in seconds, and nitrogen content; noticeable increase in the bacterial reduction % and UPF values; and slight increase in K/S value and decrease in L* value. In contrast, the preactivation of DF samples with N_2 plasma for 120 s and subsequent treatment with SiO_2 NPs (5 or 10 g/L) are accompanied by no change in wetting time (<1 s), slight decrease in N%, remarkable improvement in bacterial reduction % (*S. aureus* > *E. coli*), noticeable increase in UPF, slight increase in K/S value, and decrease in L* value. The higher the SiO_2 NP concentration in the Post-treatment step, the longer the fixed and immobilized NPs on the plasma-treated substrate, and hence the better the imparted antibacterial and UV-protection functionalities. The significant increase in the antibacterial and anti-UV functionalities imparted to the N_2 plasma-pretreated/post-finished DF samples reflects the photocatalytic activity of the loaded SiO_2 NPs and the generation of highly active species, as well as the creation of new cationic sites by N_2 plasma pretreatment. These changes lead to the highest antibacterial activity and enhanced UV-protection efficacy due to the combined effect of the indigo dye, as a UV absorber, and the SiO_2 NPs as UV-blockers [15, 47, 48]. The extent of variation in the abovementioned performance properties is governed by the particle size, extent of fixation and immobilization of the used MO NPs during the microwave fixation step, and by the photocatalytic activity, UV-shielding ability, and synergistic effect of MO NPs with N_2 plasma-treated indigo dye under the given treatment conditions.

3.4. Post-treatment with ascorbic or salicylic acid

The results in Table 3 demonstrate that finishing untreated DF samples using ascorbic or salicylic acid, as ecologically acceptable phenolic compounds, results in an increase in wetting time, decrease in N%, reasonable improvement in bacterial reduction and UV-protection, increase in K/S value, and decrease in L* value, keeping other parameters constant. The variation in the abovementioned properties is affected by both type and concentration of the phenolic compound in the finishing bath. The higher the acid concentration, the more protective the finished DF against the tested pathogenic microorganisms, with efficacy in the order of salicylic acid > ascorbic acid >> none, regardless of the bacterial type. The improvement in UV-protection follows the order ascorbic acid > salicylic acid > none, for constant acid concentration.

Table 2. Effect of post-treatment with ZnO_2 NPs or SiO_2 NPs

Post-loaded functional agent	Conc. g/L	Plasma exposure time (s)	WT (s)	N (%)	Bacterial reduction (%)		UPF	Color properties	
					S. aureus	E. coli		K/S	L*
Untreated	0	None	<1	0.254	0.00	0.00	34	10.74	30.13
N_2-Plasma treated	0	120	<1	0.456	47.54	41.20	31	10.22	31.42
ZnO NPs	5	None	>180	0.247	50.32	39.48	219	10.72	31.29
	10		>180	0.238	55.14	44.16	285	10.40	32.34
	5	120	55	0.429	96.35	85.40	425	8.90	32.59
	10		61	0.435	99.01	93.40	441	9.02	33.37
SiO_2 NPs	5	None	5	0.230	27.61	21.48	50	10.87	30.03
	10		7	0.225	33.23	29.34	64	10.95	29.81
	5	120	<1	0.432	89.73	83.53	79	11.21	29.40
	10		<1	0.443	94.98	85.70	112	11.55	28.09

Plasma-modification: N_2-plasma exposure time (60, 120 s).
Post-loading of functional agents: solubilized in water aqueous solutions of ZnO_2 NPs and SiO_2 (5, 10 g/L), LR 1:20 at 30°C for 30 min. using a sonicator bath, microwave fixation at 450 w for 6 min.
%N: nitrogen content, WT: wetting time, UPF: UV-protection factor, K/S: color strength, L*: lightness.

Table 3. Effect of post-treatment with ascorbic or salicylic acid

Post-loaded functional agent	Conc. g/L	Plasma exposure time (s)	WT (s)	N (%)	Bacterial reduction (%)		UPF	Color properties	
					S. aureus	E. coli		K/S	L*
Untreated	0	None	<1	0.254	0.00	0.00	34	10.74	30.13
N_2-Plasma treated	0	120	<1	0.456	47.54	41.20	31	10.22	31.42
Ascorbic acid	5	None	8	0.244	28.61	21.68	108	11.22	28.41
	10		12	0.238	38.64	32.99	130	12.54	29.63
	5	120	3	0.460	91.57	79.12	213	10.92	30.25
	10		4	0.471	93.28	85.78	340	11.18	29.58
Salicylic acid	5	None	<1	0.250	40.67	28.72	39	10.07	30.27
	10		2	0.248	49.28	43.93	47	10.19	31.82
	5	120	<1	0.453	94.69	89.39	57	10.84	30.54
	10		<1	0.449	98.79	93.80	63	11.10	29.70

Plasma-modification: N2-plasma exposure time (60, 120 s).
Post-loading of functional agents: solubilized in water aqueous solutions of ascorbic and salicylic acid (5, 10 g/L), LR 1:20 at 30oC for 30 min. using a sonicator bath, microwave fixation at 450 w for 6 min
%N: nitrogen content, WT: wetting time, UPF: UV-protection factor, K/S: color strength, L*: lightness.

The variation in the aforementioned functional properties, using ascorbic or salicylic acid as the active ingredient, reflects their differences in chemical structure; functional groups; extent of fixation onto the indigo-dyed DF samples; antibacterial activity; mode of interaction; ability to change cell morphology and cell membrane permeability; and ability to damage DNA, protein synthesis, and other metabolic processes to cause cell lysis and death [49, 51]. In contrast, the variation in the UPF of phenolic acid-loaded DF samples is ascribed to their differences in extent of loading and fixation onto/within the fabric structure, variation in fabric porosity, variation in coloration properties, and differences in their absorption of and shielding capacity against harmful UV-B radiation [49].

The results shown in Table 3 demonstrate that the pretreatment of DF samples with N_2 plasma followed by Post-treatment with ascorbic or salicylic acid as a functional agent has a marginal or a slight effect on the wetting time, N%, and coloration properties at a fixed acid concentration.

In contrast, preactivation of DF samples with N_2-atmospheric plasma for 120 s followed by ascorbic or salicylic acid Post-treatment at the same concentration is accompanied by a significant increase in antibacterial activity against pathogenic bacteria, as follows: salicylic acid > ascorbic acid >> none, and GPB > GNB. Additionally, the improvement in the imparted UV-protection from N_2 plasma treatment to substrates postloaded with phenolic acid follows the order ascorbic acid >> salicylic acid > none. Increasing the phenolic acid concentration up to 10 g/L in the postfinishing step has some impact, especially on the imparted fabric functionalities.

The data in Table 3 demonstrate the synergetic effect and positive impacts of N_2 plasma surface modification and subsequent loading of ascorbic or salicylic acid on upgrading the antibacterial and UV-protection functionalities of the indigo-dyed DF samples.

3.5. Post-finishing with selected functional formulations

The data in Table 4 indicate that post-finishing of N_2 plasma-preactivated DF samples with vanillin/ZnO NPs, vanillin/salicylic acid, and ZnO NPs/salicylic acid functional formulations individually results in a marginal increase in wetting time, as in the case of using vanillin/salicylic acid (1 s), or noticeable increase in wetting time, as in the case of using vanillin/ZnO NPs (28 s) or ZnO NPs/salicylic acid (35 s), which reflects the differences in the extent of their loading and fixation onto the plasma-treated fabric surface, the change in the fabric surface morphology and chemistry, and their ability to form a thin hydrophilic or hydrophobic coating on the modified substrate [40].

The positive change in N% of the developed samples varies as vanillin/salicylic acid > vanillin/ZnO NPs > ZnO NPs/salicylic acid ≈ none, which could be discussed in terms of the positive impact of the postfinishing step on enhancing the extent of fixation of the generated N-containing active sites, as well as the N-containing indigo dye, during the microwave fixation step [10, 49].

Table 4. Effect of post-treatment of N_2-plasma preactivated DF samples using numerous functional finishing formulations

Functional formulation constituents	Conc. g/L	WT (s)	N (%)	Bacterial reduction (%)		UPF	Color properties		Metal content (%)
				S. aureus	E. coli		K/S	L*	
Untreated	0	<1	0.254	00.00	00.00	34	10.74	30.13	
N_2-Plasma treated	0	<1	0.456	47.54	41.20	31	10.22	31.42	
Vanillin/ZnO-NPs	(5/5)	28	0.467	98.41	91.65	490	9.17	33.26	5.618
Vanillin/salicylic acid	(5/5)	1	0.482	96.51	88.10	166	10.04	32.12	
ZnO-NPs/salicylic acid	(5/5)	35	0.459	99.50	94.72	251	10.52	30.51	5.000

Plasma-modification: N2-plasma exposure time (120 s).
Post-loading of functional agents: aqueous solution mixtures of Vanillin/ZnO-NPs, Vanillin/salicylic acid, and ZnO-NPs/salicylic acid (5,5 g/L), LR 1:20 at 30°C for 30 min. using a sonicator bath, microwave fixation at 450 w for 6 min.
%N: nitrogen content, WT: wetting time, UPF: UV-protection factor, K/S: color strength, L*: lightness.

Additionally, postfinishing of plasma-pretreated substrates with the selected functional formulations effects an outstanding improvement in the imparted antibacterial functionality against the tested *S. aureus* and *E. coli* pathogenic bacteria. The experimental results reveal that the destructive effect of nominated functional formulations on the bacteria follows the order ZnO NPs/salicylic acid >> vanillin/ZnO NPs > vanillin/salicylic acid >> none, which reflects the differences among the selected formulations in terms of chemical composition, extent of loading and adhesion to the preactivated fabric surface, bioactive constituents, reactive oxygen species (ROS), mode of interaction, and antimicrobial action, as discussed earlier, as well as the synergetic effect of the N_2 plasma step and post-finishing chemicals on the surface morphology, chemistry, and functionality. These, in turn, positively affect the imparted biocidal functionality against both *S. aureus* and *E. coli* [24,52]. Moreover, the imparted antibacterial functionality is governed by the type of pathogenic bacteria, with greater effect against *S. aureus* than *E. coli*, when all other parameters are constant, most likely due to their differences in cell constituents and arrangement [30].

Moreover, the improvement in anti-UV functionality, expressed as a UPF value, follows the decreasing order vanillin/ZnO NPs (UPF 490) > ZnO NPs/salicylic acid (UPF 251) > vanillin/salicylic acid (UPF 166) >> none (UPF 31), which is attributed to their differences in the extent of coating and ability to block, shield, and/or absorb harmful UV-B radiation [10, 28, 49].

The change in the K/S and L* values of preactivated and postfinished fabric samples shows a slight variation in the abovementioned properties under different finishing formulations and reflects the extent of their fixation, chemical composition, and colored constituents.

Surface activation using air plasma followed by post-functionalization

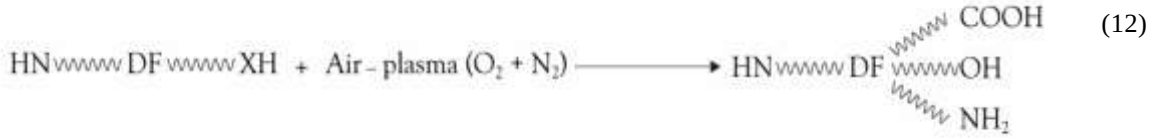
Table 5 shows that preactivation of indigo-dyed DF with air plasma, using O_2 and N_2 gas constituents, is accompanied by no change in wetting time (<1 s), slight increase in N% (0.337%), noticeable improvement in antibacterial functionality against *S. aureus* (44.51%) and *E. coli* (36.37%), slight decrease in both the UPF and K/S values, and slight increase in L* value compared with the untreated DF. The change in the aforementioned properties reflects the impact of air plasma premodification on the surface activation and creation of new functional groups, e.g., -COOH and -NH_2, the generation of active species on the plasma-treated fabric surface, and their negative impacts against the tested pathogenic bacteria [24, 53]. It also reflects the partial oxidation of the indigo-dyed fabric, which in turn affects the UPF, K/S, and L*values [16, 54].

Table 5. Effect of Post-loading of air-plasma treated denim fabric samples with selected active ingredients

Post-loaded functional agent	Conc. g/L	WT (sec.)	N (%)	Bacterial reduction (%)		UPF	Color properties	
				S. aureus	E. coli		K/S	L*
Untreated	0	<1	0.254	00.00	00.00	34	10.74	30.13
Air-Plasma treated	0	<1	0.337	44.51	36.37	30	10.16	30.26
Vanillin	(10)	5	0.342	89.10	84.15	319	8.79	34.45
ZnO-NPs	(10)	>180	0.351	95.33	90.81	419	10.18	31.90
Salicylic acid	(10)	3	0.329	92.49	88.62	83	10.32	32.76

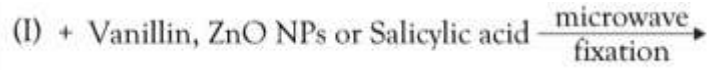
Plasma-modification: air-plasma exposure time (120 s).
Post-loading of functional agents: aqueous solution of Vanillin, ZnO-NPs, and salicylic (10 g/L), LR 1:20 at 30oC for 30 min. using a sonicator bath, microwave fixation at 450 w for 6 min.
%N: nitrogen content, WT: wetting time, UPF: UV-protection factor, K/S: color strength, L*: lightness.

On the other hand, the data in Table 5 indicate that Post-treatment of air plasma-activated fabric samples with vanillin or salicylic acid (10 g/L) results in an increase in wetting time, marginal variation in N%, and remarkable increase in antibacterial properties against *S. aureus* as salicylic acid (92.49%) > vanillin (89.10%) > none (44.51%), and against *E. coli* as salicylic acid (88.62%) > vanillin (84.15%) > none (36.37%). Additionally, Post-loading of ZnO NPs (10 g/L) onto O_2 plasma-preactivated substrates brings about a remarkable increase in the extent of *S. aureus* (95.33%) and *E. coli* (90.81%) reduction. The variation in the antibacterial properties imparted to the preactivated fabric surface samples could be discussed in terms of their differences in chemical composition, extent of loading and adhesion to the modified fabric active sites, and functional groups, as described in Eqs. 12 and 13 [24], considering both the biocidal activity and mode of action discussed previously [14, 28, 44].



Preactivated substrate

(I) (12)



(13)

Vanillin, ZnO NPs or Salicylic acid loaded denim fabric

Further, the Post-treatment of air plasma-preactivated fabric samples with the nominated functional materials is accompanied by a remarkable improvement in UV-protection (>50), irrespective of the additive used, reflecting their ability to block, as in case of ZnO NPs, and/or absorb the harmful UV-B radiation, as in case of vanillin and salicylic acid [10, 28].

Moreover, the variation in the K/S and L* values upon using the aforementioned functional additives may be attributed to their chemical constituents, inherent color, mode of interaction, and/or fixation onto the indigo-dyed DFs.

*3.6. Multifunctionalized **DF***

The data in Table 6 demonstrate that the premodification of DF samples with N_2 plasma followed by Post-treatment with aloe vera, neem, cinnamon, vanillin, or ZnO NPs is accompanied by a remarkable increase in their antibacterial and UV-protection functionalities. The extent of improvement follows the order N_2 plasma → ZnO NPs > N_2 plasma → vanillin > N_2 plasma → neem > N_2 plasma → cinnamon > N_2 plasma → aloe vera >> N_2 plasma alone, which reflects their differences in chemical structure, chemical composition, active constituents, extent of loading onto/within the plasma-treated surface, mode of antibacterial action, and UV absorption or blocking [44, 49, 51].

The increase in fabric hydrophobicity, expressed as water contact angle, follows the decreasing order:

N_2 plasma → ZnO NPs ≈ N_2 plasma → cinnamon > N_2 plasma → aloe vera ≈ N_2 plasma → neem >> N_2 plasma alone (Fig. 1), which could be attributed to their differences in chemical constituents, hydrophobic components, ability to block hydrophilic active sites, surface fabric porosity, ability to develop surface roughness, and ability to create micro- and nanosurfaces with low surface energy [46].

Additionally, Post-treatment of N_2 plasma-treated DF samples with cinnamon or vanillin results in the development of multifunctional DF samples with a fragrance-emitting property, expressed as an SIR value. In contrast, the K/S values of the functionalized DF samples are governed by both the N_2 plasma pretreatment as well as the functional additive used in the postfinishing formulation.

As indicated in Table 6, the functionalized DF samples demonstrated high functionality and exhibited a pleasant aroma, as in the case of using cinnamon and vanillin as functional additives, even after 10 washing cycles.

Table 6. Options for imparting multifunctionalities to indigo dyed-DF

Treatment sequence	Bacterial reduction (%)		UPF	WCA (°)	SIR	K/S
	S. aureus	E. coli				
Untreated	0.00 (0.00)	0.00 (0.00)	34 (30)	wet (wet)	None (None)	10.74 (9.62)
N_2-Plasma pretreated (120 s)	47.54 (41.00)	41.20 (35.52)	31 (25)	wet (wet)	None (None)	10.22 (9.18)
N_2-Plasma → Aloe vera (10 g/L)	82.22 (77.44)	65.89 (50.12)	120 (105)	121 (110)	None (None)	13.82 (12.10)
N_2-Plasma → Neem (10 g/L)	91.50 (87.32)	79.03 (75.00)	180 (170)	124 (115)	None (None)	13.07 (11.43)
N_2-Plasma → Cinnamon (10 g/L)	86.02 (81.00)	76.91 (72.50)	170 (160)	144.4 (130)	5 (4)	13.98 (12.20)
N_2-Plasma → Vanillin (10 g/L)	96.97 (90.32)	91.41 (84.02)	377 (345)	wet (wet)	5 (5)	9.48 (8.60)
N_2-Plasma → ZnO NPs (10 g/L)	99.01 (95.01)	93.40 (87.25)	441 (420)	145.9 (135)	None (None)	9.02 (8.06)

N_2-Plasma pre-modification for 120s.

Post loading of functional additives: N_2-Plasma pretreatment followed by subsequent treatment with functional additive solution or dispersion using a sonicator bath, followed by microwave fixation

Values between parentheses correspond to the retained functional properties after 10 launder cycles.

UPF: UV-protection factor; WCA (°): water contact angle, SIR: scent intensity rate; K/S: color strength.

3.7. SEM and EDX analysis of selected samples

The change in surface morphology of untreated and N_2-plasma pre-activated / post-functionalized samples were evaluated using SEM. Fig. 2 (a) shows the smooth surface of untreated denim cotton fabric. SEM images of all pre-activated and post-functionalized ones, Fig's. 2 (c), (e) and (g), exhibit a remarkable morphological change as a direct consequence of post-loading and high deposition of post finishing bath constituents onto the modified fabrics surfaces. The extent of loading and deposition is governed by type and chemical composition of the utilized active ingredients, mode of interaction and fixation onto the generated N_2-containing active sites of pre-activated fabric surface during microwave fixation step as discussed earlier.

Additionally, EDX analysis Fig's. 2 (b), (d), (f), (h) confirm: i) nitrogen element related to the fixed indigo dye as well as the generated -NH_2 groups due to N_2-plasma pre-treatment, ii) Zn element, Fig's. 2 (d) and (h) as a direct consequence of fixation of ZnO NPs onto the developed substrates, and iii) silicon element, Fig. 2 (f) related to immobilization and fixation of SiO_2 NPs onto the finished denim cotton fabric during microwave fixation step.

4. Conclusion

The main goal of the present study is to explore the feasibility of using N_2 or air plasma as a green tool for surface modification and preactivation of DFs, followed by Post-treatment with environmentally sound functional materials, individually and in selected combinations, to impart enhanced multifunctional properties, such as an antibacterial response, UV-protection, and hydrophobicity. The functional materials considered were aloe vera, neem, cinnamon, vanillin, ascorbic acid, salicylic acid, ZnO NPs, and SiO_2 NPs. The experimental results demonstrate that a combination of plasma pretreatment and functional postfinishing results in a remarkable improvement in the imparted antibacterial efficacy and UV-protection functionality, along with some changes in the wettability and coloration of the finished DFs. The variation in the imparted functional, wetting, and coloration properties is generated by the atmospheric plasma, via its ability to modify the fabric surface, and the extent of oxidation and/or discoloration of the indigo-dyed substrate. The type of functional additive, i.e., its chemical composition, extent of fixation, antibacterial action, ability to absorb or block harmful UV radiation, hydrophobic or hydrophilic components, and extent of interaction with the indigo dye, plays a positive or negative role in the imparted physical, functional, and coloration properties. Moreover, the imparted functional properties, along with a pleasant smell, showed a noticeable durability to wash. The presented multifunctional finishing strategy provides a novel, environmentally sound, and sustainable method to develop multifunctional DFs with durable, desirable, and highly demanded functionalities to satisfy the ever-growing customer needs.

5. Conflicts of interest

In accordance with our policy on Conflict of interest please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

6. Formatting of funding sources

List funding sources in a standard way to facilitate compliance to funder's requirements.

7. References

[1] F. Kalaoglu, R. Paul, Finishing of jeans and quality control, in: Denim, Woodhead Publishing, 2015, pp. 425-459.
[2] K. Amutha, 2 - Environmental impacts of denim, in: S.S. Muthu (Ed.) Sustainability in Denim, Woodhead Publishing, 2017, pp. 27-48.
[3] R. Paul, Denim and jeans: An overview, in: R. Paul (Ed.) Denim, Woodhead Publishing, 2015, pp. 1-11.
[4] A.K. Patra, A.K. Pattanayak, Novel varieties of denim fabrics in: R. Paul (Ed.) Denim, Woodhead Publishing, 2015, pp. 483-506.
[5] A. Kumari, K. Khurana, Regenerated cellulose-based denim fabric for tropical regions: an analytical study on making denim comfortable, Journal of Textiles, 2016 (2016).
[6] N. Özdil, Stretch and bagging properties of denim fabrics containing different rates of elastane, Fibres & Textiles in Eastern Europe, 16 (2008) 66.
[7] A. Colomera, H. Kuilderd, Biotechnological washing of denim jeans in: R. Paul (Ed.) Denim, Woodhead Publishing, 2015, pp. 357-403.
[8] A.S. Maryan, M. Montazer, A cleaner production of denim garment using one step treatment with amylase/cellulase/laccase, Journal of Cleaner Production, 57 (2013) 320-326.
[9] A.K. Roy Choudhury, Sustainable Textile Wet Processing: Applications of Enzymes, in: S.S. Muthu (Ed.) Roadmap to Sustainable Textiles and Clothing: Eco-friendly Raw Materials, Technologies, and Processing Methods, Springer Singapore, Singapore, 2014, pp. 203-238.
[10] N.A. Ibrahim, B.M. Eid, M.S. Abdel Aziz, S.M. Hamdy, S.E. Abd Allah, Green surface modification and nano-multifunctionalization of denim fabric, Cellulose, 25 (2018) 6207-6220.
[11] A. Madhu, J.N. Chakraborty, Developments in application of enzymes for textile processing, Journal of Cleaner Production, 145 (2017) 114-133.
[12] B.M. Eid, N.A. Ibrahim, Recent developments in sustainable finishing of cellulosic textiles employing biotechnology, Journal of Cleaner Production, 284 (2021).
[13] A.S. Maryan, M. Montazer, T. Harifi, Synthesis of nano silver on cellulosic denim fabric producing yellow colored garment with antibacterial properties, Carbohydrate Polymers, 115 (2015) 568-574.
[14] N. Becenen, Ö. Altun, Applications of TiO2, ZnO and Ag Nanomaterials to Denim Fabric, J. Nanosci. Nanotechnol., 16 (2016) 5359-5363.
[15] S. Talebi, M. Montazer, Denim Fabric with Flame retardant, hydrophilic and self-cleaning properties conferring by in-situ synthesis of silica nanoparticles, Cellulose, 27 (2020) 6643-6661.
[16] M. Radetić, P. Jovančić, N. Puač, Z.L. Petrović, Z. Šaponjić, Plasma-induced Decolorization of Indigo-dyed Denim Fabrics Related to Mechanical Properties and Fiber Surface Morphology, Textile Research Journal, 79 (2009) 558-565.
[17] M. Ghoranneviss, B. Moazzenchi, S. Shahidi, A. Anvari, A. Rashidi, Decolorization of Denim Fabrics with Cold Plasmas in the Presence of Magnetic Fields, Plasma processes and Polymers, 3 (2006) 316-321.
[18] M. Sumithra, V.N. Raaja, Antifungal Activity of Herbal Finish on 100% Cotton Denim Fabric, J. Fashion Technol. Textile Eng., 3 (2014).
[19] M. Sumithra, N.V. Raaja, Antibacterial efficacy analysis of Ricinus communis, Senna auriculata and Euphorbia hirta extract treated on the four variant of denim fabric against Escherichia coli and Staphylococcus aureus, Journal of Textile Science & Engineering, 2: 111 (2012) 1-4.
[20] M. Sumithra, N. Vasugi Raaja, Effect of medicinal herb extracts treated on cotton denim fabric, Mintage journal of Pharmaceutical and Medical Sciences, 2 (2013) 6-9.
[21] D. Vijayalakshmi, T. Ramachandran, A Study on The Anti-Bacterial Property Of Essential Oils And Metal Oxides In Denim Garments, International Journal of Textile and Fashion Technology, 5 (2015) 49-54.
[22] N.A. Ibrahim, M.M. Hashem, M.A. Eid, R. Refai, M. El-Hossamy, B.M. Eid, Eco-friendly plasma treatment of linen-containing fabrics, The Journal of The Textile Institute, 101 (2010) 1035-1049.
[23] C.X. Wang, S.L. Chen, Fragrance-release Property of β-Cyclodextrin Inclusion Compounds and their Application in Aromatherapy, Journal of Industrial Textiles, 34 (2005) 157-166.
[24] N.A. Ibrahim, B.M. Eid, M.S. Abdel-Aziz, Effect of plasma superficial treatments on

antibacterial functionalization and coloration of cellulosic fabrics, Applied Surface Science, 392 (2017) 1126-1133.
[25] S. Shahidi, N. Aslan, M. Ghoranneviss, M. Korachi, Effect of thymol on the antibacterial efficiency of plasma-treated cotton fabric, Cellulose, 21 (2014) 1933-1943.
[26] M.I.H. Mondal, J. Saha, Antimicrobial, UV Resistant and Thermal Comfort Properties of Chitosan- and Aloe vera-Modified Cotton Woven Fabric, Journal of Polymers and the Environment, 27 (2019) 405-420.
[27] S.W. Ali, R. Purwar, M. Joshi, S. Rajendran, Antibacterial properties of Aloe vera gel-finished cotton fabric, Cellulose, 21 (2014) 2063-2072.
[28] N.A. Ibrahim, N.A. Abd El-Ghany, B.M. Eid, E.M. Mabrouk, Green options for imparting antibacterial functionality to cotton fabrics, International Journal of Biological Macromolecules, 111 (2018) 526-533.
[29] N.A. Ibrahim, E.M.R. El-Zairy, B.M. Eid, Eco-friendly modification and antibacterial functionalization of viscose fabric, The Journal of The Textile Institute, 108 (2017) 1406-1411.
[30] N.A. Ibrahim, B.M. Eid, F.H.H. Abdellatif, Advanced Materials and Technologies for Antimicrobial Finishing of Cellulosic Textiles, in: Handbook of Renewable Materials for Coloration and Finishing, 2018, pp. 301-356.
[31] Z. Breijyeh, B. Jubeh, R. Karaman, Resistance of Gram-Negative Bacteria to Current Antibacterial Agents and Approaches to Resolve It, Molecules (Basel, Switzerland), 25 (2020) 1340.
[32] N.A. Ibrahim, B.M. Eid, E.R. El-Zairy, Antibacterial functionalization of reactive-cellulosic prints via inclusion of bioactive Neem oil/βCD complex, Carbohydrate Polymers, 86 (2011) 1313-1319.
[33] M.F. Khurshid, M. Ayyoob, M. Asad, S.N.H. Shah, Assessment of eco-friendly natural antimicrobial textile finish extracted from aloe vera and neem plants, Fibres & Textiles in Eastern Europe, (2015).
[34] K. Vaideki, S. Jayakumar, R. Rajendran, G. Thilagavathi, Investigation on the effect of RF air plasma and neem leaf extract treatment on the surface modification and antimicrobial activity of cotton fabric, Applied Surface Science, 254 (2008) 2472-2478.
[35] K. Vaideki, S. Jayakumar, G. Thilagavathi, R. Rajendran, A study on the antimicrobial efficacy of RF oxygen plasma and neem extract treated cotton fabrics, Applied Surface Science, 253 (2007) 7323-7329.
[36] N.A. Ibrahim, B.M. Eid, M.A. Youssef, H.M. Ibrahim, H.A. Ameen, A.M. Salah, Multifunctional finishing of cellulosic/polyester blended fabrics, Carbohydr Polym, 97 (2013) 783-793.
[37] J. Shah, R. Padhye, R.D. Pachauri, Studies on UV protection and antimicrobial functionality of textiles, Journal of Natural Fibers, (2021) 1-12.
[38] Y. El Atki, I. Aouam, F. El Kamari, A. Taroq, K. Nayme, M. Timinouni, B. Lyoussi, A. Abdellaoui, Antibacterial activity of cinnamon essential oils and their synergistic potential with antibiotics, J Adv Pharm Technol Res, 10 (2019) 63-67.
[39] N.A. Ibrahim, B.M. Eid, S.M. Sharaf, Functional Finishes for Cotton-Based Textiles: Current Situation and Future Trends, in: M. Shabbir (Ed.) Textiles and Clothing, John Wiley & Sons, Inc. and Scrivener Publishing LLC USA, 2019, pp. 131-190.
[40] C. Panisello, B. Peña, G. Gilabert Oriol, M. Constantí, T. Gumí, R. Garcia-Valls, Polysulfone/Vanillin Microcapsules for Antibacterial and Aromatic Finishing of Fabrics, Industrial & Engineering Chemistry Research, 52 (2013) 9995-10003.
[41] Z. Yang, Z. Zeng, Z. Xiao, H. Ji, Preparation and controllable release of chitosan/vanillin microcapsules and their application to cotton fabric, Flavour and Fragrance Journal, 29 (2014) 114-120.
[42] P.L. Nostro, L. Fratoni, P. Baglioni, Modification of a cellulosic fabric with β-cyclodextrin for textile finishing applications, Journal of Inclusion Phenomena and Macrocyclic Chemistry, 44 (2002) 423-427.
[43] N.A. Ibrahim, B.M. Eid, M.A. Youssef, S.A. El-Sayed, A.M. Salah, Functionalization of cellulose-containing fabrics by plasma and subsequent metal salt treatments, Carbohydrate Polymers, 90 (2012) 908-914.
[44] N.A. Ibrahim, A.A. Nada, B.M. Eid, M. Al-Moghazy, A.G. Hassabo, N.Y. Abou-Zeid, Nano-structured metal oxides: synthesis, characterization and application for multifunctional cotton fabric, Advances in Natural Sciences: Nanoscience and Nanotechnology, 9 (2018) 035014.
[45] S.W. Kim, Y. An, Effect of ZnO and TiO 2 nanoparticles preilluminated with UVA and UVB light on Escherichia coli and Bacillus subtilis, Appl Microbiol Biotechnol, 95 (2012).
[46] M.Z. Khan, V. Baheti, M. Ashraf, T. Hussain, A. Ali, A. Javid, A. Rehman, Development of UV protective, superhydrophobic and antibacterial textiles using ZnO and TiO 2 nanoparticles, Fibers and Polymers, 19 (2018) 1647-1654.

[47] S. Palaskar, A. Desai, S. Shukla, Development of multifunctional cotton fabric using atmospheric pressure plasma and nano-finishing, The Journal of The Textile Institute, 107 (2016) 405-412.
[48] N.A. Ibrahim, B.M. Eid, E.A. El-Aziz, T.M.A. Elmaaty, S.M. Ramadan, Loading of chitosan – Nano metal oxide hybrids onto cotton/polyester fabrics to impart permanent and effective multifunctions, International Journal of Biological Macromolecules, 105 (2017) 769-776.
[49] N.A. Ibrahim, B.M. Eid, E.M. El-Zairy, E. Emam, S. Barakat, Environmentally sound approach for imparting antibacterial and UV-protection functionalities to linen cellulose using ascorbic acid, International Journal of Biological Macromolecules, 135 (2019) 88-96.
[50] M. Tajkarimi, S.A. Ibrahim, Antimicrobial activity of ascorbic acid alone or in combination with lactic acid on Escherichia coli O157:H7 in laboratory medium and carrot juice, Food Control, 22 (2011) 801-804.
[51] A. Kantouch, A.A. El-Sayed, M. Salama, A. Abou El-Kheir, S. Mowafi, Salicylic acid and some of its derivatives as antibacterial agents for viscose fabric, International Journal of Biological Macromolecules, 62 (2013) 603-607.
[52] S. Shahidi, Novel method for ultraviolet protection and flame retardancy of cotton fabrics by low-temperature plasma, Cellulose, 21 (2014) 757-768.
[53] N.A. Ibrahim, B.M. Eid, M.S. Abdel-Aziz, Green synthesis of AuNPs for eco-friendly functionalization of cellulosic substrates, Applied Surface Science, 389 (2016) 118-125.
[54] C.W. Kan, C.W. Yuen, Effect of atmospheric pressure plasma treatment on the desizing and subsequent colour fading process of cotton denim fabric, Coloration Technology, 128 (2012) 356-363.