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Dyeing of polyester with disperse dyes: Part 3. Characterization of ZnO nanoparticles treated polyester fabrics for antibacterial, self-cleaning and UV protective

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Abstract: The aim of this study is to utilize (ZnO) nanoparticles for obtaining the added value of the dyed fabrics. The average size of nano ZnO particles used is less than 100 nm. Polyester fabrics were treated with ZnO nanoparticles to improve its light fastness, antibacterial activities, UV-protective, self-cleaning.

Keywords: Nanotechnology; UV-protective; Self-cleaning; Polyester fabrics; light fastness.

Introduction

Last decade ZnO nanoparticles are studied materials attributable to their exceptional antibacterial activities, optical, and photocatalytic [1,2,3]. Decomposition of ozone layer has become risky to human life. As ultraviolet radiation generates free radicals, durable exposure of human skin to ultraviolet radiation can be the occasion of a series pessimistic health belongings such as aging, skin cancer, and skin reddening[4]. The ultraviolet radiation can broadcast through fabrics, consequently, to build up ultraviolet -protective textile fabrics is of great value. ZnO nanoparticles have well-organized ultraviolet absorptivity, hence, they were extensively used to produce ultraviolet-protective materials, self-cleaning and antibacterial activities[5,6,7]. In the current study, we have treated polyester fabrics with ZnO nanoparticles, for enhancing antibacterial activities, ultraviolet-protective, self-cleaning and better light fastness for polyester fabrics. The optimum ratio of ZnO nanoparticles were investigated.

Experimental

Fabrics

Scoured and bleached 100% polyester fabric was supplied by El-Mahalla El-Kobra Company, Egypt. The fabrics were scoured in aqueous solution having a liquor ratio of 1:50 and containing 2 g/L of nonionic detergent solution (Hostapal; Clariant, Swiss) and 2 g/L of Na_2CO_3 at 50 °C for 30 min to remove waxes and impurities, then rinsed thoroughly in cold tap water, and dried at room temperature.

Dyeing process

All dyes were used as pure powder in the same form as prepared without milling. Fabric samples (2 g) were introduced into a flask containing a dyebath of 2% (o.w.f) dye shade and Matexil DA-N (supplied by ICI Company, UK) as dispersing agent at 130 °C with a 1:50 liquor ratio; during dyebath preparation, the dye was mixed with 10 drops of DMF and then mixed with dispersing agent, and water was added to prepare a homogeneous dispersion of the dye. The pH was adjusted to 4.5 by using acetic acid. At the end of the dyeing process, the dyed samples were removed, rinsed in warm water, and subjected to reduction clearing in a solution comprising 2 g/L of sodium hydrosulphite and 2g/L of sodium hydroxide (caustic soda) for 10 min at 60 °C, with a liquor ratio of 1:40, and the reduction-cleared sample was rinsed thoroughly in water. The dyed samples were removed, rinsed in tap water, and allowed to dry in the open air.

Color Measurements

The colorimetric parameters of the dyed polyester fabrics were determined on a reflectance spectrophotometer. The color yields of the dyed samples were determined by using the light reflectance technique performed on an UltraScan PRO D65 UV/VIS Spectrophotometer. The color strengths, expressed as K/S values, were determined by applying the Kubelka-Munk equation [8].

$$K/S = (1- R)^2 / 2R$$

Where, R is the reflectance of colored samples and K and S are the absorption and scattering coefficients, respectively.

CIE Lab Difference

$$\Delta E=[\Delta L^2+\Delta a^2+\Delta b^2]^{½}$$

ΔE: the total color difference between the sample and the standard: (*L*) represents the white-black axis, (*a*) represents the red-green axis and finally (*b*) represents the yellow-blue axis.

Color fastness to light

The light fastness test was carried out in accordance with the ISO 105-B02:1988 test method [9], using a carbon arc lamp and continuous light for 35 h. The effect on the color of the tested samples was recorded by reference to the blue scale for color change.

Fabric Treatment with zinc oxide

Pre-treatment

The fabric samples were soaked for 10 min. in 10 g/l nonionic detergent solution (Hostapal, Clariant), dispersion of ZnO nanoparticles (0-2.5% w/w) under gentle stirring for 15 min. The fabrics were squeezed to remove the excess dispersion and dried in an oven at 70 ºC for 10 min. The fabrics were querying at 140 ºC for 3 min. The fabrics were washed in aqueous solution with a liquor ratio1:50 containing 3 g/l nonionic detergent solution (Hostapal, Clariant) at 60 ºC for 15 min.

Post-treatment

The fabric samples were soaked for 10 min. in 10 g/l nonionic detergent solution (Hostapal, Clariant), dispersion of ZnO nano particles (0-2.5% w/w) under gentle stirring for 15 min after dyeing. The fabrics were squeezed to remove the excess dispersion and dried in an oven at 70 ºC for 10 min. The fabrics were querying at 140 ºC for 3 min. The fabrics were washed in aqueous solution with a liquor ratio1:50 containing 3 g/l nonionic detergent solution (Hostapal, Clariant) at 60 ºC for 15 min.

UV- blocking measurements of nano ZnO treated polyester fabrics

UV-blocking measurements were performed by measuring transmittance with duple beam UV-Vis. spectrophotometer attached with integrating sphere at National Institute for Standards, Cairo, Egypt [10].

Photo-induced Discoloration onto polyester Fabric

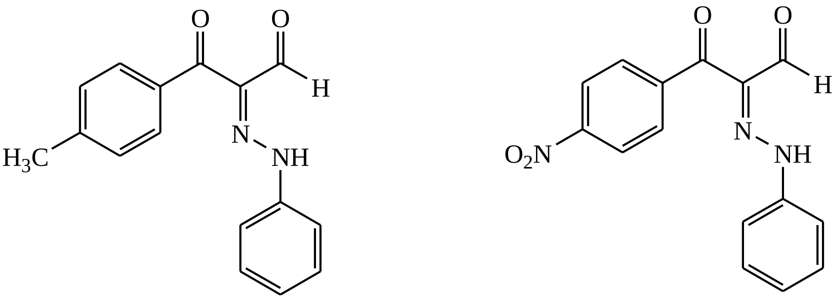
60 µl coffee or methyl red (2.5 g/10 ml) were spotted on untreated and ZnO treated polyester fabric. The samples were irradiated by UV lamp for 24 hours.

Antimicrobial Activities Test

The antimicrobial activity of the dyed polyester fabrics were detected against some pathogenic microorganisms namely, *Staphyllococcus aureus, Candida albicans, Escherchia coli, Bacillus subtilis* and *Klebsiella pneumoniae.* These microorganisms were provided by Soil Microbiology Unit, Desert Research Center, Cairo, Egypt. The antimicrobial activity was determined by agar diffusion technique using filter paper discs[11, 12].

Results and Discussion

Disperse dyes **1**, **2** have been recently synthesized by us[13, 14] *via* coupling of enaminones with phenyl diazonium salts, hence these disperse dyes were applied for dyeing polyester fabrics (Figure 1).



1 **2**

Figure 1: Disperse dyes 1 and 2

Herein, in an attempt to improve the light fastness of the dyed samples and also to acquire added-value, e.g. antibacterial, self cleaning and UV protective, zinc oxide nanoparticles was used. To optimize the ZnO nanoparticles ratio of the treated polyester fabrics, color strength (K/S) and the color difference ΔE were measured.

UV protective properties of untreated and treated polyester fabrics with ZnO nanoparticles

To acquire ultraviolet-protective properties, ultraviolet protection factor (UPF) was measured. UPF is a factor that gives ultraviolet-protective properties of materials like polyester fabrics and is articulated as a number between 15 and 50. It is called 50+ if it has over 50 UPF. UPF factors were calculated by evaluating the transmission measurements. UV blocking measurements of ZnO nanoparticles treated polyester fabrics is given in Figure 2. The UPF data listed in Table 1 reveals that ZnO nanoparticles treated polyester fabrics have 145.51 and 173.25 for disperse dye **1** and 131.55 and 190.59 for disperse dye **2**, respectively, that indicates UPF values of post-treated is much higher than pre-treated polyester fabrics for both disperse dyes. Also, Table 1 shows that the UPF values of treated is bigger than untreated polyester fabrics 141.88 for dye **1** and 122.37 for dye **2**, respectively.

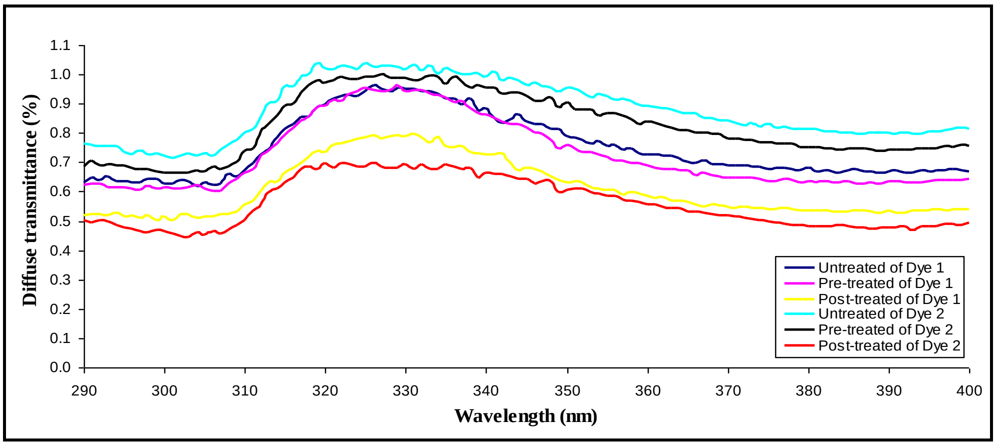


Figure. 2. UV transmission measurements of untreated, treated polyester fabrics with ZnO nanoparticles

Table 1: UPF parameters of blank, untreated, treated polyester fabrics with ZnO nanoparticles

Dye No	Treatment	ZnO %	UPF (Ultraviolet Protection Factor)
1	Blank	0	19.420
	Untreated	0	141.88
	Pre-treated	2.5	145.51
	Post-treated	2.0	173.25
2	Untreated	0	122.37
	Pre-treated	2.5	131.55
	Post-treated	2.5	190.59

Self-cleaning of untreated and treated polyester fabrics with ZnO nanoparticles

One of the efficiencies of nanoparticles treated polyester fabrics is transforming the absorbed light into the self-cleaning materials to disband its stain. Photodegradation of coffee and methyl red adsorbed on nano ZnO treated polyester fabrics was investigated to obtain self-cleaning properties of nano ZnO particles. Tables 2, 3 shows the effect of coffee and methyl red stains on ZnO nanoparticles treated polyester fabrics after 24 hours ultraviolet-irradiation. A partial discoloration of coffee and methyl red stains induced by ultraviolet-light was observed for ZnO nanoparticles treated polyester fabrics. The treatment of polyester fabric with ZnO nanoparticles is led to the formation of thin layer ZnO nanoparticles which rises its hydrophobic properties. The idea of produce hydrophobic surfaces was enlarged derived from Lotus effect [15]. A hydrophobic surface prevents the adsorption of dirt, leaving the surface of polyester clean all times. It was found that the highest photodegradation percentage on surface as 60-70% at the end of 24 hours for coffee and methyl red stains. The photocatalytic mechanism is established that when light with energy higher or equal to the band gap lighten on nano ZnO particles, an electron(e^-) in the valence band (VB) can be agitated to the conduction band (CB) with the simultaneous generation of a hole (h^+) in the valence band, hence electron–hole pairs ($e^- h^+$) exist. The holes and electrons might create ($O_2^{-\bullet}$) and $OH^\bullet$ radicals, which have high oxidative properties that might easily corrupt molecules like coffee and methyl red[16-18].

Table 2: Effect of Coffee Stain on ZnO nanoparticles treated polyester fabrics

Dye No	Treatment	ZnO %	L*	a*	b*	ΔE*	K/S
1	Pre-treated	untreated	81.87	-6.82	60.22	66.77	5.98
		0.5	82.21	-6.46	50.82	57.41	3.45
		1.0	82.26	-7.20	45.31	52.1	2.78
		1.5	82.86	-6.31	50.94	57.45	3.45
		2.0	83.64	-6.95	48.29	54.85	2.82
		2.5	83.17	-7.13	52.13	58.71	3.61
	Post-treated	0.5	83.28	-6.60	47.6	54.16	2.88
		1.0	83.57	-6.91	46.08	52.67	2.66
		1.5	83.62	-7.12	46.47	53.09	2.86
		2.0	83.50	-6.97	46.51	53.12	2.78
		2.5	82.10	-6.04	57.00	63.47	4.99
2	Pre-treated	untreated	76.36	6.74	44.50	51.92	3.99
		0.5	76.37	6.90	46.88	54.24	4.27
		1.0	75.75	8.05	51.23	58.72	5.05
		1.5	76.97	6.00	47.73	54.85	4.31
		2.0	77.24	5.77	47.77	54.82	4.19
		2.5	76.50	7.00	53.54	60.71	4.79
	Post-treated	0.5	77.81	4.67	44.08	51.02	3.96
		1.0	77.26	5.53	44.66	51.76	3.90
		1.5	76.44	5.22	42.80	50.11	4.24
		2.0	77.50	5.21	43.15	50.21	3.95
		2.5	75.79	6.70	49.07	56.47	4.88

Table 3: Effect of Methyl red Stain on ZnO nanoparticles treated polyester fabrics

Dye No	Treatment	ZnO %	L*	a*	b*	ΔE*	K/S
1	Pre-treated	untreated	82.4	-6.8	60.74	67.23	5.63
		0.5	82.34	-6.21	54.71	61.21	4.36
		1.0	83.35	-6.81	46.82	53.41	2.84
		1.5	83.45	-6.78	46.83	53.41	2.73
		2.0	83.82	-6.47	44.51	51.04	2.37
		2.5	83.43	-6.45	46.79	53.32	2.72
	Post-treated	0.5	82.99	-7.41	53.59	60.20	4.03
		1.0	83.03	-7.4	52.79	59.41	3.84
		1.5	83.13	-6.96	54.35	60.88	4.08
		2.0	82.53	-7.88	48.63	55.44	3.23
		2.5	82.85	-7.19	53.77	60.36	3.92
2	Pre-treated	untreated	77.13	5.93	42.80	50.02	3.63
		0.5	76.64	6.75	45.29	52.62	4.15
		1.0	76.27	7.17	46.96	54.36	4.37
		1.5	76.70	6.39	46.03	53.29	4.27
		2.0	77.28	5.90	45.66	52.76	3.76
		2.5	76.88	6.63	49.06	56.23	3.93
	Post-treated	0.5	77.26	5.27	47.41	54.42	4.31
		1.0	77.24	5.78	48.28	55.32	4.28
		1.5	76.00	5.63	47.05	54.37	4.43
		2.0	77.22	5.25	46.69	53.73	4.12
		2.5	76.57	5.82	53.11	60.18	5.37

Light fastness of untreated and treated polyester fabrics with ZnO nanoparticles

The color difference ΔE for all dyed samples pre- and post-treated of polyester fabrics with ZnO nanoparticles of disperse dyes **1** and **2** were measured which shows more significant results. Table 4 reveals that utilizing of ZnO nanoparticles becomes more effective in case of pre-treated polyester fabrics than post-treated samples. Moreover, the light fastness of treated polyester fabrics is higher than the untreated samples[13,14] for both disperse dyes **1** and **2** under investigation.

Table 4: Light fastness of the untreated and treated polyester fabrics with ZnO nanoparticles

Dye No	Treatment	ZnO %	ΔE*	Light Fastness
1	Pre-treated	untreated	51.61	3-4
		0.5	50.37	5
		1.0	43.49	2-3
		1.5	42.80	2-3
		2.0	47.57	3-4
		2.5	45.00	3
	Post-treated	0.5	47.58	3
		1.0	46.24	3
		1.5	47.89	3
		2.0	44.94	3
		2.5	47.45	3
2	Pre-treated	untreated	52.21	4
		0.5	54.44	5
		1.0	54.69	5
		1.5	55.70	5
		2.0	51.56	5
		2.5	52.78	4-5
	Post-treated	0.5	52.39	5
		1.0	51.97	5
		1.5	46.13	4
		2.0	49.11	4-5
		2.5	50.39	4-5

Antimicrobial activity of untreated and treated polyester fabrics with ZnO nanoparticles

The untreated and treated polyester fabrics are presented against *Bacillus subtilis* and *Staphylococcus aureus* as Gram positive, *Escherichia coli*, *Klebsiella pneumonia*e as Gram negative and *Candida albicans* as yeast, respectively. It is clear from Table 5 that untreated and post-treated with nano ZnO of polyester fabrics have not exhibit antibacterial activity against all of the microorganisms. Nano ZnO pre-treated polyester fabrics of disperse dye **1** exhibit antibacterial activity against only *Bacillus subtilis*, while nano ZnO pre-treated polyester fabrics of disperse dye **2** exhibit antibacterial activity against both *Bacillus subtilis* and *Klebsiella pneumonia*e. The pre-treated with nano ZnO of polyester fabrics have not exhibit antibacterial activity against *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans*. Nano ZnO has antibacterial activity for bacteria and its mechanism *via* either ZnO nanoparticles may influence the membrane of bacteria and slow down their growth [19, 20] or nano ZnO may provide the formation of peroxide that may afford antibacterial activities[21].

Table 5. Inhibition zone diameters of the dyed polyester fabrics of disperse dyes 1 and 2 against Gram positive, Gram negative bacteria and Yeast.

Dye No	ZnO% & Treatment	Inhibition zone diameter (Nearest mm)				
		G^+ inhibition zone		G^- inhibition zone		Yeast
		Bacillus subtilis	*Staphylococcus aureus*	*Escherichia coli*	*Klebsiella pneumoniae*	*Candida albicans*
1	Untreated	ND	ND	ND	ND	ND
	2.5 Pre-treatment	11	ND	ND	ND	ND
	2.5 Post-treatment	ND	ND	ND	ND	ND
2	Untreated	ND	ND	ND	ND	ND
	2.5 Pre-treatment	8	ND	ND	10	ND
	2.5 Post-treatment	ND	ND	ND	ND	ND

(ND) Not Detected

Conclusion

We treat polyester fabrics with ZnO microparticles to acquire polyester fabrics with added value, as better light fastness, UV irradiation protection, antibacterial and self clean. The optimum ratio of ZnO microparticles was studied. Ultraviolet protecting factor (UPF) indicating ultraviolet-blocking properties of nano ZnO treated polyester fabrics were measured as 145.51 and 173.25 for disperse dye **1** and 131.55 and 190.59 for disperse dye **2**, respectively. Also, self-cleaning ability was determined by investigating photocatalytic activity of coffee and methyl red stains. Good light fastness was obtained. Moreover, the antimicrobial activities of the dyed samples of disperse dyes against Gram positive, Gram negative bacteria and yeast were conducted.

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