Egypt. J. Chem. **Vol. 67**, No. 9 pp. 415 - 426 (2024)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Effect of Plasma /Copper Oxide Nanoparticles on Silk Fabric Printability with Some Natural Dyes Using Ultraviolet Fixation

Heba M. Khalil [a], Azaa A. El-Halwagy [b], Usama M. Rashed [c], Wafaa M. Raslan [d], and Hend M. Ahmed [b]*

[a] *Helwan University, Faculty of Applied Arts, Printing, Dyeing and Finishing Department, Benha, Egypt*

[b] *National Research Centre (Scopus affiliation ID 60014618), Textile Research and Technology Institute, Dyeing, Printing, and Intermediate Auxiliaries Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt*

[c] *Physics Dept. Faculty of Science, Al-Azhar University, Cairo, Egypt,*

[d] *National Research Centre (Scopus affiliation ID 60014618), Textile Research and Technology Institute, Protienic, and Synthetic Fiber Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt*

Abstract

This study investigated the effect of treatment with Nano copper oxide and Cu NPs in the form of sonicated copper sulfate after O2 plasma treatment on the printability of silk fabric. The silk fabric was treated with various concentrations (0.5-1.5 wt %) of CuO NPs using the padding technique, squeezing to 100 % pick up, and then thermal treated at 120 °C for 30 min. The treated silk was printed with some natural dyes such as coffee, deer blood, and red cabbage dyes. The printability of the treated fabric was evaluated by measuring the color strength (K/S) as well as its fastness properties. The results showed that the treatments with plasma/ CuO NPs as well as CuSO4 improved the printability of silk fabric with the aforementioned natural dyes. A higher concentration of CuO NPs after O2 plasma treatment resulted in higher color strength and color fastness. The use of natural dyes also resulted in a unique range of color shades and hues, which are not possible with synthetic dyes. This study highlights the potential of natural dyes for enhancing the printability of silk fabric and providing a sustainable and environmentally friendly alternative to synthetic dyes.

Keywords: silk, natural dyes, plasma, nanoparticles, copper oxide, copper sulfate.

1. Introduction

Surface treatments of textiles could be carried out with plasma causing etching and other deformation on the fabric surface. Low-pressure plasma was applied for surface modification of textiles. [1, 2] Nanotechnology has recently been used to increase the added value of textiles and improve their properties. [3, 4] Nanoparticle treatments impart antibacterial, water, or oil repellence, antistatic properties, self-cleaning, and flame retardancy as well as improving coloration properties. [5-26] The surface etching resulting from plasma treatment is suitable for introducing nanoparticles on textiles. [27-30] The adsorption of NPs on the fiber surface increases with plasma treatments. New functional groups such as carbonyl, carboxylic, and hydroxyl produced by plasma on the fiber surface depend on the used gas (air, oxygen, nitrogen … etc.).

Silk is a proteinic fiber and is found in the form of filaments. Silk is soft and gloss fibers having good moisture regain breathability, and excellent draping. [31, 32] Silk could be attacked by bacteria causing damage to the fiber such as degradation and/or deformation. [31, 33-37] Antibacterial reagents such as TiO2, ZnO, Ag, and Pt NPs could be applied on textile substrates. ZnO NPs play an important role in UV protection, self-cleaning, and antibacterial

* Corresponding author e-mail: hend_plasma@yahoo.com.; (Hend M. Ahmed).
Received date 21 November 2023; revised date 14 February 2024; accepted date 03 March 2024
DOI: 10.21608/EJCHEM.2024.250348.8901

activity. Plasma treatment could improve ZnO desorption onto silk fabric. [38, 39]

The functionalization of textiles with cupric oxide (CuONPs) gives antibacterial properties for textiles. [40] CuO is a semiconductor. Application of CuONPs on textiles could be carried out by different techniques. The in situ process could be carried out by the synthesis of NPs in the presence of the textile fibers. [41] Another methodology is the ex-situ technique that is carried out in two steps; 1st step is the formation of NPs and 2nd step is the application of NPs on textiles. [42]

This work investigates the treatment of silk fabric with CuONPs as well as sonicated $CuSO_4$ solution to improve its printability with some natural dyes such as coffee, red cabbage, and deer blood. Fixation of dyes was tried either thermally and /or by subjecting them to UV irradiation. The treated silk was examined by SEM, TEM, FTIR, and mechanical properties as well as antibacterial activity. As shown in part I of this work.

2. Experimental

2.1. Material

2.1.1. Fabric

Grey silk was offered by a private company. The fabric was degummed using a 15% (o. w. f) aqueous solution of Asp icon 1030 soap at a temperature of 95-100°C for 1-2 hrs. The fabric was thoroughly washed with warm water, followed by cold water, then, squeezed and air dried.

2.1.2. Chemicals

CuO Nanoparticles are supplied by Orchid Pharmaceutical Company, Obour City, Egypt, Nonionic detergent, urea, and Ammonium persulfate $(NH_4)_2S_2O_8$ as thermal initiators are supplied from Merck, Germany. Bercolin metal CM as a thickener is supplied by Berssa, Turkey. Thermal curing binders and $CuSO_4$ were laboratory-grade chemicals. Dyestuffs: Coffee, Gomphrena Glo bosa (deer blood), and red cabbage were bought from the local market.

2.2. Methods

2.2.1. Fabric Treatments

Silk fabric was treated with O_2 plasma at 17.35 Watts for 15 min followed by padding treatment with CuONPs or sonicated $CuSO_4$ solution then squeezed to 100 % pickup. Treated samples were dried at 120°C for 30 mins. The concentration of NPs ranged from 0.5 to 1.5 g/100g fiber.

2.2.2. Dye extraction

Coffie was extracted according to previously reported work.

2.2.3. Plasma Set up

The textile fabrics were exposed to low-temperature plasma generated by DBD under atmospheric pressure. A schematic drawing of the experimental arrangement is depicted in Fig 1. The DBD cell consisted of two electrodes of stainless-steel discs; each had a diameter of 25.5 cm and a thickness of 2 mm. The lower electrode was fixed to a Perspex base that was 30 cm in diameter and 2 cm in thickness and connected to the earth.

The upper electrode was connected to a high-voltage AC power supply that had a 50 Hz frequency and a variable voltage of 0-20 kV. A dielectric material of glass that had a thickness of 1.7 mm was pasted to the upper electrode. The gap distance (d) between the dielectric glass and the lower electrode was 3 mm. The discharge voltage and discharge current were measured using a two-channel digital storage oscilloscope (HM-407). The discharge voltage was connected to the oscilloscope via a 2000:1 resistive potential divider. The discharge current that flowed through the DBD cell was measured as a voltage across a resistor of 1 k connected in a series to the ground. The DBD was in an airtight Plexi-glass box and the used gas (oxygen) was injected from the inlet of the electrode box.

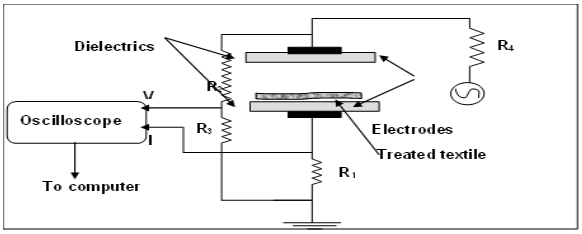

Fig 1: Schematic diagram of the discharge cell used for the treatment of the textile.

2.2.4. Preparation of Printing Paste

The composition of the printing paste was as follows: [43-46]

The printing paste recipe:	
Dye concentration	
Synthetic thickener	2 g
Binder	5-20 g
Urea	4 g
Sodium dihydrogen phosphate	0.5 g
Dyes	2 g
Water	X g
	100 g

All the printed samples were fixed via thermo-fixation at 180°C for 3min and washed as follows:

- Rinsing thoroughly with cold water
- Treatment with hot water
- Treatment at 60°C with 2g/l nonionic detergent

- Washing with hot water
- Rinsing with cold water
- Finally, the samples were dried and assessed for color strength measurement.

Other printed samples are fixed by exposure to UV irradiation for a variety of times.

2.3. Measurements

2.3.1. Color Assessment (K/S)

The color strength of the printed samples was evaluated by Hunter Lab Ultra scan PRO. The color strength (K/S) of each printed sample was measured using a Data Color SF 600 plus Colorimeter. [47, 48]

2.3.2. Fastness Properties

The color fastness of the printed fabrics was assessed by the AATCC Test Method 16-2014 (color fastness to light), AATCC Test Method 61-2013(colorfastness to laundering), and AATCC Test Method 8-2016 (color fastness to rubbing and color fastness to perspiration). [49-51]

3. Result and Discussions

The results of untreated and treated silk fabrics were evaluated by measuring the color strength, and fastness properties.

3.1. Color Strength

The effect of plasma/CuONPs treatment on the color strength of printed silk fabric with coffee solution, red cabbage, and deer blood dyes was investigated upon applying different concentrations of CuONPs and different methods for dye fixation either thermally or by UV irradiation. Tables 1-6 illustrate the results of color strength (K/S) for printed silk with coffee, deer blood, and red cabbage fixed thermally at 100 ° C for 30 min and by UV irradiation for 48 hours.

3.1.1. Printability of silk with coffee

Table 1 shows that the color strength (K/S) of treated silk fabric with CuONPs and printed with coffee, increases gradually with increasing the concentration of CuONPs. K/S of samples treated with O_2 plasma followed by treatment with CuONPs were higher than that treated with only CuO without subjecting to plasma. All the treated printed samples fixed thermally give color strength higher than untreated ones.

Table 1 also presents the color strength of printed silk with coffee fixed via UV irradiation for 48 hours. It can be concluded that fixation of coffee-printed silk samples with UV irradiation could improve their color strength as well as improve dye fastness properties as shown later.

Table 2 shows the printability of silk with coffee upon treatment with sonicated $CuSO_4$ solution for 10 min after pre-treatment of O_2 plasma. A high improvement in printability is noticed. The results are approximately close to that obtained upon treatment of silk with CuONPs.

Table 1: Color strength of coffee printed silk treated* with O_2 plasma / CuONPs

Type of Sample	Plasma Power (watt)	Plasma Exposure time (min)	Conc. of CuO wt. %	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	2.74	2.75
O_2 plasma-treated silk	17.35	15	zero	3.5	3.59
CuONPs treated silk	_	_	0.5 1 1.5	6.76 7.70 7.89	7.22 8.08 8.44
O_2 plasma/ CuONPs treated silk	17.35	15	0.5 1 1.5	9.43 11.79 11.94	10.01 11.98 11.96

* Treatment: 100% pick up, 120 ° C, 30 min.
Fixation: Thermally at 100 ° C, for 30 min / Ultraviolet for 48 h.

Table 2: Effect of O2 plasma/CuSO4 treatment* on printability of silk with coffee.

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. Of $CuSO_4$ (wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	5.27	5.49
O_2 plasma-treated silk	17.35	15	Zero	6.86	6.89
Treated silk with Cu SO_4 solution	_	_	0.5 1 1.5	7.01 8.25 7.99	7.9 8.79 8.21
Treated silk with O_2 plasma/$CuSO_4$	17.35	15	0.5 1 1.5	7.44 9.88 9.11	10.2 12.34 11.99

*Treatment: 100% pick up, 120 ° C, 30 min.
Fixation: Thermally at 100 ° C, for 30 min / Ultraviolet for 48 h.

3.1.2. Printability of silk with deer blood dye

Table 3 shows the color strength of silk fabric treated with O_2 plasma /CuONPs at different concentrations of NPs and printed with deer blood dye. The fixation of dye was carried out thermally at 100°C for 30 min or by subjecting it to UV irradiation for 48h. It can be observed that the enhancement in color strength (K/S) of treated silk with CuO concentration is dependent and increases gradually with increasing concentration. It is also observed that the fixation of printed silk by UV irradiation is more effective in enhancing K/S than thermal fixation. Combined O_2 plasma/CuONPs treatments give the best color strength results of deer blood dye.

Replacement of CuONPs by sonicated $CuSO_4$ solution in the treatment of silk affects positively on printability of silk with deer blood dye (Table 4). The color strength (K/S) results are promising as well as fastness properties (Table 3, 4).

Table 3: Color strength of CuONPs treated* silk printed with deer blood dye.

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. of CuO (Wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	1.76	1.84
O_2 plasma-treated silk	17.35	15	Zero	4.04	5.05
CuONPs treated silk	_	_	0.5	8.83	9.01
			1	9.48	9.99
			1.5	9.98	10.02
O_2 plasma/ CuONPs treated silk	17.35	15	0.5	11.63	12.98
			1	13.32	14.67
			1.5	14.0	15.55

*Treatment: 100% pick up, 120 ° C, 30 min.
Fixation: Thermally at 100 ° C, for 30 min / Ultraviolet for 48 h.

Table 4: Effect of O_2 plasma/$CuSO_4$ treatment* on printability of silk with deer blood dye

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. of $CuSO_4$ (wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	7.9	8.93
O_2 plasma-treated silk	17.35	15	zero	8.03	9.97
Treated silk with Cu SO_4 solution	_	_	0.5	10.51	12.95
			1	12.36	13.38
			1.5	12.5	13.98
Treated silk with O_2 plasma/$CuSO_4$	17.35	15	0.5	12.86	15.32
			1	13.73	17.21
			1.5	13.34	17.50

*Treatment: 100% pick up, 120 ° C, 30 min.
Fixation: Thermally at 100 ° C, 30 min / Ultraviolet for 48 h.

3.1.3. Printability of silk with red cabbage dye

Table 5 collects the values of color strength (K/S) of treated silk with CuONPs in the presence and absence of O_2 plasma treatments and printed with red cabbage dye. The printed silk is fixed either thermally or by subjecting it to UV irradiation. It can be seen that the K/S values of treated silk with O_2 plasma are approximately doubled compared to the untreated sample. It can be also noticed that the color strength (K/S) values increase gradually with increasing the concentration of CuONPs. The (K/S) values of printed samples fixed by UV irradiation are better than those fixed thermally. The combined O_2 plasma/ CuONPs treatment gives the best results.

3.1.4. Effect of UV exposure time on the printability of silk

Both sonicated $CuSO_4$ solution and O_2 plasma/$CuSO_4$ treatments affected markedly the color strength (K/S) of printed silk with coffee and deer blood which are fixed at different times of UV irradiation (Table 6). It was also noticed that increasing UV exposure time from 18 to 48h enhances slightly the K/S values. It could be concluded from Tables 1-6 that the printed samples with natural dyes which were fixed via UV irradiation have relatively higher color strength than their corresponding samples fixed thermally.

3.2. Fatness Properties

Tables 7-16 presented the fastness properties of treated silk with CuONPs and sonicated CuSO4 solution either without or with O_2 plasma exposure. The washing (Alt, St), rubbing (Dry, Wet), perspiration (Acid, Alkali), and light fastness properties were examined. Tables 7-12 give the fastness properties of CuONPs treated silk printed with coffee, deer blood, and red cabbage, followed by fixation either; thermally or by UV irradiation. Tables 13-16 give the corresponding values when silk is treated with sonicated $CuSO_4$ solutions and printed with coffee and deer blood dyes. All fastness properties of treated silk were found to be improved upon applying these treatments either by NPs only or combined with O_2 plasma CuONPs. Most values of washing, rubbing, and perspiration fastness are 5 or 4-5 compared to 3-4 or 2-3 for untreated ones. While the light fastness ranged between 6-7 and 7 for treated samples compared to 5-6 for untreated one. It was also observed that treatment of silk with O_2 plasma followed by treatment with Cu NPs either in the form of CuO or $CuSO_4$ is found to give the highest fastness values. Also, the fixation of printed samples with all applied natural dyes via UV irradiation is better than thermos-fixation.

Table 5: Printability with red cabbage of CuONPs treated* silk

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	Conc. Of CuO (Wt. %)	K/S	
				Fixed thermally	Fixed by UV
Untreated silk	-	-	Zero	1.75	2.14
O2 plasma-treated silk	17.35	15	zero	3.59	4.77
CuONPs treated silk	_	_	0.5 1 1.5	6.49 6.98 6.89	7.33 8.78 9.09
O2 plasma/ CuONPs treated silk	17.35	15	0.5 1 1.5	7.33 8.32 9.18	9.38 10.98 11.77

*Treatment: 100% pick up, 120 º C, 30 min.
Fixation: Thermally at 100 º C, for 30 min / Ultraviolet for 48 h.

Table 6: Printability of treated* silk with sonicated CuSO4 at different UV exposure times

Type of Sample	Plasma Power (watts)	Plasma Exposure time (min)	CuSO4 conc wt.%	K/S at different UV exposure times (hours)					
				Coffee			Deer blood		
				18h	24h	48h	18h	24h	48h
Untreated silk	-	-	-	5.18	5.23	5.49	8.5	8.81	8.93
O2 plasma-treated silk	17.35	15	-	6.34	6.56	6.86	9.56	9.85	9.97
Treated silk with CuSO4	_	_	0.5	7.47	7.88	7.9	12.69	12.9	12.95
			1.0	8.36	8.68	8.79	13.35	13.43	13.38
			1.5	7.97	8.01	8.21	16.98	17.01	17.5
O2 plasma/ CuSO4 treated silk	17.35	15	0.5	9.97	9.99	10.2	14.64	15.01	15.32
			1.0	11.69	12.01	12.34	16.76	16.98	17.21
			1.5	10.95	11.3	11.99	16.98	17.01	17.5

*Treatment: 100% pick up, 120 º C, 30 min.

Table 7: Fastness properties of CuONPs treated* silk fabrics printed with coffee dye fixed** thermally

Type of sample	Conc CuO Wt. %	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6

Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	4-5	4	4	4-5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	4-5	5	5	4-5	4-5	6-7
Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	4-5	5	5	4-5	4-5	5	7
Treated silk with CuONPs	1.5	-	-	5	5	4-5	5	4-5	5	7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	5	5	4-5	5	4-5	4-5	7

*Treatment: 100% pick up, 120 º C, 30 min.
**Fixation: Thermally at 100 º C, for 30 min.

Table 8: Fastness properties of CuONPs treated* silk fabrics printed with coffee dye fixed** by UV irradiation.

Type of sample	Conc wt% CuONPs	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	4-5	4-5	5	4-5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	5	5	5	4-5	5	7
Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	5	5	5	5	4-5	5	7
Treated silk with CuONPs	1.5	-	-	5	5	4-5	5	4-5	5	6-7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	5	4-5	5	5	5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: UV for 48 h.

Table 9: Fastness properties of CuONPs treated* silk fabrics printed with deer blood dye fixed** thermally.

Type of sample	Conc wt% CuONPs	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	5	5	4-5	5	6-7
Treated silk with CuONPs	1.0	-	-	5	4-5	5	4-5	4-5	5	7

Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	4-5	4-5	4-5	4-5	5	5	7
Treated silk with CuONPs	1.5	-	-	4-5	4-5	5	5	4-5	4-5	6-7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	5	4-5	4-5	5	5	4-5	6-7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: Thermally at 100 o C, for 30 min.

Table 10: Fastness properties of CuONPs treated* silk fabrics printed with deer blood dye fixed** by UV.

Type of sample	Conc wt% CuONPs	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	4-5	4-5	5	5	4-5	6-7
Treated silk with CuONPs	1.0	-	-	5	5	5	5	4-5	5	7
Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	4-5	4-5	4-5	5	5	5	7
Treated silk with CuONPs	1.5	-	-	4-5	5	5	5	5	4-5	7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	5	5	5	5	5	4-5	6-7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: UV for 48 h.

Table 11: Fastness properties of CuONPs treated* silk fabrics printed with cabbage dye fixed** thermally.

Type of sample		Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs	0.5	17.35	15	4-5	5	4-5	5	4-5	5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	4-5	4-5	4-5	5	4-5	6-7
Treated silk with O2 plasma/ CuONPs	1.0	17.35	15	5	5	4-5	5	5	4-5	6-7
Treated silk with CuONPs	1.5	-	-	5	4-5	5	4-5	5	4-5	7
Treated silk with O2 plasma/ CuONPs	1.5	17.35	15	4-5	4-5	4-5	4-5	4-5	4-5	6-7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: Thermally at 100 o C, for 30 min.

Table 12: Fastness properties of CuONPs treated* silk fabrics printed with red cabbage dye fixed** by UV irradiation

Type of sample				Washing fastness	Rubbing fastness	Perspiration fastness	Lightfastness

	Conc wt% of CuONPs	Plasma power (watt)	Exposure time (min)	Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuONPs	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuONPs		17.35	15	5	5	4-5	5	4-5	5	6-7
Treated silk with CuONPs	1.0	-	-	4-5	5	5	5	5	5	6-7
Treated silk with O2 plasma/ CuONPs		17.35	15	5	5	5	5	5	4-5	7
Treated silk with CuONPs	1.5	-	-	5	5	4-5	5	4-5	4-5	6-7
Treated silk with O2 plasma/ CuONPs		17.35	15	5	4-5	5	4-5	4-5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: UV for 48 h.

Table 13: Fastness properties of CuSO4 treated* silk fabrics printed with coffee dye fixed** thermally

Type of sample	Conc wt.% of CuSO4	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO4	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4	4	4	6-7
Treated silk with CuSO4	1.0	-	-	4-5	4-5	5	5	4-5	4-5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	5	4-5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	4-5	5	4-5	5	4-5	4-5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	4-5	5	4-5	4-5	7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: Thermally at 100 o C, 30 min.

Table 14: Fastness properties of CuSO4 treated* silk fabrics printed with coffee dye fixed** by UV irradiation.

Type of sample	Conc wt.% of CuSO4	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO4	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7

Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4-5	5	4-5	6-7
Treated silk with CuSO4	1.0	-	-	4-5	5	5	5	4-5	5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	5	5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	4-5	5	4-5	5	4-5	5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	5	5	5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: UV for 48 h.

Table 15: Fastness properties of CuSO4 treated* silk fabrics printed with deer blood dye fixed** thermally

Type of sample	Conc wt% of CuSO4	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO4	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4	4	4	7
Treated silk with CuSO4	1.0	-	-	4-5	4-5	4-5	4-5	4-5	5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	5	4-5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	5	4-5	4-5	4-5	4-5	5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	4-5	5	4-5	4-5	7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: Thermally at 100 o C, for 30 min.

Table 16: Fastness properties of CuSO4 treated silk fabrics printed with deer blood dye fixed by UV irradiation.

Type of sample	Conc wt.% of CuSO4	Plasma power (watt)	Exposure time (min)	Washing fastness		Rubbing fastness		Perspiration fastness		Lightfastness
				Alt	St	dry	wet	acid	alkali	
Untreated silk	-	-	-	3-4	4	2-3	3	3-4	3-4	5-6
Treated silk with O2 plasma	-	17.35	15	4	4	3-4	3-4	4	4	6
Treated silk with CuSO4	0.5	-	-	4	4-5	3-4	4	4	4-5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	4-5	5	4-5	4-5	5	4-5	6-7
Treated silk with CuSO4	1.0	-	-	4-5	5	4-5	5	4-5	5	6-7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	5	4-5	5	4-5	5	7
Treated silk with CuSO4	1.5	-	-	5	5	4-5	5	4-5	5	7
Treated silk with O2 plasma/ CuSO4		17.35	15	5	4-5	5	5	5	5	7

*Treatment: 100% pick up, 120 o C, 30 min.
**Fixation: UV for 48 h.

4. Conclusion

The color strength of samples treated with O2 plasma followed by treatment with CuONPs was higher than that treated with only CuO without subjecting to plasma.

The treated printed samples with coffee fixed via UV irradiation for 48 hours have higher color strength values compared to thermally fixed samples that acquired color strength higher than untreated ones.

It can be concluded that fixation of coffee-printed silk samples with UV irradiation not only improves their color strength but also improves dye fastness properties.

The enhancement in color strength (K/S) of treated silk with CuO is dependent to a great extent on its concentration and increases gradually. Combined O2 plasma/CuONPs treatments give the best color strength results of deer blood dye.

The K/S values of treated silk with O2 plasma and printed with red cabbage dye are approximately doubled compared to the untreated sample and it increases gradually with increasing the concentration of CuONPs.

All fastness properties of treated silk were improved upon applying these treatments either by NPs only or combined with O2 plasma Cu NPs. Most values of washing, rubbing, and perspiration fastness are 5 or 4-5 compared to 3-4 or 2-3 for untreated ones.

Light fastness ranged between 6-7 and 7 for treated samples compared to 5-6 for untreated ones. Also, the treatment of silk with O2 plasma followed by treatment with Cu NPs either in the form of CuO or CuSO4 gives the highest fastness values. As well as fixation of printed samples with all applied natural dyes via UV irradiation is better than thermos-fixation.

5. Funds

There is no available fund

Acknowledgments

The authors are gratefully grateful to acknowledge the Faculty of Applied Arts, Helwan University. Furthermore, the authors are gratefully grateful to acknowledge the Central Labs Services (CLS) and Centre of Excellence for Innovative Textiles Technology (CEITT) in Textile Research and Technology Institute (TRTI), National Research Centre (NRC) for the facilities provided.

6. Author Declarations

The authors declare that the data supporting the findings of this study are available in the article

The authors declare that there is no conflict of interest.

7. References

[1]. N. Karthikeyan, K.A. Vijayalakshmi, K. Vignesh, Study on nano particles coated viscose fabric using low temperature plasma, International Journal of Chemical and Physical Sciences 4(6) (2015) 94-98.

[2]. N. Zakaria, A. Shahin, H. Othman, A.G. Hassabo, Enhancing the properties of textile fabrics using plasma technology, Egy. J. Chem. (2024) -.

[3]. L. Guo, W. Yuan, Z. Lu, C.M. Li, Polymer/nanosilver composite coatings for antibacterial applications, Colloids and Surfaces A: Physicochemical and Engineering Aspects 439 (2013) 69-83.

[4]. W. Yu, T. Kuzuya, S. Hirai, Y. Tamada, K. Sawada, T. Iwasa, Preparation of ag nanoparticle dispersed silk fibroin compact, Appl. Surf. Sci. 262 (2012) 212-217.

[5]. K.A. Abdel Salam, N.A. Ibrahim, D. Maamoun, S.H. Abdel Salam, A.I. Fathallah, M.S. Abdelrahman, H. Mashaly, A.G. Hassabo, T.A. Khattab, Anti-microbial finishing of polyamide fabric using titanium dioxide nanoparticles, J. Text. Color. Polym. Sci. 20(2) (2023) 171-174.

[6]. E.F. Attia, T.W. Helal, L.M. Fahmy, M.A. Wahib, M.M. Saad, S. Abd El-Salam, D. Maamoun, S.A. Mahmoud, A.G. Hassabo, T.A. Khattab, Antibacterial, self-cleaning, uv protection and water repellent finishing of polyester fabric for children wheelchair, J. Text. Color. Polym. Sci. 20(2) (2023) 181-188.

[7]. M. Mahmoud, N. Sherif, A.I. Fathallah, D. Maamoun, M.S. Abdelrahman, A.G. Hassabo, T.A. Khattab, Antimicrobial and self-cleaning finishing of cotton fabric using titanium dioxide nanoparticles, J. Text. Color. Polym. Sci. 20(2) (2023) 197-202.

[8]. A.L. Mohamed, T.A. Khattab, A.G. Hassabo, Color-tunable encapsulated perylene-labeled silica fluorescent hybrid nanoparticles, Results in Chemistry 5 (2023) 100769.

[9]. A.L. Mohamed, A.G. Hassabo, Composite material based on pullulan/silane/zno-nps as ph, thermo-sensitive and antibacterial agent for cellulosic fabrics, Adv. Nat. Sci.: Nanosci. Nanotechnol. 9(4) (2018) 045005 (1-9).

[10]. A.L. Mohamed, A.G. Hassabo, Core–shell titanium@silica nanoparticles impregnating in poly (itaconic acid)/poly (n-isopropylacrylamide) microgel for multifunctional cellulosic fabrics, J. Polym. Res. 29(2) (2022) Article number: 68 (1-18).

[11]. N.A. Ibrahim, A.A. Nada, A.G. Hassabo, B.M. Eid, A.M. Noor El-Deen, N.Y. Abou-Zeid, Effect of different capping agents on physicochemical and antimicrobial properties of zno nanoparticles, Chem. Pap. 71(7) (2017) 1365-1375.

[12]. A.L. Mohamed, A.G. Hassabo, Engineered carbohydrate based material/silane as a thermo and ph-

sensitive nanogel containing zinc oxide nanoparticles for antibacterial textile, International Conference on Medical Textiles and Healthcare Products (MedTex 2015), Department of Material and Commodity Sciences and Textile Metrology, Faculty of Material Technologies and Textile Design, Lodz University of Technology, Lodz, Poland, 2015.
[13]. A.G. Hassabo, A.A. Nada, H.M. Ibrahim, N.Y. Abou-Zeid, Impregnation of silver nanoparticles into polysaccharide substrates and their properties, Carbohydrate Polymers 122 (2015) 343-350.
[14]. A.L. Mohamed, M.E. El-Naggar, T.I. Shaheen, A.G. Hassabo, Laminating of chemically modified silan based nanosols for advanced functionalization of cotton textiles, Int. J. Biol. Macromol. 95 (2017) 429–437.
[15]. A.L. Mohamed, T.A. Khattab, M.F. Rehan, A.G. Hassabo, Mesoporous silica encapsulating zns nanoparticles doped cu or mn ions for warning clothes, Results in Chemistry 5 (2023) 100689.
[16]. A.L. Mohamed, A.G. Hassabo, Modified cellulose acetate membrane for industrial water purification, Egy. J. Chem. 65(13) (2022) 53-70.
[17]. A.G. Hassabo, S. Shaarawy, A.L. Mohamed, A. Hebiesh, Multifarious cellulosic through innovation of highly sustainable composites based on moringa and other natural precursors, Int. J. Biol. Macromol. 165 (2020) 141-155.
[18]. 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, Adv. Nat. Sci.: Nanosci. Nanotechnol. 9(3) (2018) 035014.
[19]. A.G. Hassabo, A.L. Mohamed, Novel flame retardant and antibacterial agent containing mgo nps, phosphorus, nitrogen and silicon units for functionalise cotton fabrics, Biointerf. Res. Appl. Chem. 9(5) (2019) 4272 - 4278.
[20]. A.L. Mohamed, M.E. El-Naggar, T.I. Shaheen, A.G. Hassabo, Novel nano polymeric system containing biosynthesized core shell silver/silica nanoparticles for functionalization of cellulosic based material, Microsys. Technol. 22(5) (2016) 979-992.
[21]. A.G. Hassabo, A.L. Mohamed, T.A. Khattab, Preparation of cellulose-based electrospun fluorescent nanofibres doped with perylene encapsulated in silica nanoparticles for potential flexible electronics, Luminescence 37(1) (2022) 21-27.
[22]. A.L. Mohamed, M.E. El-Naggar, A.G. Hassabo, Preparation of hybrid nano-particles to enhance the electrical conductivity and performance properties of cotton fabrics, Journal of Materials Research and Technology 12 (2021) 542-554.
[23]. M.E. El-Naggar, A.G. Hassabo, A.L. Mohamed, T.I. Shaheen, Surface modification of sio2 coated zno nanoparticles for multifunctional cotton fabrics, J. Colloid Interface Sci. 498 (2017) 413-422.
[24]. A.G. Hassabo, E.M. Reda, H. Ghazal, H.A. Othman, Synthesis of agnps and znonps using tea leaves extract and their utilization to improve dyeability, printability and functionality of cotton and wool fabrics, Inorg. Chem. Commun. 150 (2023) 110525.
[25]. M. Zayed, H. Ghazal, H.A. Othman, A.G. Hassabo, Synthesis of different nanometals using citrus sinensis peel (orange peel) waste extraction for valuable functionalization of cotton fabric, Chem. Pap. 76(2) (2022) 639-660.
[26]. A.P. Periyasamy, H. Venkatesan, Eco-materials in textile finishing, Handbook of ecomaterials (2019).
[27]. D.M. Hamdy, H.A. Othman, A.G. Hassabo, A recent uses of plasma in the textile printing J. Text. Color. Polym. Sci. 19(1) (2022) 1-10.
[28]. E. Abdel-Aziz, M. Bakr, M. Zayed, H. Othman, A.G. Hassabo, Microencapsulation and its application in textile wet processing: A review, J. Text. Color. Polym. Sci. 19(2) (2022) 189-202
[29]. E. El-Sayed, A.G. Hassabo, Recent advances in the application of plasma in textile finishing, J. Text. Color. Polym. Sci. 18(1) (2021) 33-43.
[30]. A.G. Hassabo, M. Bakr, M. Zayed, H.A. Othman, Review on some fabric pretreatment via plasma to improve their printability using various types of colorants and dyes, Materials International (Accept 2022).
[31]. M. Abd El-AAty, M. Mohamed, A. Hashad, S. Moawaed, A.G. Hassabo, H. Othman, E. Abdel-Aziz, Investigation of the discharge printing of cotton and silk fabrics dyed with reactive and natural dyes, J. Text. Color. Polym. Sci. 19(2) (2022) 203-210.
[32]. W. Shao, F. Gu, C. Li, M. Lu, Highly efficient dye-sensitized solar cells by using a mesostructured anatase tio2 electrode with high dye loading capacity, Indust. Eng. Chem. Res. 49(19) (2010) 9111-9116.
[33]. Y. Gao, R. Cranston, Recent advances in antimicrobial treatments of textiles, Textile Research Journal 78(1) (2008) 60-72.
[34]. E. Abd El-Aziz, S.S. El-Desoky, G.A. El-Bahrawy, H.A. Ezat, R. Abd El-Rahman, A. abdelraouff, A.G. Hassabo, Nanotechnology to improve the performance of silk fabric, J. Text. Color. Polym. Sci. 21(1) (2024) 33-38.
[35]. E. Abd El-Aziz, H.A. Ezat, R. Abd El-Rahman, A. abdelraouff, S.S. El-Desoky, G.A. El-Bahrawy, A.G. Hassabo, Improve the quality of coloring performance of silk fabric, J. Text. Color. Polym. Sci. 21(1) (2024) 11-22.
[36]. H. Othman, H.A. Ezat, S.S. Moawaed, R. Abd El-Rahman, A. abdelraouff, S.S. El-Desoky, G.A. El-Bahrawy, A.G. Hassabo, Various printing techniques of silk fabric to enhancing its performance properties, J. Text. Color. Polym. Sci. 21(1) (2024) 23-32.

[37]. H. Othman, N. Gamal, A. Sediek, F. Saad, B.M. Hegazy, H.M. Elmorsy, A.G. Hassabo, Printing techniques of silk fabric, J. Text. Color. Polym. Sci. 21(1) (2024) 1-10.
[38]. W.M. Raslan, A.A. El-Halwagy, H.S. El-Sayad, Recent advances in plasma/nanoparticles treatments of textile fibers, J. Text. Color. Polym. Sci. 17(2) (2020) 87-105.
[39]. H.M. Ahmed, H. El-Sayad, W. Raslan, U. Rashed, A. El-Halwagy, Natural dyes printability of modified silk fabric with plasma/nano particles of metal oxides, Egy. J. Chem. 65(12) (2022).
[40]. L.E. Román, E.D. Gomez, J.L. Solís, M.M. Gómez, Antibacterial cotton fabric functionalized with copper oxide nanoparticles, Molecules 25(24) (2020) 5802.
[41]. A.G. Hassabo, M.E. El-Naggar, A.L. Mohamed, A.A. Hebeish, Development of multifunctional modified cotton fabric with tri-component nanoparticles of silver, copper and zinc oxide, Carbohydrate Polymers 210 (2019) 144-156.
[42]. L. Tamayo, M. Azócar, M. Kogan, A. Riveros, M. Páez, Copper-polymer nanocomposites: An excellent and cost-effective biocide for use on antibacterial surfaces, Materials Science and Engineering: C 69 (2016) 1391-1409.
[43]. A.A. Ragheb, S. Tawfik, J.I.A.E. Thalouth, M.M. Mosaad, Development of printing natural fabrics with curcuma natural dye via nanotechnology, International Journal of Pharmaceutical Sciences and Research 8(2) (2017).
[44]. S.A. Ebrahim, H.A. Othman, M.M. Mosaad, A.G. Hassabo, Eco-friendly natural thickener (pectin) extracted from fruit peels for valuable utilization in textile printing as a thickening agent, Textiles 3(1) (2023) 26-49.
[45]. F. Saad, A.L. Mohamed, M. Mosaad, H.A. Othman, A.G. Hassabo, Enhancing the rheological properties of aloe vera polysaccharide gel for use as an eco-friendly thickening agent in textile printing paste, Carbo. Polym. Technol. App. 2 (2021) 100132.
[46]. F. Saad, A.G. Hassabo, H.A. Othman, M.M. Mosaad, A.L. Mohamed, Improving the performance of flax seed gum using metal oxides for using as a thickening agent in printing paste of different textile fabrics, Egy. J. Chem. 64(9) (2021) 4937 - 4954.
[47]. P. Kubelka, F. Munk, Ein beitrag zur optik der farbanstriche, Z. Tech. Phys. 12 (1931) 593.
[48]. K.T. Mehta, M.C. Bhavsar, P.M. Vora, H.S. Shah, Estimation of the kubelka--munk scattering coefficient from single particle scattering parameters, Dyes Pigm. 5(5) (1984) 329-340.
[49]. AATCC Test Method (61-2013), Color fastness to laundering: Accelerated, Technical Manual Method American Association of Textile Chemists and Colorists, 2017, p. 108.
[50]. AATCC Test Method (8-2016), Colorfastness to crocking, crockmeter method, Technical Manual Method American Association of Textile Chemists and Colorists, 2018, pp. 17-19.
[51]. AATCC Test Method (16.1-2014), Colour fastness to light: Outdoor, Technical Manual Method American Association of Textile Chemists and Colorists, 2015, pp. 33-48.