



New Natural Dye Printing Paste Functional on Various Kinds of Fabrics Enhanced by Plasma Irradiation

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IN coloration of fabrics, natural dye shows more environmental advantages than synthetic dyes; however, the product has poorer color and fastness properties. The present study showed the suitability of printing most kind of fabrics (natural synthetic and blends) with natural dye using pigment printing technique assist by plasma radiation with high product quality. The effect of different factors was studied as plasma conditions (power & exposure time), binder's concentration, fabric type and structure of natural dye. Various measurements as SEM, AFM, and EDX evaluated the effect of plasma treatment on the fabric surface. The gained results of both color strength (K/S) and fastness properties showed a great extent in enhancing printability and indicating that plasma treatment of printed fabrics with natural dye has high K/S values and excellent fastness properties comparing with the blank sample.

Keywords : Atmospheric pressure plasma, Natural dye, Cotton, Cotton / Polyester, Color Strength.

Introduction

Natural dyes are known for their use in coloring natural fabrics like wool, silk, cotton, and flax as major areas of application since ancient times. They may have a wide range of shades and can be obtained from various parts of the plants, including roots, bark, leaves, flowers, and fruit [1]. Since 1856, owing to the advent of widely available and cheaper synthetic dyes having moderate to excellent colorfastness properties, the use of natural dyes having poor to moderate wash and light fastness had declined to a great extent. However, nowadays, there has been a revival and growing interest in the application of natural dyes on natural fiber sowing to environmental consciousness worldwide [2]. Several commercial dyers and small textile export houses have started

looking at the possibilities of using natural dyes for regular basis dyeing and printing of textiles to overcome environmental pollution caused by the synthetic dyes. The natural dyes have several remarkable advantages, such as they do not pose any hazards to health, are easily harmonized with nature, have little chemical reactivity, and have no adverse environmental problems [3].

Pigment printing is not only the oldest but also the easiest printing method as far as simplicity of application is concerned. It has the advantages such as ease of near-final print at the printing stage itself, quality of the prints, and applicability to almost every kind of fabric or blends, as well the ability to avoid any washing processes after fixation [4,5]. Dyes that have no attraction for any fabric are used in a finely spread form.

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Received 26 / 10 / 2019; Accepted 16 / 1 / 2020

DOI: 10.21608/ejchem.2020.18694.2153

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Film-forming binders are used to fix these dyes to the substrate by adhesion. The binders used in pigment printing are usually based on styrene-butadiene, styrene-acrylate, or vinyl acetate-acrylate copolymers [6]. In the printing process, three-dimensional binder films have occurred in hot air ambient owing to pH changing. Kind and amount of the chemical polar groups of fabrics influence fixation conditions and adhesion strength of the binder-to-fiber bond (important for rubbing fastness). Consequently, the helpfulness of coating binder affects the final properties of pigment printed fabric [7,8].

In general, pigment offers good light and washing fastness. However, the poor crocking fastness and low build-up of pigment dyeing, especially for cotton, does not satisfy coloring requirements in the new century. Printability of different fabrics with pigments paste contained natural dyes could be improved by atmospheric pressure plasma treatment [9–11].

Plasma process is extremely easy to handle and requires only a short treatment time; the depth of surface modification of the material subjected to plasma varies from 100 to several micrometers; the bulk of the polymer remains intact; and mechanical, physiochemical, and electro physical properties of the original material are retained [12,13]. Plasma is a complex gaseous mixture of ions, electrons, metastable, neutrals, photons, and radicals. High concentration of neutral reactive species in oxygen plasma etches the fiber surface, generating cracks and grooves [14–16]. The free oxygen radicals increase surface polarity by introducing new polar carboxylic and hydroxyl derivatives [17–19] either during the treatment and/or immediately after the plasma treatment on exposure to the atmosphere [20,21].

This article studies the ability to print various textile fabrics (natural, synthetic, and blends)

with natural dyes (which have no affinity for some of the fibers) by using the pigment-printing technique .

Materials and Methods

Materials

Fabrics: cotton, wool, polyester, polyamide, cotton/polyester (60/40), and wool /polyester (80/20) were produced by Misr Helwan Spinning and Weaving Company, Misr Helwan, Egypt.

Chemicals: nonionic detergent, urea, and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), as thermal initiator, were obtained from Merck, Germany, and bercolin metal CM, as thermal curing binder, was supplied by Berssa, Turkey; all were of laboratory grade. Regarding dyestuffs, henna powder, was supplied by Tag Cosmetics Ltd., Omdurman, Sudan, and Curcuma tinctoria, pomegranate peel, and madder were purchased from the local market.

Methods

Treatment with plasma

Fabrics samples (20×20cm) were exposed to low-temperature atmospheric pressure plasma. Different conditions of plasma discharge powers (12.5, 24.5, and 41.5W) and exposure times (3, 5, 7, and 10min) were applied. The fabric samples are treated using two techniques :

The first technique

Plasma treatment → printing process → fixation → washing → air-drying.

The second technique*

Printing process → fixation by plasma → washing → air-drying.

*Plasma was used as a treatment for cotton and PET/cotton fabrics and dye fixation at the same time.

The schematic diagram of Glow Dielectric Barrier Discharge (GDBD) reactor used for the treatment of different textile fabrics is shown in Fig.1.

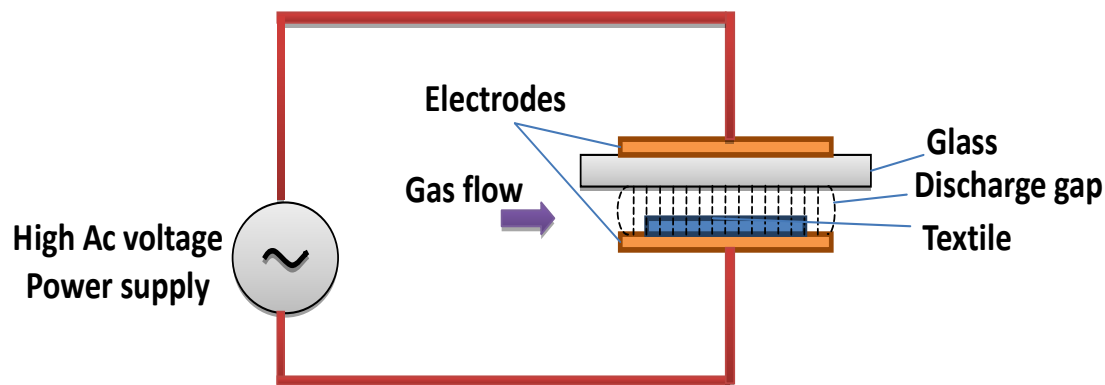


Fig. 1. The schematic diagram of GDBD reactor used for the treatment of different textile fabrics. .

Fabric printing

The printing paste was prepared according to the following recipe :

Synthetic thickener	2g
Binder	5–20g
Urea	4g
Dyes	3g
Water	x
100g	

For the first technique, the printed samples were fixed via thermo fixation at 180°C for 3min, and for the second technique, plasma is used as a fixing tool. All samples are washed twice with cold and hot water, and then air dried.

Measurements and material characterization

All samples were investigated by a scanning electron microscope (SEM, JSMT-20; JEOL, Okohama Japan), NRC. Surface morphology of the treated and untreated samples was studied by using a wet-SPM9600 Scanning Probe Microscope (Shimadzu made in Japan). Color strength and fastness properties were evaluated using the AATCC standard test method.

Results and Discussion*Electrical parameters of GDBD reactor characteristics*

Voltage and current waveforms of the GDBD reactor were measured at different applied voltages. Figure 2 shows the waveforms of the voltage functional to the reactor and the supplementary discharge current at applied voltages of 8.5kV, 11.25kV, and 13.35KV, correspondingly.

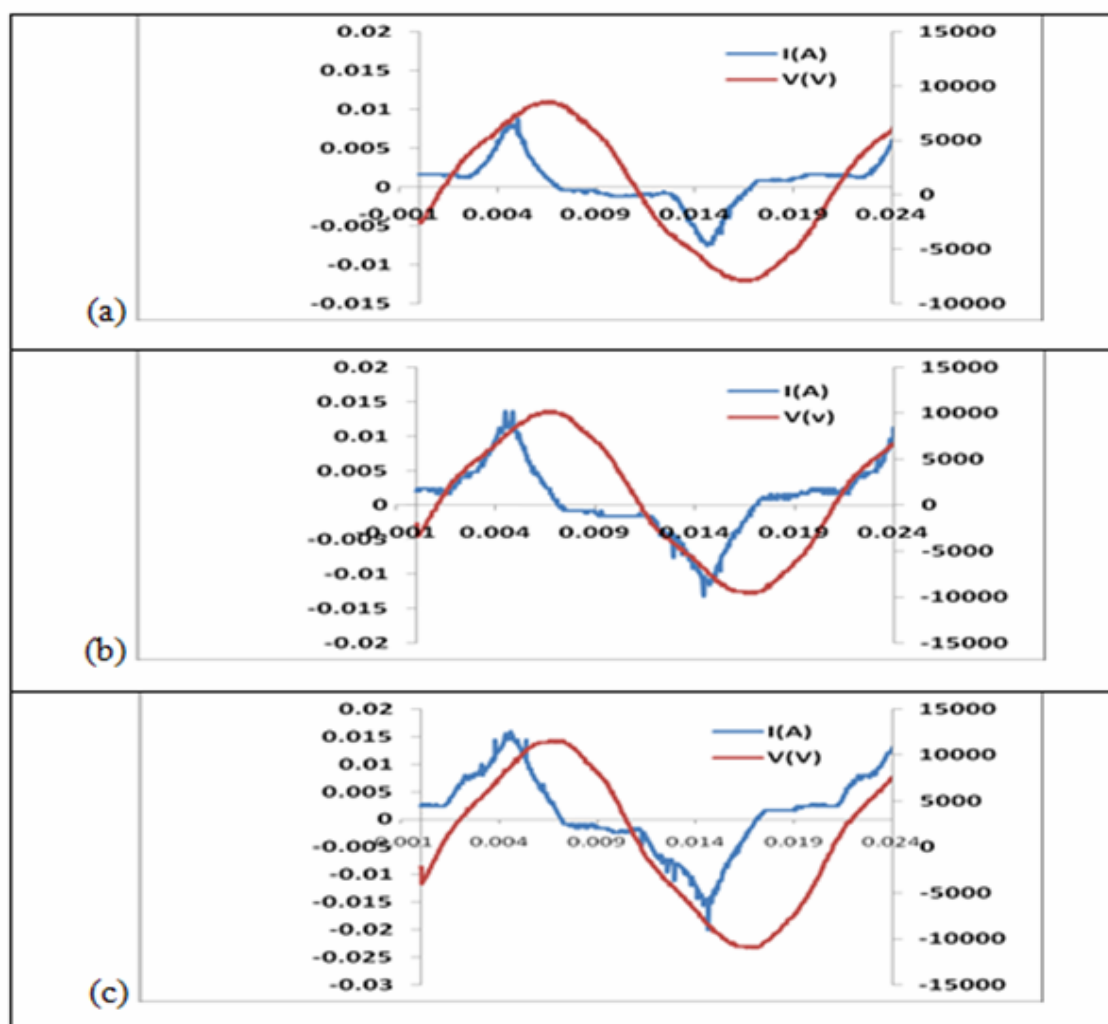


Fig. 2. The voltage and current waveforms of GDBD at applied voltages (a) 8.5 kV, (b) 11.25 kV and (c) 13.35KV respectively.

From Fig. 2, it was noticed that GDBD current waveform is characterized by a large hump of duration in milliseconds (glow component) with a small component of microfilaments that are superimposed on the glow component. The glow component can be attributed to the special configuration of the porous fiber sheets, which are characterized by the existence of microholes, and an internal discharge takes place inside the micro holes of the porous fiber [22]. Massines and Gouda [23] stated that this internal discharge provides seed electrons sufficient for the initiation and growth of the discharge in the GDBD form inside gas between the two electrodes.

Discrete current spikes characterize the small component of microfilaments. The amplitude and the number of these spikes increase with the increase in applied voltage. These spikes were connected to the development of micro discharges of tens of nanosecond interval in the gap space [24].

The discharge power of GDBD reactor was determined from a voltage–charge Lissajous figure (U-Q diagram). This can be achieved simply by

putting a capacitance in series with the GDBD experiment. The voltage across this measuring capacitor is proportional to the charge. It can be strongly shown that the area of U-Q diagram always represents the energy consumed during one period [25–27]. Lissajous diagrams were taken at diverse applied voltages where the voltage change between the two electrodes has been dignified as a function of the charge transmitted within the discharge gap. Figure 3 shows Lissajous diagrams of GDBD at applied voltages of 8.5, 11.25, and 13.35kV. It was noted that the area of a parallelogram increases with the applied voltage owing to energy consumption associated with the parallelogram region. The Lissajous figure of the GDBD is characterized by a smoothing area with a very small filamentary formation. The smoothing area of Lissajous reflects the homogeneity of discharge (glow mode) [28].

The calculation of energy consumed by multiplying space parallelogram frequency AC power source AC user (50Hz). Table 1 shows the values of the energy consumed in different voltages applied across GDBD reactor.

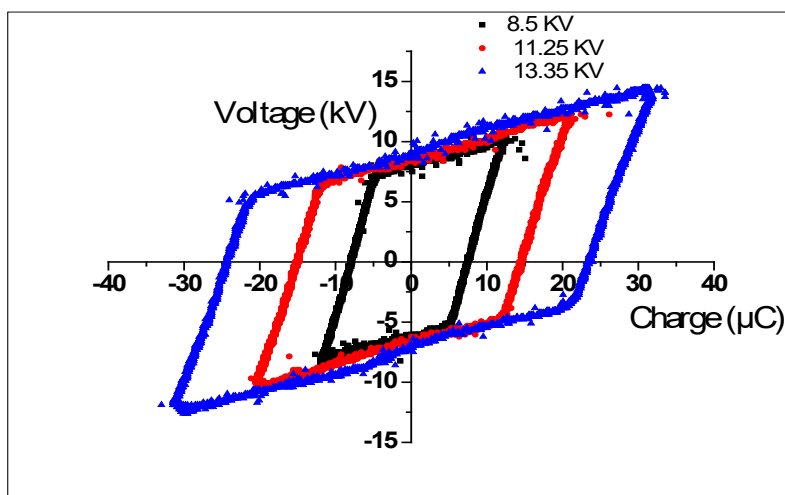


Fig. 3. U-Q Lissajous diagrams of GDBD at applied voltages 8.5- 13.35 kV.

TABLE 1. The relation between the applied voltage and the consumed power in the GDBD cell.

Applied voltage (kV)	Consumed power (W)
8.5	12.5
11.25	24.5
13.35	41.46

It was noticed that the consumed power within the GDBD reactor increased with the increase in applied voltage. The values of consumed power are greater than that of the usual consumed power of GDBD at the same voltages.

The effect of plasma conditions on color strength (K/S) and related parameters

To study the influence of treatment time and power, plasma treatment was carried out – using the two techniques – at 12.5, 14.5, and 41.5 watts discharge power for 3, 5, 7 and 10min duration. The pigment printing method was carried out one day after plasma treatments for the first technique. The results are shown in Figs 4 and 5 for cotton and polyester/cotton blend treated with the first technique, whereas Figs 6 and 7 represent the results of the second technique for the same fabrics order. It is obvious that K/S values increased with increase in the plasma exposure time and power. These results hold true for the fabrics used regardless of the technique. The K/S values for cotton fabric at power 12.5 watts are 13.33 and 15.17 for 3 and 10min (using first technique) against 15.5 and 17.04 at the same exposure time (using the second technique). The color strength K/S of the untreated cotton fabric is 12.5. The K/S values of polyester/cotton fabrics are 15.5 and 17.01 (first technique) and 15.6 and 18.02 (second technique) at the same power (12.5W) for exposure times 3 and 10min, respectively, whereas the untreated PET/cotton had K/S of 8.93. The phenomenon of K/S increase can be attributed to the increase in the number of plasma-created polar groups such as – COOH, – OH, and – CO, as well as increase in the surface roughness owing to etching and other chemical changes of the surface [29]. It can be seen in Figs 4 –7 that higher K/S values were obtained when using plasma as a treatment and a fixation tool at the same time for dye (second technique). Moreover, the best K/S was obtained when the two fabrics were treated for an exposure time of 5min at discharge power of 24.5 watts. Further increase in the plasma treatment time or other plasma conditions, the K/S slightly increased or became nearly constant. Overall, the printability after plasma treatment was quite acceptable.

Tables 2 and 3 represent the color parameters and color difference (ΔE) of the prints at optimum conditions using the two techniques. Color parameters and the color difference of printed fabrics values are evaluated using CIE Lab system. The color difference is calculated as follows :

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

where $\Delta L=L-L^*$; $\Delta a=a-a^*$; $\Delta b=b-b^*$.

Where L refers to lightness-darkness values from 100 to 0 representing white to black, values run from negative (green) to positive (red), b values run from negative (blue) to positive (yellow) and a .

It can be seen from Tables 2 and 3 for the two techniques that L values decreased in all the printed samples, indicating that the samples became darker compared with that of the control sample. As seen from a and b values, that the color hue changed to reddish-yellow. For color difference (ΔE) values, there is a significant color difference between the printed samples and the control samples, although the dye concentration is constant. Chroma is calculated as $(a^2+b^2)^{1/2}$, as the chromaticity increases, the color becomes more intense, and as it decreases, the color becomes dull, and this is clear from Table 3 that the chroma of samples increased [30].

Effect of binder's concentration on the color strength

Binders play an important role in pigment printing achieving high color strength and act as adherent agent between the fiber and the pigment. The relation between the binder's concentration and the color strength (K/S) values of both untreated and plasma treated cotton and PE/C fabrics (using second technique) is represented by Fig.8.

It is obvious that varying binder's concentration affects –to a great extent – the color strength of the prints. Using 5% concentration, the color strength values are 18 and 17 for treated cotton and PET/C fabrics against the values 9 and 12 for cotton and PET/cotton prints, respectively, on using 1% concentration. It is also noticed that increasing the binder's concentration more than 5% has an influence on the color strength (K/S) regardless of the fabric type. This indicates that 5% concentration of binder is the optimum in this pigment printing paste.

On the contrary, at zero binder concentration, reasonable K/S values are acquired by plasma-treated fabrics compared with the untreated ones owing to the increase of polar groups that increased the amount of linkage between binder and fiber and resistance of chemical bonds.

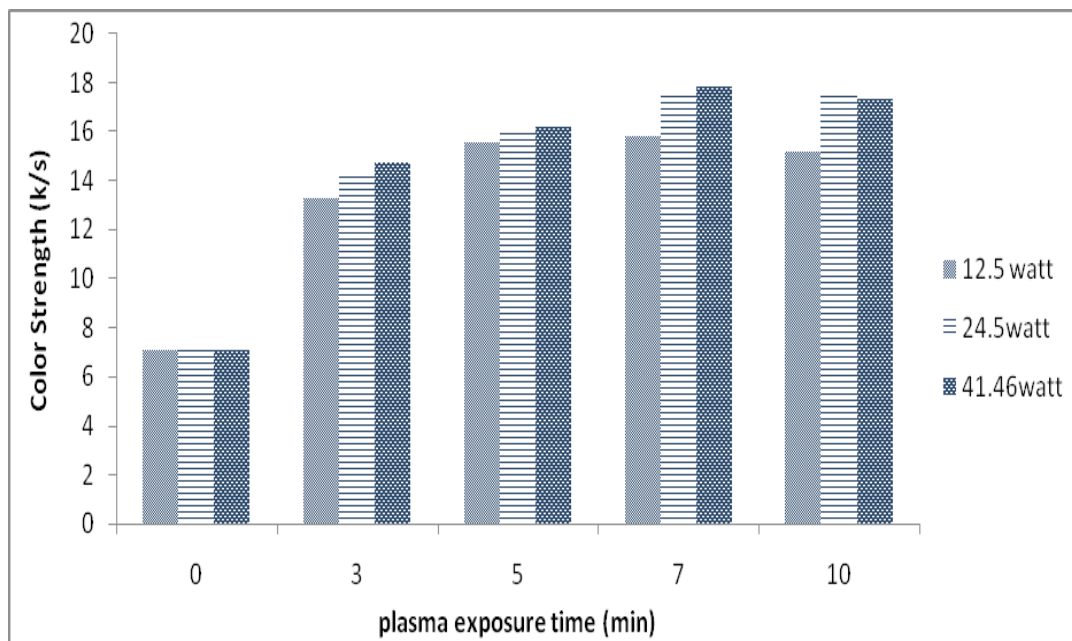


Fig. 4. Color strength of plasma treated printed cotton fabric with natural dye (Curcuma), using 1st technique and plasma conditions; discharge discharge powers 12.5, 14.5 & 41.5 watts and exposure times 3, 5, 7 & 10 min.

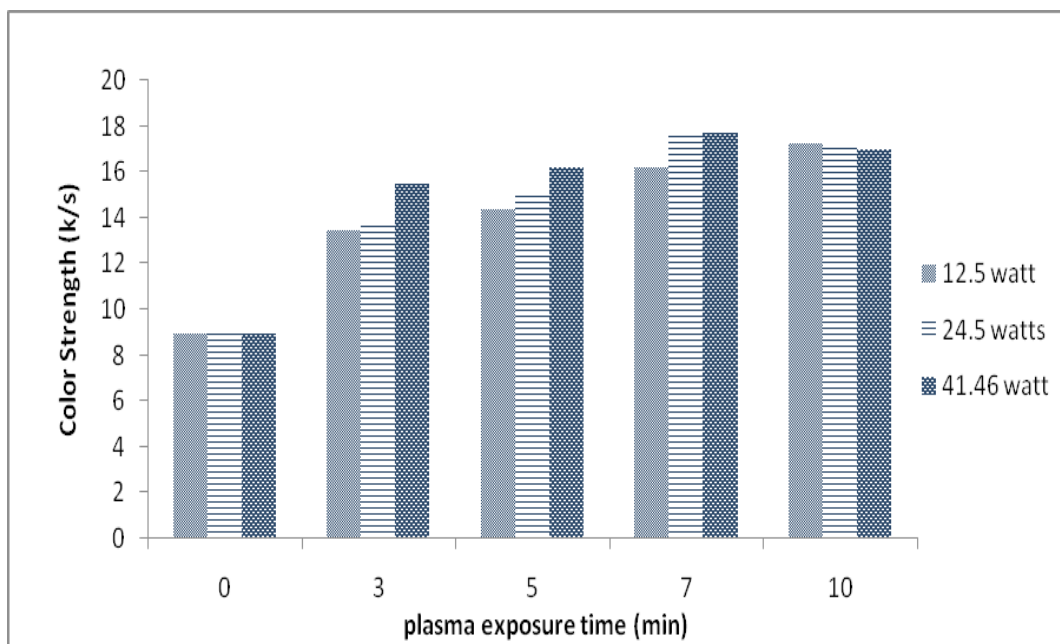


Fig. 5. Color strength of plasma treated printed PE/C fabric with natural dye (Curcuma), using 1st technique and plasma conditions; discharge discharge powers 12.5, 14.5 & 41.5 watts and exposure times 3, 5, 7 & 10 min.

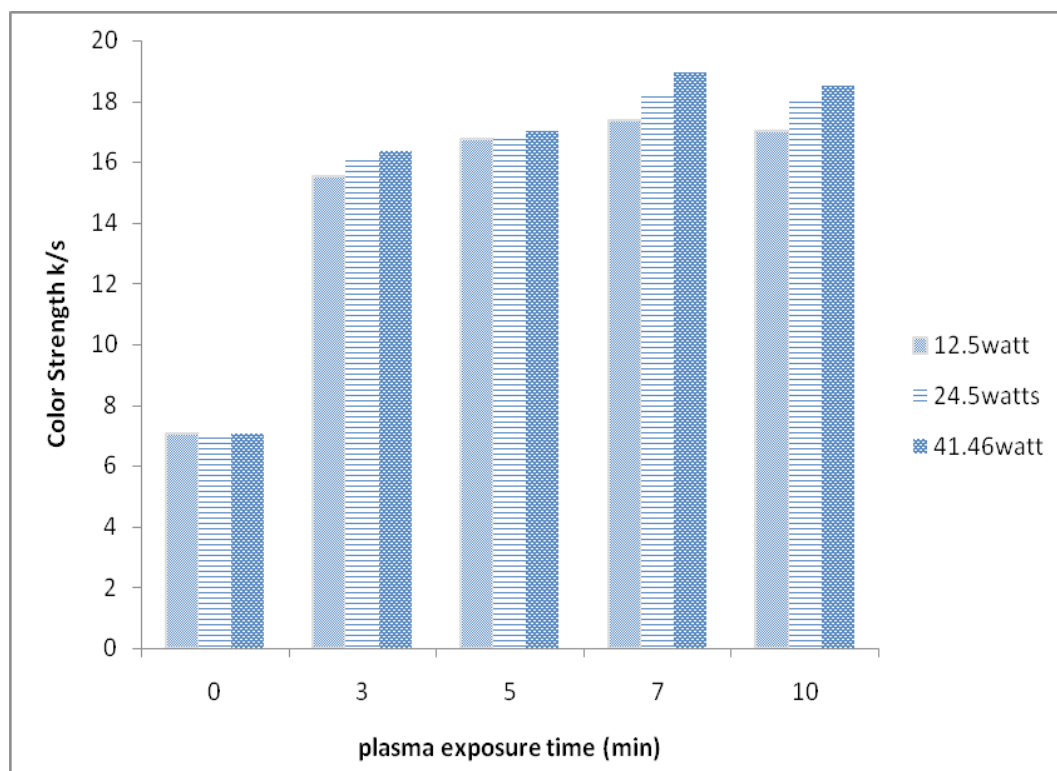


Fig. 6. Color strength of plasma treated printed cotton fabric with natural dye (Curcuma), using 2nd technique and plasma conditions; discharge discharge powers 12.5, 14.5 & 41.5 watts and exposure times 3, 5, 7 & 10 min

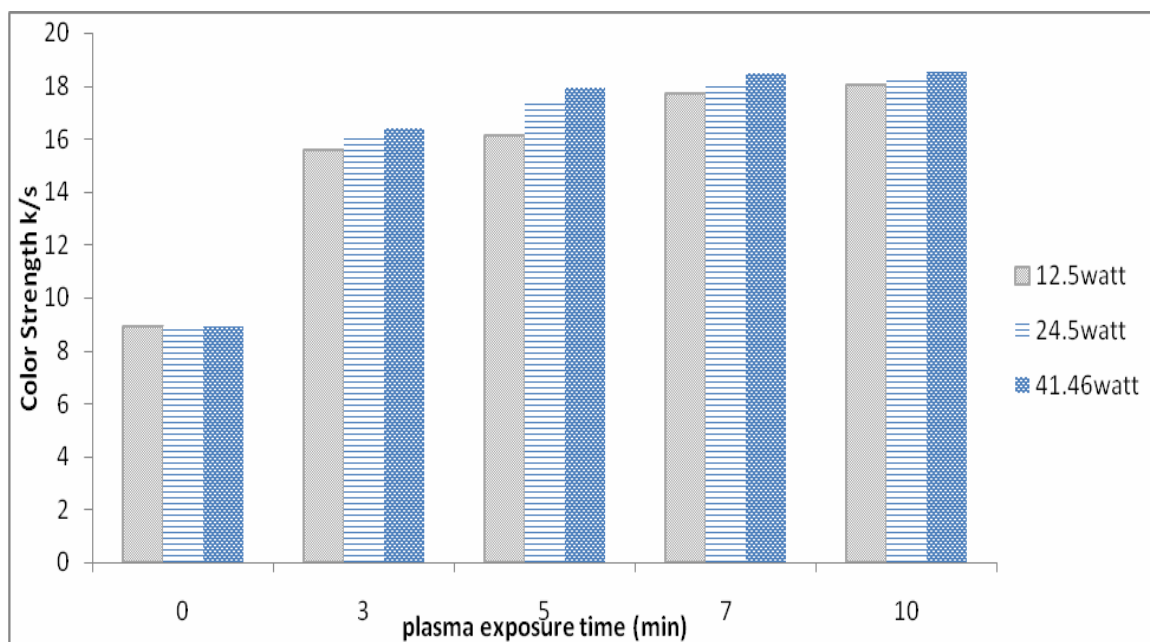


Fig. 7. Color strength of plasma treated printed PE/C fabric with natural dye (Curcuma), using 2nd technique and plasma conditions; discharge powers 12.5, 14.5 & 41.5 watts and exposure times 3, 5, 7 & 10 min.

TABLE 2. Color parameter and color difference of fabrics printed with curcuma at the optimum conditions (7min, 24.5W).

Printed sample	First technique											
	L	a	b	L*	a*	b*	ΔL	Δa	Δb	ΔE	C_{ab}^{**}	
Untreated cotton	66.77	14.70	17.75	7.08	-2.17	70.27	70.74	8.78	5.48	73.75	13.5	45.9
Treated cotton	70.50	16.20	22.3	9.9	-4.21	85.6	85.96	10.4	6.87	86.8	15.9	55.9
Untreated PE/C	69.97	14.96	14.53	78.86	-5.2	68.88	65.29	17.49	20.40	73.01	39.9	55.6
Treated PE/C	82.1	17.8	16.9	87.65	-3.1	75.9	76.01	19.56	24.76	83.9	42.6	65.9

TABLE 3. Color parameter and color difference of Fabrics printed with Curcuma at the optimum conditions (7min, 24.5W).

Printed sample	Second technique											
	L	a	B	L*	a*	b*	ΔL	Δa	Δb	ΔE	C_{ab}^{**}	
Untreated cotton	69.74	8.78	5.48	7.08	-2.17	70.27	75.56	9.8	-24.1	79.90	14.2	50.3
Treated cotton	78.9	10.8	7.9	9.43	-3.1	84.7	86.3	11.9	-22.1	88.5	16.5	65.3
Untreated PET/cotton	65.29	17.49	20.40	78.86	-5.2	68.88	87.53	1.48	-8.3	78.41	41.4	63.1
Treated PET/cotton	79.9	19.65	23.6	86.8	-8.8	79.0	88.6	2.1	-6.3	90.01	55.4	73.6

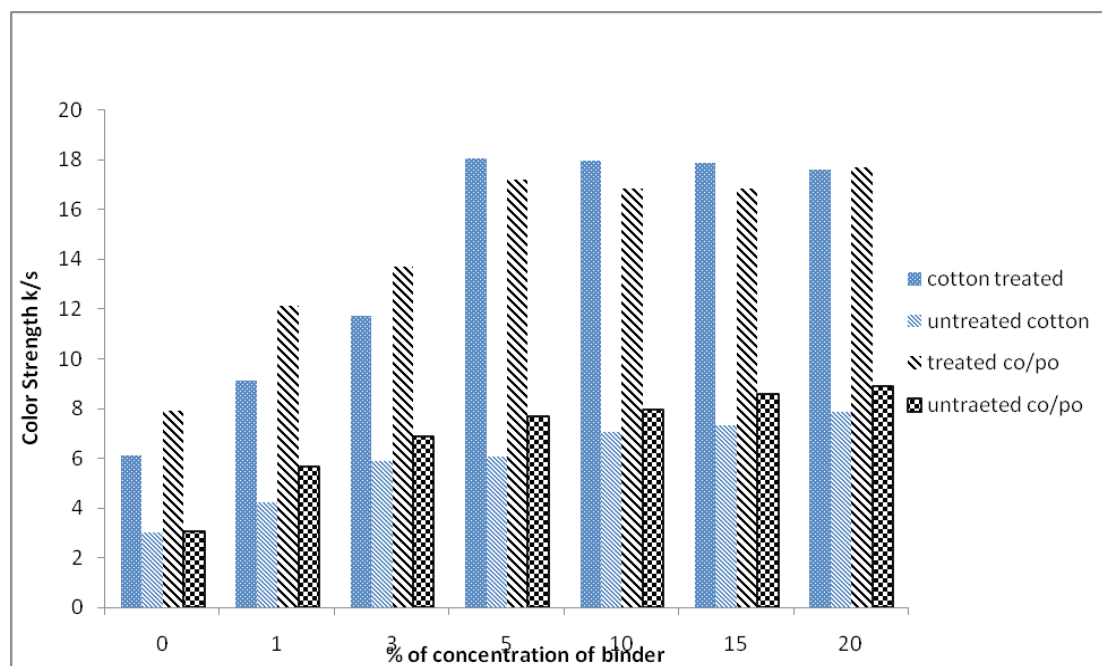


Fig. 8. Effect of binder's concentration variation on the color strength of untreated & plasma treated cotton and PET/C fabrics at 24.5 watts for exposure time 7 minutes.

Further applications— using the second technique – were carried out on different fabrics (polyester, polyamide, wool, and PE/W) and printed with various natural dyes (Curcuma, henna, madder, and pomegranate) using the second technique. The results obtained were very good, saving effort, time, and energy, where in the second technique, plasma had a bi-function role at the same time, that is, treating and fixing dyes on fabrics' surfaces.

Fastness properties

Tables 4–9 indicate the fastness properties and the best color strength obtained when treated all fabrics – cotton, polyester, wool, polyester/cotton, polyester/wool, and polyamide – at discharge power of 24.5–W for exposure time 7 min. As mentioned before, all the plasma-treated fabrics and printed with different natural dyes acquired very high color strength values that, nearly, increased to triple compared with the untreated fabrics.

Good results of rubbing, washing, perspiration, and light fastness of treated fabrics were obtained owing to plasma treatment that improved the binder film strength, where it creates more linkage between binder and fiber owing to the increase of polar groups [31]. Wet rubbing fastness is poorer compared with dry rubbing owing to the presence of water, which may dissolve the binder

and cause more dye removal from the fiber surface during rubbing process. This phenomenon holds true for all treated fabrics and dye used.

Scanning electron microscope

SEM image was observed to comprehend the alteration of surface morphology of cotton treated fabric. Figure 9a and c shows the SEM of untreated cotton fabric before and after printing with the new natural dye paste. However, Fig. 9b and d displays the SEM images of plasma-treated cotton and plasma-treated printed cotton, respectively, at a discharge power of 24.5 watts for exposure time of 7 min. Fig. 9a demonstrates clearly free roughness and smooth surface of the untreated fiber with no damage on its surface. However, Fig. 9b illustrates some cracks leading to a change in the fiber surface morphology owing to plasma treatment that created polar groups and increased fabric surface energy. This caused etching effect of plasma-active species through bombardment of the cotton surface and development of cracks into voids and holes formed on the surface of the treated fabric. Figure 9c shows the coagulation and levelness of dye carried out in the untreated printed fabric, whereas Figure 9d clarifies how plasma treatment improved the fabric adhesion to the printing paste and enhanced the linkage between treated fabric, binder, and natural dye to become more strengthened and gave a well-bonded and homogenous fabric surface.

TABLE 4. Fastness properties and K/S of untreated and plasma treated cotton samples.

Printed cotton samples using dyes	Color strength K/S	Rubbing fastness						Washing fastness						Perspiration fastness						
		Wet	Dry	Alt	St	Alt	St	Wet	Dry	Alt	St	Alt	St	Wet	Dry	Alt	St	Alt	St	Light fastness
Untreated curcuma	3.025	1-2	2	3	3	3-4	3-4	3	3-4	3	3-4	3-4	3	3-4	3	3-4	3	3-4	3	4
Treated fabric curcuma +binder	18.08	4-5	4-5	5	5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6-7
Untreated henna	3.89	1-2	1-2	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	4-5
Treated fabric henna +binder	11.29	4	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6
Untreated madder	4.06	2	2	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	5
Treated fabric madder+binder	18.2	4	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5-6
Untreated pomegranate	5.5	1-2	1-2	3	3-4	3	3-4	3	3-4	3	3-4	3	3-4	3	3-4	3	3-4	3-4	3-4	5
Treated fabric Pomegranate. +binder	14.05	4-5	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6

TABLE 5. Fastness properties and K/S of untreated and plasma treated PE/C samples.

Printing sample for difference dyes	Color strength K/S	Rubbing fastness						Washing fastness						Perspiration fastness						
		Wet	Dry	Alt	St	Alt	St	Wet	Dry	Alt	St	Alt	St	Wet	Dry	Alt	St	Alt	St	Light fastness
Untreated curcuma	3.04	1-2	2	3-4	4	3-4	3-4	4	3-4	3-4	3-4	3-4	4	3-4	4	3-4	4	3-4	4	5
Treated curcuma +binder	17.2	4	3-4	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6
Untreated henna	4.14	1	1-2	3-4	4	3-4	3-4	4	3	3-4	3-4	3-4	3	3-4	3	3-4	3	3-4	3	5-6
Treated henna+binder	11.10	4	4-5	5	4-5	4-5	4-5	5	4-5	4-5	4-5	4-5	5	4-5	5	4-5	5	5	5	6-7
Untreated madder	5.09	1-2	2	4	3-4	4	3-4	4	3	3-4	4	3-4	4	3-4	4	3-4	4	3-4	4	5
Treated madder+binder	10.34	4	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6-7
Untreated Pomegranate	5.56	1-2	2	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	5
Treated pomegranate+binder	17.13	4	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6-7

TABLE 6. Fastness properties and K/S of untreated and plasma treated polyester samples.

Printing sample for difference dyes	Color strength K/S	Perspiration fastness															
		Rubbing fastness				Washing fastness				Acid				Alkaline			
		Wet	Dry	Alt	St	Wet	Dry	Alt	St	Wet	Dry	Alt	St	Wet	Dry	Alt	St
Untreated Curcuma	4.54	2	2	3-4	3-4	4	3	4	4	4	4	4	4	4	4	4	5-6
Treated curcuma +binder	18.18	4	4-5	5	4-5	5	4-5	5	5	5	5	4-5	5	5	5	5	6
Untreated henna	4.66	1-2	2	3-4	4	3-4	3	4	4	4	4	3	4	4	4	4	5
Treated Henna +binder	8.96	4-5	4-5	5	5	5	4-5	4-5	5	5	4-5	4-5	5	5	5	5	6-7
Untreated madder	3.04	1-2	2	3-4	3-4	4	3-4	4	4	4	4	3-4	4	4	4	4	5
Treated madder+binder	8.18	4	4	5	5	5	4	4-5	4-5	4-5	4-5	4	4	4	4-5	4-5	6-7
Untreated pomegranate	4.1	2	2	3-4	4	3-4	4	4	4	4	4	4	4	4	4	3-4	4-5
Treated pomegranate+binder	13.75	4	4-5	4	5	5	5	5	5	5	5	5	5	5	5	4	5-6

TABLE 7. Fastness properties and K/S of untreated and plasma treated wool samples.

Printing sample for difference dyes	Color strength K/S	Perspiration fastness															
		Rubbing fastness				Washing fastness				Acid				Alkaline			
		Wet	Dry	Alt	St	Wet	Dry	Alt	St	Wet	Dry	Alt	St	Wet	Dry	Alt	St
Untreated curcuma	4.99	2	2	4	4	3-4	3-4	4	4	4	3-4	3-4	3-4	3-4	3-4	3-4	5
Treated curcuma+binder	17.85	4	4-5	5	5	5	4	4	4	4	5	5	5	5	5	5	6
Untreated henna	6.04	1-2	2	3-4	4	3-4	3-4	3-4	4	4	3-4	3-4	3-4	4	4	4	5
Treated henna+binder	15.3	4-5	4-5	5	5	5	4-5	4-5	5	5	5	5	5	5	5	5	6-7
Untreated madder	5.89	1-2	2	3-4	3-4	4	3-4	4	4	4	3-4	3-4	3-4	4	4	4	5-6
Treated madder+binder	7.85	3-4	4	5	5	5	5	5	5	5	5	5	5	5	5	5	6-7
Untreated pomegranate	6.14	3	3	4	4	3-4	3-4	4	4	4	3-4	3-4	4	4	4	4	5
Treated pomegranate+binder	18.9	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6

TABLE 8. Fastness properties and K/S of untreated and plasma treated PE/W samples.

Printing sample for difference dyes	K/S	Rubbing fastness						Perspiration fastness					
		Wet		Dry		Washing fastness		Acid		Alkaline		Light fastness	
		St	Alt	St	Alt	St	Alt	St	Alt	St	Alt	St	Alt
Untreated curcuma	4.97	1-2	3-4	1-2	3-4	4	3	3-4	4	3-4	4	3-4	5
Treated curcuma +binder	8.99	4-5	4-5	4-5	4-5	5	4	4-5	5	5	5	5	6
Untreated henna	5.99	2	3-4	2	3-4	4	3-4	3	3-4	4	3-4	4	5
Treated henna+binder	14.2	4	4-5	4-5	4	5	4	3-4	4-5	4-5	4-5	4-5	6-7
Untreated madder	4.14	1-2	3	2	3-4	3-4	3-4	4	3-4	4	3-4	4	5
Treated madder+binder	9.59	3-4	4	4	4-5	4	4	4-5	4	4-5	4	4-5	6
Untreated pomegranate	6.09	2	3-4	2	3-4	3-4	4	3	3-4	3	3-4	3	4-5
Treated pomegranate+binder	17.4	4-5	5	4-5	5	5	5	4-5	4-5	5	4-5	5	6

TABLE 9. Fastness properties and K/S of untreated and plasma treated polyamide samples.

Printing sample for difference dyes	Color strength K/S	Rubbing fastness						Washing fastness						Perspiration fastness					
		Wet		Dry		Acid		Alkaline		Acid		Alkaline		Acid		Alkaline		Light fastness	
		St	Alt	St	Alt	St	Alt	St	Alt	St	Alt	St	Alt	St	Alt	St	Alt	St	Alt
Untreated curcuma	4.99	2	4	2	4	4	4	3-4	4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	5	5
Treated curcuma+binder	17.85	4	4-5	4-5	5	5	5	4	4	4	4	5	5	5	5	5	5	6	6
Untreated henna	6.04	1-2	3-4	2	3-4	4	3-4	3-4	4	3-4	3-4	3-4	3-4	4	4	4	4	5	5
Treated henna+binder	15.3	4-5	4-5	4-5	5	5	5	4-5	5	4-5	5	5	5	5	5	5	5	6-7	6-7
Untreated madder	5.89	1-2	2	2	3-4	3-4	4	4	3-4	4	3-4	3-4	4	4	4	4	4	5-6	5-6
Treated madder+binder	7.85	3-4	4	4	5	5	5	5	5	5	5	5	5	5	5	5	5	6-7	6-7
Untreated pomegranate	6.14	3	4	3	4	4	4	3-4	4	3-4	3-4	4	4	4	4	4	4	5	5
Treated pomegranate+binder	18.9	4-5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	6	6

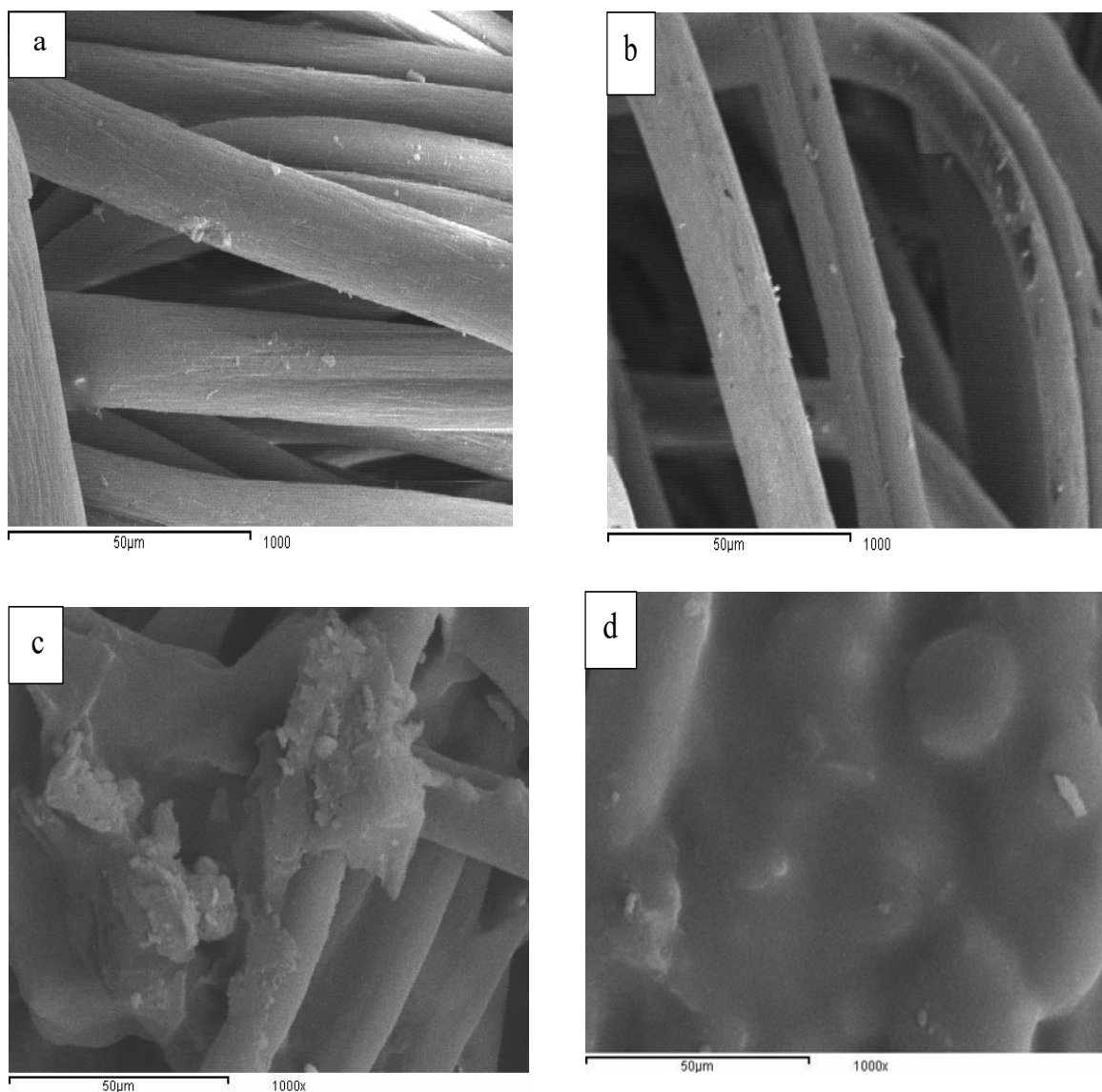


Fig. 9 . SEM images of (a) the untreated cotton (b) plasma treated cotton (c) untreated printing cotton, and (d) plasma treated printed cotton. Plasma conditions; discharge power 24.5watts & exposure time 7 min.

X-Ray analysis

Energy dispersive X-ray analysis (EDX) is used to provide elemental identification and quantitative compositional information of the material. Data resulting from the analysis of EDX spectra show peaks corresponding to the constituent elements of the real composition of the sample being analyzed and image analysis. All are represented by Fig. 10a and b for untreated and plasma treated cotton fabrics, respectively.

The EDX analysis in Fig.10b revealed the change in quantitative surface composition after plasma treatment. The results represented in the tables show that the oxygen atomic percentage decreased after plasma treatment compared with

the untreated sample, which may be owing to the removal of hydroxyl group and replaced by the attachment of $\text{Si} - (\text{CH}_3)_3$ groups.

Atomic force microscope

Figure 11a– drepresents the atomic force microscope (AFM) images of cotton samples that were untreated, plasma treated, untreated printed with curcuma, and plasma-treatedprinted with curcuma, respectively.

The topography in Fig.11a shows inhomogeneity surface for the untreated cotton specimen (control) compared with the untreated printed one (Fig. 11b), which gives more homogeneity surface owing to the printing layer

that covers all the protrusions in the control specimen surface. A visual analysis clearly highlights changes in the textile surface topography after plasma treatment (Fig. 11c), where plasma treatment caused an increase in surface roughness of the sample owing to the etching

effect as mentioned before. Figure 11d represents the plasma-treated printed fabric that looks smoother owing to the presence of the printing layer that filled all the rougher parts on the surface giving a smoothness and homogeneity surface.

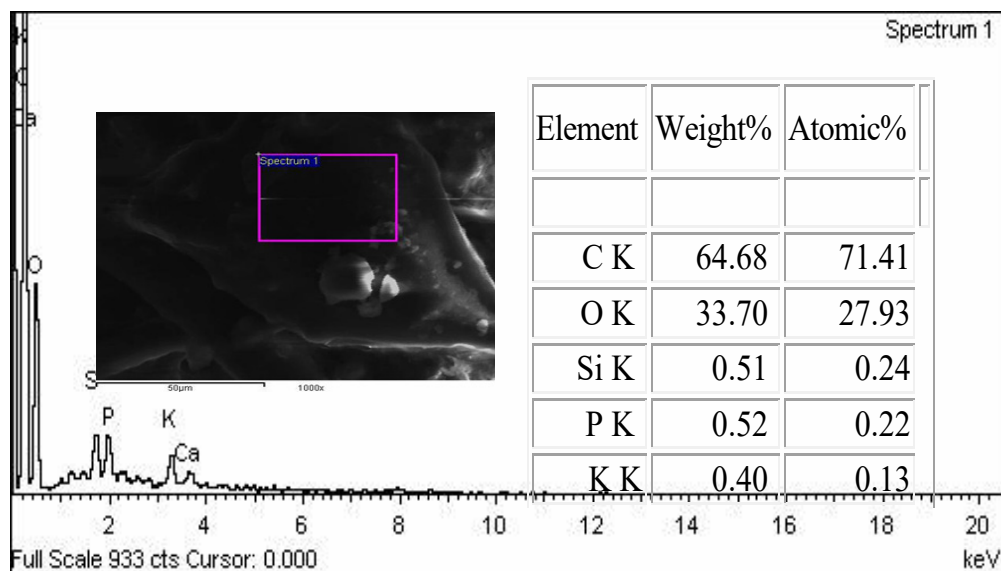


Fig.10 a. EDX of untreated cotton fabric.

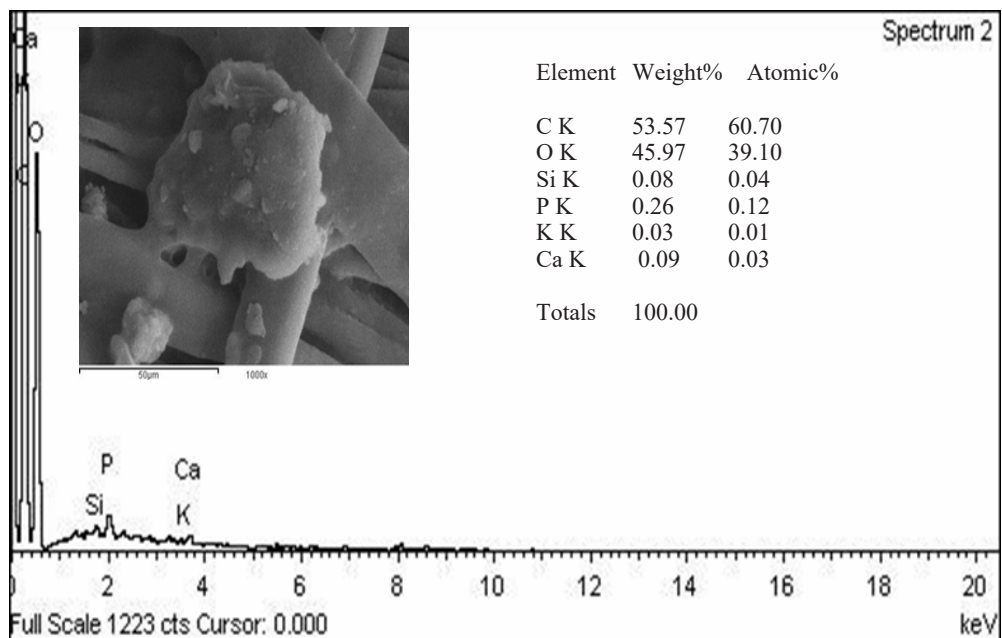


Fig. 10 b. EDX analysis of plasma treated cotton fabric.

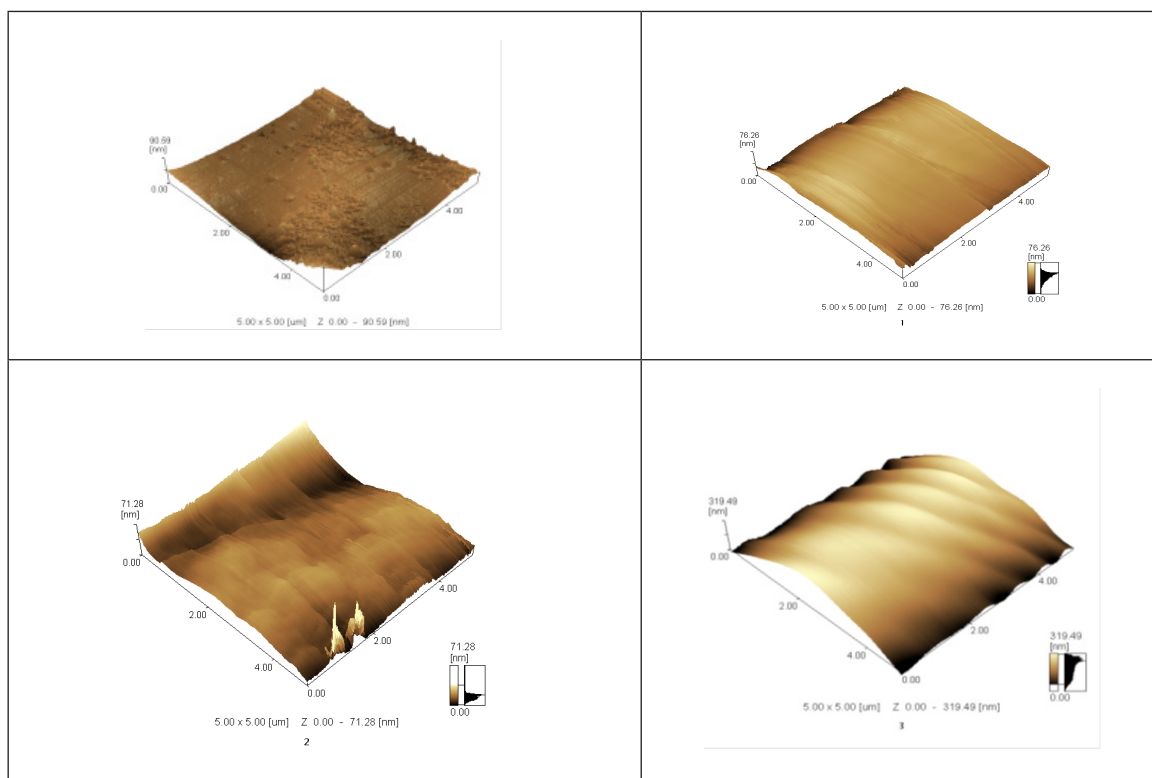


Fig. 11. AFM images of ; (a) untreated (b) untreated printed (c) plasma treated (d) plasma treated printed cotton fabric. Optimum plasma conditions; (15 W & 7 min).

Conclusion

- (1) Cotton, polyester, wool, and their blends with polyester could be, successfully, printed with pigment technique recipe containing natural dyes.
- (2) In this study, pigment printing paste could be used without a mordant and with very low percentage of the binder.
- (3) DBD plasma enhanced the printability of all treated fabrics and increased their color strength, nearly, to the triple compared with the control ones.
- (4) Fastness properties (rubbing, washing, perspiration, and light) are all improved – ranged from good to excellent – after DBD plasma treatment.
- (5) The ability of using plasma technique as a treatment and fixation tool at the same time is useful.

Conflicts of interest

The authors declare that there is no conflict of interest

References

1. Nattadon Rungruangkitkrai, Rattanaphol Mongkhorrattanasit, RMUTP International Conference: Textiles & Fashion, July 3-4, Bangkok Thailand, (2012).
2. Samanta, A. K. & Agarwal, P.: Application of natural dyes on textiles, *Indian Journal of Fibre & Textile Research*, Vol. 34, No. 4, pp. 384-399, ISSN 0975-1025, (December 2009).
3. Rahman Bhuiyan, M. A., Ali, A., Islam, A., Hannan, M.A., Fijul Kabir, S. M., and Islam, M. N., *Fash Text*, 5:2., (2018).
4. Ali, N.F., El-Khatib, E.M., EL-Mohamedy, R.S.R., *Egypt. J. Chem.* Vol. 62, Special Issue (Part 1), pp. 35-36 (2019).
5. Yaman, N., Ozdogan, E., Seventekin, N., *Journal of Engineered Fibers and Fabrics*, Vol. 7, Issue 2, (2012).
6. Neral B., Šoštar-Turk, S., and Vončina, B., *Dyes and Pigments*, Vol. 68, No. 2-3, pp. 143-150, (2006).
7. Mohamed A.A., Fouda A., Elgamel M.S., Hassan S.E., Shaheen T.I and Salem S., *Egypt. J. Chem.* The 8th. Int. Conf. Text. Res. Div., Nat. Res. Centre, Cairo (2017), pp. 63-71 (2017).

8. El-Asasery M.A., Abdelghaffar R.A., Kamel M.M., Kamel M.M., Youssef B.M. and Haggag K.M., *Egypt. J. Chem. The 8th. Int. Conf. Text. Res. Div., Nat. Res. Centre, Cairo* (2017) pp. 143 - 151 (2017).
9. Bahmani, S.A., East, G.C., and Holme, I., *Coloration Technology, Vol.116, No.4*, pp. 94-99, (2000).
10. Yaman N. Ph.D. Thesis, Ege University, Textile Engineering Department, pp. 278, (2008).
11. Abou Taleb, M., Haggag, K., Mostafa, T.B., Abou El-Kheir, A. and El-Sayed, H., *Egypt. J. Chem. The 8th. Int. Conf. Text. Res. Div., Nat. Res. Centre, Cairo*, pp. 15- 31 (2017).
12. Mana, W.S., Kan, C.W., Ng, S.P., *Vacuum, Vol. 99*, pp.7-11, (2014).
13. Essa D.M. , Ibrahim S.F. , Elnagar K. , Ahmed M. Abdel-Razik and Adel A. H. Abdel-Rahman, *Egypt.J.Chem. Vol. 62, Special Issue (Part 1)*, pp. 75 - 90 (2019).
14. Fang, K.J., Wang, S.H., Wang, C.X., Tian, A.L., *Journal of Applied Polymer Science*, :107:, 2949e55 , (2008).
15. Zhang, C.M., Fang, K.J., *Surface and Coatings Technology*, :203:2058e63, (2009) .
16. Knittel, D., Schollmeyer, E., *Journal of the Textile Institute*, Vol. 91, No.3:151e65, (2000) .
17. Ahmed, H. M., Ahmed, K. A., Mashaly, H. M., and El-Halwagy, A. A., *Indian Journal of Science and Technology*, Vol. 10, No.10, March (2017).
18. Ahmed, H. M., Abd-El Thalouth, J. I., Rashed, U. M. and El-Halwagy, A.A., *International Journal of Science and Research (IJSR)*, Vol. 5 Issue 12, December(2016).
19. Kuvshinov,D., Siswanto,A., Lozano-Parada J. and Zimmerman,W.B., *International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering*, Vol. 8, No.1, pp.80-83, (2014).
20. Moubarak, D., Abd Al-Halim, M., Abu-Hashem, A. and Elbasha, Y.H., *Egypt. J. Chem. Vol. 62, No. 7*, pp. 1335- 1341 (2019).
21. Gupta, B., Hilborn, J., Hollenstein, C.H., Plummer, C.J.G., Houriet, R. and Xanthopoulos, N., *Journal of Applied Polymer Science*, Vol. 78,1083e91(2000).
22. Ren, Y., Wang, C.X. and Qiu, Y.P., *Surface and Coatings Technology*;202:2670e6 (2008) .
23. Ahmed, H.A., El-Hennawi, H.M., Ahmed, K.A., El-Halwagy, A.A., A. Samir, A. and Garamoon, A.A., *Egypt.J.Chem. Vol. 62, No. 6*. pp. 1025 - 1036 (2019).
24. Shin, Y. and Yoo, D.I., *Journal of Applied Polymer Science*, Vol. 108, 785e91(2008) .
25. Inagaki, N., *Plasma surface modification and plasma polymerization. Lancaster,PA: Technomic; (1996).*
26. Garamoon, A.A., El-zeer, D.M., *Atmospheric pressure glow discharge plasma in air at frequency 50 Hz', Plasma Sources Sci. Technol*, Vol. 18, No.3, pp.194–201(2009).
27. Massines, F., Gouda, G., *A comparison of polypropylene- surface treatment by filamentary, homogeneous and glow discharges in helium at atmospheric pressure', J. Phys. D: Appl. Phys. Vol.31, pp.3411–3420 (1998).*
28. Gherardi,N., Gouda,G., Gat,E., Ricard,A., and Massines,F., *Plasma Sources Sci. Technol.*, Vol. 9, pp.340-346 (2000).
29. Kogelschatz,U., Eliasson,B., and Egli, W.,*J. Physique, IV, 7 (C4) ,pp.47- 66 (1997).*
30. Falkenstein, Z. and Coogan, J.J., *J. Phys. D: Appl. Phys. Vol.30, 817 (1997).*
31. Wagner, H.E., Brandenburg, R., Kozlov,K.V., Sonnenfeld, A. and Michel, P., J.F. Behnke, *The barrier discharge: basic properties and applications to Surface treatment, Vacuum, Vol. 71, pp.417–436, (2003).*
32. Kostov, K.G., Honda, R. Y., Alves, L.M.S. and Kayama, M.E., *'Characteristics of Dielectric Barrier Discharge Reactor for Material Treatment', Brazilian Journal of Physics, Vol. 39, No.2, June, pp.322-325 (2009).*
33. Stefano, Z., Silvia, F., Attilio, C. and Claudia, R., *Surface & Coatings Technology* , Vol.292, pp.155–160 (2016) .
34. Abdou, E. S., El-Hennawi, H. M., and Ahmed, K. A., *Journal of Chemistry, Vol.10, No.8, Article ID 5958 (2013) .*
35. Hamilton, L.E., Chiweshe, A., and Lincoln, N.E., *Starch/Stärke, Vol. 50, pp.213-217(1998).*
36. Hanna, A.A, Mohamed. W.A.A., and Galal. H.R., *Egypt. J. Chem. Vol.57, No. 5,6 pp. 423- 433 (2014)*