

Naphthalene-Based Azo Dyes: Synthesis, Characterization and Dyeing Performance on Polyester Fibers

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ABSTRACT

In the present study, five naphthalene-based azo dyes were obtained using classical azo coupling reactions. The structure of the dyes was characterized and confirmed by the UV-Vis, FT-IR, ¹H NMR and ¹³C NMR analyzes. The solvatochromic behavior of the dyes was studied in a set of 10 solvents with different polarity and considerable results were obtained. The dyes were applied as disperse dyes to polyester fiber and their dyeing properties were evaluated. The fastness properties of the dyed fabrics such as wash, light and rubbing fastness degrees were measured by standard methods. Additionally, the prepared dyes were evaluated for antioxidant activity by ferric reducing antioxidant power method. Prog. Color Colorants Coat. 8 (2015), 317-327 © Institute for Color Science and Technology.

1. Introduction

Dyes play an essential role in human history since ancient time. Dyes are widely used in a number of industries such as food, textile dyeing, cosmetics, pigments and paints, and other advanced application industries. Azo dyes represent one of the most attractive known classes of organic dyes. Since their discovery in the 19th century, azo compounds have been extensively used as colorants and account for over 50% of all commercial dyes. In addition, the bis-azo

dyes are valuable for providing high intensity of color and good technical properties such as fastness to light, heat, water and other solvents [1-3]. On the other hand, several synthetic ways have been developed to synthesis azo and bis-azo derivatives. However, the common methods for synthesis of these classes of dyes are the using of diazotization-coupling reactions by aromatic amines, diamines or phenols [4-6].

The scale and growth of the dye industry is

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inextricably linked to that of the textile industry. Consequently, dye manufacturers tend to concentrate their efforts on producing dyes for two most important cotton and polyester textile fibers. Their inexpensive production from petrochemical raw materials and excellent textile properties alone and in combination with natural fibers guarantee polyester fibers universal applicability. Polyester fibers can be dyed easily with disperse dyes including water-insoluble, small molecular weight properties. Furthermore, more than 50% of disperse dyes are azo compounds [2, 7-14].

On the other hand, there is increasing evidence to suggest that many degenerative diseases could be the result of cellular damage caused by free radicals (Aruoma, 1998). Moreover, antioxidants may play an important role in disease prevention. Antioxidants are of importance due to their ability to retard disease progression by reducing the damage caused by free radical oxidative stress in a patient. These compounds may act independently or in combination as anti-

microbial agents by a variety of mechanisms. Additionally, colorants with antioxidant activity have received much attention during recent years, mainly owing to their application in the various industries [15-21].

In view of the above facts and in continuation of our studies on the organic colorants [21-25], two novel bis-azo and three mono-azo dyes based on 1,5-diaminonaphthalene and 1-aminonaphthalene as the diazo components are synthesized and fully characterized for the first time.

The aim of this study is to evaluate the dyeing properties of synthesized bis-azo dyes in comparison to related mono-azo dyes on polyester fibers, to investigate the solvatochromic behavior of the dyes in solvents with different polarity, and to assay the antioxidant activity of compounds including hydroxyl groups with radical scavenging activity. General formula of the prepared dyes is as given in Figure 1.

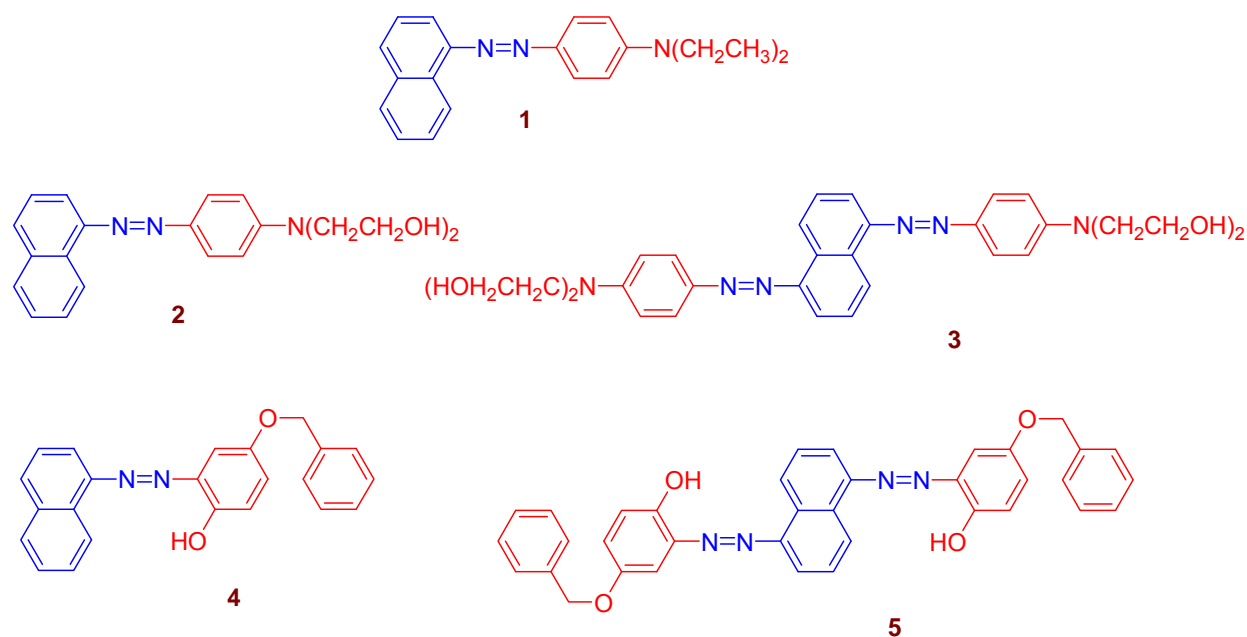


Figure 1: The structure of synthesized dyes 1-5.

2. Experimental

2.1. Materials and apparatus

All compounds used in this study were obtained from Merck Chemical Company and were used without further purification. All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu 8400 FT-IR spectrophotometer. Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained on a FT-NMR (400 MHz) Bruker apparatus spectrometer, and the chemical shifts are expressed in δ ppm using TMS as an internal standard and J values are given in Hz. The visible spectra were measured using a Pharmacia Biotech Spectrophotometer. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

2.2. Synthesis of naphthalene-based azo dyes 1-3 using aromatic amines

The diazonium salts were prepared in good yield from equimolar mixture of corresponding naphthylamines and nitrous acid according to previously described methods [21, 23]. After completion of diazotization, the azo liquor was slowly added to a stirred solution of amine coupling components dissolved in 10 mL of glacial acetic acid and 2-3 mL of DMF in acidic medium by adjusting the pH at 5.5-6.0 by addition of sodium acetate and the temperature was maintained at 0-4 °C. The resulting mixture was stirred for 2.5-3 h in an ice bath then allowed to reach room temperature. After completion of the reaction, the pH of the solution was maintained at 6.5-7.5 by addition of sodium acetate. The solid product was collected by filtration and washed two times with water. The crude products (1-3) were purified by recrystallization from DMF/H₂O.

2.3. Synthesis of naphthalene-based azo dyes 4 and 5 using 4-benzyloxy phenol

The diazonium salts were prepared in good yield from equimolar mixture of corresponding naphthylamines and nitrous acid according to previously described methods. After completion of the diazotization procedure, the diazonium salt solution was added drop

wise to the solution of 4-benzyloxy phenol in sodium hydroxide and water. The resulting solution was vigorously stirred at 0-5 °C for 1.5 h, while the pH of the reaction mixture was maintained close to 8-9 by adding 2.5 % sodium hydroxide solution. The progress of the reaction was followed by TLC using an ethyl acetate-petroleum ether mixture (4:1). After completion of the reaction, the pH of the reaction mixture was regulated at 5-5.5 by means of a 10% hydrochloric acid solution. The resulting solid was filtered, washed thoroughly with cold water and dried. Recrystallization from DMF-EtOH afforded pure crystals of the dyes. The Physical and spectroscopic data of prepared dyes are given below.

Dye 1: Brown solid; yield 76%; mp; 92-94 °C; FT-IR (KBr) ν (cm⁻¹): 2970 (=CH), 2886 (-CH), 1510 (N=N). ^1H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 1.14 (t, 6H, J = 7.2 Hz, CH₃), 3.46 (q, 4H, J = 6.8 Hz, CH₂), 6.82 (d, 2H, J = 8.8 Hz, Ar-H), 7.60 (d, 2H, J = 7.6 Hz, Ar-H), 7.63 (t, 1H, J = 6.4 Hz, Ar-H), 7.72 (d, 1H, J = 7.2 Hz, Ar-H), 7.91 (d, 2H, J = 8.4 Hz, Ar-H), 8.00 (t, 2H, J = 7.6 Hz, Ar-H), 8.85 (d, 2H, J = 8.4 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-*d*₆) δ (ppm): 12.9, 44.5, 111.4, 111.5, 123.4, 125.9, 126.4, 126.8, 127.0, 128.4, 129.7, 130.7, 134.4, 143.5, 147.7, 150.6.

Dye 2: Orange solid; yield 75%; m.p. 139-140 °C; FT-IR (KBr) ν (cm⁻¹): 3232 (OH), 2921 (=CH), 2873 (-CH), 1596 (N=N). ^1H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.58 (t, 4H, J = 5.2 Hz, CH₂), 3.63 (t, 4H, J = 5.2 Hz, CH₂), 4.87 (t, 2H, J = 4.8 Hz, OH), 6.90 (d, 2H, J = 8.8 Hz, Ar-H), 7.59 (d, 1H, J = 7.6 Hz, Ar-H), 7.63 (d, 1H, J = 7.2 Hz, Ar-H), 7.66 (t, 1H, J = 6.8 Hz, Ar-H), 7.71 (d, 1H, J = 7.2 Hz, Ar-H), 7.90 (d, 2H, J = 8.8 Hz, Ar-H), 8.01 (t, 2H, J = 6.8 Hz, Ar-H), 8.84 (d, 1H, J = 8.4 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-*d*₆): δ (ppm): 53.7, 58.6, 111.4, 111.8, 123.4, 125.7, 126.4, 126.8, 127.0, 128.4, 129.8, 130.7, 134.4, 143.6, 147.7, 151.5.

Dye 3: Light Brown solid; yield 66%; mp; 243-244 °C; FT-IR (KBr) ν (cm⁻¹): 3407 (OH), 2932 (=CH), 2871 (-CH), 1594 (N=N). ^1H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.60 (t, 8H, J = 4.8 Hz, CH₂), 3.65 (t, 8H, J = 4.8 Hz, CH₂), 4.89 (t, 4H, J = 4.8 Hz, OH), 6.62 (d, 4H, J = 8.8 Hz, Ar-H), 7.75 (t, 2H, J = 9.6 Hz, Ar-H), 7.81 (d, 2H, J = 7.6 Hz, Ar-H), 7.93 (d, 4H, J = 8.8 Hz, Ar-H), 8.93 (d, 2H, J = 8.4 Hz, Ar-H). ^{13}C NMR (125 MHz, DMSO-*d*₆) δ (ppm): 53.8, 58.6, 111.8, 111.9, 125.8, 127.0, 131.7, 143.7, 147.8, 151.7.

Dye 4: Dark Brown solid; yield 78%; mp; 105-106 °C; FT-IR (KBr) ν (cm⁻¹): 3446 (OH), 2928 (=CH), 1592 (N=N). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 5.17 (s, 2H, CH₂), 7.06 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.19 (d, 1H, *J* = 6 Hz, Ar-H), 7.35 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.42 (t, 3H, *J* = 7.2 Hz, Ar-H), 7.51 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.67 (t, 2H, *J* = 7.6 Hz, Ar-H), 7.75 (t, 1H, *J* = 7.6 Hz, Ar-H), 8.06 (m, 2H, Ar-H), 8.13 (d, 1H, *J* = 8 Hz, Ar-H), 10.19 (s, 1H, OH). ¹³C NMR (125 MHz, DMSO-*d*₆) δ (ppm): 70.3, 103.2, 113.1, 119.6, 122.9, 123.1, 126.3, 127.1, 127.7, 128.1, 128.2, 128.6, 128.9, 130.8, 131.7, 134.4, 137.7, 139.8, 147.0, 151.2, 152.1.

Dye 5: Red solid; yield 78%; mp; 193-194 °C; FT-IR (KBr) ν (cm⁻¹): 3443 (OH), 2946 (=CH), 1592 (N=N). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 5.18 (s, 4H, CH₂), 7.07 (d, 2H, *J* = 9.2 Hz, Ar-H), 7.20 (dd, 2H, *J* = 2.8 Hz, Ar-H), 7.35 (t, 2H, *J* = 7.2 Hz, Ar-H), 7.42 (t, 6H, *J* = 7.2 Hz, Ar-H), 7.52 (d, 4H, *J* = 7.2 Hz, Ar-H), 7.88 (t, 2H, *J* = 8 Hz, Ar-H), 8.15 (d, 2H, *J* = 7.6 Hz, Ar-H), 8.99 (d, 2H, *J* = 8.4 Hz, Ar-H), 10.30 (s, 2H, OH). ¹³C NMR (125 MHz, DMSO-*d*₆) δ (ppm): 70.3, 102.6, 113.5, 119.7, 123.2, 126.6, 127.5, 128.1, 128.3, 128.9, 131.7, 137.7, 139.9, 147.2, 151.6, 152.1.

2.4. Ferric reducing antioxidant power (FRAP) assay

The FRAP assay was performed according to Benzie and Strain method with minor modifications. The principle of this method is based on the reduction of a ferric 2,4,6-tris(2-pyridyl)-1,3,5-triazine (Fe³⁺-TPTZ) to ferrous, in the presence of synthesized compounds. FRAP reagent was prepared from 0.3 M acetate buffer (pH = 3.6), 10 mmol TPTZ solution in 40 mmol HCl and 20 mmol iron (III) chloride solution in proportions of 10:1:1 (v/v), respectively. The FRAP reagent was freshly prepared before analysis and warmed to 37 °C prior to use. 100 μ l diluted compounds (2-50 μ M) was added to 1.4 mL of the FRAP reagent. The absorbance of the reaction mixture was measured after 5 min against blank at 593 nm. Increased absorbance of the reaction mixture is an indicative of higher reducing power. A standard curve was prepared using different concentrations (0.5-10 mM) of ferrous sulfate. All determinations were carried out three times.

2.5. Dyeing procedure and determination of fastness properties

The dyeing was carried out in an Infra Color apparatus using liquor ratio (L:G) of 30:1 and pH was adjusted to 5-6 using acetic acid. The concentrations of the dye dispersions were 0.1, 0.4, 0.8, 1.2, 2 and 4% owf. The owf indicates wt% of a dye relative to fiber weight of a dried fiber. The dyeing was carried out by raising the dye bath temperature from 40 to 100 °C at a rate of 2 °C/min and the bath temperature was maintained at 100 °C for 60 min. After that, the bath was rapidly cooled down to 70 °C at a rate of 3 °C/min. Finally, the fabrics were washed off with cold water and dried.

The light fastness was tested in accordance with ISO 105-B02:2013 under irradiation in a commercial xenon arc weather meter. The black panel temperature was 50 °C and the power of light was 1500 W. The changes in color were evaluated based on the blue scale 1-8 where one is poor and eight is excellent.

For assessment of color fastness to washing, the dyed fibers were attached to the same size undyed polyester fibers and immersed in a bath of 0.5% detergent at 35 °C and at a liquor ratio of 50:1. After 30 min, the samples were removed, washed twice with deionized water, washed with tap water, and air-dried. Changes in shade and staining of adjacent fabrics were evaluated with the aid of gray-scale 1-5 for color change and transfer. Wash fastness was measured according to ISO 105-C10:2006. Rubbing fastness was measured using a Crockmeter in accordance with ISO 105-X12:1993(E). This property was also determined according to the gray scale.

3. Results and discussion

3.1. Synthesis and spectral characteristics

All the investigated azo dyes 1-5 in this paper were synthesized by coupling two aromatic amines and 4-benzyloxy phenol as couplers and corresponding aromatic diazonium salts using a classical reaction for the synthesis of azo compounds [26, 27]. The structures of prepared dyes were confirmed by analyzing their spectral characteristics.

Physical and spectral data of the dyes are given in the experimental section. ¹H NMR spectrum of dyes 2 and 3 in DMSO at T = 298 K showed the hydroxyl proton signals at about δ 4.87 and 4.89 in the form of triplets with coupling constant of 4.8 Hz. The methylenic protons signals in dyes 2 and 3 appeared at about δ 3.58 and 3.6 as triplet. In dyes 4 and 5, the hydroxyl proton occurred as broad singlet at about δ

10.19-10.30 ppm. Protons of benzylic moiety in dyes 4 and 5 displayed a broad singlet at about δ 5.17-5.18 ppm. For all synthesized compounds, the aromatic protons appeared in the region of δ 6.8-8.99 ppm in the form of singlet, doublet, triplet and multiples. In addition, the number of carbon signals and their chemical shifts correspond to the structure of synthesized dyes. The UV-Vis absorption spectra of all the synthesized dyes showed a strong band at about 388-498 nm, which can be attributed to $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ electronic transitions of unsaturated azo group [28]. These results prove the structure of the prepared dyes 1-5.

3.2. The UV-Visible spectra and solvatochromic studies

It has long been known that absorption spectra of chemical compounds, mainly colorants, are influenced by the solvent media. Therefore, the absorption spectra of the colorant materials in solution depend strongly on the solvent nature and solvent-solute interactions [29-31]. In order to study the solvatochromic behavior of

the prepared dyes, we recorded their absorption spectra in solvents with different polarity at a concentration of 10^{-4} - 10^{-5} M at room temperature, in which the solvents are arranged in the order of increasing polarity (Table 1). As shown in Table 1, the electronic absorption spectra of all studied compounds in different solvents exhibit the wavelengths of absorption maxima (λ_{\max}) in the range of 398-498 nm due to the $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ electronic transitions of azo chromophore. The absorption spectra of the dyes 1-5 in DMSO are shown in Figure 2.

The changes induced by solvents were evaluated using solvent polarity scale (π^*). However, we believe that solvatochromic behavior should be evaluated using Kamlet-Taft equation [32, 33]. As can be seen in Table 1, there is a strong solvent dependency for dyes 1-5 with solvent polarity parameter (π^*), indicating bathochromic effect (positive solvatochromism) in more polar solvents (Figure 3) [34]. For example, in the absorption spectrum of dye 4, the λ_{\max} is shifted from 390 to 426 nm ($\Delta\lambda_{\max} = 36$ nm) by changing the solvent from Cyclohexane ($\pi^* = 0.00$) to DMSO ($\pi^* = 1.00$).

Table 1: Experimental electronic absorption maxima for dyes 1-5 and solvent dipolarity/polarizability parameter (π^*).

| Solvents | π^* | Dye 1 | Dye 2 | Dye 3 | Dye 4 | Dye 5 |
|---------------------|---------|-------|-------|-------|-------|-------|
| Cyclohexane | 0.00 | 432 | 430 | 452 | 390 | 448 |
| Butanol | 0.47 | 440 | 442 | 476 | 396 | 460 |
| Ethanol | 0.54 | 456 | 444 | 476 | 398 | 454 |
| THF | 0.55 | 442 | 446 | 478 | 396 | 464 |
| Chloroform | 0.58 | 438 | 428 | 456 | 392 | 474 |
| Methanol | 0.60 | 442 | 450 | 476 | 400 | 454 |
| Glacial Acetic acid | 0.64 | 400 | 428 | 468 | 388 | 460 |
| Dichloromethane | 0.82 | 444 | 438 | 466 | 394 | 474 |
| DMF | 0.87 | 458 | 452 | 490 | 424 | 458 |
| DMSO | 1.00 | 456 | 456 | 498 | 426 | 456 |

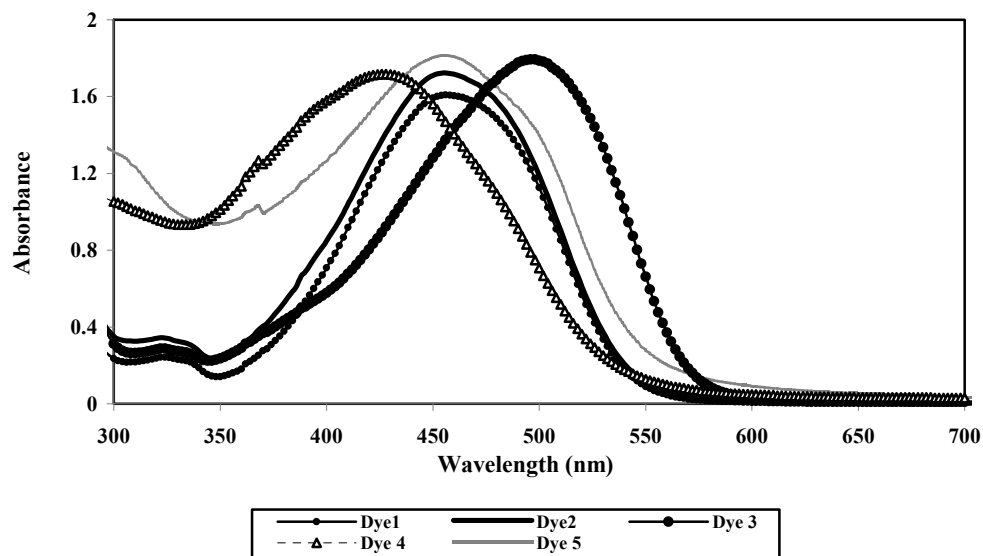


Figure 2: UV-Visible normalized absorption spectra of dyes 1-5 in DMSO.

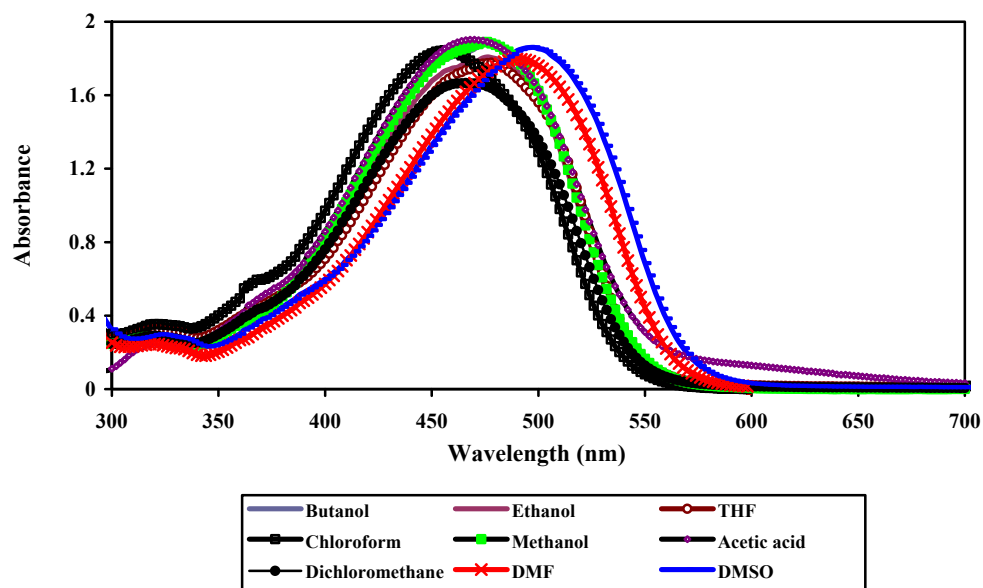


Figure 3: Normalized absorption spectra of dye 3 in selected solvents.

It was found that the wavelength of maximum absorbance for dyes, show acceptable correlation with solvent dipolarity/polarizability parameter (π^*). The obtained correlation coefficients values (R) for studied solvents were $R = 0.556$ for Dye 1, $R = 0.437$ for Dye 2, $R = 0.548$ for Dye 3, $R = 0.522$ for Dye 4 and $R = 0.150$ for Dye 5. These results would seem to indicate the ground state of the mono-azo dyes is better

stabilized by solvation than the molecule in the excited state in polar solvents. On the other hand, it is clear that the bis-azo dye 5 with electron-donating groups on the benzene rings cannot be used as solvent polarity indicator (Figure 4).

The absorption maxima of bis-azo dyes 3 and 5 were observed at longer wavelength region (bathochromic shift) compared to the similar mono-azo

dyes 2 and 4 due to extended resonance systems as shown in Table 1 and Figure 5. Also, the azo dyes 1-3 derived from amino coupling components show a

slightly bathochromic shifts compared to the similar azo dyes 4-5 derived from phenolic coupler.

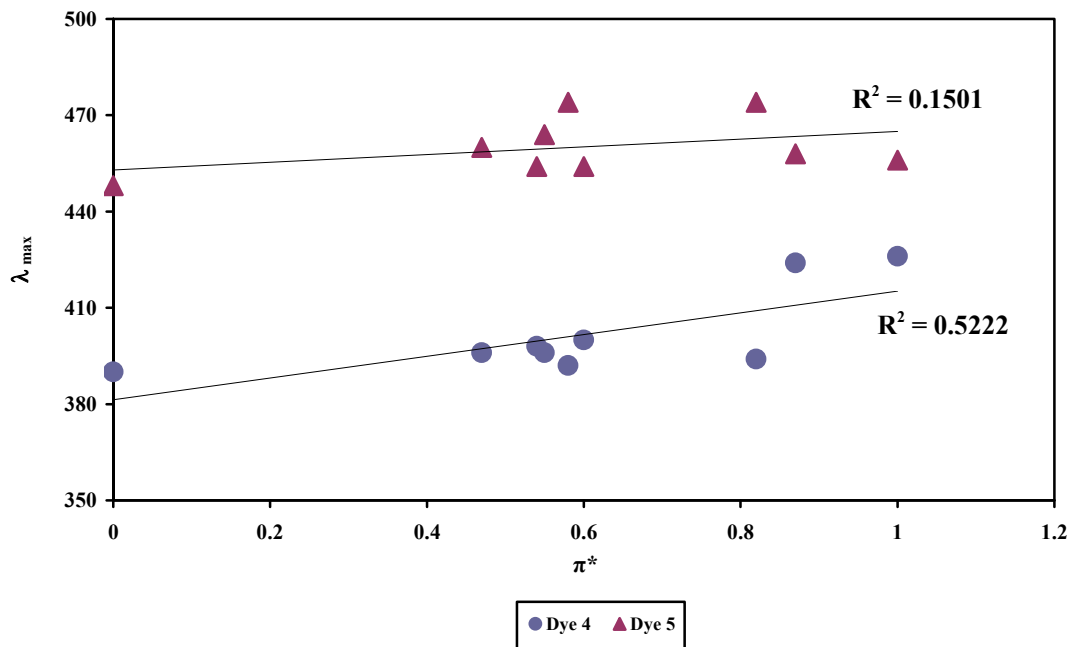


Figure 4: Variation of λ_{max} (nm) of dyes 4 and 5 as a function of π^* .

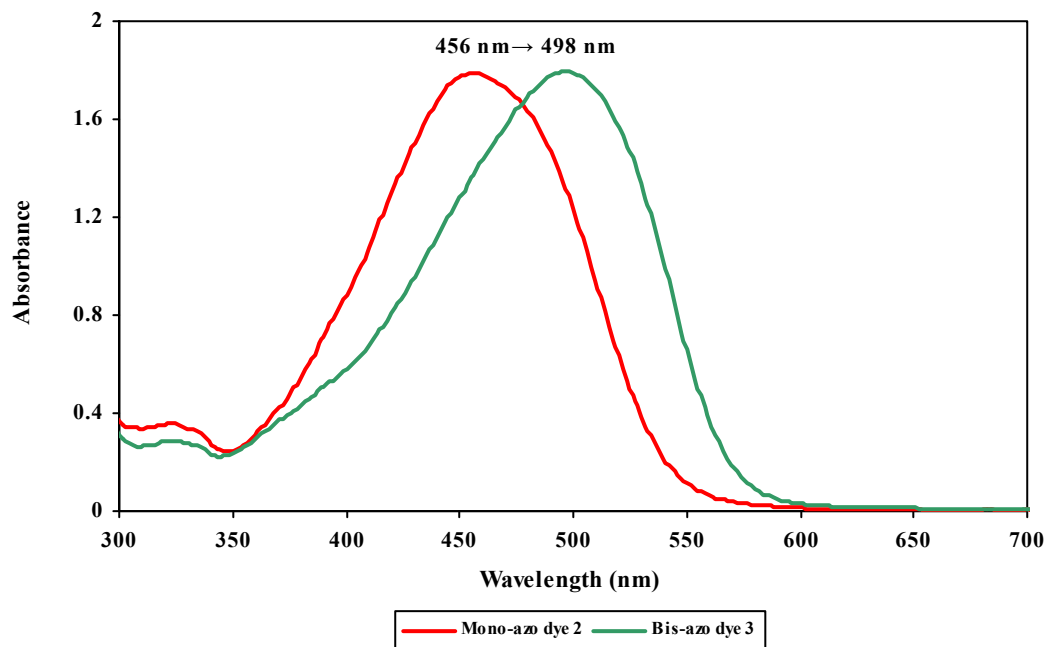


Figure 5: Normalized absorption spectra of dyes 2 and 3 in DMSO.

3.3. Dyeing properties of synthesized dyes

The measurement of dye uptake in polyester fabric was determined by absorption method according to the Beer Lambert law [35]. The results of dye uptake for synthesized dyes 1-5 on polyester are shown in Figure 5. The results showed that the mono azo dyes 1, 2 and 4 had moderate to excellent uptake on the polyester fiber related to their similar bis-azo dyes 3 and 5. This fact can be attributed to the physicochemical properties of dyes 1, 2 and 4 with small and planar structures. These properties allow the dyes to penetrate between the polymer chains and into the bulk of the fiber [2, 36]. In addition, the bis-azo dyes 3 and 5 had moderate uptake on the polyester fiber due to high molecular weight. Therefore, from this point of view, these two dyes do not seem to be good for uptake on the polyester fiber.

The measurement of fastness properties of novel dyes on fibers is important to determine that they are good colorants. In this part, the dyes 1-5 were applied to polyester fibers by high-temperature pressure method [37]. Wash, light and rubbing fastnesses of

prepared dyes on polyester fibers are listed in Table 2. The results indicate that the dyeing on polyester fibers show excellent fastness to washing and rubbing tests. This may be attributed to the good penetration and hard removal of synthesized dyes on polyester fibers. According to Table 2, the light fastness results are good except for compounds 4 and 5 with phenolic coupler.

3.4. Antioxidant assay

Antioxidant activity of newly synthesized compounds 1-5 was measured by FRAP method [38]. The results are presented in Table 3. The concentration values of Fe^{2+} indicated that all the synthesized dyes exhibited significant antioxidant properties, and this activity enhanced in the dyes including hydroxyl and amino groups. This noteworthy antioxidant activity may be rationalized on the basis that the prepared dyes possess phenolic, amine and hydroxyl moieties as well-known antioxidants [39, 40]. Among the tested compounds, azo dyes 1-4 have exhibited good radical scavenging activity. However, dye 5 exhibited moderate activity.

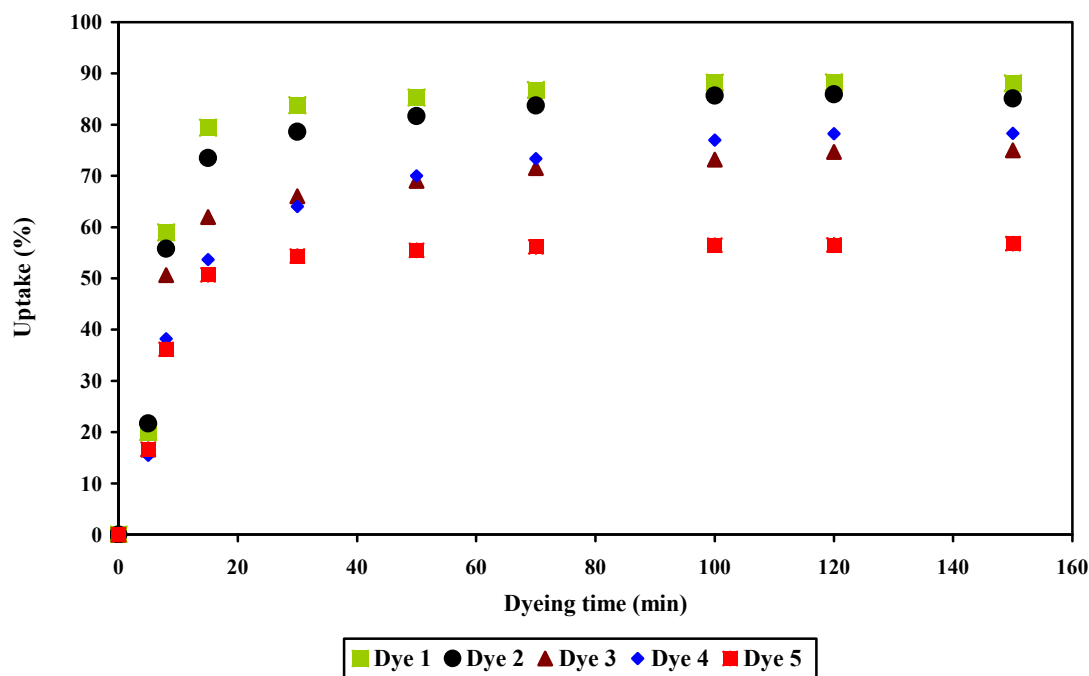


Figure 6: Uptake of the dyes 1-5 on polyester fibers.

Table 2: Fastness properties of the dyes 1-5 on polyester fibers.

| Dyes | Color | Washing | | Rubbing | | Light |
|------|--------|-----------------|-----------------------|---------|-----|-------|
| | | Change in shade | Staining on polyester | Dry | Wet | |
| 1 | Brown | 4 | 4 | 4 | 4 | 4 |
| 2 | Orange | 4-5 | 4-5 | 4 | 4 | 6 |
| 3 | Brown | 4-5 | 4-5 | 4 | 4 | 6 |
| 4 | Brown | 4 | 4 | 4 | 4 | 2 |
| 5 | Red | 4-5 | 4-5 | 4 | 4 | 2 |

Table 3: Antioxidant Activity of dyes 1-5 assayed by FRAP method.

| Dyes | FRAP (μM), Fe^{2+} (Con.) |
|------|---|
| 1 | 154 \pm 1.2 |
| 2 | 172 \pm 1.0 |
| 3 | 168 \pm 1.4 |
| 4 | 144 \pm 1.0 |
| 5 | 142 \pm 1.5 |

4. Conclusions

In summary, we have synthesized five naphthalene-based azo dyes in this work. The structures of prepared dyes were confirmed by ^1H NMR, ^{13}C NMR, FT-IR and UV-Vis spectroscopy. The electronic absorption spectra of synthesized dyes were recorded in solvents with different physicochemical properties. A large bathochromic shift of these compounds was observed upon increasing the solvent polarity (π^*). In addition, the prepared disperse dyes were investigated for their dyeing characteristic on polyester fibers and they showed moderate to excellent light, washing and rubbing fastness. The measurement of dye uptake on

the polyester fiber indicated that the mono azo dyes 1, 2 and 4 have a larger uptake than that of the bis azo dyes 3 and 5, which resulted in the obtained molecular weight and physicochemical properties for the studied dyes. Finally, the results of antioxidant measurements indicated that these dyes effectively showed antioxidant capacity as confirmed by the ferric reducing antioxidant power method.

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