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# Synthesis, spectral properties, biological activity and application of new 4-(benzyloxy)phenol derived azo dyes for polyester fiber dyeing

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ABSTRACT

A series of hetaryl-azophenol dyes were prepared by coupling 4-benzyloxyphenol with eight heterocyclic amines in nitrosyl sulphuric acid. The structure of the prepared azo dyes was characterized by UV-Vis, FT-IR and $^1$H-NMR spectroscopic techniques, as well as elemental analysis (CHN). The solvatochromism of dyes was evaluated with respect to the wavelength of maximum absorption ($\lambda_{max}$) in various solvents. The effects of temperature, concentration as well as acid and base on the visible absorption maxima are also reported. The newly synthesized dyes were screened for their potential antibacterial activities against four bacterial species and the results revealed significant activity against the test microorganisms *in vitro*. In addition, the dyes were applied to polyesters and afforded red-orange shades with excellent wash fastness properties.



## 1. Introduction

Azo dyes (–N N–) are an important class of organic colorants used in many practical applications [1–4]. They are successfully employed as LCD color filters [5], chromophoric substrates for redox enzymes [6], optical switches [7,8] chemical sensors [9,10], textile dyes [11–14], lasers [15], optical data storage [16], non-linear optics [17–21]; and also they have advanced applications in organic synthesis [22]. Azo dyes containing sulfur and/or nitrogen atoms have been the subject of many studies recently. These dyes provide bright and strong shades that range from red to green and blue [23–26]. In addition, azothiazole and azobenzothiazole dyes have been attracted great attention for their spectral and eco-friendly features. They illustrate bathochromic shift as compared to corresponding azobenzene dyes [27–29]. In this regard, a number of studies have been devoted to the characterization, purification and application of azo dyes as antibacterial agents [30–36]. Thus, the aim of the present work was to prepare some new dyestuffs containing heterocyclic moieties having acceptable antibacterial activities and fastness properties. The latter was a requirement as the dyes would be used to dye polyester, wool nylon and garments which would be in direct contact with human skin.

Accordingly, in this paper, we report the synthesis of some hetaryl azophenol compounds (1–8) using 4-benzyloxyphenol as coupling component and evaluation of their visible absorption spectra with respect to the influence of solvent. The effects of acid and base on the visible absorption maxima of the dyes are reported. In addition, their unique application in polyester fiber dyeing was investigated. The compounds structures are shown in Scheme 1.

## 2. Results and discussion

### 2.1. Synthesis and characterization

Following the general procedure for preparation of azo dyes, diazotization was performed by treatment of heterocyclic amines with nitrosyl sulfuric acid, then the resulting diazonium salts were reacted with alkaline solution of 4-benzyloxyphenol to afford azo dyes 1–8 in high yields (Scheme 1). The structure of the synthesized dyes was confirmed by FT-IR, $^1$H-NMR and elemental analyses. The prepared dyes may exist in two tautomeric forms, azo form (A) and hydrazone (B), as depicted in Scheme 2. Deprotonation of two tautomers leads to common anions ($A_1$ and $B_1$).

The IR spectra of all synthesized dyes showed the O–H stretching at 3350–3450 cm$^{-1}$. In addition, absorption bands at 3021–3100 cm$^{-1}$ and 2872–2970 cm$^{-1}$ were attributed to the aromatic and aliphatic C–H stretching vibrations, respectively. The $^1$H-NMR spectra were recorded in $CDCl_3$ at room temperature and showed singlets at 2.45 ppm (–$CH_3$, 3), 3.90 ppm (–$OCH_3$, 4), 5.10 to 5.16 ppm for benzylic protons (–$CH_2$Ar), a multiplet from 7.00 to 8.70 ppm for aromatic protons (Ar–H) and a broad peak from 11.23 to 12.45 ppm for hydroxylic proton (–OH). The $^1$H-NMR of dyes 6 and 7 exhibit one broad peak,

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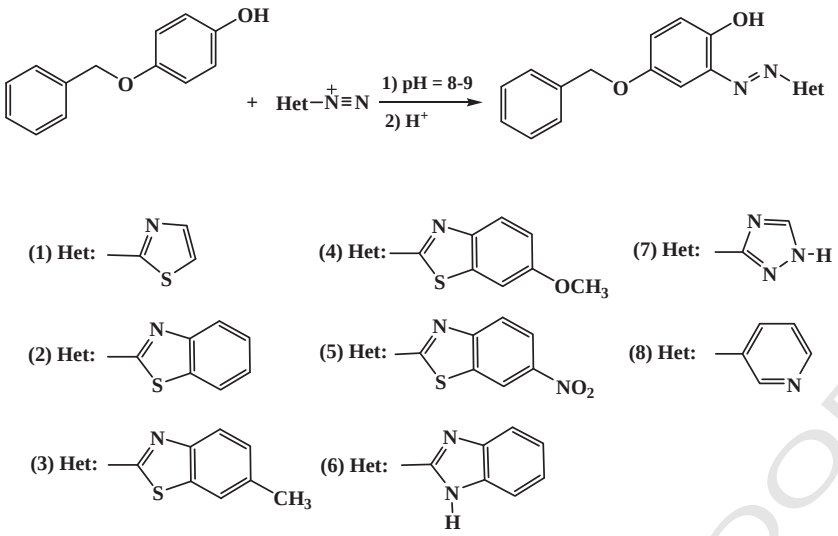



**Scheme 1.** Synthesis of azo dyes 1–8.

related to –NH protons, at 14.70 and 15.20 ppm, respectively. Spectroscopic results suggest that the synthesized dyes are predominantly in azo form (A), both in solid state and in chloroform.

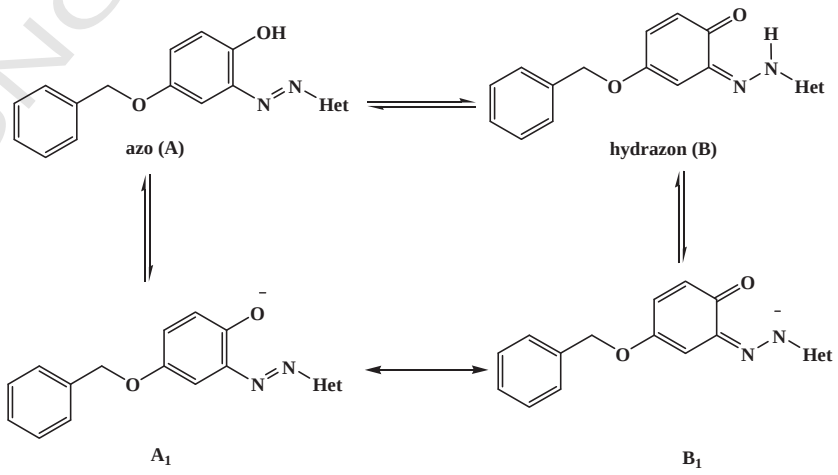
### 2.2. Solvent effect on UV-Vis spectra

Since the tautomeric equilibriums strongly depend on the nature of the media, the behaviors of dyes in various solvents were studied. For this purpose, the UV-Vis absorption spectra of dyes 1–8 were measured in various solvents at $10^{-6}$ to $10^{-8}$ mol $L^{-1}$. The results are summarized in Table 1. Visible absorption spectra of the dyes exhibited a strong solvent dependence; however, no regular variation with the solvent polarity was observed.

The benzothiazole azo dyes 1–5 showed three absorbances in DMSO and DMF and single absorbance in methanol, chloroform, acetonitrile and acetic acid. It was observed that the $\lambda_{max}$ values of dyes 1–5 showed bathochromic shifts in high polar basic solvents, e.g. DMSO and DMF, as shown in Table 1. A typical example is shown in Fig. 1. The large bathochromic shifts in basic solvents are due to deprotonation of the dyes, which leads to anionic forms, $A_1$ and $B_1$. It can be suggested that these dyes may be a mixture of tautomeric form (A) and anionic forms ($A_1$ and $B_1$) in DMSO and DMF, while they are predominantly in the single tautomeric form in other solvents. As it can be seen in Fig. 1, the absorption curves of dye 1 almost pass through an isobestic point, approximately at 536 nm, which is characteristic of equilibrium. This equilibrium may exist between the azo tautomeric form and the anionic forms $A_1$ and $B_1$.

Dye 6 showed two absorption maxima in all used solvents, indicative of two tautomeric forms existing simultaneously in solution. In contrast, dye 8 indicated just one absorption maximum, confirming the fact that the azoic form dominated. Interestingly, dye 7 in DMSO and acetic acid exhibited one $\lambda_{max}$. However, the maximum in DMSO was related to the anionic form whereas in acetic acid it was related to the azoic form. In other solvents, it showed two absorption maxima, emphasizing that both forms are present simultaneously in solution (Fig. 2).

It was also observed that the absorption curves of the synthesized dyes are not significantly sensitive to acid, whilst they are sensitive to base. Absorption spectra of the dyes in methanol did not change significantly by addition of 0.1 M HCl and the absorption curves are similar to those in acetic acid. However, the $\lambda_{max}$ of dyes 1–8 showed large bathochromic shifts when a small amount of 0.1 M KOH solution




**Scheme 2.** The tautomerism and anionic form of hetraylazo 4-benzyloxyphenoles.



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**Table 1**
Influence of solvents on the $\lambda_{max}$ of dyes 1–8.

| Dye | DMSO | DMF | Acetonitrile | Methanol | Acetic acid | Chloroform |
|---|---|---|---|---|---|---|
| 1 | 474, 591 s, 624 s | 483, 585, 621 s | 471 | 470 | 470 | 480 |
| 2 | 488, 588 s, 623 s | 490, 584 s, 619 s | 486 | 492 | 498 | 496 |
| 3 | 495, 596 s, 636 s | 497, 594 s, 626 s | 481 | 492 | 493 | 490 |
| 4 | 502, 597, 639 s | 499, 595 s, 637 s | 492 | 483 | 498 | 492 |
| 5 | 517, 588 s, 642 s | 514, 586 s, 638 s | 507 | 506 | 532 | 520 |
| 6 | 443 s, 478 | 440 s, 474 | 430, 464 s | 434, 454 s | 428, 554 s | 481, 617 s |
| 7 | 550 | 452 s, 540 | 468, 550 s | 441, 548 s | 444 | 454, 632 s |
| 8 | 440 | 437 | 429 | 427 | 430 | 431 |

s = shoulder.

was added to each dye solution in methanol. A typical example is shown in Fig. 3. These results indicate that the dyes may exist in a dissociated (anionic) tautomeric form in strongly basic solutions.

The absorption spectra of dyes 1 to 8 were determined in aqueous solution in different pH values at room temperature and are given in Table 2. Each compound exhibits two bands in the region of 479–588 nm and 421–528 nm for anionic and the molecular species, respectively. As the pH value of the solution increases, the height of the former band increases and simultaneously that of the latter band decreases. From the optical spectra, in each case, the isobestic points indicate that two species are in equilibrium (Fig. 4).

For all of these dyes, the changes of color were extremely sharp and clear in the pH range 7.02–9.20 (Table 2). Sensitive acid–base reaction property of the compounds can be explained by the formation of a π system within the whole dye structures. From the UV-Vis absorption spectra based on the varying basicity, a pH-dependent equilibrium between molecular species (HIn) (acidic medium) and its deprotonated form ($In^-$) (basic medium) was established in a mixture of sodium hydroxide and EtOH/$H_2O$ system. The dyes were yellow or red in acidic medium (0.1 mol $L^{-1}$ HCl). While, as the pH values were increased, the color of the medium changed dramatically to blue-violet in the pH range 7.02–9.20. As a result of the reaction between acid and base forms, a considerable increase in the absorption intensity was observed in this pH range, exhibiting the color transition property necessary for pH indicators. Also color changes were reversible and the dyes were stable in acidic and alkali conditions. Consequently, these compounds could potentially be used as pH indicators.

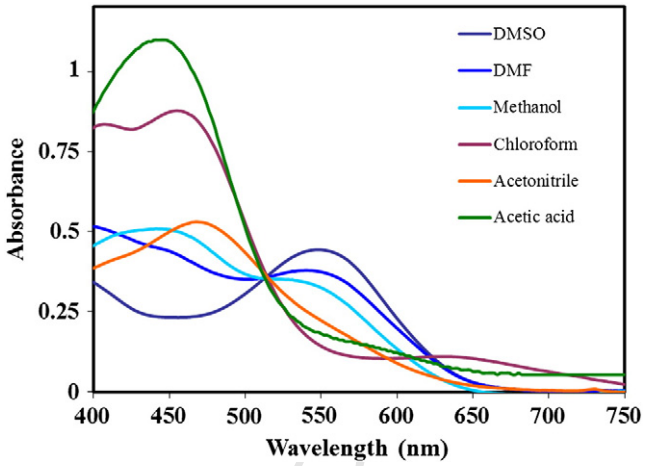


**Fig. 2.** Absorption spectra of dye 7 in various solvents.

Buffer standard solutions with pH 1.33, 2.01, 4.37, 6.71, 7.02, 8.27, 8.57, 8.87, 9.20, 10.12, 12.39, and 13.47 were prepared with traditional procedure from distilled deionized water and ethanol with HCl, NaOH, $H_3PO_4$, $KHC_8H_4O_4$, $KH_2PO_4$, $H_2B_4O_7$, $NaHCO_3$, KCl, and $Na_2CO_3$. In most cases, the pH needed to be adjusted using a pH meter and the drop wise addition of either 1 M HCl or 1 M NaOH to 1 L of solution. The accurate pH for each buffer solution was measured with a Jenway model 3505 digital pH meter. Typical absorbance–pH curve is showed in Fig. 5.

As an example, Fig. 6 shows the photograph of the 2-thiazolylazo-4-benzyloxy phenol (dye 1) solutions at different pHs obtained from buffer solutions. It is possible to appreciate the pH-dependence of the color variation in solution.

To further our study, we evaluated the effects of substituent and extension of resonance system on absorption maximum of the synthesized heterocyclic dyes (Table 1). Evaluations show that thiazolyl derivatives have a higher maximum wavelength relative to dyes containing isoxazole, triazole and pyridine. This bathocromic shift in absorption maximum of thiazolyl dyes has been attributed to the existence of sulfur, either alone or in combination with nitrogen atoms in the chemical structures of such dyes. As it is apparent in Table 1, the introduction of an electron-accepting nitro group into position 6 on benzothiazole ring results in a hypsochromic shift in all solvents as compared to electron-donating, methyl and methoxy groups (for dye 3 $\Delta\lambda = 30$ nm and for dye 4 $\Delta\lambda = 28$ nm, relative to dye 5 for spectra in chloroform). Also dye 2, including benzothiazole ring,

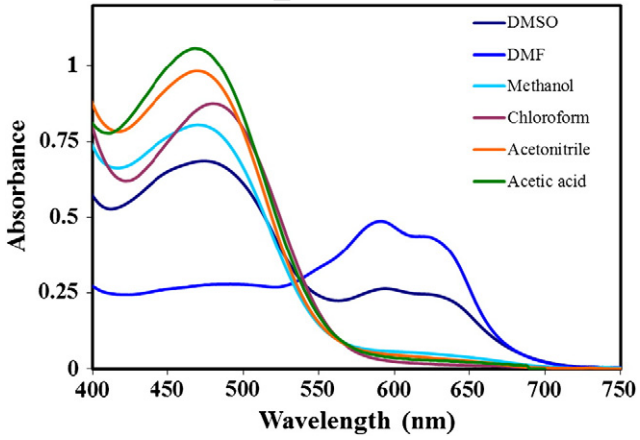


**Fig. 1.** Absorption spectra of dye 1 in various solvents.

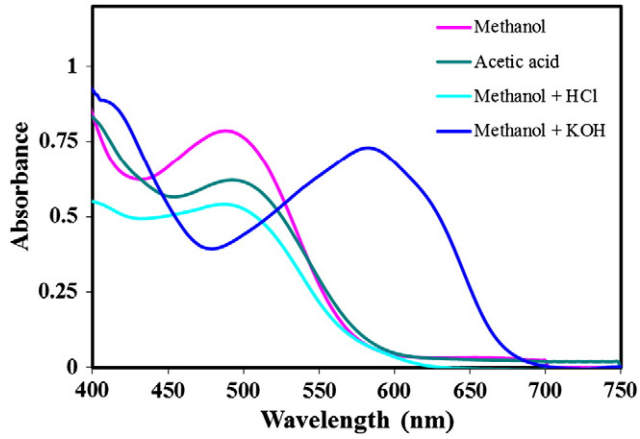


**Fig. 3.** Absorption spectra of dye 3 in acidic and basic solutions.

**Table 2**
Influence of pH on $\lambda_{max}$ of dyes 1–8.

| Dye | pH 1.33 | pH 2.01 | pH 4.37 | pH 6.71 | pH 7.02 | pH 8.27 | pH 8.57 | pH 8.87 | pH 9.20 | pH 10.12 | pH 12.39 | pH 13.47 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 471 | 469 | 471 | 469 | 469 | 472, 561 s | 473, 563 s | 473, 565 s | 561, 472 s | 563 | 563 | 565 |
| 2 | 493 | 492 | 491 | 491 | 491 | 492, 610 s | 493, 584 s, 617 s | 493, 584 s, 617 s | 614, 584, 492 s | 588 | 585 | 588 |
| 3 | 488 | 488 | 490 | 490 | 491 | 491, 618 s | 492, 584 s, 618 s | 492, 584 s, 618 s | 618, 584, 493 s | 586 | 588 | 588 |
| 4 | 492 | 492 | 492 | 492 | 492 | 500, 582 s, 620 s | 502, 582 s, 620 s | 502, 582 s, 620 s | 620, 583, 502 s | 584 | 586 | 587 |
| 5 | 520 | 521 | 521 | 528 | 528 | 518, 585 s, 634 s | 518, 585 s, 635 s | 518, 585 s, 635 s | 635, 585 s, 518 s | 586 | 587 | 587 |
| 6 | 421 | 422 | 428, 538 s | 428 | 429 | 442, 479 s | 442, 479 s | 442, 479 s | 442, 479 s | 479 | 481 | 481 |
| 7 | 431 | 432 | 432 | 435 | 435 | 441, 547 s | 441, 548 s | 442, 549 s | 442, 542 s | 542 | 542 | 543 |
| 8 | 431 | 432 | 432 | 432 | 437 | 437 | 439 | 439 | 439, 510 s | 510 | 514 | 514 |

s = shoulder.

shows bathochromic shifts due to the extended resonance system in comparison with dye 1.

The effects of concentration and temperature on the absorption maxima of dyes were also examined and the results are listed in Table 3. The $\lambda_{max}$ values of synthesized dyes did not change significantly by altering the dye concentration in chloroform, acetonitrile, methanol, DMSO and DMF, except for dye 4 and dye 8 in acetonitrile, in which a red shift appeared as the concentration increased. Considering the influence of temperature, a solution of each dye in chloroform, acetonitrile, methanol, DMSO and DMF were prepared and examined in a temperature range of 25–70 °C. The results show few changes in $\lambda_{max}$ values of the dyes 1–8 as the temperature was increased.

### 2.3. Antibacterial activity

The antibacterial activity of the dyes at various concentrations is shown in Tables 4 to 7. The comparative effect of all the dyes on *Pseudomonas aeruginosa* is shown in Fig. 7, as an example. In general, dye 5 showed the most potent effect, being comparable to tetracycline and penicillin (Fig. 8). Dye 7 showed the second highest activity against the bacteria. It may be speculated that these two dyes were more active due to the presence of more polar groups or formation of hydrogen bonds with groups on bacterial surfaces. *Escherichia coli* and *Micrococcus luteus* strains were more sensitive to the dyes than the *Bacillus subtilis* or *Pseudomonas aeruginosa* strains. This is not surprising as the two latter species are some of the most resistant environmental bacteria. It can also be observed that antibacterial effect of the dyes is not Gram-specific, as *Escherichia coli* and *Pseudomonas aeruginosa* are Gram negative, whilst *Bacillus subtilis* and *Micrococcus luteus* are Gram positive.

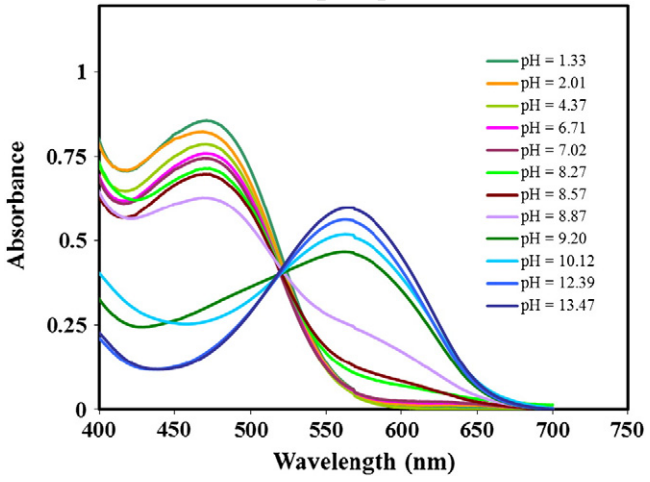


**Fig. 4.** Absorption spectra of dye 1 at different pH values.

## 3. Experimental

### 3.1. Materials and methods

All reagents were purchased from Merck and Aldrich Chemical Companies and used without further purification. IR spectra were recorded on a shimadzu 8400 FT-IR spectrophotometer. $^1$H-NMR spectra of the dyes were recorded on a Bruker 400 spectrometer in $CDCl_3$ as solvent and TMS as the internal standard. Microanalytical data for CHN were performed on a Perkin-Elmer 2400 (II) elemental analyzer. The absorption spectra of the compounds were scanned on a Cary UV-Vis double-beam spectrophotometer (Model 100). Melting points were recorded with an Electro-thermal apparatus.

### 3.2. The general procedure for the synthesis and purification of disperse azo dyes

For the preparation of dyes 1–8, the diazonium coupling reaction was employed. The procedure is presented in Scheme 1. Nitrosyl sulfuric acid solution was prepared from concentrated sulfuric acid (1.5 mL) and sodium nitrite (0.14 g, 2 mmol) at 70 °C and then cooled to 5 °C. This solution was added dropwise, with stirring, to a mixture of 3 mL of acetic acid and propionic acid (5:1 v/v) containing 2 mmol of heterocyclic amines in an ice bath. The mixture was then stirred for 1.5 h at 0–5 °C. After completion of the diazotization procedure, the diazonium salt solution was added dropwise to the solution of coupling compound (2 mmol) in sodium hydroxide (2 mmol) and water (3 mL). 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 5–6 by means

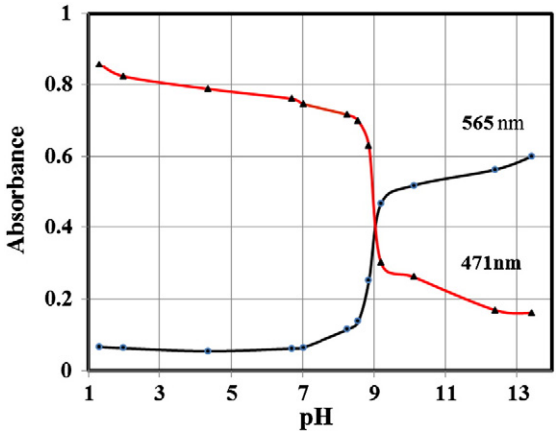


**Fig. 5.** Effect of pH on the maximum absorption intensity of 2-thiazolylazo-4-benzyloxy phenol (dye 1, 0.1%, *w*/*v* in 80% ethanol).

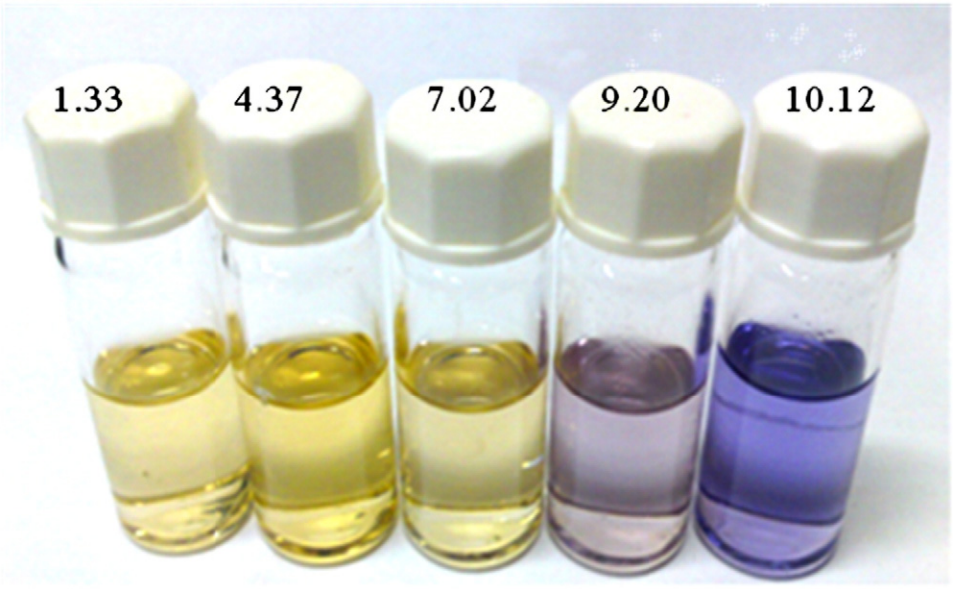


**Fig. 6.** Color observed for dye 1 solution at different pH values.

**Table 3**
Influence of temperature and sample concentration on absorption maxima of dyes 1–8.

| Dye | DMSO conc. (25 °C) | DMSO dil. (25 °C) | DMSO (70 °C) | DMF conc. (25 °C) | DMF dil. (25 °C) | $\lambda_{max}$ (nm) DMF (70 °C) | A. nitrile conc. (25 °C) | A. nitrile dil. (25 °C) | Meth. conc. (25 °C) | Meth. dil. (25 °C) | Chl. conc. (25 °C) | Chl. dil. (25 °C) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 472, 591 s, 624 s | 472, 591 s, 620 s | 474, 590 s, 621 s | 483, 582, 624 s | 485, 588, 622 s | 483, 584, 621 s | 471 | 471 | 472 | 470 | 480 | 480 |
| 2 | 485, 591 s, 623 s | 486, 588 s, 623 s | 488, 586 s, 623 s | 492, 580 s, 620 s | 491, 582 s, 622 s | 490, 584 s, 619 s | 484 | 482 | 494 | 492 | 492 | 496 |
| 3 | 495, 596 s, 636 s | 495, 596 s, 636 s | 495, 635 s | 495, 596 s, 628 s | 497, 594 s, 626 s | 497, 592 s, 626 s | 480 | 484 | 488 | 489 | 491 | 491 |
| 4 | 499, 597, 639 s | 502, 597, 639 s | 500, 597, 640 s | 499, 598 s, 637 s | 501, 595 s, 638 s | 500, 595 s, 637 s | 504 | 492 | 482 | 485 | 494 | 495 |
| 5 | 517, 588, 640 s | 515, 583, 641 s | 517, 584, 642 s | 512, 582, 639 s | 512, 581, 640 s | 515, 587, 641 s | 505 | 506 | 503 | 502 | 521 | 520 |
| 6 | 443 s, 478 | 440 s, 477 | 443 s, 478 | 442 s, 472 | 442 s, 474 | 440 s, 474 | 432, 464 s | 430, 464 s | 436, 452 s | 434, 454 s | 481, 617 s | 481, 617 s |
| 7 | 554 | 550 | 551 | 455 s, 540 | 452 s, 540 | 452 s, 540 | 470, 552 s | 466, 552 s | 441, 548 s | 441, 548 s | 454, 632 s | 454, 632 s |
| 8 | 440 | 440 | 442 | 438 | 438 | 437 | 442 | 429 | 429 | 430 | 432 | 431 |

Chl.: chloroform, Meth.: methanol, A. nitrile: acetonitrile, conc.: concentrated, dil.: diluted.

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.

Supplementary data are also available for the products showed in Scheme 1.

### 3.3. Determination of antimicrobial activity

The antibacterial activities of the dyes were determined against *Escherichia coli*, *Pseudomonas aeruginosa*, *Micrococcus luteus* and *Bacillus subtilis*, using the well diffusion method. Each bacterium

**Table 4**
Antibacterial activity of test compounds against *Escherichia coli* (diameter of inhibition zone (mm)).

| Test compound | Concentration | | | |
|---|---|---|---|---|
| | 50 μg/mL | 100 μg/mL | 150 μg/mL | 200 μg/mL |
| 1 | 12 | 15 | 17 | 20 |
| 2 | – | 9 | 13 | 15 |
| 3 | 14 | 18 | 22 | 24 |
| 4 | 8 | 13 | 16 | 19 |
| 5 | 16 | 19 | 24 | 28 |
| 6 | 10 | 12 | 16 | 20 |
| 7 | 9 | 13 | 16 | 19 |
| 8 | – | 9 | 12 | 14 |
| Std[a] | 19 | 22 | 27 | 33 |
| Std[b] | 16 | 18 | 23 | 26 |

–: Resistant.
[a] Tetracycline is used as standard.
[b] Penicillin is used as standard.

**Table 5**
Antibacterial activity of test compounds against *Pseudomonas aeruginosa* (diameter of inhibition zone (mm)).

| Test compound | Concentration | | | |
|---|---|---|---|---|
| | 50 μg/mL | 100 μg/mL | 150 μg/mL | 200 μg/mL |
| 1 | – | 9 | 12 | 13 |
| 2 | 11 | 15 | 18 | 20 |
| 3 | 10 | 12 | 15 | 19 |
| 4 | 10 | 12 | 16 | 18 |
| 5 | 11 | 13 | 17 | 22 |
| 6 | 8 | 10 | 12 | 16 |
| 7 | 10 | 12 | 17 | 19 |
| 8 | – | 9 | 14 | 16 |
| Std[a] | 18 | 19 | 21 | 24 |
| Std[b] | 17 | 21 | 24 | 29 |

–: Resistant.
[a] Tetracycline is used as standard.
[b] Penicillin is used as standard.

**Table 6**
Antibacterial activity of test compounds against *Micrococcus luteus* (diameter of inhibition zone (mm)).

| Test compound | Concentration | | | |
|---|---|---|---|---|
| | 50 μg/mL | 100 μg/mL | 150 μg/mL | 200 μg/mL |
| 1 | 17 | 21 | 24 | 28 |
| 2 | – | – | 11 | 13 |
| 3 | 14 | 18 | 22 | 26 |
| 4 | 14 | 18 | 23 | 25 |
| 5 | 18 | 21 | 25 | 29 |
| 6 | 11 | 14 | 21 | 24 |
| 7 | 8 | 9 | 12 | 15 |
| 8 | – | 9 | 11 | 12 |
| Std[a] | 18 | 23 | 27 | 30 |
| Std[b] | 9 | 10 | 12 | 14 |

–: Resistant.
[a] Tetracycline is used as standard.
[b] Penicillin is used as standard.

**Table 7**
Antibacterial activity of test compounds against *Bacillus subtilis* (diameter of inhibition zone (mm)).

| Test compound | Concentration | | | |
|---|---|---|---|---|
| | 50 μg/mL | 100 μg/mL | 150 μg/mL | 200 μg/mL |
| 1 | 8 | 10 | 12 | 13 |
| 2 | – | – | 9 | 10 |
| 3 | – | – | 9 | 10 |
| 4 | – | – | 10 | 13 |
| 5 | 9 | 11 | 15 | 18 |
| 6 | – | – | 9 | 12 |
| 7 | 12 | 18 | 22 | 25 |
| 8 | – | 8 | 12 | 15 |
| Std[a] | 14 | 16 | 19 | 21 |
| Std[b] | 8 | 10 | 12 | 16 |

–: Resistant.
[a] Tetracycline is used as standard.
[b] Penicillin is used as standard.

was inoculated into 3 mL of nutrient broth (Merck) and after overnight growth at 37 °C, 50 μL was transferred onto nutrient agar (Merck) plates. The inoculum was spread using a sterile glass spreader. Wells were formed in the nutrient agar by removing the agar gel using a sterile Pasteur pipette end. The dyes were prepared at 4 different concentrations (50, 100, 150 and 200 μg/mL) in DMSO and 50 μL was added to the wells. After overnight growth at 37 °C, the diameters of zones of growth inhibition were measured. Tetracycline and penicillin were used as positive control.

### 3.4. Dye uptake determination

#### 3.4.1. Spectrophotometric analyses

In order to measure the dyes uptake, for the synthesized dyes 50 mg of the dyes (1–5 and 7) were dissolved in 10 mL of water-DMF (25:1 v/v) solutions and sonicated for 10 minutes. The prepared solutions were then diluted to 50 mL and absorption spectra of the obtained solutions were recorded and used for characterization of the peak position, $\lambda_{max}$, and the molar absorptivity, ε, according to Beer–Lambert law. Different portions (0.1, 0.2, 0.4, 0.6, 0.8 and 1 mL) of each solution were subsequently diluted to 10 mL deionized water-DMF (25:1, v/v) for making proper series of the standard samples. Absorptions of these standard samples were recorded and the obtained data were used for development of standard curves.

#### 3.4.2. Uptake measurements

The prepared standard solution were diluted to 50% of their initial concentrations and set as first concentrations, $C_0$ for each dye. The polyester fibers (100 mg) were then immersed and stirred according to the following profile: 5 min/25 °C, 10 min/35 °C, 15 min/50 °C, 25 min/60 °C, 50 min/90 °C, 85 min/95 °C, 100 min/95 °C and 120 min/95 °C. At the end of the each period, 1 mL of the bath solution was removed and diluted to 10 mL with deionized water-DMF (25:1 v/v) and the absorption was recorded at $\lambda_{max}$. According to the dye standard curve, the concentration of the dye in the bath solution was evaluated ($C_i$). Subsequently, the uptake percentage was calculated according to the following equation:

$$\text{Uptake } \% = \frac{C_0 - C_i}{C_0} \times 100\%$$

Fig. 9 and Table 8 show the uptake of dyes 1–5 and 7. The dye uptake percentage increased as the temperature increased. It suggested that the dye molecules interact more effectively with the fiber functional groups and penetrate into the fiber structure more easily, as the temperature is raised. This means that the dyestuff dyes the fiber more easily at higher temperatures.

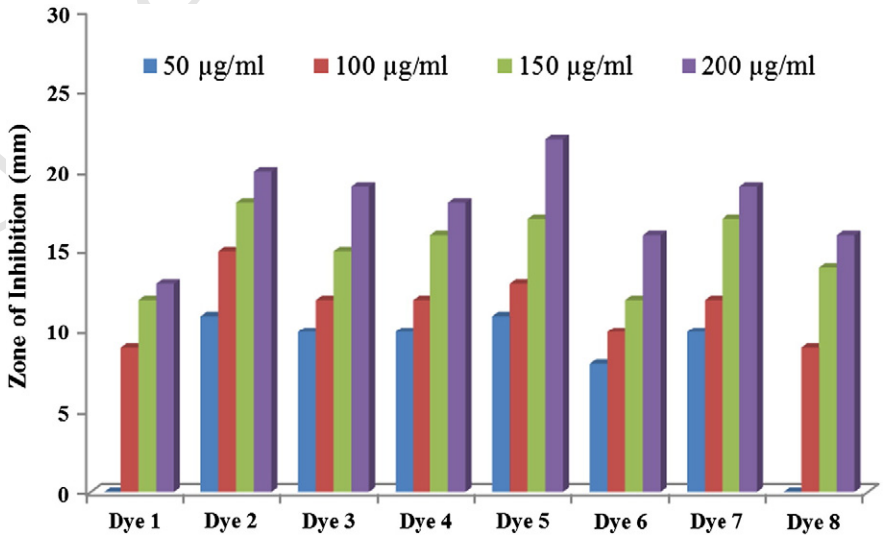


**Fig. 7.** Statistical representation for biological activity of dyes 1–8 against *Pseudomonas aeruginosa*.



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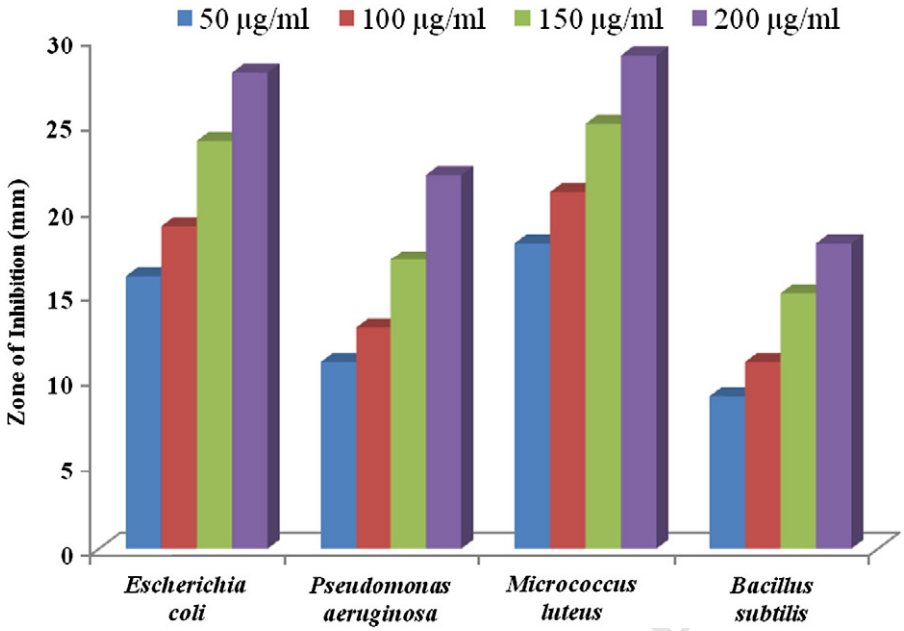


**Fig. 8.** Statistical representation for biological activity of dye 5.

### 3.4.3. Colorfastness assessment

The wash fastness of dyed fabrics was evaluated using AATCC test method 61-1996 No. 2A and the resultant fabrics were evaluated for color change and staining [37]. The dyed fabric was rinsed with water, dried at room temperature and ironed. The dyes (1–5 and 7) gave a narrow range of color, varying from orange to red, with excellent brightness, depth on fabric and deeper shade with high tinctorial and excellent levelness. The washing fastness properties of the dyed polyesters were evaluated and are shown in Table 9. For the assessments, a rating scale of 1 to 5 was used. Where 1 = poor, 2 = fair, 3 = moderate, 4 = good, and 5 = excellent. All of the used dyes showed moderate (3–4) to fairly good (4–5) fastness to wash on fabric.

## 4. Conclusions

In this study, we have synthesized some hetaryl-azo dyes by linking various heterocyclic amines with 4-benzyloxyphenol as the coupling component. The solvatochromic behaviors of these dyes in various solvents were evaluated. The study of substituent effects showed that the withdrawing group on the diazo moiety has significant influence (red shift) on the electron absorption spectra of these dyes. It was also observed that the absorption curves of the dyes changed slightly with acid, but significantly with base.

In acidic aqueous medium, the dyes were intense yellow or red. As the pH value of the solution increased, they showed a gradual bathochromic shift with sharp, clear and reversible color changes in the pH range 7.02–9.20. A few drops of the dye in 50 mL of solution will turn the solution from yellow or red to a strong blue-violet color in the mentioned pH range. As a result, the possible use of these azo dyes as an acid–base endpoint indicator should be considered.

All the dyes exhibited antibacterial activity. The most active, was dye 5, followed by dye 7. Presence of more polar groups in these dyes is likely to increase their antibacterial activities. Antibacterial activity exhibited was not Gram-specific and therefore, the activity is probably related to bacterial cytoplasmic membrane or to interference

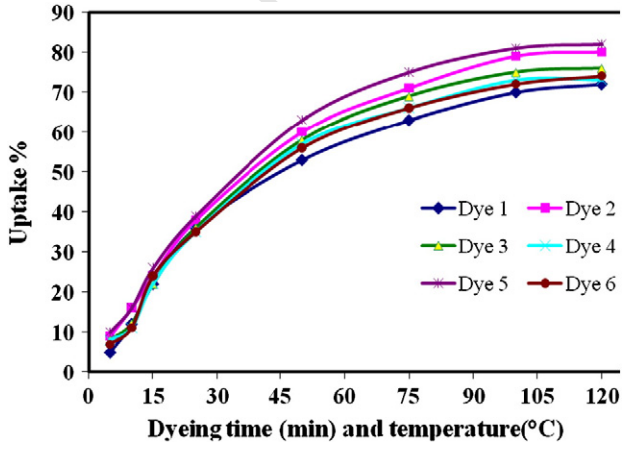


**Fig. 9.** Uptake of the dyes 1–5 and 7 on polyester fiber at 1 % (omf).

**Table 8**
Effect of dyeing time and temperature on the dye uptake percentage.

| Dyeing profile | Dye uptake (%) | | | | | |
|---|---|---|---|---|---|---|
| | Dye 1 | Dye 2 | Dye 3 | Dye 4 | Dye 5 | Dye 7 |
| 5 min/25 °C | 5 | 9 | 8 | 8 | 10 | 7 |
| 10 min/35 °C | 12 | 16 | 12 | 11 | 16 | 11 |
| 15 min/50 °C | 22 | 24 | 22 | 22 | 26 | 24 |
| 25 min/60 °C | 36 | 38 | 36 | 35 | 39 | 35 |
| 50 min/90 °C | 53 | 60 | 58 | 57 | 63 | 56 |
| 75 min/95 °C | 63 | 71 | 69 | 66 | 75 | 66 |
| 100 min/95 °C | 70 | 79 | 75 | 73 | 81 | 72 |
| 120 min/95 °C | 72 | 80 | 76 | 73 | 82 | 74 |

**Table 9**
Wash fastness properties for dyes 1–5 and 7 on polyester.

| Dye | Wash fastness | | |
|---|---|---|---|
| | color | Change in Shade | Staining on polyester |
| 1 | Red | 3–4 | 4 |
| 2 | Red | 4–5 | 3–4 |
| 3 | Dark red | 4 | 4–5 |
| 4 | Dark red | 4 | 4–5 |
| 5 | Reddish black | 4–5 | 4 |
| 7 | Brick orange | 3 | 4 |

in an intracellular cytoplasmic process. Further investigations are necessary to determine the mechanism of activity.

The dyeing of polyester fiber was also studied. Wash fastness results of the new azo dyes are excellent, both in change in shade and color staining.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2012.12.030.

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