Color, Fastness, Antibacterial, and Skin Sensitivity Properties of High Lightfastness Azo Disperse Dyes Incorporating Sulfamide Groups

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Abstract: A series of cationic and disperse dyes has been applied on to the nylon and acrylic fabrics in order for their dyeing properties to be investigated. The build-up values and the fastness properties of the dyed fabrics such as wash, light, and rubbing fastness degrees were measured by standard methods. Moreover, the color gamut of the synthesized dyes was measured on polyamide and acrylic fibers. The results showed that the synthesized dyes were able to dye polyamide fabrics with deep shades. However, synthesized azo dyes did not show good dyeing ability on acrylic fiber. The antimicrobial properties of dyed polyamide fabrics were evaluated against various bacteria and fungi. The dyed fabrics exhibited excellent antimicrobial efficacy against both Gram-positive, Gram-negative bacteria, and fungi. The skin irritation test on azo dyes and dyed polyamide fibers with this dye was carried out. The results showed that none of the dye and dyed polyamide fibers created any skin irritation.

Keywords: Dyeing, Polyamide and Acrylic fabrics, Antimicrobial properties, Fastness properties, Skin irritation

Introduction

Intensive research efforts have been made for the past four decades in the area of disperse dyes that have been used for the coloration of hydrophobic fabrics [1-3]. A wide range of dyes are nowadays available in the market for dyeing of nylon (polyamide) textiles and among them acid, metal complex, reactive dyes, and disperse dyes are being extensively used [4-6].

Before 1950, almost all the disperse dyes used were prepared from the anthraquinone class and had the limitations of poor discharge ability and sensitivity to oxides of nitrogen. Red and blue azo dyes with good discharge ability for use in printing were developed [7].

Investigation of the use of heterocyclic diazo components was stimulated by the discovery of Dickey JB of Eastman Kodak in 1950 [7]. In 1953, they prepared bright blue heterocyclic azo disperse dyes from 2-amino-5-nitrothiazole with adequate light fastness combined with excellent discharge ability, gas fastness, and dye ability on cellulose acetate [8]. The commercial success of such bright blue azo disperse dyes for cellulose acetate showing considerable interest in this class of dyes. With the exceptional of the 5nitro derivatives for discharge printing of dyeing cellulose acetate fabrics, 2-thiazolylazo dyes have so far achieved only secondary importance as bright blue dyes for polyester. Early dyes showed moderate light fastness on cellulose acetate and polyesters, and light fastness on polyamides was very poor [8]. Dyes with increased light fastness were prepared from aniline type coupling components containing one or more N-alkyl groups substituted with groups such as cyano, alkoxy, pyridinium, and sulfato were used as coupling components [9,10].

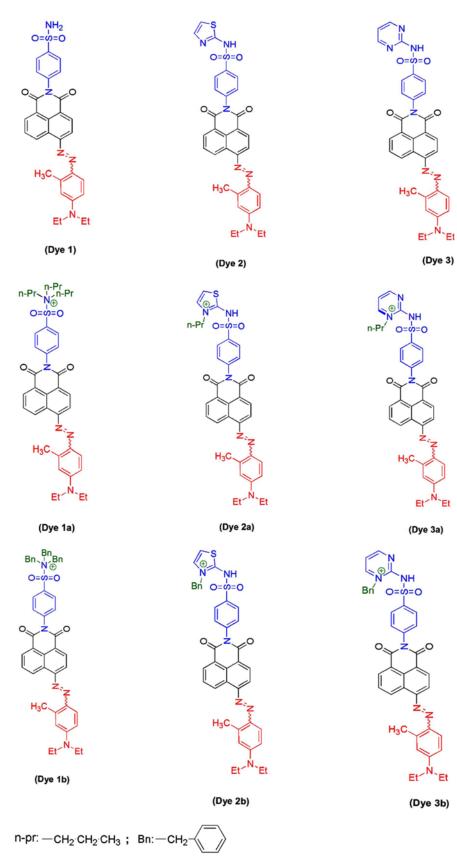
During the last ten years, the level of interest as indicated by the patent literature has grown in the field of sulfanilamide disperse dyes [11-14]. Sulfonamide azo dyes are attractive candidates to synthetic chemists due to the ability of the motif to access a wide range of functional group transformations [15-18]. Furthermore, one of the ways to increase the lightfastness property of azo dyes on fibers is to use azo dyes including sulfonamide group (sulfonamide azo dyes) [19]. These compounds also produce antimicrobial properties in the fibers. It seems that no report is available on the use of azo disperse dyes including sulfonamide moiety on fibers that improved lightfastness property and caused antimicrobial properties of the fibers. Therefore, we reported dyeing of polyamide fibers with azo disperse and azo cationic dyes whose synthesis has been published in our previous work [10] and investigated dyeing, antibacterial, antifungal, and skin sensitivity properties.

Experimental

Materials and Instrumentation

All compounds used in this study were of analytical grade unless otherwise stated. The UV-visible spectra were measured by a Cecil 9200 double beam spectrophotometer. Nylon 6 fabrics (Alyaf Co., Iran) were utilized throughout the study. The colorimetric data of the dyed fabrics were processed by a Gretag Macbeth 7000A spectrophotometer (D65 illumination, 10 ° observer). The light, wash, and rubbing fastness degrees of all the synthesized dyes were measured according to standard. Skin sensitivity test was performed on rabbit skin according to ISO 10993-10 standard. To study the antibacterial effects, the Grampositive bacteria and the Gram-negative bacteria were provided by The Culture Collection Centre, Shahid Beheshti University, Tehran, Iran.

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Scheme 1. Chemical structures of synthesized dyes (1-3, 1a-3a and 1b-3b).

Preparation of Disperse and Cationic Dyes

All azo disperse and cationic dyes used in this study were of synthetic grade. These dyes were synthesized according to our previous study (Scheme 1: dyes 1-3, 1a-3a, and 1b-3b) [10].

Preparation of Nylon and Acrylic Fabrics and Dye Dispersion

Nylon and acrylic fabrics was scoured with 5 g/l nonionic detergent at 80 °C for 30 min, liquor ratio (L:R) of 40:1, rinsed and air dried. Nine dispersions containing dye (0.5 g), dispersing agent (Lyoprint EV, Ciba, 1 g), and water (2 ml) were milled for 60 min in a mortar. The resulting mixture was diluted with 20 ml of water, transferred to a ball mill and milled again for another 20 h. The volume of the dispersion was adjusted to 100 ml and filtered through a 5 μ m Micro-Prazisions Sieb Fritsch.

Dyeing Method

Dyeing was carried out in an Infra Colour apparatus (Rossari Labtech) using liquor ratio (L:G) of 50:1, and pH was adjusted to 5-6 for acrylic and 3-4 for polyamide using acetic acid. Dyeing temperature was T=105 °C and T=100 °C for acrylic and polyamide, respectively. The concentrations of the dye dispersions were 0.1 %, 0.4 %, 0.8 %, 1.2 %, 2 %, 4 %, and 6 % owf (on the weight of fiber). The dyeing of polyamide and acrylic was carried out by raising the dye bath temperature from 40 °C to 100 °C and 105 °C, respectively, at a rate of 2 °C/min and the bath temperature was maintained at 100 °C and 105 °C for 1 h for polyamide and acrylic. After that, the bath was rapidly cooled down to 70 °C. Finally, the fabrics were washed off with cold water and dried.

Dyeing ability of various dyes was monitored by changes in dye up-take ability of substrates as expressed by color strength (*K/S*) values. *K/S* values were calculated at λ_{max} (wavelength of maximum absorption) using Kubelka-Munk equation as follows:

$$(K/S)_{\lambda max} = (1-R)^2 / 2R \tag{1}$$

where *R* is the reflectance, *K* and *S* are the absorbance and scattering coefficients, respectively.

Fastness Properties

Wash fastness was measured by the standard ISO105-A02:1993 method. The washing was conducted for 30 min at 40 °C, rinsed with cold water, air dried, and analyzed with grey scale. Light fastness test BS 1006-1990 UK-TN was evaluated with the xenon arc lamp using blue reference samples for 72 h. The rub fastness test was performed according to ISO 105-X12:1993(E) standard using a crockmeter. For the wet rub test, the testing squares were thoroughly immersed in distilled water; the rest of the procedure was the same as in the dry test. The staining on

the white test cloth was assessed according to the gray scale.

Antimicrobial Activity of the Treated Fabrics

Antimicrobial properties of treated fabrics were examined according to AATCC test method 100-2004. Antimicrobial activity was evaluated against S. aureus and M. luteus as gram-positive bacteria, E. coli and P. aeruginosa as gramnegative bacteria, and C. albicance as a fungi. In this method, about 1 g of circular fabric swatches in disposable petri dishes was challenged with 1.0 ± 0.1 ml bacteria inoculum (containing 10^{5-6} colony forming unit of bacteria). After a certain period of contact time, the challenged fabric swatches were transferred to 250 ml containers filled with 100 ml of sterilized water, and the resultant supernatant was diluted to 10^1 , 10^2 , 10^3 , and 10^4 , respectively. Then 100 ml of each dilution were placed on a nutrient agar and incubated at 37 ± 2 °C (99±3 °F) for 18-24 h [20,21]. The same procedure was applied to an untreated fabric swatch as a control. Finally, viable bacteria colonies on the agar plate were counted and the antimicrobial activity was expressed in terms of reduction of the organisms (%) after contacting test specimen compared to the number of bacterial cells surviving after contacting the control. The percentage reduction was calculated using equation (2) follows:

Reduction percentage (%) = $(A - B)/A \times 100$ (2)

where *A* and *B* represent the bacterial colonies in control and the dyed fabrics, respectively. The test was repeated three times and the results were reported as mean percentage reduction of the bacterium $\pm SD$.

Skin Sensitivity Test

The skin sensitivity test on the skin of the rabbit was carried out in accordance with ISO 10993-10 [22]. Mature rabbits weighing 2 to 3 kg were kept under human care in a laboratory with a temperature of 22 ± 2 °C and a humidity of 60-50 %. Samples of synthetic dyestuffs were tested both ointment and after application on the fabric, in the form of a dyed fabric on the skin of the rabbit. How to prepare the ointment was as follows: the first of 0.2 g of each of the synthetic dyes was spread in 1 g of glycerin to completely disperse and dissolve, and then add Vaseline about 3 grams. The dye in glycerin was completely spread in Vaseline and continued to stir for 30 min (Figure 1).

After preparing the ointment, the next step was to prepare the area for the rabbit, the hair was cut from the back of the rabbit and the skin was sterilized and prepared (Figure 1). After preparing the rabbits, the prepared ointment from each of the synthesis dyes was applied to the rabbit's skin and then the rabbits were placed in a special cage (Figure 1). Also, in order to evaluate the lack of skin sensitivities by a dyed fabric with synthesized dye, a piece of dyed product of 10×5 cm² on a rabbit skin was glued with anti-allergic adhesive (Figure 1). The criterion for creating or not creating

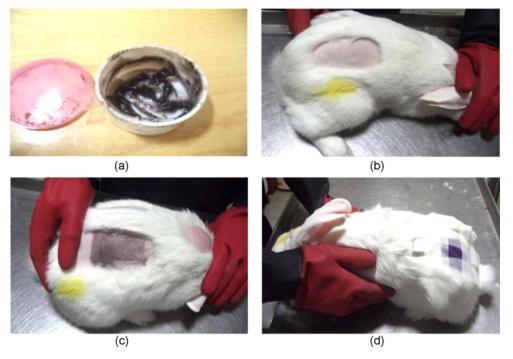


Figure 1. Prepared ointments from synthetic dyes (a), preparation of rabbits for testing (b), apply ointment made of dyes on rabbit skin (c), and how to put dyed fabric on rabbit skin (d).

skin sensitivity is the visual observation of the presence or absence of redness and swelling on the skin of rabbits. The results of visual observations were investigated at 24, 48, and 72 h.

Results and Discussion

Solvatochromic Effect

All azo dispersant and cationic dyes used in this study were synthesized according to our previous study (Scheme 1: dyes 1-3, 1a-3a, and 1b-3b) [10]. The chemical structures of synthesized dyes are illustrated in Scheme 1. The UVvisible absorption data of azo dyes were recorded in various solvents such as n-hexane, acetone, acetic acid, ethanol at a concentration of 10⁻⁵ M, and the results are summarized in Table 1. It is known that the ability of a chemical substance to change color due to a change in solvent polarity is called solvatochromism [23]. In other words, the λ_{max} shifts of the prepared dyes in various solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvent (Table 1). The absorption spectra of synthesized dyes were recorded in various solvents at a concentration of 10⁻⁵ M, their results and dielectric constant (ε) of solvents are summarized in Table 1. By changing acetic acid to DMF, positive solvatochromism was observed ($\Delta \lambda_{max}$ of 15-18 nm). The λ_{max} of the dyes in acetic acid varied from 530 to 540 nm, whereas in the more polar solvent (DMF) they lay between 547 and 558 nm. As

Table 1. λ_n	_{nax} (nm) of synt	hesized dyes i	n various solvo	ents
	Acetic acid $\varepsilon = 6.15$	Acetone $\varepsilon=20.7$	Ethanol $\varepsilon=24.5$	DMF ε=36.7
Dye 1	537	537	547	553
Dye 2	540	549	552	558
Dye 3	539	538	549	555
Dye 1a	533	531	538	549
Dye 2a	535	535	546	552
Dye 3a	534	537	539	550
Dye 1b	530	531	535	547
Dye 2b	535	535	543	550
Dye 3b	532	535	537	549

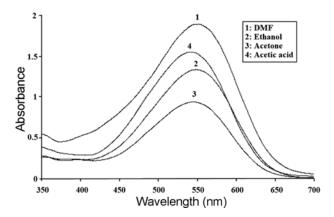


Figure 2. Absorption spectra of dye 2 in various solvents.

an example, Figure 2 shows UV-Vis absorption spectra of dye **2** in various solvents.

Colorimetric Properties

CIE Lab values of dyed polyamide and acrylic fabrics with 4 % owf dye are given in Tables 2 and 3. It is apparent that treatment with dyes resulted in noticeable changes in color of fabric. In general, dyed treated fabrics exhibited darker shades. Depending on the dyestuff used, a^* and b^* and accordingly chroma values (C^*) varied in different manner. The leveling properties of the dyes are excellent for all the synthesized dyes.

The a^* and b^* values of polyamides dyed with D_7 - D_{11} , D_{13} , and D_{14} dyes indicate that these dyes produce color in the red (*a* positive) and blue (*b* negative) range and the values of a^* and b^* of polyamides dyed with D_{12} and D_{15} show that the color of the dyed fabrics is in the red (*a* positive) and yellow (*b* positive) range. Dyed acrylic fabrics showed same pattern as dyed polyamides did.

The visual evaluation of the values of L^* , a^* , b^* , c^* , and h of dyed polyamides shows that the nature of the alkyl section in the amine group of the coupler affects the absorption and dyeing intensity and the adsorption intensities

 Table 2. Spectrophotometric data of the dyed polyamide at 1/1 standard depth

Dye	ĥ	c^{*}	b^{*}	<i>a</i> *	L^{*}	K/S
Dye 1	335.41	13.57	-4.54	12.29	40.24	5.95
Dye 2	321.86	14.52	-5.84	10.88	38.88	6.59
Dye 3	330.64	10.85	-4.18	8.48	39.12	6.06
Dye 1a	315.18	16.03	-7.06	13.63	35.87	8.21
Dye 2a	311.43	17.32	-8.68	15.34	32.46	9.54
Dye 3a	41.68	8.67	0.95	8.95	33.75	8.28
Dye 1b	331.47	15.82	-6.84	13.25	38.98	6.64
Dye 2b	316.54	15.36	-8.05	12.95	36.15	7.25
Dye 3b	42.84	9.52	0.982	7.98	36.42	7.23

 Table 3. Spectrophotometric data of the dyed acrylic at 1/1 standard depth

Standard (aopun					
Dye	ĥ	c^{*}	b^{*}	a^*	L^{*}	K/S
Dye 1	338.26	10.57	-4.12	10.42	26.64	13.75
Dye 2	330.02	17.12	-8.55	14.83	23.75	15.68
Dye 3	328.44	11.85	-5.68	9.25	29.12	15.14
Dye 1a	322.58	18.12	11.02	13.56	33.38	9.98
Dye 2a	331.53	11.22	-4.49	10.82	30.85	10.84
Dye 3a	44.06	7.15	1.23	8.83	31.19	10.01
Dye 1b	326.45	10.99	-10.35	9.97	29.65	8.28
Dye 2b	329.6	17.03	-9.3	15.26	24.21	9.45
Dye 3b	45.25	8.98	1.25	9.12	31.54	9.25

are higher and dyed fabrics are purple or reddish-purple and reddish-yellow.

Fastness Properties

Textiles are exposed to repeated washing, rubbing, and lighting during their usage. Hence, durability of the finish applied on textile materials at these conditions is very important. Fastness data of dyed nylon and acrylic fabrics, measured according to standard methods, are presented in Tables 4 and 5, respectively.

According to the results, the wash fastness of all dyes was 5 and 4-5 and their staining effect was 5 and 4-5 on polyamide and acrylic, respectively. These results show that all the dyes synthesized had excellent washing stability on polyamide and acrylic fabric. The excellent wash fastness of the dyes is mainly due to that the dyes used in the fabric are relatively large and insoluble, and its large size and insolubility in water and aqueous solutions due to high washing-resistant performance [24]. Rubbing fastness of the samples measured in dry and wet conditions was in very good level as well.

As we know, light causes electron transfer. In other words, changing the chemical structure makes changes in the absorption spectra of dyes and thus changes in their color hues. It is now well established that there is an effective relationship between the optical stability of the dyed fabrics and the physical and chemical structures of the dye and fabrics.

The optical stability of the dyes was measured according to ISO105-B02: 1994 (E). The optical stability of the dyed fabrics in this study is higher than the fabrics dyed with other naphthalimide dyes in previous investigations [25-27]. In this study, the optical stability of some dyed fabrics was 6 and a 2 degree increase in optical stability compared to previous studies. The measurement results of fastnesses on

 Table 4. Color fastness of dyed polyamide fibers at 1/1 standard depth

	Was	shing fastnes	S	Rubl fast	bing ness	Light
Dye	Change	Staini	ng	Polya	mide	fastness
	polyamide	Polyamide	Cotton	Wet	Dry	
Dye 1	5	5	5	4-5	4	4-5
Dye 2	5	5	5	4	4	6
Dye 3	4-5	5	5	4-5	4-5	5-6
Dye 1a	5	5	5	4-5	4-5	4
Dye 2a	5	5	5	3-4	4-5	4-5
Dye 3a	4-5	4-5	5	4-5	4-5	4-5
Dye 1b	5	5	5	5	4-5	4
Dye 2b	5	5	5	4-5	5	5
Dye 3b	4-5	4-5	5	4-5	5	5

	Was	shing fastı	ness	Rubbing	fastness	T 1.1.4
Dye	Change	Stair	ning	Acr	ylic	Light
	acrylic	Acrylic	Cotton	Wet	Dry	lustiless
Dye 1	5	5	5	4-5	5	4-5
Dye 2	5	5	5	5	5	5-6
Dye 3	4-5	5	5	5	5	4
Dye 1a	5	5	5	4-5	4-5	4
Dye 2a	5	5	5	4	4-5	6
Dye 3a	4-5	4-5	5	4-5	4-5	5-6
Dye 1b	5	5	5	5	5	4-5
Dye 2b	5	5	5	4-5	5	6
Dye 3b	5	4-5	5	5	5	4-5

 Table 5. Color fastness of dyed acrylic fibers at 1/1 standard depth

polyamide and acrylic are shown in Tables 4 and 5.

In general, in azo dyes, the electron acceptor groups on the diazonium salt component and the electron donations on the coupler component cause higher wavelength and higher buildup of the dye and this usually increases the dye concentration on the fabric and it enhances higher optical stability [28].

In the present study, sulfonamides are included in the imide section of the dyes which have two strong S=O receptor electron groups, these groups increase the accepting electron of the azo part, color strength, and concentration of dyes on the fabric and subsequently increased optical stability.

Dyeing Properties

In this research, after applying the synthesized dyes on polyamide fabrics, the color strength $(K/S)_{\lambda max}$ of dyed fabrics was drawn based on the concentration of dyes (Figures 3 and 4). A reflectance spectrophotometer is used for the colorimetric measurements on the dyed samples. *K/S* values given by the reflectance spectrophotometer are

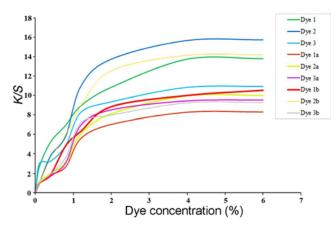


Figure 3. Build up curves of the dyes on polyamide fiber.

Figure 4. Build up curves of the dyes on acrylic fiber.

calculated at λ_{max} and are directly correlated with the dye concentration on the substrate according to the Kubelka-Munk equation.

Figures 3 and 4 illustrate the build-up curves of all dyes on nylon and acrylic fabrics. Generally, the build-up $(K/S)_{\lambda max}$ of the dyes synthesized on polyamide fabric is higher than acrylic. The factor which causes dyes to become absorbed by polyamide fabrics is that cationic dyes can bond to polyamide through ionic bonding.

The low build-up of cationic dyes synthesized on acrylic can be attributed to the presence of large groups of dye molecules that make them difficult for the dye to penetrate the fiber. In other words, the dye with larger molecules cannot easily penetrate into this fiber. As it is clear from Figures 3 and 4, they generally flatten off at dye concentrations of around 4 % owf.

Antimicrobial Properties

Numerous standard methods are being used to evaluate the antibacterial properties of textiles. In this study, antimicrobial properties of the fabrics were investigated according to AATCC test method 100-1999, a quantitative antimicrobial test method performed under dynamic contact conditions against *E. coli*, *P. aeruginosa* as negative bacteria, *S. aureus*,

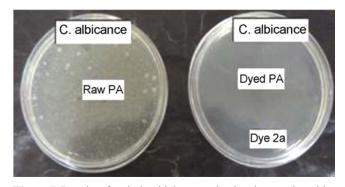


Figure 5. Results of antimicrobial test on dyed and raw polyamide against microorganism.

Dye	S. aureus	M. luteus	E. coli	P. aeruginosa	C. albicance
Dye 1	98.96±0.02	98.95±0.01	98.12±0.01	98.93±0.04	97.35±0.07
Dye 2	98.97±0.02	98.99±0.03	98.75±0.03	98.65±0.04	$97.88 {\pm} 0.05$
Dye 3	98.97±0	98.96±0.03	98.94±0.02	98.93±0.4	97.45±0.03
Dye 1a	99.65±0.04	99.85±0.02	98.88 ± 0	98.99±0.03	97.94±0.01
Dye 2a	99.99±0.04	99.99±0.01	99.97±0.02	99.93±0.03	98.86±0.03
Dye 3a	99.95±0.03	99.96±0.03	99.9±0	99.9±0.04	98.64±0.03
Dye 1b	99.89±0.03	99.9±0.03	98.98 ± 0.02	98.96±0.04	98.09 ± 0.05
Dye 2b	99.92±0.02	99.94±0.01	99.85±0.04	99.88±0.05	98.85±0.02
Dye 3b	99.89±0.03	99.86±0.01	99.65±0.05	89.54±0.04	98.59±0.06
Raw polyamide	-	-	-	-	-

Table 6. Antimicrobial efficacy of the dyed polyamide fabrics with various dyes

M. luteus as positive bacteria, and *C. albicance* as a fungi. The results are presented in Table 6.

The concentration of dyes used on the polyamide fabric was 0.2 g/l in this evaluation. This technique was repeated three times. In this test, dyed polyamides and raw polyamide as a control were cut into circles with a diameter of 1 cm and were contacted with the bacterial and fungal suspensions for 24 h.

After this time, different concentrations of the bacterial and fungal suspension were transferred to plates containing solid culture medium and the plates were incubated for 24 and 48 h in bacteria and fungi, respectively. After this time, the results showed that the microorganisms were completely grown in the presence of untreated polyamide, whereas in the presence of dyed polyamide was observed no growth or a limited number were grown, as shown in Figure 5. The results clearly showed strong microbial reduction in cases of all the gram positive and gram negative bacteria. The results of this test showed that dyed fabric with all the dyes synthesized can inhibit 97-99.9 % of bacterial growth.

Skin Sensitivity

The skin sensitivity test was performed on all azo dyes and dyed polyamide fabric according to ISO 10993-2. The criterion for measuring this test is the presence or absence of redness and swelling on the skin of rabbits after exposure to dyes and commodities. Results at each 24, 48, and 72 hour period showed that dyes and dyed fabrics have no irritation on the intact skin of rabbits, as shown in Figure 6.

Certificate of confirmation of no skin sensitivity of synthesized dyes and dyed fabrics is issued by the Quality Control Laboratory of Shahid Beheshti University School of Pharmacy (Figures 7 and 8). This certification is approved by the Ministry of Health.



Figure 6. No skin allergies after applying the dye (after 24, 48, and 72 h).

PRODUCT CHARACTERISTICS Product Name Dy ? state Powder Sample presenter Haatek Skalu Batch No. Bio batch Q.C. Inh. No. 9403-857-445 References EPA OPPTS 870-2500 Intritation Test (In vivo) Intritation test Method: Skin inritation test Test Animal : Ablins Rabbits Results: No akin inritation was seen	roduct Name Dye 7 tate Powder ande presenter Hasiek Shahi Sich No. Bio batch CC. Lik No. Bio batch Sich No. 9403-8F-445 seterroaces EPA OPTIS 870.2500 rritation Test (In vivo) tetchod: Skin irritation test Cet Animal : Albino Rabbits cets Results: No skin irritation was seen analyst: Dr Mehrdad Faizi	CER	
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Figure 7. Certification of non-skin allergic for ointment made of synthesized dye.

Conclusion

In this study, azo disperse and cationic dyes were applied on polyamide and acrylic fabrics. The results showed that most of these dyes exhibited good build-up on polyamide fabrics. So, the dyeing ability of azo dyes synthesized on acrylic was lower than that of polyamide. They are capable of dyeing polyamide and acrylic fabrics to purple, purplish red, and yellowish red hues with very good wash and rubbing fastness and medium to good light fastness. Antimicrobial activity against Gram-positive, Gram-negative bacteria, and fungi was evaluated.

The results showed that the percentage of reduction of microorganisms in contact with the dyed fabric is about 97-99.9 %, indicating that these fabrics are capable of inhibiting the growth of the tested microorganisms. The skin sensitivity test was also performed on azo dyes and dyed polyamide fabrics. The results showed that the dyes and dyed fabrics did not produce any skin irritation on the rabbit skin.

CER	ATIFICATE OF ANALYSIS
	PRODUCT CHARACTERISTICS
Product Name state	Dye 7 Fiber Hanieh Shaki
Sample presenter Batch No. Q.C. Iab. No.	Bio batch 9403-SF-454 EPA OPPTS 870.2500
References Irritation Test (In vivo)	EPA OPPTS \$70.2300
Method:	Skin irritation test
Test Animal : Results:	Albino Rabbits No skin irritation was seen
24	1

Figure 8. Certification of non-skin allergic dyed fabric.

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