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## Usage of Cotton Fabric Substrate for Synthesis Mono Azo Dye.

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### ABSTRACT

Azo dyes are one of the important structures of dyes that these structures usually were classified by their functions. One of the properties of these dyes is to may have the irreversible properties; therefore some of these dyes cannot be removed from substrate of polymers. Due to the dyes properties of azo, some of the dyes were able to remain insoluble in fibers. Furthermore, this classifies of dyes can caused high wet fastness properties. Azo dye with one azo group has the colors between yellow to red. According to some synthesis methods of azo dyes, using of coupling and diazotaion process are common. In this study we use a novel method for dyeing cellulosic fabric with simultaneous synthesis mono azo dye on cotton. Therefore, the effect of pH, time, temperature and concentration of synthesis materials for azo dye (e.g. sodium nitrite, 2, 4, dinitroaniline,  $\beta$ -naphtol) were measured. Furthermore, parameter pH with three levels with different temperature, time and various concentrations were studied. For analyses of samples properties, reflectance (R) values and  $L^*a^*b^*$  values of the dyed samples were measured. The results of the synthesis was shown the optimum conditions with pH=11, temperature=70°C, time=30 min and concentration=2%OWF for dyeing cotton fabric. To study the surface morphology we used SEM and internal morphology of the fibers XRD.

**Keywords:** dyeing, synthesis, cotton, azo dye.

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## INTRODUCTION

Over the years, azo compounds consist one of the largest classes of industrially synthesized organic compounds [1, 2]. In fact, 60-70% of all dyes stuff in use and production fall in this group [3]. According to a statistical data survey, one million tons of such dyes are produced annually worldwide [4, 5]. It can simply be defined as any class of artificial dyes that contains the azo group (-N=N-). When describing a dye molecule, nucleophiles are referred to as *auxochromes*, while the aromatic groups are called *chromophore*. Together, the dye molecule is often described as a *chromogen* [6]. Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxy-groups are commonly used coupling components [7].

The traditional application field of the synthetic azo dyes still remains the textile industry, and the finishing of fibrous materials. The emergence of diverse classes of synthetic dyes including azo dyes occurred due to constant effort to find specific dye for application in diverse materials of industrial importance which include, but not limited to textile fabric [8]. Leather, aluminum sheet, ink-jet printer, paper, electro-optical devices [9]. Furthermore, azo dye compounds also have a lot of applications in industry and photodynamic therapy as well as photosensitive species in photographic or electro photographic systems and are dominant organic photoconductive materials [10, 11].

## MATERIAL AND METHODS

### Materials

#### Cotton

Cotton fabric was purchased from local market in Iran. Before use, the fabric was treated with a solution containing detergent 2g/L, 1g/L soda ash in 100°C for 30 minutes and liquor to goods ratio (L.R.) of 50:1. Then, the fabric was desized with a solution containing H<sub>2</sub>O<sub>2</sub> (1% W/V), 1 g/L soda ash, detergent 0.1 % W/V in 100°C for 30 minutes, Then the fabric was thoroughly washed with water and air dried at room temperature.

#### Chemical materials

$\beta$  naphthol (C<sub>10</sub>H<sub>8</sub>O), sodium tetra borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O), 2,4-dinitroaniline (C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>O<sub>4</sub>), sodium nitrite (NaNO<sub>2</sub>), soda ash (Na<sub>2</sub>CO<sub>3</sub>), ethanol (C<sub>2</sub>H<sub>6</sub>O), methanol (CH<sub>4</sub>O), calcium carbonate (CaCO<sub>3</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), acetone (C<sub>3</sub>H<sub>6</sub>O), Hydrochloric acid (HCl), carbon tetra chloride, Ethanol and Methanol purchased from Merck company and the Distilled water was purchased from Arian mehr company.

#### Synthesis of Schaffer acid

Schaffer acid synthesized with 5g of  $\beta$  naphthol, 0.6 mL Sulfuric acid with a purity of 98% and 20 mL Distilled water in 80°C for 2 hours in auto clove machine. Then the flask was cooled in room temperature. Then the gained material was dried in room temperature for 4 days.

#### Coupling

The coupling process began with preparing a solution containing 1g Schaffer acid as coupling compound, which dissolved in 10 mL NaOH 10% in a tab with a temperature of 5°C, then dissolving 0.5g 2,4 dinitroaniline in 40 mL water and then 0.3g sodium nitrite in 20 mL water. Finally the sodium nitrite solution was added to the 2, 4 dinitroaniline solution, and the prepared solution was added to the Schaffer acid solution and mixed with Magnetic stirrer in 30 minutes.

#### Dyeing and in situ coupling

For this purpose, like the coupling stage all the steps were followed and then the fabric was added to the coupling bath and dyed in various range of time (5, 10, 15, 20, 30, 45, 60, 120 minutes), temperatures (20-70°C) and different percentage of coupling materials concentration (2, 2.5, 3, 3.5% W/V).

## Experimental

### Examination of dyed fabrics

#### Color Strength (K/S)

Due to the dyes parameters which one of them is Color Strength, we measure the reflectance (R) values of the dye samples were measured and the K/S values were assessed using the Kubelka – Munk equation. (Equation 1)

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

Where R is the observed reflectance, K the adsorption coefficient, and S the light scattering coefficient.

#### Color difference

The values of CIELAB and K/S of samples were measured at a  $\lambda_{max}$  580 nm. The color difference ( $\Delta E$ ) of dyed fabric samples in different conditions t were calculated with equation 2.

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

Where L\* is lightness, b\* is yellowish-bluish and a\* is Reddish-greenish.

#### FTIR/ATR

Analacts PerkinElmer Spectrum Fourier transform infrared spectroscopy was taken for acquiring infrared spectrum using pressed disc method.

#### SEM

Scanning electron microscopy (SEM) (KYKY-EM3200) analysis was applied on the cotton samples (raw and in situ dyed cotton fabric) to observe the dye particles on surface of treated cotton samples.

#### XRD

X-ray diffraction (XRD) (X-Pert Philips) analysis was applied on the dyed cotton samples (raw and in situ dyed cotton) to observe the crystallinity of the fabric, before and after in situ dyeing. The FWHM values were calculated with the equation 3 .

$$\text{Scherrer equation } \tau = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

Where K is constant and is equal to 0.9 ,  $\lambda$  is the wavelength of the X radiation and is equal to 1.54065,  $\beta$  is the value of the FWHM (Full Weight at Half Maximum,),  $\tau$  is the shred dimension, and  $\theta$  is the bragge's angel.

#### Thin layer chromatography (TLC)

Compounds (synthesized dye and synthesized Schaffer acid) were routinely checked by TLC on silica gel G plates using three different eluting solvents depending on the polarity disparity. The solvent systems are water: Acetone (5: 5, v/v), Ethanol: Distilled water (5:5, v/v), and also pure Distilled water, Acetone, carbon tetra chloride, Ethanol and Methanol. In addition, the developed plates were visualized using UV lamp. For the presence of spots,  $R_f$  values were duly calculated by the equation 4. Where  $d_A$  is distance traveled by the object and  $d_S$  is distance traveled by the solvent. And also the optimum range for  $R_f$  is between 0.2-0.5.

$$R_f = \frac{d_A}{d_S} \quad (4)$$

**Coding tables**

These tables are designed for the samples in different Tests situation which are shown in table 1-3

**Table 3-1- coding samples (different buffers and times of dyeing)**

Buffer	7			9			11			11							
Temp (°C)	40	70	100	40	70	100	40	70	100	70							
Time(minute)	60									5	10	15	20	30	45	60	120
Concentration (OWF %)	% 0.5									%0.5							
Code	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	A <sub>7</sub>	A <sub>8</sub>	A <sub>9</sub>	A <sub>10</sub>	A <sub>11</sub>	A <sub>12</sub>	A <sub>13</sub>	A <sub>14</sub>	A <sub>15</sub>	A <sub>16</sub>	A <sub>17</sub>

**Table 3- 2 – coding samples (Different concentrations and different Temperatures)**

Buffer	11				11				
Temp(°C)	70				20	40	50	60	70
Time	30				30				
Concentration (OWF %)	2	2.5	3	3.5	2				
Code	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>

**Table 3-3- coding samples (Raw and optimized sample)**

Buffer	-	11
Temp(°C)	-	70
Time(minute)	-	30
Concentration (OWF %)	-	2
Code	Raw sample (R)	Optimized sample (B)

**RESULTS AND DISCUSSION**

**The effect of pH on K/S, ΔE, and L\*a\*b\* values**

The K/S, ΔE and L\*a\*b\* values of dyed cotton samples are listed in Table4-1. The results show that highest ΔE and K/S value is for sample which dyed in pH=11 and 70°C (A<sub>8</sub>), that is the result of good absorption in alkanic pHs. The a\* and b\* values shows that the reddish and yellowish of this sample is higher than the others but the higher L\* value cause highest lightness and lowest purity of the sample. The results indicate that decrease in Abs% leads to increase of absorption of cotton fabric. It means that the amount of dye in Waste water decrease and this sample is darker than other samples. The Abs values conformed above results. The results show that lowest Abs values is for the sample dyed in pH=11 and 70°C. (See table4-1)

**The effect of time on K/S, ΔE, L\*a\*b\* and Abs values**

Increase in time of dyeing leads to increase the interaction between dye molecules, due to this fact the greater interaction, make more absorption. The K/S, ΔE, L\*a\*b\* and Abs values of dyed cotton samples are listed in Table 4-2. The results show that highest ΔE and K/S value is for sample which dyed in pH=11 and 70°C and 30 minutes, after that the sample which dyed in pH=11, 70°C and 120 minutes has the highest ΔE and K/S value. The Initial absorption of dye occur in first 30 minutes of dying process and in the next 1,5 hour the dyeing might have Non-uniformity. The results indicates that decrease in Abs% leads to increase of absorption of cotton fabric. It means that the amount of dye in Wastewater decrease and these samples is darker than other samples. The Abs values conformed above results. The results show that lowest Abs values is for the sample dyed in pH=11, 70°C and 30 minutes dyeing process. (See table4-2)

**The effect of dye concentration on K/S, ΔE, L\*a\*b\* and Abs values**

The K/S, ΔE, L\*a\*b\* and Abs values of dyed cotton samples are listed in Table 4-3. The results show that highest ΔE and K/S value is for sample which dyed in pH=11 and 70°C and 30 minutes with 2% of concentration of dye. Mono azo dyes are insolvent in water, so the dye molecules are able to have Aggregation. Increase in concentration of dye leads to increase of aggregation and decrease in absorption of dye molecules. The results indicate that decrease in Abs% leads to increase of absorption of cotton fabric. It means that the amount of dye in Wastewater decrease and this sample is darker than other samples. The Abs values conformed above results. The results show that lowest Abs values is for the sample dyed in pH=11, 70°C, 30 minutes dyeing process and 2% OWF of dye. (See table4-3)

**The effect of temperature on K/S, ΔE, and L\*a\*b\* and Abs values**

The K/S, ΔE, L\*a\*b\* and Abs values of dyed cotton samples are listed in Table 4-4. The results show that highest ΔE and K/S value is for sample which dyed in pH=11 and 70°C and 30 minutes with 2% of concentration of dye. Because of the swelling of the cotton fibers in high temperature, dye molecules can absorb more, so increasing the temperature up to 70°C leads to increase of absorption of the dye molecules. The b\* values show the highest yellowish of the sample and the lowest L\* value show the highest absorption by the fabric.

**Surface morphology**

Scanning electron microscopy (SEM) of cotton samples (scoured and in situ dyed) is presented in Fig.1. The results show that dye molecules cover the surface of fabric.

**Internal morphology**

From fig.2 it was determined that the crystalline content of cotton fabric decrease from 15% (scoured cotton fabric) to 9.4 % (in situ dyed cotton fabric). This change is because of the temperature increase in fiber and also the in situ dyeing process. With temperature increase, fiber start to swell and this leads to a change between functional groups and their bonds. So the crystalline of the fabric begins to change. The results in table 4-5 approve the changes in the fabric crystalline with the lowest value for the optimum sample in the same angle (42°) of the raw sample.

**Thin-layer chromatography (TLC)**

Purity of dye was determined by a thin-layer chromatography (TLC) using silica gel-G coated Al-plates (0.5 mm thickness, Merck). Fig.3 shows the synthesized dye purity. The results show that in situ synthesized dye was pure and the spots were unit. And also the R<sub>f</sub> values for the synthesized dye are listed in table 4-6. The results show that the ethanol/water solvent with the R<sub>f</sub> = 0.3 which is in the optimum range, is the best solvent for the dye.

**Table 4-1: ΔE, L\*a\*b\*, K/S, yellowness, whiteness and Abs values affected by pH**

sample	dyed			K/S	yellowness	Whiteness	ΔE	Abs
	L*	a*	b*					
A <sub>1</sub>	87.268	-0.144	-0.681	1.4371	74.604	0.181	0.870	0.181
A <sub>2</sub>	88.790	0.252	-0.503	1.5151	74.061	0.211	1.121	0.211
A <sub>3</sub>	87.631	0.007	-0.543	1.5155	73.206	0.084	1.453	0.084
A <sub>4</sub>	81.377	-0.157	-0.307	1.4642	60.733	0.088	1.124	0.088
A <sub>5</sub>	80.836	-0.166	-0.837	1.4832	62.566	0.232	0.757	0.232
A <sub>6</sub>	82.449	0.069	-0.780	1.4225	65.118	0.087	1.332	0.087
A <sub>7</sub>	81.945	-0.094	-0.841	1.4669	64.51	0.127	0.870	0.127
A <sub>8</sub>	81.822	-0.125	-0.433	1.5369	62.19	0.073	1.353	0.073
A <sub>9</sub>	81.339	-0.210	-0.080	1.4023	59.495	0.237	1.121	0.237

Table 4-2:  $\Delta E$ ,  $L^*a^*b^*$ , K/S, yellowness, whiteness and ABS values affected by time

sample	dyed			K/S	yellowness	Whiteness	$\Delta E$	Abs
	L*	a*	b*					
A <sub>10</sub>	72.420	-2.452	29.451	2.8242	54.069	-122.084	21.29	0.086
A <sub>11</sub>	72.729	-1.877	23.013	3.8117	44.304	-85.62	25.96	0.074
A <sub>12</sub>	72.303	-0.164	23.496	3.9605	47.098	-88.837	26.51	0.065
A <sub>13</sub>	72.634	-1.975	28.004	4.9496	52.295	-113.307	30.74	0.062
A <sub>14</sub>	76.899	-2.180	19.302	5.8403	36.048	-53.56	36.44	0.058
A <sub>15</sub>	75.242	-3.075	32.226	5.5572	56.149	-127.573	31.90	0.061
A <sub>16</sub>	73.104	-0.112	29.392	4.7997	56.086	-112.28	31.51	0.060
A <sub>17</sub>	74.610	-1.414	34.372	5.6971	61.137	-139.911	32.21	0.061

Table 4-3:  $\Delta E$ ,  $L^*a^*b^*$ , K/S, yellowness, whiteness and ABS values affected by dye concentration

sample	dyed			K/S	yellowness	Whiteness	$\Delta E$	Abs
	L*	a*	b*					
C <sub>1</sub>	22.507	-2.709	76.059	24.780	-73.353	41.259	3.3457	0.050
C <sub>2</sub>	21.102	-2.794	77.280	23.038	-62.302	38.386	3.2962	0.051
C <sub>3</sub>	22.477	-1.937	75.045	24.637	-75.89	42.407	3.147	0.051
C <sub>4</sub>	22.471	-2.085	75.154	24.757	-75.588	42.186	2.8952	0.053

Table 4-4:  $\Delta E$ ,  $L^*a^*b^*$ , K/S, yellowness, whiteness and ABS values affected by temperature

sample	dyed			K/S	yellowness	Whiteness	$\Delta E$	Abs
	L*	a*	b*					
D <sub>1</sub>	20.6174	-53.16	35.456	2.9257	16.910	-0.325	79.264	0.063
D <sub>2</sub>	24.2022	-73.82	44.518	2.9977	19.887	2.268	77.798	0.066
D <sub>3</sub>	24.8747	-67.02	39.275	2.7934	23.003	-4.399	75.525	0.052
D <sub>4</sub>	25.7437	-75.78	42.922	3.3643	23.943	-2.749	71.913	0.051
D <sub>5</sub>	34.3339	-125.79	58.597	4.1218	32.324	-0.678	70.147	0.050

Table 4-5- The FWHM values for the cotton samples

sample	2 $\theta$	FWHM	Crystalline
B	23.0120	0.9446	1.4979
	42.3058	0.1574	9.4454
	49.0482	0.4723	3.2270
	72.3634	0.5510	3.1177
	87.5790	0.8659	2.2183
R	15.0664	0.9446	1.4807
	17.0431	0.9446	1.4842
	22.9539	0.9446	1.4977
	42.2937	0.0984	15.1088
	49.0885	0.5510	2.7664

Table 4-6- The R<sub>f</sub> values for the synthesized dye

Solvent	R <sub>f</sub>
Methanol	0.2
Ethanol	0.1
Acetone	0.7
Ethanol/ Water	0.3
Acetone/water	0.2
Water	0.1

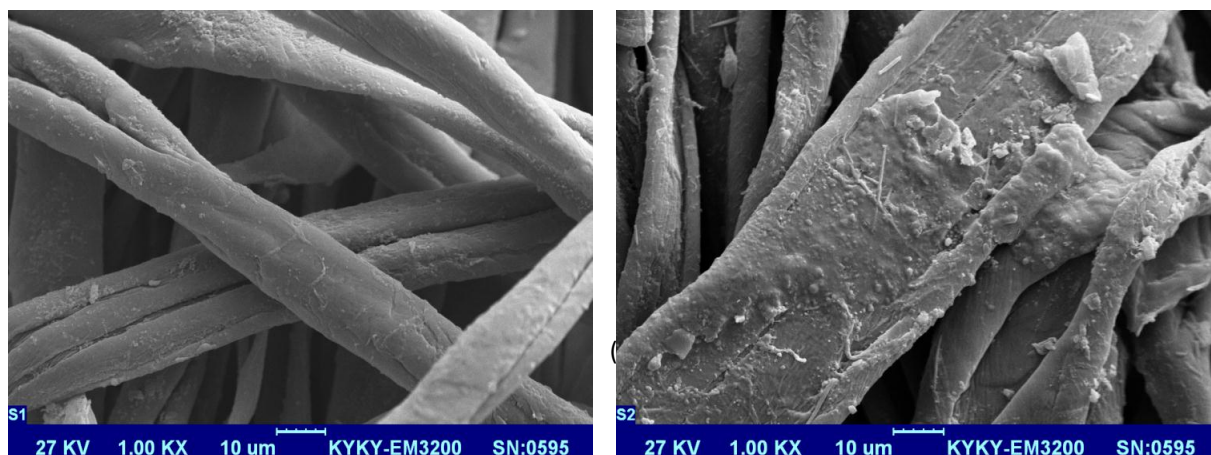


Figure 1: Surface morphology of (a): scoured cotton (b): in situ dyed cotton

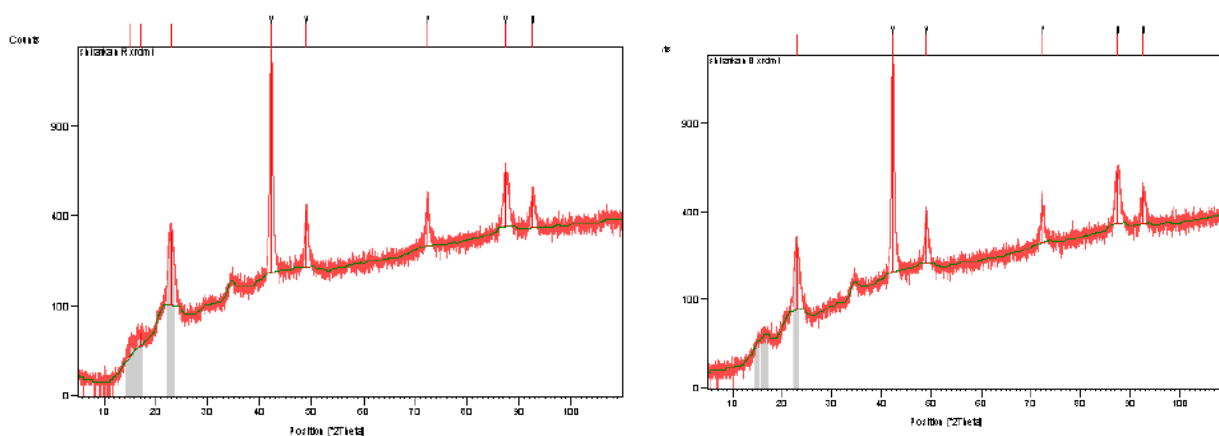


Figure 2: Internal morphology of (a): scoured cotton (b): in situ dyed cotton

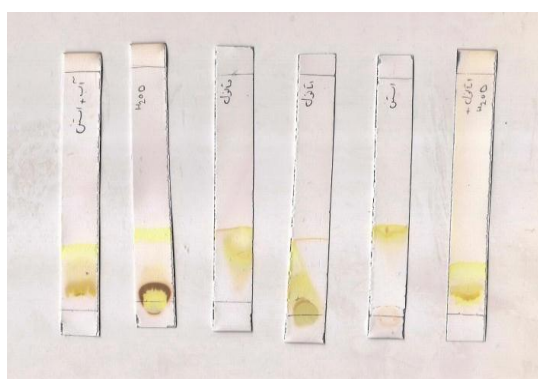


Figure 3: TLC of the synthesized dye

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