Fibers and Polymers 2022, Vol.23, No.4, 1040-1049
DOI 10.1007/s12221-022-4476-6

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Synthesis, Application, and Recovery of Alkali-Clearable Disperse Dyes Containing Azo Pyridone Structure

Liang Jin[1], Tao Qian[2], Tao Zhu[3], Ren-Liang Wang[4], Wei-Guo Chen[1,5], Hua Jiang[1,5], and Zhi-Hua Cui[1,5]*

[1]*Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China*
[2]*Hangzhou Jihua Polymer Material Co., Ltd., Hangzhou 310018, China*
[3]*Shangyu Industrial Technology Research Institute Co., Ltd., Zhejiang Sci-Tech University, Shangyu 312300, China*
[4]*Zhejiang Longsheng Group Co., Ltd., Shangyu 312368, China*
[5]*Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education of China, Hangzhou 310018, China*

(Received May 11, 2021; Revised July 12, 2021; Accepted August 18, 2021)

Abstract: Carboxylic acid ester disperse dyes containing an azo pyridone structure have a high molar extinction coefficient, excellent washing color fastness, and simple synthetic methods. Dyes were readily synthesized through a conventional diazo coupling reaction between the reactant ethyl *p*-aminobenzoate and a coupling component containing an azo pyridone structure. Subsequently, the molecular structures of the target products were characterized by FTIR, mass spectrometry, ^{1}H NMR, ^{13}C NMR, UV-vis absorption spectroscopy, and elemental analysis. The synthesized dyes were used to dye poly(ethylene terephthalate) fabric, and their washing and rubbing color fastness properties were tested and compared under different post-treatment methods. Moreover, under the condition of alkali clearing, the relationships among different alkali concentrations and clearing effects were studied to determine the optimal alkali clearing process conditions for dyed fabrics, and the minimum alkali consumption required to obtain the best results was determined. It was found that carboxylic ester disperse dyes containing an azo pyridone structure showed good dyeing performance and alkali-clearable properties on polyester fibers. In addition, in hydrolyzate recovery, $BaCl_2$ (salting out) can be used instead of acidification to recover the dye hydrolyzate, which has good environmental benefits.

Keywords: Alkali-clearable, Pyridone, Synthesis, Salting out, Recovery

Introduction

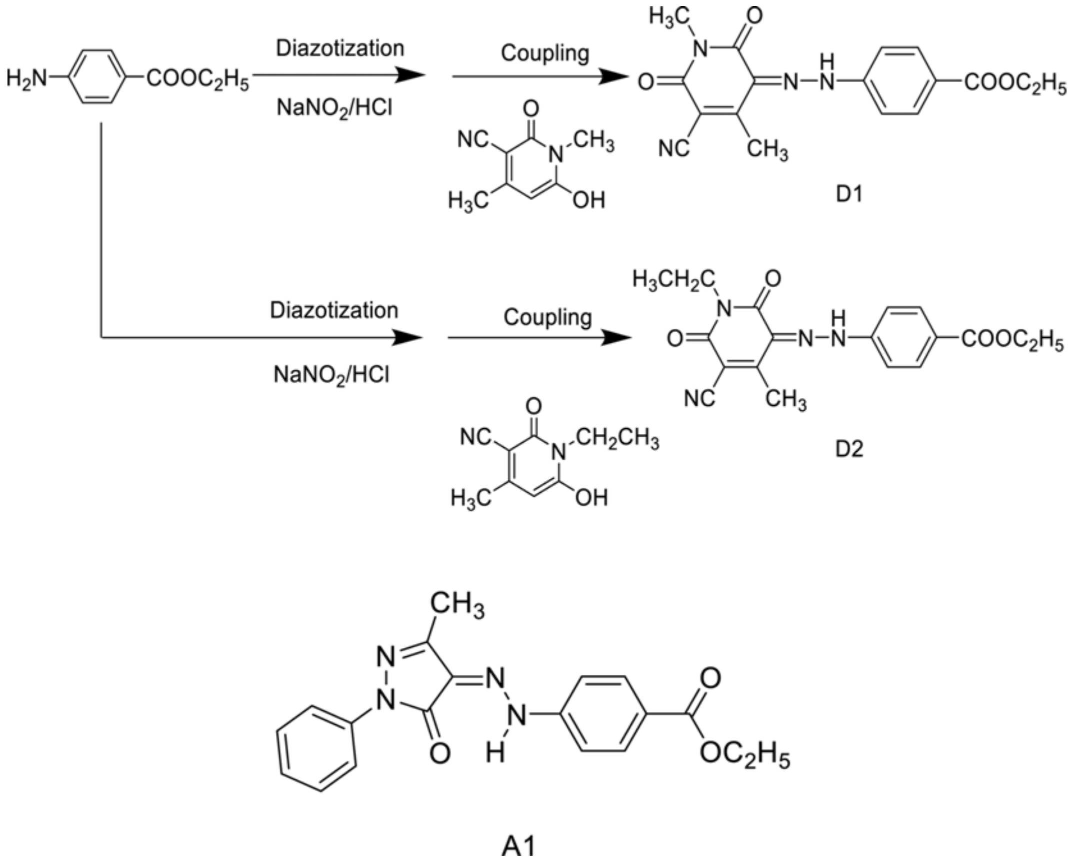
Disperse dyes with complete chromatograms and various types have always occupied an important position in the dye industry. Their molecular structure does not contain water-soluble groups such as sulfonate or carboxylate groups and only contains a small number of polar groups, so such dyes are widely used for the coloration of hydrophobic fibers such as polyester. Some dye particles may remain on the fiber surface after dyeing is completed, and these particles will affect the brightness of fabric as well as its fastness to washing and rubbing [1,2]. Therefore, after polyester fabric is dyed, a reduction clearing method (1.7 g/*l* sodium hydrosulfite and 1 g/*l* sodium hydroxide at 70 °C for 15 min) is usually necessary to remove the insoluble dye particles on the fiber surface [3]. In this process, although the dispersed dye particles can be decomposed into small water-soluble molecules through the action of reduction clearing, serious environmental pollution also occurs due to the addition of chemicals and the formation of potentially carcinogenic aromatic amines [4]. This consequence not only increases the difficulty of treating wastewater but also endangers human health.

Following the rapid development of disperse dyes in recent years, alkali-clearable disperse dyes have provided a solution to the environmental problems caused by the reduction clearing process [5]. Some disperse dyes containing phthalimide and sulfonyl fluoride have been reported due to their alkali-clearable properties [6-9]. Alkali-clearable disperse dyes containing phthalimide and sulfonyl fluoride groups can be converted to water-soluble dyes under relatively mild alkali conditions, and these water-soluble dyes generated after alkali clearing are readily washed off without the generation of harmful primary aromatic amines [10]. In view of the lower toxicity of hydrolyzates of carboxylic ester groups than sulfonyl fluoride and phthalimide groups under alkali conditions, the incorporation of carboxylic ester groups into the structure of alkali-clearable azo disperse dyes has become a good choice [11].

On the other hand, *N*-substituted pyridone-containing disperse dyes show a high molar extinction coefficient, bright color, excellent light fastness, excellent fastness to washing, and some fluorescence and have important uses in industrial fields such as dyes and medicine [12-17]. Therefore, combining pyridone structures with carboxylic ester groups is an effective strategy to improve the related properties of dyes. In this paper, two alkali-clearable azo disperse dyes with high color strength (see Scheme 1) were synthesized with a pyridone structure derivative as the coupling component and ethyl *p*-aminobenzoate as the diazo

---

*Corresponding author: zhhcui@zstu.edu.cn



Scheme 1. Synthetic routes of alkali-clearable disperse dyes **D1**, **D2** containing azo pyridone structure, and the structure of the control dye **A1**.

component. Their molecular structures were characterized and confirmed. The synthetic disperse dyes containing carboxylic acid esters of azo pyridone [18-20] and the control dye **A1** [21] (see Scheme 1) were then applied to dyeing poly(ethylene terephthalate) (PET) fabric, and their color fastness properties with different post-treatment methods (reduction clearing and alkali clearing) were examined and compared. In addition, based on the clearing of polyester fabric with the sole action of alkali after dyeing, this paper investigates the UV-vis absorption spectra of the dye particles remaining on the surface of the fabric after alkali clearing with different alkali concentrations to minimize the amount of alkali required to achieve the best results. Furthermore, this study provides broad application prospects in the process of dye preparation and production to save production costs and reduce the difficulty of sewage treatment.

Experimental

Materials and Instruments

Polyester fabric (PET, 100 %, plain, 20 tex/48F) was scoured in boiled water containing 0.5 % sodium dodecyl benzenesulfonate for 10 min before use.

The reagents ethyl *p*-aminobenzoate, 1,4-dimethyl-3-cyano-6-hydroxy-2-pyridone, *N*-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone, sodium hydroxide, sodium nitrite, concentrated hydrochloric acid (37 %), sodium carbonate, sodium hydrosulfite, sodium chloride, *N*,*N*-dimethylformamide, ethanol, *p*-nitroaniline, and acetone were purchased from Aladdin Chemical Co., Ltd. (Shanghai, P.R. China). The dispersant sodium methylenedinaphthalene disulfonate (NNO) was provided by Zhejiang Longsheng Group Co., Ltd. (Shangyu, Zhejiang Province, P.R. China).

^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 NMR spectrometer with TMS as the internal standard in $CDCl_3$. IR spectra were measured with an FT/IR-430 spectrophotometer. Mass spectra (MS) were recorded on a Thermo Fisher LCQ Fleet using an electrospray ionization (ESI) source. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Lambda 900UV/vis spectrophotometer.

Synthesis of Dye 1

The disperse dye **D1** containing an azo pyridone carboxylic ethyl ester structure was synthesized by a conventional diazo coupling reaction. First, ethyl *p*-aminobenzoate (1.67 g, 10 mmol) was dissolved in an ice-water mixture and stirred well, and then a sodium nitrite (0.76 g, 11 mmol) aqueous solution was rapidly mixed with the ethyl *p*-aminobenzoate solution. Second, the mixed solution was cooled in an ice-water bath maintained at approximately 0-5 °C and then rapidly poured into the ice-cooled dilute hydrochloric acid (13 m*l*, 2.3 mol/*l*) solution already in the vessel. The coupling reaction was carried out by adding the prepared diazonium salt solution to 1,4-dimethyl-3-cyano-6-hydroxy-2-pyridone (coupling component) in sodium hydroxide solution (8.2 g, 10 mmol) at 0-5 °C and pH 4.5-5.5 for 3 h. The pH value of the coupling liquor was controlled by adding sodium carbonate powder. A color reaction with H-acid was used to confirm the reaction endpoint. The dye was filtered, washed and dried in an oven at 70 °C to afford the product. Crude yield: 3.22 g (94.7 %); FTIR (KBr, cm^{-1}): 2960, 2930 (CH_3, CH_2), 2227 (CN), 1699 (C=O, carboxylic ester), 1665 (C=O, pyridone); ^1H NMR (400 MHZ, $CDCl_3$): δ14.98 (s, 1H, NH), 8.18 (d, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 4.45 (q, 2H, CH_2), 3.42 (s, 3H, N-CH_3), 2.69 (s, 3H, C=C-CH_3), 1.46 (t, 3H, CH_3); ^{13}C NMR (125 MHZ, $CDCl_3$): δ165.41, 161.75, 159.80, 158.34, 144.03, 131.53, 128.96, 123.95, 116.54, 114.01, 61.31, 53.41, 26.41, 16.60, 14.32; ESI MS (m/z, %): 341.1 $[M+H]^+$; elemental analysis: found (%): C, 60.19, H, 4.67, N, 16.24; calcd (%): C, 60.00, H, 4.74, N, 16.46. The crude product was purified by recrystallization from ethanol (55.9 % yield).

Synthesis of Dye 2

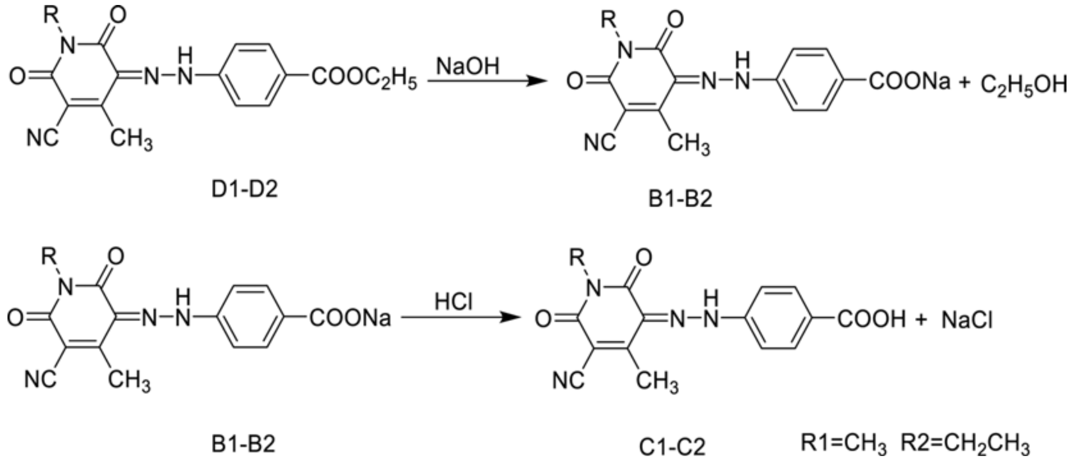
The disperse dye **D2** containing an azo pyridone carboxylic ethyl ester structure was also synthesized by a conventional diazo coupling reaction. The method for synthesizing the diazonium salt of dye **D2** was the same as that used for dye **D1**. The coupling reaction was carried out by adding the aforementioned diazonium salt solution to *N*-ethyl-3-cyano-4-methyl-6-hydroxy-2-pyridone (coupling component) solution (8.34 g, 10 mmol) at 0-5 °C and pH 4.5-5.5 for 3 h. The pH value of the coupling liquor was controlled by adding sodium carbonate powder. A color reaction with H-acid was used to confirm the reaction endpoint. The dye was filtered, washed and dried in an oven at 70 °C to afford the product. Crude yield: 3.64 g (102.8 %); FTIR (KBr, cm^{-1}): 2960, 2930 (CH_3, CH_2), 2227 (CN), 1699 (C=O carboxylic ester), 1665 (C=O pyridone); ^1H NMR (400 MHZ, $CDCl_3$): δ15.02 (s, 1H, NH), 8.19 (d, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 4.45 (q, 2H, CH_2), 4.1 (q, 2H, CH_2), 2.68 (s, 3H, CH_3), 1.46 (t, 3H, CH_3), 1.30 (t, 3H, CH_3); ^{13}C NMR (125 MHZ, $CDCl_3$): δ165.64, 161.38, 159.51, 158.32, 144.1, 131.53, 128.80, 124.09, 116.50, 114.06, 61.30, 53.41, 35.31, 16.60, 14.33, 12.96; ESI MS (m/z, %): 353.2 $[M-H]^-$; elemental analysis: found (%): C, 61.42, H, 5.03, N, 15.04; calcd (%): C, 61.01, H, 5.12, N, 15.81. The crude product was purified by recrystallization from ethanol (yield 70.6 %).

Synthesis of Carboxylate Dyes

Dyes **D1** and **D2** (6.86 mmol) were dissolved in 1 g/*l* sodium hydroxide solution, stirred continuously, and hydrolyzed at 85 °C for 1 h. After hydrolysis was completed, an aqueous solution containing sodium carboxylate dyes **B1** and **B2** was obtained. **B1** ESI MS (m/z, %): 311 $[M-Na]^-$; **B2** ESI MS (m/z, %): 325 $[M-Na]^-$.

To facilitate the characterization of the molecular structure of the sodium carboxylate dyes, it was necessary to separate the dyes from the aqueous solution. Here, acid precipitation was used to separate the dyes from the alkaline solution: 10 % dilute hydrochloric acid was slowly added to the sodium carboxylate solution until the dye precipitated, and the solution was allowed to stand for 24 h. Dyes **C1** and **C2** were filtered, washed and dried in an oven at 70 °C to afford the product.

C1: crude yield: 1.75 g (81.7 %); FTIR (KBr, cm^{-1}): 2231 (CN), 1720 (C=O, COOH), 1664 (C=O, pyridone); ^1H NMR



Scheme 2. Synthetic route and acid precipitation process of sodium carboxylate dye.

(400 MHZ, DMSO): δ14.50 (s, 1H, OH), 13.04 (s, 1H, NH), 8.05 (d, 2H, Ar-H), 7.82 (d, 2H, Ar-H), 5.78 (s, 3H, CH_3), 3.48 (s, 3H, CH_3); ^{13}C NMR (125 MHZ, DMSO): δ167.14, 162.45, 160.14, 159.36, 131.40, 128.48, 124.72, 117.61, 115.38, 55.40, 27.45, 34.98, 16.91; ESI MS (m/z, %): 311 $[M-H]^-$; elemental analysis: found (%): C, 57.60, H, 3.86, N, 17.86; calcd (%): C, 57.69, H, 3.87, N, 17.94.

C2: crude yield: 1.86 g (83.2 %); FTIR (KBr, cm^{-1}): 2225 (CN), 1760 (C=O, COOH), 1667 (C=O, pyridone); ^{1}H NMR (400 MHZ, DMSO): δ14.51 (s, 1H, OH), 13.04 (s, 1H, NH), 8.05 (d, 2H, Ar-H), 7.82 (d, 2H, Ar-H), 3.93 (q, 2H, CH_2), 2.56 (s, 3H, CH_3), 1.17 (t, 3H, CH_3); ^{13}C NMR (125 MHZ, DMSO): δ167.09, 162.78, 160.23, 159.63, 131.47, 128.68, 124.77, 117.61, 115.40, 55.40, 36.26, 34.99, 16.92, 13.13; ESI MS(m/z, %): 325 $[M-H]^-$; elemental analysis: found (%): C, 58.60, H, 4.25, N, 17.45; calcd (%): C, 58.89, H, 4.32, N, 17.17.

Dyeing

Dyebath dispersions of the azo pyridone carboxylic acid ester structure-containing dyes **D1-D2** and the control dye **A1** were prepared by milling an aqueous suspension of the powdered dye with glass beads (0.2 mm diameter) for 10 h in the presence of the dispersing agent NNO, which had a similar mass to the dyes. Dyeing was carried out at a 100:1 liquor-to-goods ratio in sealed stainless steel dyeing pots of 200 m*l* capacity in a Roaches-Rotee dyeing machine. An appropriate volume of the dye solution was placed in each pot to give the required quantity of dye. The dyebath pH was adjusted to 5.0 using acetic acid/sodium acetate buffer solution. A sample of preweighed PET fabric was placed in each pot, and dyeing was carried out by raising the dyebath temperature from room temperature to 130 °C at a rate of 2 °C/min and holding at dyeing temperature for 60 min before cooling to room temperature. The dyed PET fabric was then rinsed with cold water and air-dried.

Washing Methods and Color Fastness Test

At the end of the dyeing process, the dyed fabric was treated by heat-setting at 180 °C for 30 s. Subsequently, the fabric was treated in three different ways (no treatment, reduction clearing and alkali clearing). Reduction clearing was performed at a liquor ratio of 80:1 using 1.7 g/*l* sodium hydrosulfite and 1 g/*l* sodium hydroxide for 15 min at 70 °C. Alkali clearing was undertaken using an 80:1 liquor ratio and a certain concentration of sodium hydroxide for 15 min at 70 °C. After clearing, the samples were rinsed with cold water and air dried.

Washing and rubbing color fastness tests of the dyes on PET fabrics were carried out according to ISO 105-C10:2006 and ISO 105-X12:2001, respectively [22].

Acetone Extraction Experiment

The dyed fabrics after alkali clearing with different alkali concentrations and reduction clearing were put in 20 m*l* of acetone solution and extracted for 15 min at room temperature. After extraction, the absorbance of residual dye on the fiber surface after different post-treatment methods was measured by UV-visible absorption spectroscopy. Then, the residual content (R%) of dye on the fiber surface after clearing was calculated according to equation (1):

$$R(\%) = \{A(\text{treated}) / A(\text{untreated})\} \times 100 \tag{1}$$

where A (treated) is the absorbance value (at the absorption maximum) of the extracted acetone solution of residual dye on the surface of the dyed fabric after clearing. A (untreated) is the absorbance value (at absorption maxima) of the extracted acetone solution of residual dye on the surface of the dyed fabric.

Shade Depth

The *K/S* values of dyed PET fabrics were evaluated at maximum absorption wavelength (λ_{max}) using a UV-vis spectrophotometer. The *K/S* value is a function of the reflectance R, as expressed by the equation (2). Each sample was measured in four different areas and the average value was recorded [23].

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

Dye Exhaustion

The dye in the residual dyebath and the staining inside the dyeing pot were rinsed with acetone and dissolved into 50/50 acetone/water. The optical absorbance of the solutions was determined according to the Beer-Lambert law at the maximum absorption wavelength of each dye by UV-vis spectrophotometer. Subsequently, the dye exhaustion (%S) was calculated using equation (3):

$$\%S = \{(A_1 - A_2)/A_1\} \times 100 \tag{3}$$

where A_1 and A_2 are the absorbance of the dyebath dissolved into 50/50 acetone/water before and after dyeing.

Recovery Experiment of Hydrolyzate

Different molar ratios of metal salt were added to a certain concentration of carboxylate solution after alkali clearing, and the concentration ratios of salt and carboxylate were 0.5:1, 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1. Carboxylate (0.78 mmol) and salt in the above ratios were dissolved in a certain volume of aqueous solution, stirred to achieve full mixing and allowed to stand for 24 h. Finally, the supernatant of each group of samples was filtered with a Buchner funnel, and the absorbance of the filtrate was measured with a UV-vis spectrophotometer and recorded as A. Similarly, an equivalent concentration of carboxylate solution that had not been treated with salt was prepared. The absorbance of the carboxylate filtrate measured with a UV-vis spectrophotometer was recorded as A_0. Subsequently, the yield Y of hydrolyzate under different salt concentrations was calculated using equation (4):

$$Y = \{(A_0 - A)/A_0\} \times 100 \tag{4}$$

Results and Discussion

Design, Synthesis, and Characterization

A pyridone structure and carboxylic ester groups were combined for the synthesis of two dyes; the resulting structures combined the dye's high molar extinction coefficient, excellent color fastness, and alkali-clearable properties and expanded the scope of application of the dye. Given the current difficulties in treating wastewater from dye companies, these dyes have the advantage of alkali-clearable properties, and the dye hydrolyzate can be recovered to reduce the color of the solution. Ethanol is used to purify synthetic dyes to remove other possible by-products. After the dyes were filtered, washed, and dried, the crude yields of both dyes were above 90 %. In addition, the properties of the yellow disperse dye **A1** containing carboxylate groups and synthesized previously by us are presented here for comparison.

The alkali-clearable disperse dyes **D1-D2** containing an azo pyridone structure were synthesized by a simple diazo coupling reaction. Ethyl *p*-aminobenzoate (diazo component) reacts with two different coupling components containing a pyridone structure to form a dye. The chemical structures of dyes **D1-D2** were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis.

Spectral Properties

The change in polarity on both sides of the azo chromophore may affect the spectral properties of dyes in solvents and their dyeing properties on fabrics. Therefore, the UV-visible absorption curves for dyes **D1-D2** and the control dye **A1** in acetone and DMF were measured. The UV-visible absorption spectra for dyes **D1-D2** and the control dye **A1** in acetone are described in Figure 1, and data on the visible absorption maxima (λ_{max}) and the molar extinction coefficients (ε_{max}) of dyes **D1-D2** and **A1** in acetone and DMF are listed in Table 1. Comparing **D1-D2** in Figure 1, the very small polarity difference between the -CH_3 and -CH_2CH_3 moieties in the two dyes resulted in little change in the λ_{max} in acetone. The change in λ_{max} of dyes **D1-D2** and **A1** comes exclusively from the electron-withdrawing ability of the coupling component [24] because the three dyes were synthesized using the same diazo component (ethyl *p*-aminobenzoate). The coupling component of **D1-D2** has a strong electron-withdrawing group (-CN). The resulting enhanced electron-withdrawing ability leads to a decrease in the HOMO-LUMO energy gap of **D1-D2**, which might be helpful for electron transition. The molar extinction coefficient can indicate the amount of dye needed in dyeing, and a higher molar extinction coefficient signifies a lower dosage of the dye. Table 1 shows that the ε values of dyes **D1-D2** in acetone are even higher than 55,000 $l \cdot mol^{-1} \cdot cm^{-1}$, which are better than those of **A1**. Therefore, dyes **D1-D2**, whose coupling component was a pyridone structure, possessed excellent dyeing properties and a notably higher molar extinction coefficient than **A1**.

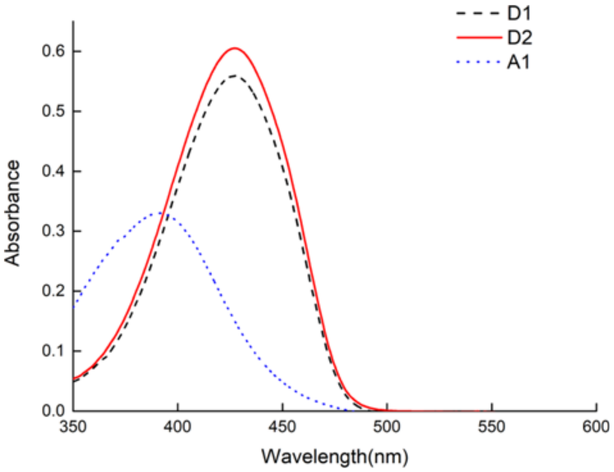


Figure 1. UV-vis absorption spectra of **D1-D2** and **A1** in acetone (1×10^{-5} mol/l).

Table 1. Spectral properties of **D1**, **D2**, and **A1** in acetone and DMF

Dye	Acetone		DMF	
	λ_{max}	$\varepsilon\times10^4$ (l/mole·cm)	λ_{max}	$\varepsilon\times10^4$ (l/mole·cm)
D1	427	5.59	431	3.32
D2	427	6.05	433	3.34
A1	392	3.31	406	1.92

In view of the effect of solvent polarity, the λ_{max} of dyes **D1-D2** dissolved in DMF shifted to a longer wavelength compared with those of dyes dissolved in acetone, where a bathochromic effect ($\Delta\lambda_{max}$=4-6 nm) was observed. This bathochromic shift can be explained by the increase in solvent polarity from 5.40 (acetone) to 6.40 (DMF) [25]. When the dye was dissolved in DMF, the superior stabilization of the dye's excited electronic state led to a lower energy gap between the ground and excited states of the dye molecules, which resulted in a bathochromic shift [26].

Color Build-up

In consideration of the importance of high dye sorption for the textile industry, which means lower dye consumption and high affinity between dyes and fibers, some other dyeing

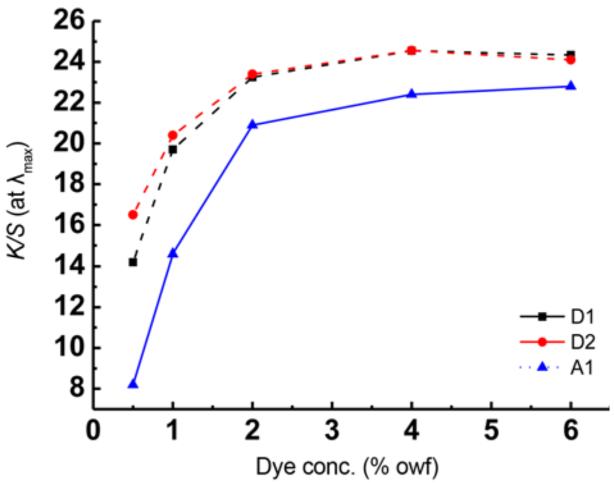


Figure 2. Color build-up of azo pyridone disperse dyes and the control dye on PET fabric (dyeing conditions: liquor-to-goods ratio 70:1, maintained at 120 °C for 60 min).

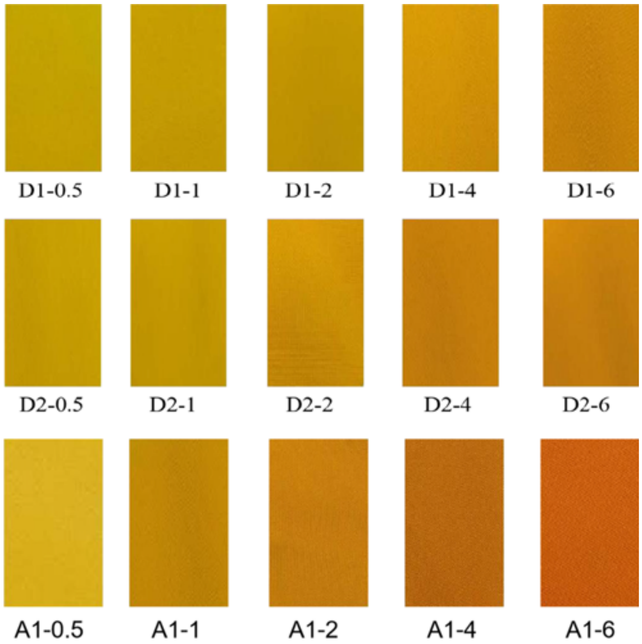


Figure 3. Digital photos of the dyed PET fabrics under D_{65} illuminant.

performance indicators, such as color build-up and color fastness properties, in addition to the dye sorption of the three dyes, were further investigated. Figure 2 illustrates the different build-up profiles of dyes **D1-D2** and **A1** on PET fabric. Compared with the yellow control dye **A1**, **D1-D2** containing pyridone structures show a higher color depth. **D1-D2** give yellow hues and exhibit good build-up properties on PET fabric, and the color strength of the two dyes reaches saturation at 4.0 % owf (the depth of each dye reaches a *K/S* value over 20). Our initial dyeing attempt of polyester fabrics resulted in yellow shades with excellent color uniformity (Figure 3).

Table 2. Color properties of the dyed PET with **D1**, **D2**, and **A1** at 1 % owf dyeing concentration

Dye	λ_{max} (nm)	*K/S*	L^*	a^*	b^*	C^*	*h*
D1	440	19.7	82.27	-1.6	95.6	95.6	90.9
D2	440	20.7	82.25	-0.7	98.2	98.2	90.4
A1	410	14.6	80.39	8.37	73.1	73.6	83.4

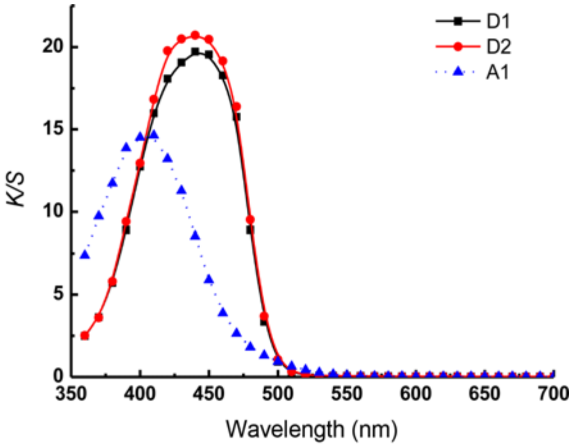


Figure 4. *K/S* curves of dyes **D1-D2** and **A1** at 1 % owf (data collected from Figure 2).

The dyed samples were assessed using the CIELAB system in terms of L*, a* and b*, and the color values are shown in Table 2. The a* values of dyes **D1-D2** are considerably smaller than those of dye **A1**, suggesting that the color hue of dye **A1** tends towards red more than does that of dyes **D1-D2**. Compared with the b* value of dye **A1**, those of dyes **D1-D2** are considerably larger; hence, the color hue of dyes **D1-D2** tends to be more pure yellow than that of **A1**. Compared with **A1**, the *K/S* curves of **D1-D2** exhibit a redshift from a λ_{max} of 410 to 440 nm (Figure 4). The reason for this shift may be caused by the difference in electron-withdrawing ability of the coupling components of dyes **D1-D2** and **A1**.

Dyeing Properties and Color Fastness Test

To further study the effect of fabric dyeing after alkali clearing at different alkali concentrations, dyed fabric was treated in three different ways (no treatment, reduction clearing, and alkali clearing), in which the alkali clearing process was set to five different sodium hydroxide concentrations: 0.2 g/*l*, 0.4 g/*l*, 0.6 g/*l*, 0.8 g/*l*, and 1.0 g/*l*. The post-treatment dyed fabric was extracted using a certain volume of acetone for 15 min at room temperature. The

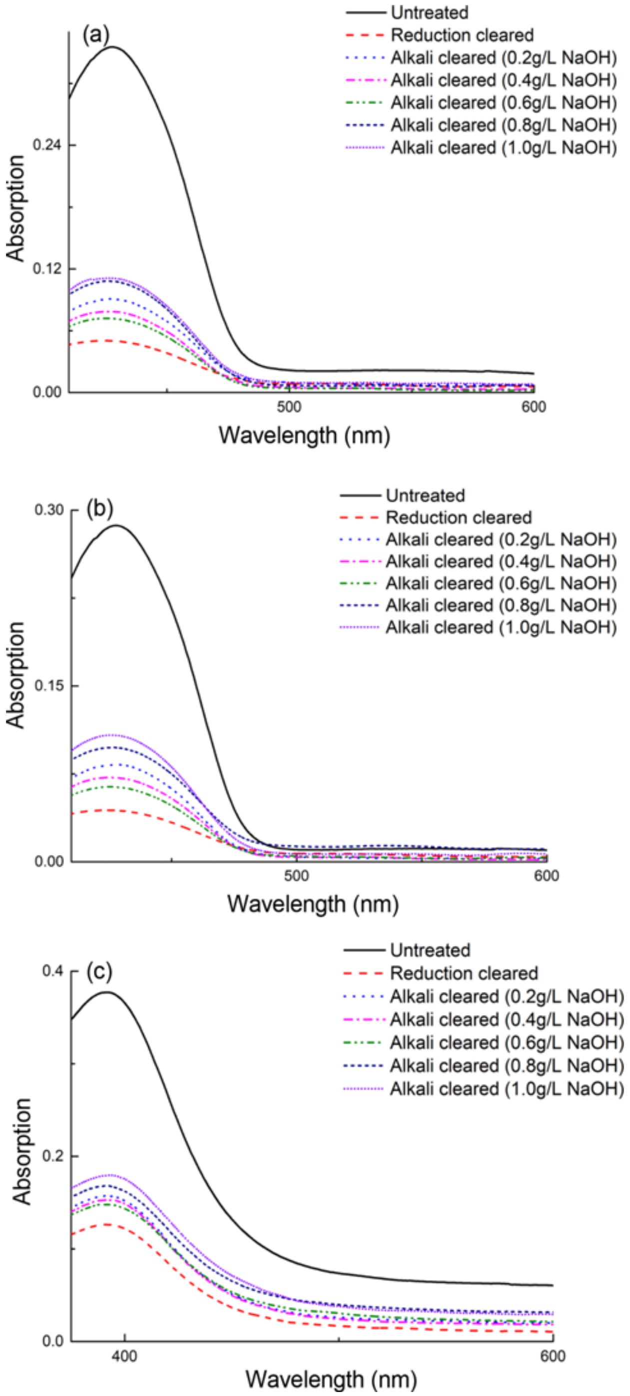


Figure 5. UV-vis absorption spectra of the disperse dye particles remaining on the surface of the dyed fabric after acetone extraction; (a) **D1**, (b) **D2**, and (c) **A1**.

optimal alkali concentration was determined by comparing the absorption spectra of the disperse dye particles remaining on the surface of the dyed fabric dissolved in the acetone solution after different post-treatment methods. Figure 5 shows the UV-vis absorption spectrum of each

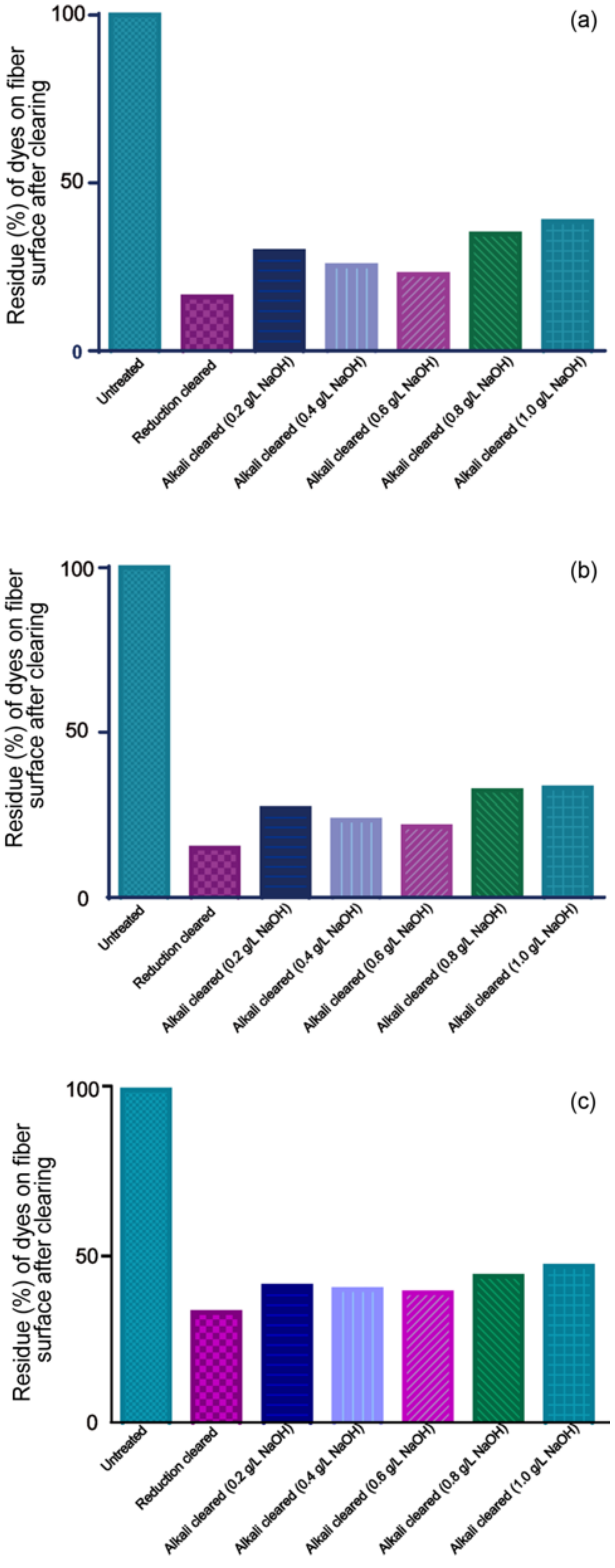


Figure 6. Residues of dye on fiber surface after different post-treatment methods (data collected from Figure 5); (a) **D1**, (b) **D2**, and (c) **A1**.

group of acetone solution. Figure 6 shows the residual contents (%) of the dyes on the fiber surface after clearing based on the results of Figure 5. It can be seen from the untreated absorption spectrum of Figure 5 that the absorbance of (c) is higher than that of (a) and (b). This result indicates that the amount of dye **A1** remaining on the fiber surface is more than that of **D1-D2** for untreated dyed fabrics. This may be the reason why the color fastness of **A1** is worse than that of **D1-D2**. In addition, the absorbance of the three dyes remaining on the fiber surface after reduction clearing is lower than that of the untreated fabric because the untreated fabric surface contains more insoluble dye than do the samples after reduction clearing. As seen in Figure 6, the residual content (%) of dye on the fiber surface after clearing in (c) is generally higher than that in (a) and (b), and the residual content (%) of dye on the fiber surface in (b) is the lowest after reduction clearing and alkali clearing with different alkali concentrations. This result shows that the alkali clearing effect of **D2** is better than those of **A1** and **D1**. The alkali clearing effect with 0.6 g/*l* sodium hydroxide is better than those at other concentrations of sodium hydroxide, and there is less insoluble dye on the surface of the fabric, which has an absorbance close to that obtained with reduction clearing. The greater absorbance of samples treated with 1.0 g/*l* and 0.8 g/*l* may be due to the excessive alkali concentration destroying the surface structure of the fibers, resulting in an increase in the specific surface area of the fabric in contact with the acetone solution and dissolving more dye.

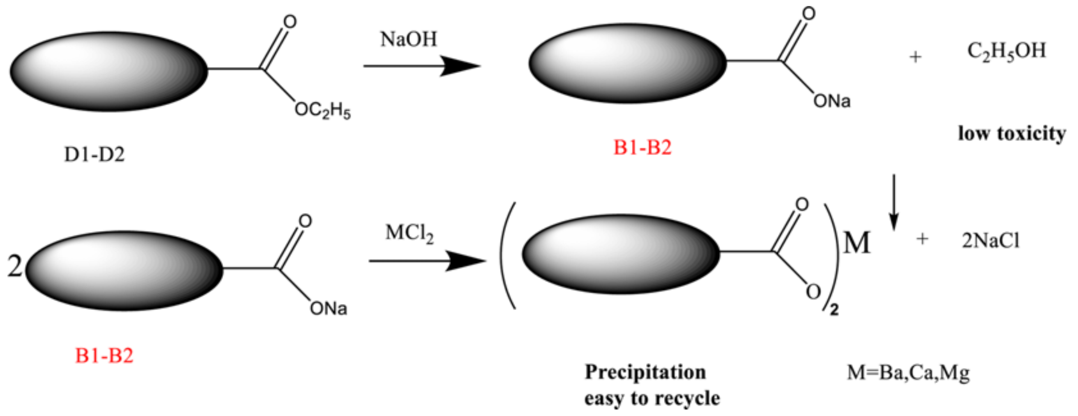
The dye exhaustion and *K/S* values of dyes **D1-D2** and **A1** on PET fabrics are listed in Table 3. All samples showed high exhaustion (>90 %) and satisfactory *K/S* values (>15) for the color fastness tests, and the light fastness of the three dyes reached level 6. Table 3 also shows the washing and rubbing color fastness test results of dyes **D1-D2** and **A1** on PET fabrics with various treatment methods. The samples of dyes **D1-D2** and **A1** treated by reduction clearing and alkali clearing show better rubbing fastness and washing color fastness against color changes than do the untreated samples. This result confirms the effectiveness of the clearing processes to remove the insoluble dye particles around the fibers. For the carboxylic acid ester dyes **D1-D2** containing azo pyridone structures, the samples treated by alkali clearing show nearly equal fastness properties to the samples treated by reduction clearing. In other words, the reductant-free treatment method can achieve the same color fastness results and simplify the after-treatment process of dyeing effluent. Table 3 also indicates that the color fastness of **D1-D2** containing an azo pyridone structure is better than that of **A1**.

Recovery of Hydrolyzed Dyes

Additionally, the carboxylic acid ester dyes **D1-D2** containing an azo pyridone structure have some other advantages in the application and after-treatment of dyeing effluents. The hydrolyzates of dye **D1-D2** include hydrolyzates **B1-B2** (see Scheme 3) and ethanol, of which ethanol has low toxicity and **B1-B2** can easily be recovered by acidification, precipitation, and filtration. This paper uses salting out instead of acidification to recover **B1-B2**, which can greatly reduce the amount of precipitant required to obtain high recovery. There are three main precipitating agents for the recovery of **B1-B2** by salting out: $CaCl_2$, $MgCl_2$, and $BaCl_2$. When calcium chloride and magnesium chloride were added to hydrolyzed carboxylate solution, the OH^- in the solution reacted with Ca^{2+} and Mg^{2+} and then formed precipitates. This led to a decrease in the precipitation efficiency of **B2** (Figure 7). Barium hydroxide has better solubility than calcium hydroxide and magnesium hydroxide, as well as higher precipitation efficiency. Therefore, barium chloride was the best choice as the precipitant in the recovery experiment. Figure 8 shows the recovery rate of dyes **B1-B2** at different Ba^{2+} concentrations. The rising trends of **B1-B2** are similar, and the recovery rate of the dyes reaches 92.56 % at 5:1. However, in the process of acidification, the pH needs to be neutralized from 12 to 1 to

Table 3. Dyeing and color fastness properties of carboxylic acid ester dyes **D1-D2** containing azo pyridone structure and the control dye **A1** on PET fabrics after heat-set treatment at 2 % owf

Dye	Dye exhaustion (%)	*K/S*	Aftertreatment	Washing fastness			Rubbing fastness		Light fastness
				Color change	Staining		Dry	Wet	
					Acetate	Nylon			
D1	94.56	23.2	Untreated	4	3-4	3	3-4	3	6
		23.4	Reduction clearing	5	4-5	5	5	4-5	6
		24.1	Alkali clearing	5	4-5	5	5	4-5	6
D2	95.89	23.4	Untreated	4	3-4	3-4	3-4	3	6
		22.8	Reduction clearing	5	5	5	5	5	6
		23.3	Alkali clearing	5	5	5	5	5	6
A1	95.60	20.9	Untreated	3-4	3	2-3	3	2-3	6
		20.6	Reduction clearing	4	3-4	4-5	4-5	4-5	6
		20.2	Alkali clearing	4	3-4	4-5	4-5	4-5	6



Scheme 3. The alkal-hydrolysis of alkali-clearable azo disperse dyes containing a carboxylic ethyl ester moiety and the recovery of their hydrolyzates.

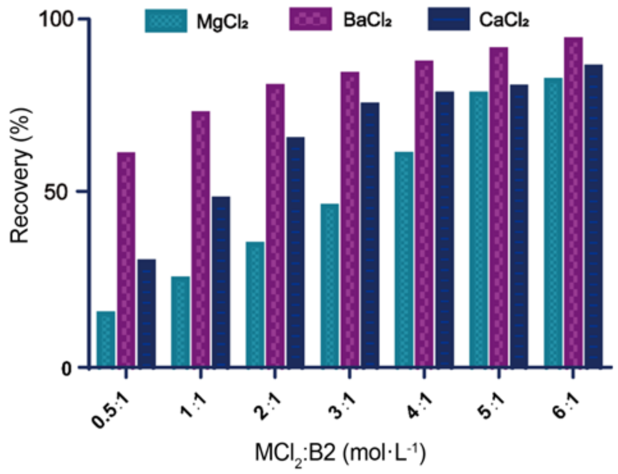


Figure 7. B2 recovery rate under different salt concentrations.

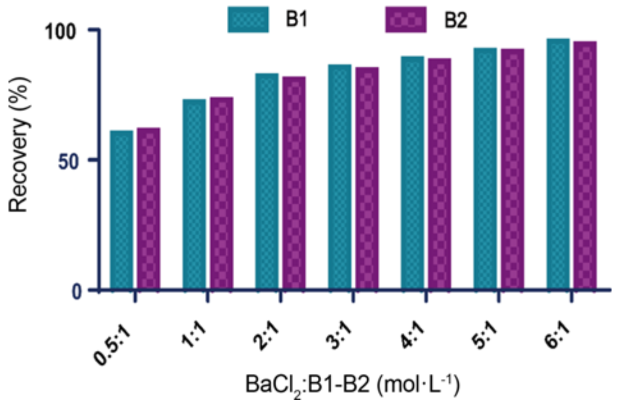


Figure 8. B1-B2 recovery rate under different Ba^{2+} concentrations.

obtain a high recovery rate of **B1-B2**. The molar ratio of acid to carboxylate exceeds 340:1 [27], thus requiring more precipitant to obtain a higher recovery rate than salting out. Therefore, the method of salting out to recover dye not only effectively reduces the amount of precipitant and the difficulty of sewage treatment but also saves costs. This recovery test proves the effectiveness of barium chloride as a precipitating agent. By allowing the hydrolyzate dye to settle down, the color of the solution can be greatly reduced, which is beneficial for post-treatment and provides a reliable solution for the reuse of the dye.

Conclusion

Alkali-clearable disperse dyes containing an azo pyridone structure were facilely synthesized by traditional diazo coupling reactions. Introducing a pyridone structure into disperse dyes containing an ester group structure combined the bright color and alkali-clearable properties of dyes. The ester-containing, alkali-clearable dyes could be applied to polyester fabrics and attain the same excellent color fastnesses after alkali clearing treatment without the utilization of reductants as that obtained with reduction clearing treatment. By analysing the UV-vis absorption spectra of the disperse dye particles remaining on the surface of the fabric after alkali clearing, the alkali-clearable effect of different sodium hydroxide concentrations was tested. The difficulty of wastewater treatment can be further reduced by reducing the amount of alkali used. Salting out ($BaCl_2$) could be used instead of acidification to recover the hydrolyzate, which not only obtains a higher recovery rate with less precipitant but also provides the possibility for the reuse of dyes.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No.21808210), Zhejiang Provincial Natural Science Foundation of China (LY21B060010), Zhejiang Provincial Key Research and Development Program of China (2021C01058) and '521' Talent Project of Zhejiang Sci-Tech University.

References

1. J. Koh, H. Y. Yoo, and J. P. Kim, *Color. Technol*., **120**, 156 (2004).
2. J. Koh, *Dyes Pigm*., **64**, 17 (2005).
3. GB/T 2394-2013, "Disperse Dyestuff-Determination of Shade and Relative Strength", Standardization Administration of the People's Republic of China, 2013.
4. J. H. Choi, J. Y. Choi, E. M. Kim, J. P. Kim, A. D. Towns, and C. Yoon, *Color. Technol*., **129**, 352 (2013).
5. J. S. Koh and J. P. Kim, *Dyes Pigm*., **37**, 265 (1998).
6. J. Koh, H. Kim, and J. Park, *Fiber. Polym*., **9**, 143 (2008).
7. J. Koh and A. J. Greaves, *Dyes Pigm*., **50**, 117 (2001).
8. J. Koh, J. D. Kim, and J. P. Kim, *Dyes Pigm*., **56**, 17 (2003).
9. J. Koh, *Dyes Pigm*., **69**, 233 (2006).
10. J. S. Kohand and J. P. Kim, *J. Soc. Dyer. Colour*., **114**, 121 (1998).
11. Z. H. Cui, X. H. Cheng, X. Li, H. H. Lu, X. D. Wang, and W. G. Chen, *Chinese Chem. Lett.*, **25**, 1121 (2014).
12. M. A. Weaver and L. Shuttleworth, *Dyes Pigm*., **3**, 81 (1982).
13. G. Hallas and J. H. Choi, *Dyes Pigm*., **42**, 249 (1999).
14. H. R. Maradiya and V. S. Patel, *J. Braz. Chem. Soc*., **12**, 710 (2001).
15. L. B. Cheng, X. Chen, K. Y. Gao, and J. Z. Hu, *Dyes Pigm*., **7**, 373 (1986).
16. M. A. Metwally, E. Abdel-Galil, A. Metwally, and F. A. Amer, *Dyes Pigm*., **92**, 902 (2012).
17. C. W. Ghanavatkar, V. R. Mishra, and N. Sekar, *Spectrochim. Acta A Mol. Biomol. Spectrosc*., **230**, 118064 (2020).
18. A. M. Al-Etaibi and M. A. El-Apasery, *Int. J. Environ. Res. Public Health*, **17**, 4714 (2020).
19. A. M. Al-Etaibi and M. A. El-Apasery, *Int. J. Environ. Res. Public Health*, **17**, 1377 (2020).
20. A. M. Al-Etaibi and M. A. El-Apasery, *Int. J. Environ. Res. Public Health*, **16**, 4603 (2019).
21. Z. H. Cui, G. Xia, J. R. Gao, W. G. Chen, N. P. Liu, Q. Ou, and R. L. Wang, *Fiber. Polym*., **18**, 1708 (2017).
22. J. J. Qiu, J. Q. Xiao, B. T. Tang, B. Z. Ju, and S. F. Zhang, *Dyes Pigm*., **160**, 524 (2019).
23. S. H. Amirshahi and M. T. Pailthorpe, *Text. Res. J.,* **64**, 357 (1994).
24. Y. Z. Zhan, X. Zhao, and W. Wang, *Dyes Pigm*., **146**, 240 (2017).
25. G. Wypych, "Handbook of Solvent", 1st ed., ChemTec Publishing, New York, 2001.
26. C. Reichardt, "Solvents and Solvent Effects in Organic Chemistry", 3rd ed., p.330, Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim, 2003.
27. X. H. Cheng, Master Degree Thesis, Zhejiang Sci-Tech University Hangzhou, China, 2016.