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Graphical Abstract



Synthesis and efficient dyeing of anthraquinone derivatives on polyester fabric with supercritical carbon dioxide

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Abstract

Two series of anthraquinone dye derivatives [CNU-1 to CNU-7 and CNU-8 to CNU-10] have been successfully synthesized from commercially inexpensive and readily available starting materials by using simple and convenient methods. All synthesized anthraquinone dyes were characterized by ¹H NMR, ¹³C NMR, and UV-Vis spectroscopy and HRMS. The UV-Vis spectra of the dyes indicated that the absorption wavelengths of dyes were approximately 590 - 655 nm, which indicated that these are blue dyes. Polyester fabrics were dyed with these compounds using supercritical carbon dioxide as a green medium. All the compounds displayed deep color shades and excellent dye fixation even at low concentrations (0.5%). In the fastness experiments, compounds CNU-1 to CNU-10 all exhibited excellent results in washing (4-5), sweat (4-5) and lightfastness [CNU-1 to 7 (4-5), CNU-8 to 10 (2-3)]. Hence, our results revealed that these types of anthraquinone dyes are commercially most acceptable, and they practically exhibited satisfactory color uniformity.

Keywords

Anthraquinone dyes; Blue color; Supercritical carbon dioxide; polyester fabric (PET).

1. Introduction

When using conventional water-based dyeing methods, the textile industry requires more water to dye polyester fabrics and requires several chemical additives, such as dispersing agents and surfactants, to enhance the solubility of the dyes in water [1, 2]. This method produces enormous quantities of polluted water, which is very expensive to purify and harmful to the environment [3, 4]. Therefore, the textile industry seeks an ecofriendly process to replace the conventional water-based dyeing method. To overcome the ecological and economic disadvantages of the traditional method, supercritical fluid dyeing processes have been introduced [5-10].

In supercritical fluid dyeing, supercritical fluids are used as the dye solvents instead of water. A supercritical fluid can be defined as a substance above its critical temperature (Tc) and pressure (Pc). Under these described conditions, the substance has unique properties in that it exists as a vapor and liquid in equilibrium. Carbon dioxide is particularly attractive due to its green properties, such as recyclability, nontoxic, and nonflammability [11, 12]. In the dyeing process, the critical conditions required to generate supercritical carbon dioxide (Tc = 304.34 K, Pc = 7.38 MPa) are easily attainable, and it does not require any dispersing agents or surfactants [13]. In the traditional wet dyeing process, more energy is required in the washing and drying steps, whereas in the supercritical fluid dyeing process, this energy can be saved, as this process requires only one step (either washing or drying) after dyeing [6]. Furthermore, supercritical carbon dioxide has a high diffusion rate because the dye penetrates more readily into the porous textile fibers [14-18].

Polyester (polyethylene terephthalate or PET) fabrics have compact, nonpolar, and highly crystalline structures. Therefore, for the dyeing of PET fabrics with supercritical carbon dioxide,

nonpolar dyes are used to ensure dissolution. Due to the wide range of available hues and excellent fastness, disperse dyes are used for the dyeing of polyester fabrics [19-23]. Anthraquinone disperse dyes play a vital role in the dyestuffs industry [24]. These molecules are more stable under experimental conditions and in various organic solvents during calibration studies. The molar absorption coefficients ($B^{v}v$) of anthraquinone dyes allow their spectroscopic determination even at very low concentrations [25]. The design and development of new anthraquinone disperse dye derivatives has become a hot research area in modern textile chemistry. Previously, our group synthesized various dyes and used them to dye polyester fabrics [19, 26-30]. In a continuation of our work, we have synthesized two series of anthraquinone dyes and used them to dye polyester fabrics with supercritical carbon dioxide as the medium.

2. Experimental

2.1. Materials and methods

Starting materials and commercial reagents were purchased from Sigma Aldrich and Alfa Aesar. ¹H and ¹³C NMR spectra were recorded using an AVANCE III spectrometer operating at 600 MHz and 150 MHZ, respectively, with CDCl₃ as the solvent. The chemical shift (δ) values are given in ppm downfield from an internal standard of tetramethyl silane. UV-visible absorption spectra were acquired with an Agilent 8453 spectrophotometer, and reflectance spectra were recorded using a Shimadzu UV 26000 spectrophotometer. HRMS data were recorded on a Bruker micrOTOF-Q spectrometer. Melting points were recorded visually in a capillary tube on Electrothermal IA9100/OA series melting point apparatus. The capillary tube was filled with the synthesized dyes ~3 mm high and placed in melting temperature apparatus. Set the MEL-TEMP to the appropriate power level, and increased temperature is 2 \square min⁻¹. We observed the melting

process with the magnifying lens. These experiments were done in triplicate. The purity of synthesized dyes **CNU-1** to **CNU-10** was determined by using Ultimate-3000 ISQ EC high performance liquid chromatography by calculate percentage of peak area in relation to total area of peaks under interests or in relation to main peak (small impurities determined). The HPLC conditions in this study were mobile phase composition is 0.1% formic acid in acetonitrile (0.0%), flow rate (0.3 mL/min). The corresponding HPLC spectra were placed at supporting information (**Fig. S31** to **Fig. S40**).

2.2. Synthesis

The main task of the current work was to develop the new designed anthraquinonederived blue dyes that would be commercially most accessible to supercritical carbon dioxide application in near future. We have synthesized anthraquinone dyes from previous literature reports with slight modifications [31, 32]. These dyes were applied to polyester fabrics using ecofriendly supercritical carbon dioxide dyeing conditions. Herein, we planned to synthesize two series of 10 anthraquinone dyes namely **CNU-1** to **CNU-10**.



Scheme 1. Synthesis of CNU-1 to CNU-7 supercritical dyes.

In the case of the first series of compounds, 1,8-dihydroxy-4,5-dinitroanthracene-9,10dione (I) was chosen as the starting material. A condensation reaction was performed between the starting material (I) and the appropriate aryl amines (II a-g) in the presence of 2methoxyethanol at reflux to afford compounds **CNU-1** to **CNU-7** (Scheme 1). By using this method, we synthesized 7 compounds by changing the substituents on the aryl amino moiety. The structures of the compounds are shown in **Fig. 1**.



Fig. 1. Chemical structures of CNU-1 to CNU-7 supercritical dyes.

For the synthesis of the second series of compounds, 1,4-dihydroxyanthracene-9,10-dione (III) was chosen as the starting material. This starting material was reacted with tosyl chloride (IV) in the presence of Et₃N to afford compound (V). Further compound (V) was reacted with excess of various substituted amines VI (a-c) under mild reaction conditions to give 1-amino-4-(tosyloxy)-anthraquinones VII (a-c) as red products. Reactions of intermediates VII (a-c) with amines VIII (a-c) in the presence of pyridine at 100 °C afforded compounds CNU-8 to CNU-10 (Scheme 2). Herein, we synthesized three compounds using this method by varying the amines, and the structures of these compounds are shown in Fig. 2.



Fig. 2. Chemical structures of CNU-8 to CNU-10 supercritical dyes.

2.3. General experimental procedure for the synthesis of dyes CNU-1 to CNU-7: A mixture of 1,8-dihydroxy-4,5-dinitroanthracene-9,10-dione (I) (0.5 g, 1.514 mmol), and aryl amines (II **a-g**) (3.028 mmol) in 2-methoxyethanol (10 mL) was stirred at 125 °C for 6 h. After completion of the reaction (as monitored by TLC), the crude reaction mixture was directly absorbed onto

silica (230-400 mesh) and subjected to column chromatography using 12 to 15% ethyl acetate: n-hexane as the eluent to afford **CNU-1** to **CNU-7** as blue solids.

2.3.1. 1-((**4**-Hexylphenyl)amino)-**4**,**5**-dihydroxy-8-nitroanthracene-9,10-dione (CNU-1): Blue solid; Yield: 86% (0.43 g), mp: 115 – 117 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.82 (s, 1H), 12.73 (s, 1H), 11.65 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 9.7 Hz, 1H), 7.20 (d, *J* = 9.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 9.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.55 (t, *J* = 7.9 Hz, 2H), 1.55 (qt, *J* = 7.1 Hz, 2H), 1.32 – 1.21 (m, 8H), 0.83 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 188.2, 176.4, 162.3, 157.9, 145.2, 141.0, 140.3, 134.3, 129.4, 128.6, 128.0, 127.2, 125.6, 123.8, 121.3, 114.5, 111.0, 107.3, 34.4, 30.6, 30.3, 27.9, 21.5, 13.0. HRMS: 459.1522 [M-H]⁺ Calcd for C₂₆H₂₃N₂O₆: 459.1556. Purity: 93%.

2.3.2. 1,8-Dihydroxy-4-nitro-5-((4-pentylphenyl)amino)anthracene-9,10-dione (CNU-2): Blue solid; Yield: 84% (0.41 g), mp: 260 – 262 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.83 (s, 1H), 12.74 (s, 1H), 11.66 (s, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 9.5 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 9.5 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 2.55 (t, *J* = 7.9 Hz, 2H), 1.56 (qt, *J* = 7.5 Hz, 2H), 1.32 – 1.23 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 189.3, 177.5, 163.3, 158.9, 146.3, 142.1, 141.3, 135.3, 130.5, 129.6, 128.2, 126.7, 124.8, 122.3, 115.6, 112.1, 108.4, 35.4, 31.4, 31.0, 22.5, 14.0. HRMS: 447.2458 [M+H]⁺. Calcd for C₂₅H₂₃N₂O₆: 447.4677. Purity: 82%.

2.3.3. 1-((4-Butylphenyl)amino)-4,5-dihydroxy-8-nitroanthracene-9,10-dione (CNU-3):
Blue solid; Yield: 83% (0.39 g), mp: 250 – 252 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.83 (s, 1H), 12.74 (s, 1H), 11.66 (s, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 9.7 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 9.7 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 2.56 (t, J = 7.7 Hz, 2H), 1.54 (qt, J = 7.7 Hz, 2H), 1.35 – 1.26 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ¹³C NMR

(CDCl₃, 150 MHz): δ 188.3, 176.5, 162.3, 157.9, 145.3, 141.1, 140.3, 134.3, 129.5, 128.6, 128.1, 127.2, 125.7, 123.8, 121.3, 114.6, 107.4, 34.1, 32.5, 21.3, 12.9. HRMS: 431.1223 [M-H]⁺. Calcd for C₂₄H₁₉N₂O₆: 431.1243. Purity: 86%.

2.3.4. 1,8-Dihydroxy-4-((**4-(2-(2-methoxyethoxy)ethoxy)phenyl)amino**)-**5-nitroanthracene-9,10-dione** (**CNU-4**): Blue solid; Yield: 69% (0.37 g), mp: 94 – 96 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.90 (s, 1H), 12.79 (s, 1H), 11.46 (s, 1H), 7.31 (d, *J* = 9.5 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.92 – 6.86 (m, 3H), 4.09 (t, *J* = 4.8 Hz, 2H), 3.81 (t, *J* = 5.0 Hz, 2H), 3.69 – 3.66 (m, 2H), 3.54 – 3.52 (m, 2H), 3.33 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 189.2, 184.0, 155.6, 155.3, 144.2, 143.6, 131.7, 129.8, 127.6, 125.1, 125.0, 124.9, 124.7, 114.5, 113.0, 112.8, 110.4, 110.3, 70.9, 69.7, 68.7, 66.7, 58.0. HRMS: 493.1276 [M-H]⁺. Calcd for C₂₅H₂₁N₂O₉: 493.1247. Purity: 85%.

2.3.5. 1,8-Dihydroxy-4-((2-methoxy-5-methylphenyl)amino)-5-nitroanthracene-9,10-dione (CNU-5): Blue solid; Yield: 85% (0.38 g), mp: 190 – 192 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.84 (s, 1H), 12.77 (s, 1H), 11.42 (brs, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 9.7 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.10 (d, J = 9.5 Hz, 1H), 7.00 – 6.98 (m, 1H), 6.97 – 6.94 (m, 1H), 6.80 (d, J = 8.2 Hz, 1H), 3.72 (s, 3H), 2.23 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 189.4, 177.6, 163.3, 159.0, 151.2, 146.0, 130.5, 130.3, 128.9, 128.6, 127.6, 127.0, 126.2, 122.2, 115.7, 112.1, 111.7, 108.6, 55.7, 20.5. HRMS: 419.0891 [M-H]⁺. Calcd for C₂₂H₁₅N₂O₇: 419.0879. Purity: 75%.

2.3.6. 1-((**4**-Heptylphenyl)amino)-4,5-dihydroxy-8-nitroanthracene-9,10-dione (CNU-6): Blue solid; Yield: 87% (0.45 g), mp: 90 – 92 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.84 (s, 1H), 12.75 (s, 1H), 11.66 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 9.5 Hz, 1H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 9.7 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 2.55 (t, *J* = 7.9 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.31 – 1.17 (m, 10H), 0.82 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 188.3, 176.5, 162.3, 157.9, 145.3, 141.1, 140.3, 134.3, 129.5, 128.6, 128.1, 127.2, 125.7, 123.8, 121.3, 114.6, 111.1, 107.3, 34.4, 30.7, 30.3, 28.2, 28.1, 21.6, 13.0. HRMS: 473.1708 [M-H]⁺. Calcd for C₂₇H₂₅N₂O₆: 473.1713. Purity: 89%.

2.3.7. 1,8-Dihydroxy-4-nitro-5-((4-propylphenyl)amino)anthracene-9,10-dione (CNU-7): Blue solid; Yield: 86% (0.39 g), mp: 238 – 240 °C; ¹H NMR (CDCl₃, 600 MHz): δ 12.81 (s, 1H), 12.72 (s, 1H), 11.65 (s, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 9.5 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 9.5 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 2.53 (t, J = 7.7 Hz, 2H), 1.63 – 1.55 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 189.3, 177.5, 163.3, 158.9, 146.3, 142.1, 141.0, 135.4, 130.5, 129.7, 129.1, 128.2, 126.7, 124.8, 122.3, 115.6, 112.1, 108.4, 37.5, 24.4, 13.7. HRMS: 417.3960 [M-H]⁺. Calcd for C₂₃H₁₇N₂O₆: 417.3981. Purity: 90%.

2.4. Synthetic procedure for the synthesis of 9,10-dioxo-9,10-dihydroanthracene-1,4-diyl bis(4-methylbenzenesulfonate) (V): A solution of 1,4-dihydroxyanthracene-9,10-dione (III) (10 g, 41.66 mmol) in acetonitrile (300 mL) was treated with Et₃N (30 mL, 214 mmol) followed by *p*-toluene sulfonyl chloride (IV) (19.2 g, 100 mmol), and the reaction mixture was stirred at reflux temperature for 5 h. After completion of the reaction, acetonitrile was removed by a rotary evaporator, and the resulting crude material was dissolved in DCM (500 mL). This mixture was washed with water (2 x 300 mL), and the organic layer was dried over Na₂SO₄ and filtered. The resulting solution was concentrated to give (V) a yellow brown solid. This crude material was triturated with diethyl ether and n-hexane to afford 9,10-dioxo-9,10-dihydroanthracene-1,4-diyl bis(4-methylbenzenesulfonate) (V) as a bright yellow solid. Yield: 86% (19.6 g); ¹H NMR (CDCl₃, 600 MHz): δ 8.05 (dd, *J* = 5.6, 4.3 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.75 (dd, *J* = 5.6, 3.3 Hz, 2H), 7.52 (s, 2H), 7.37 – 7.31 (m, 4H); ESI-MS: 549 [M+H]⁺.

2.4.1. General experimental procedure for the synthesis compounds (VII a-c): A solution of 9,10-dioxo-9,10-dihydroanthracene-1,4-diyl bis(4-methylbenzenesulfonate) (V) (2 g, 3.646 mmol) in DCM (100 mL) was added the appropriate alkyl amine (VIII a-c) (4.375 mmol) at room temperature, and the reaction mixture was stirred at this temperature for 24 h. After completion of the reaction (as monitored by TLC), the reaction mixture was concentrated under reduced pressure to afford red solids, which were used in the next step without further purification.

2.4.2. General experimental procedure for the synthesis compounds (CNU-8 to CNU-10): A solution of crude compounds (**VII a-c**) (1.0 mmol) in pyridine (20 mL) was added the appropriate amine (**IX a-c**) (1.0 mmol) at room temperature, and the reaction mixture was refluxed for 16 h. After completion of the reaction (as monitored by TLC), the crude reaction mixture was directly absorbed onto silica (230-400 mesh) and subjected to column chromatography using 4 to 7% ethyl acetate:n-hexane as the eluent to afford **CNU-8** to **CNU-10** as a blue solids.

2.4.3. 1-(**Benzylamino**)-**4**-(**heptylamino**)**anthracene-9,10-dione** (**CNU-8**)**:** Blue solid; Yield: 81% (1.2 g), mp: 139 – 141 °C; ¹H NMR (600 MHz, CDCl₃): δ 11.06 (s, 1H), 10.66 (s, 1H), 8.31 – 8.25 (m, 2H), 7.66 – 7.59 (m, 2H), 7.32 – 7.18 (m, 5H), 7.10 – 7.05 (m, 2H), 4.61 – 4.57 (m, 2H), 3.31 – 3.24 (m, 2H), 1.70 – 1.63 (m, 2H), 1.16 – 1.14 (m, 6H), 0.80 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz): δ 181.9, 181.3, 145.3, 144.7, 137.6, 133.5, 131.1, 127.8, 126.3, 125.8, 122.7, 122.4, 109.4, 108.7, 45.7, 41.8, 30.7, 28.6, 28.0, 26.1, 21.5, 13.0. HRMS: 426.2326 [M]⁺. Calcd for C₂₈H₃₀N₂O₂: 426.2307. Purity: 86%.

2.4.4. 1-(Benzylamino)-4-(tridecylamino)anthracene-9,10-dione (CNU-9): Blue solid; Yield: 78% (1.5 g), mp: 259 – 261 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.28 – 8.25 (m, 2H), 7.67 – 7.64

(m, 2H), 7.32 - 7.25 (m, 5H), 7.20 - 7.18 (m, 1H), 7.15 - 7.11 (m, 1H), 4.57 (s, 2H), 3.27 (t, J = 7.3 Hz, 2H), 1.75 - 1.68 (m, 2H), 1.42 - 1.35 (m, 2H), 1.31 - 1.15 (m, 18H), 0.80 (t, J = 7.1 Hz, 3H); 13 C NMR (CDCl₃, 150 MHz): δ 183.0, 182.4, 146.4, 145.7, 138.6, 134.6, 134.4, 132.1, 132.0, 128.8, 127.3, 126.9, 123.8, 123.4, 110.5, 109.7, 46.7, 42.9, 31.9, 29.6, 29.3, 27.1, 22.6, 14.1. HRMS: 510.3257 [M]⁺. Calcd for C₃₄H₄₂N₂O₂: 510.3246. Purity: 75%.

2.4.5. 1-((2-Ethylhexyl)amino)-4-(hexadecylamino)anthracene-9,10-dione (CNU-10):

Blue solid; Yield: 71% (1.4 g), mp: 139 – 141 °C; ¹H NMR (600 MHz, CDCl₃): δ 10.95 (brs, 1H), 10.87 (brs, 1H), 8.29 – 8.21 (m, 2H), 7.66 – 7.59 (m, 2H), 7.20 – 7.15 (m, 2H), 3.39 – 3.22 (m, 4H), 1.78 – 0.79 (m, 46H); ¹³C NMR (CDCl₃, 150 MHz): δ 182.1, 182.1, 146.5, 146.2, 134.5, 134.5, 131.8, 126.0, 125.9, 123.5, 109.6, 45.9, 45.9, 42.9, 39.4, 31.9, 31.2, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.0, 28.9, 27.1, 24.5, 23.0, 22.6, 14.1, 14.1, 10.9. HRMS: 573.4409 [M-H]⁺. Calcd for C₃₈H₅₇N₂O₂: 573.4420. Purity: 93%.

2.5. Dyeing apparatus

Fig. 3 represents the diagram of the whole apparatus. It mainly consists of a heating bath, a dyeing bath, temperature and pressure control units and a recycling unit. First, from the CO₂ cylinder, the CO₂ gas was passed through a circulated cooling bath. This cooling bath has a water and ethylene glycol mixture to maintain the temperature in the range of -10 to +5 \Box . Due to this maintaining temperature, CO₂ gas can be converted to a liquid. A high-pressure pump was equipped with a motor and had a power of 2.2 kW. The heating bath had a heating power of ~24 kW. These pressure pumps and heating baths were helped us to maintain the pressure and temperature of the liquid to above its critical conditions (critical pressure: 7.38 MPa and critical temperature (31.1 \Box). The dyeing bath was designed to be cylindrical with an autoclave with a rotating warp beam. Polyester fabrics were dyed with our synthesized anthraquinone dyes by

wrapping the fabrics around the rotating warp beam in a cyclic manner. The dyeing bath temperature was maintained by a temperature control unit with a temperature range of 40-300 \Box . After dyeing, recycling and separation of the unfixed dye and carbon dioxide is essential. Thus, depressurization was carried out while maintaining a suitable pressure (4 MPa) and temperature (25 °C) for separation. The CO₂ gas was purified by passage through a chamber containing molecular sieves. After purification, the CO₂ gas was released from the separator and stored in a recycling vessel.



Fig. 3. Schematic representation of the apparatus 1) CO₂ cylinder, 2) Circulated cooling bath, 3) CO₂ pump, 4) Heating bath, 5) Temperature controller, 6) Stirrer, 7) Dye bath, 8) Pressure regulator, and 9) Separator.

2.6. Supercritical dyeing procedure

Polyester fabrics (10 g) were suspended in a stainless steel cylinder and placed inside an autoclave. The synthesized anthraquinone dyes were loaded on the bottom surface of the vessel. Herein, we used different amounts of dye (0.5%, 1% and 1.5%) with respect to polyester fabric. The reactor was sealed and heated to the required temperature. Before heating, liquid CO_2 was pumped into the vessel via the valve. At this time, the initial pressure was 5 MPa. After 10 min,

the pressure had reached 15 MPa. After 1 h of dyeing, the heating was shut off, and the system cooled slowly. After reaching atmospheric pressure, the needle valve was opened to release the CO_2 . Then, the polyester fabric was removed from the sample vessel and washed with soap at 50 °C for 15 min and then washed with water.

3. Results and discussion

3.1. Factors affecting dyeing properties of polyethylene terephthalate (PET) fabrics

In our experiments, we investigated the effect of dyeing parameters like concentration, temperature and pressure on color strength values of the PET fabrics with our new synthesized dyes **CNU-1** to **CNU-10** under supercritical carbon dioxide medium. The corresponding results obtained in this experiments were shown in **fig. 4** and an appropriate discussion were presented below.

3.1.1. Effect of dye concentration:

According to Kubelka-Munk (K/S) equation, the measurement of K/S values are given directly correlated with the dye concentration on the dye substrate [33]. The K/S factor was first calibrated using a series of PET fabrics dyed in supercritical carbon dioxide at various concentrations of dye. The dye uptake in the fabric was extracted with hot acetone solution and the concentration of the solution was measured at a maximum wavelength. In our study the color intensities were increased with increasing the percentage of dye (0.5 to 1.5%) (**Fig. 4a**). This is attributed to the degree of solubility of anthraquinone disperse dyes are increased by increasing the percentage of dye [34, 35].

3.1.2. Effect of dyeing temperature:

The dyeing temperature (T °C) is a key factor and plays an important role in the color yield of the polyester fabrics. A series of dyeing experiments were carried out at constant

concentration (0.5%) and pressure (15 MPa) with different temperatures ranging from 80 °C to 120 °C (**Fig. 4b**). The results indicated that higher temperatures could improve the dye adsorption and liberty of the macromolecular chains of the polyester fabrics. The differences in color strength is very minor for dyes CNU-6, CNU-8, CNU-9 and CNU-10 at 80 \square and 100 \square . In our study, 120 °C provided the maximum equilibrium capacity of dye adsorption. Higher temperature generally enhances the freedom of the macromolecular chains of PET and dyes. Hence dye molecules rate of diffusion was very high and penetrated in to the polyester fabrics, resulting in good color strength of fabrics.

3.1.3. Effect of dyeing pressure:

The dyeing pressure also plays a crucial role in the color yield of polyester fabrics. A series of dyeing experiments were carried out at constant concentration (0.5%) and temperature (120 °C) with different pressures ranging from 5 to 15 MPa (**Fig. 4c**). While increasing the pressure the density of the supercritical carbon dioxide is increased at constant temperature. Therefore, the solubility of the dye molecules was increased, and they easily diffused into the amorphous region of the swelled polyester fabric. As a result, the color strength of the dyed polyester fabrics increased. **Fig. 5**. shows photo images of the PET fabrics dyed with ten anthraquinone dyes in supercritical carbon dioxide.







Fig. 4. (a) $\overline{K/S}$ values vs. amount of dye (**b**) Effect of dyeing temperature (80 \square , 100 \square , 120 \square) on $\overline{K/S}$ values. (**c**) Effect of dyeing pressure (5, 10, 15 [MPa]) on $\overline{K/S}$ values.

The solubility properties of the disperse dyes are a complex process in supercritical carbon dioxide. At low pressures the solubility of the disperse dye decreases with increasing temperature because of the decrease in carbon dioxide density. Therefore, the color strengths decrease. At high pressures the solubility of the disperse dyes is increases with increasing temperature because the decrease in carbon dioxide density cannot overcome the increase in vapor pressure [36]. The dye solubility is increases with increasing pressure at constant temperature due to increasing the density of carbon dioxide. Hence the color strengths also increase [37,38].

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Fig. 5. Photo images of PET fabrics dyed with anthraquinone dyes in supercritical CO₂.

3.2. Color strength and dye fixation

The color strength (K/S) values of the dyed PET fabrics were calculated from the Kubelka–Munk equation by substituting the reflectance (R).

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

Where K is absorbance, S is the scattering and R is the minimum reflectance. R_{min} can be recorded by using Shimadz UV 26000 spectrophotometer.

$$\overline{K/S} = \frac{1}{n} \sum_{i=1}^{n} (K/S)i, \ \lambda max$$

Where $\overline{K/S}$ is the arithmetic mean of K/S values of an individual fabric. i = 1, 2, 3,..., n (n = 5 was used in this work), refers to the different sites measured of an individual colorful PET fabric. The percentage of dye fixation (F) values were calculated from the following equation by substituting $(\overline{K/S})_{\text{extracted}}$ (after extraction) and $(\overline{K/S})_{\text{dyed}}$ (after dyeing). Soxhlet extraction method was used to extract the dye molecules from the dyed fabrics by using acetone as a solvent at 80 °C [39].

$$F = \frac{\overline{(K/S)}extracted}{\overline{(K/S)}dyed} X \ 100\%$$



Fig. 6. $(\overline{K/S})_{dyed}$, $(\overline{K/S})_{extracted}$ values of dyed PET fabrics

Fig. 6 shows the $(\overline{K/S})_{dyed}$, $(\overline{K/S})_{extracted}$ values of the dyed PET fabrics. These values were studied by using 0.5% dye concentration at 120 °C temperature, 15 MPa pressure at 1 h time. In the first series of compounds, all the compounds exhibited excellent color strength and dye fixation values. The dye fixation value for CNU-5 (93%) is significantly higher than those of the other dyes. While for CNU-4 (75%, high molecular weight PEG chain,) is lower. One explanation for this result could be that the dye molecule having lower molecular weight possessing high solubility in supercritical carbon dioxide medium. Therefore, high solubility enhanced the fixation value of the dyed fabric [39]. Compounds CNU-2 (5-carbon chain), CNU-**3** (4-carbon chain) and **CNU-7** (3-carbon chain) also displayed excellent percentages of dye fixation (88%, 86% and 83%, respectively) when compared to CNU-1 (6-carbon chain, 78%) and CNU-6 (7-carbon chain, 76%). However, by increasing the alkyl chain (-CH₂ group) length, both solubility and dye adsorption will increase due to the nonpolar nature of the alkyl chain, but we originally observed that the solubility is decreased for longer alkyl chains (chains longer than 5 carbons). This is because, in the solutions, long alkyl chains display high flexibility around the molecule. For these long alkyl chains, the mixing process is generally controlled by the less favorable entropy. Therefore, the formation of inter- or intramolecular hydrogen bonds enhances mutual solute interactions. Hence, the solubility of the dyes in supercritical carbon dioxide is decreased [40].

Our results indicate that all the compounds in the second series [CNU-8, CNU-9 and CNU-10] were also exhibited good to moderate color strength and dye fixation values. The $(K/S)_{dyed}$ and dye fixation values for these three dyes ranked in the following order: CNU-8 > CNU-9 > CNU-10. This could be attribute to that dye molecule structure (long alkyl chains) and solubilities in supercritical carbon dioxide medium. In general, molecules with lower molecular

weights and lower polarities have higher solubilities in supercritical carbon dioxide [39]. In addition, PET fabrics have hydrophobic characteristics and close structure with high crystallinity. Therefore, carbon dioxide molecules were breaking the dense area of PET fabric results swelling of the PET fabric. Thus our synthesized anthraquinone molecules easily penetrate the swelled PET fabrics. The adsorption of the dyes increased, resulting in excellent color shades.

3.3. Fastness determination

3.3.1. Washing fastness

The washing fastness represents the resistance of dyed fabrics to color changes during washings. This test was performed according to the KS K ISO 105 - C06:2014 method. Herein, we determined the color change of our dyed PET fabrics (specimen) and along with staining of color on the adjacent samples of white acetate, cotton, nylon, polyester, acryl and wool. The test specimen, along with the sample fabrics, was placed in a washing machine and treated with 0.4% detergent at 40 \Box for 30 min. After washing, the specimen was separated from the adjacent fabrics, rinsed in cold water, squeezed and dried in air. Color changes of the dyed fabrics and the staining of adjacent fabrics were evaluated by using an international grayscale. All the fabrics dyed with **CNU-1** to **CNU-10** displayed remarkable grades (grades 4-5, **Table 1**), which indicate that our synthesized dyes have excellent penetration capacity and good affinity for PET fabrics.

3.3.2. Light fastness

The light fastness test provides information about the color fading of dyed fabrics when exposed to known light. Herein, we used the KS K ISO 105 – B02:2015, xenon arc method. In

this experiment, our dyed fabrics were exposed to light for 20 h, and the color changes were determined by comparison with unexposed samples. The changes were measured by blue scales. According to the results, all compounds in the first series (CNU-1 to CNU-7) exhibited excellent light fastness (more than grade 4), whereas the second series of compounds (CNU-8 to CNU-10) exhibited weak light fastness (grades 2-3 only) (Table 1). Because, first series of compounds having 1,8-dihydroxy-4-amino functionality and it may form 6 membered rings (3 rings) with quinone group via intramolecular hydrogen bond. Whereas the second series of compounds having 1,4-diamino functionality and it may form only 2 rings. Therefore, more light energy is required to break these 3 rings for CNU-1 to CNU-7 when compared to CNU-8 to CNU-10 (Fig. 7) [41]. On the other hand, the lowest unoccupied molecular orbital (LUMO) frontier electron density on the oxygen atoms [free –OH group] is lower for the dyes CNU-1 to CNU-7, which gives them higher light fastness (4-5), whereas, the LUMO frontier electron densities on their nitrogen atoms for the dyes CNU-8 to CNU-10 is higher (electron donating alkyl groups on N atom), giving them lower fastness (2-3) [42]. Furthermore, the samples with dark shades showed good resistance to light. Darker shaded fabrics contain a larger number of dye molecules, and the small proportion of dye molecules that are involved in fading relative to the remaining content of dye molecules helps in maintaining the depth of shade. On the other hand, in the lighter shades, fewer dye molecules were present, and all are affected by exposure to light, which results in reduced light fastness.



Fig. 7. Ring formation via intramolecular hydrogen bonding

3.3.3. Sweat fastness

Fastness to perspiration was determined by using the KS K ISO 105 - E04:2015 procedure. The test samples were placed between undyed fabrics (acetate, cotton, nylon, polyester, acryl and wool) and were immersed in acid or base solutions at room temperature. After 30 min, the samples were removed and placed between two plastic plates under a force of approximately 4.5 kg. These plates were placed in an oven at $37 \square$ for 4 h. The test samples were separated from the undyed fabrics, and the color changes of the dyed fabrics and the staining of the undyed fabrics were measured using an international grayscale. The results are listed in **Table 2**. All the synthesized compounds in the first and second series reached grades 4-5. This indicates that our synthesized anthraquinone dyes have excellent affinity for PET fabrics.

Dye	Wash fastness ^a							
	Acetate	Cotton	Nylon	Polyester	Acryl	Wool	fastness ^b	
CNU-1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-3	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-6	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-7	4-5	4-5	4-5	4-5	4-5	4-5	4-5	
CNU-8	4-5	4-5	4-5	4-5	4-5	4-5	2	
CNU-9	4-5	4-5	4-5	4-5	4-5	4-5	2	
CNU-10	4-5	4-5	4-5	4-5	4-5	4-5	3	

Table 1. Wash fastness and light fastness properties of dyes CNU-1 to CNU-10 on PET fabrics

^aRate for wash fastness: 3-5 (acceptable), 1–2 (not acceptable) and

^bRate for light fastness: 4–8 (acceptable), 1–3 (not acceptable).

Sweat fastness ^a		CNU									
		-1	-2	-3	-4	-5	-6	-7	-8	-9	-10
	Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Acidic	Cotton	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Nylon	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	PET	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Acryl	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Alka- line	Cotton	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Nylon	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	PET	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Acryl	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Table 2. Sweat fastness properties of dyes CNU-1 to CNU-10 on PET fabrics

^aRate for sweat fastness: 3–5 (acceptable); 1–2 (not acceptable).

3.4. Color characteristics

All the synthesized anthraquinone dyes were soluble in many common organic solvents, such as cyclohexane, hexane, toluene, dichloromethane, acetone and tetrahydrofuran. These dyes can form deep blue colored solutions in these solvents. The UV-absorption spectra were recorded in acetone in the range of 400-800 nm, and the spectra showed single absorbance maxima for the first series of compounds at 610 nm for CNU-1, 612 nm for CNU-2, 613 nm for CNU-3, 609 nm

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for CNU-4, 612 nm for CNU-5, 613 nm for CNU-6 and 614 for CNU-7 and double absorbance maxima for the second series of compounds at 595 nm and 640 nm for CNU-8, 594 nm and 642 nm for CNU-9 and 597 nm and 652 nm for CNU-10 (Fig. 8). The reflectance spectra of the dyed PET fabrics were also recorded using BaSO₄ as the white standard. The reflectance curve minimum values were centered at approximately 630 nm for CNU-1, 631 nm for CNU-2, 630 nm for CNU-3, 631 nm for CNU-4, 632 nm for CNU-5, 629 nm for CNU-6, 633 nm for CNU-7, 649 nm for CNU-8, 647 nm for CNU-9 and 655 nm for CNU-10.





Fig. 8. a) UV-Vis absorption spectra of CNU-1 to CNU-7, b) UV-Vis absorption spectra of CNU-8 to CNU-10 in acetone $(1 \times 10^{-4} \text{ M})$.

3.5. Color assessment

The assessment of the color of the supercritical dyed polyester fabrics was conducted using the CIELAB system, which is based on the parameters of lightness (L*), chroma (C*), hue (h), a* indicates that the degree of greenness (negative) and redness (positive) and b* indicates that the degree of blueness (negative) and yellowness (positive). The color coordinates are listed in **Table 3**. These coordinates indicate that our synthetic dyes have good levelness, brightness and depth on polyester fabric. The color lightness values (L* values) of the dyes varied from 39.41 to 57.91. Compound **CNU-9** is lighter than the other compounds. The color hues of dyes **CNU-1** to **CNU-9** on the polyester fabric are shifted toward the greenish direction on the red-green axis according to the negative values of a*, and for **CNU-10**, the color hues were shifted toward the reddish direction on the red-green axis based on the positive value of a*. The color hues of all the synthesized dyes [**CNU-1** to **CNU-10**] on polyester fabric are shifted to the bluish direction on the yellow–blue axis according to the negative values of b*. The dyes under our investigation displayed deep and bright intense hues in the range of blue color on polyester fabrics at the given temperature. According to the color brightness (C*) values, compounds **CNU-8** and **CNU-4** exhibited brighter and duller colors, respectively, than the other compounds. The color strength (K/S) values of the anthraquinone dyes varied from 7.40 to 10.76.

Dye	L^*	a*	b*	C*	h	$\overline{K/S}$
CNU-1	45.90	-12.69	-33.12	35.47	249.09	8.3±0.3
CNU-2	41.30	-10.46	-32.06	33.73	251.93	9.3±0.3
CNU-3	46.36	-12.74	-28.51	31.23	245.93	9.0±0.4
CNU-4	43.29	-13.67	-21.62	25.58	242.39	7.5±.03
CNU-5	48.50	-13.21	-25.26	28.51	237.71	10.7±0.3
CNU-6	41.67	-9.84	-33.05	34.48	253.43	8.3±0.3
CNU-7	39.41	-10.77	-30.70	32.53	250.67	8.6±0.2
CNU-8	45.41	-5.76	-38.68	39.11	261.54	7.5±0.3
CNU-9	57.91	-8.72	-31.08	32.28	254.33	7.4±0.3
CNU-10	50.61	0.26	-35.66	35.66	270.41	7.4±0.3

Table 3. Color coordinates and color strength (K/S) of dyed polyethylene terephthalate fabrics

4. Conclusion

In summary, we have successfully synthesized two series of anthraquinone-derived blue dyes [CNU-1 to CNU-7 and CNU-8 to CNU-10] from commercially inexpensive and readily available starting materials. Dyeing experiments were performed on polyester fabric with the synthesized anthraquinone dyes under supercritical carbon dioxide conditions. Dyeing experiments were carried out at various temperatures and pressures. We found that the optimum dyeing temperature was 120 °C and pressure was 15 MPa. All the compounds provided deep color shades even at low concentrations (0.5%). Among the tested dyes, four compounds, CNU-5, CNU-2, CNU-3, and CNU-7, exhibited more than 80% dye fixation. In the fastness experiments, all compounds CNU-1 to CNU-10 exhibited excellent fastness properties (grades 4-5) towards washing and sweat fastness. However, in the case of the lightfastness tests, the first series of compounds (CNU-1 to CNU-7) reached acceptable results (4-5 grade) when compared to second series of compounds [(CNU-8 to CNU-10) 2-3 grade only]. Our results revealed that these types of anthraquinone molecules are more sustainable and ecofriendly for textile dyeing companies. These results will help us to apply and study the dyeing of other fabrics [nylon and polypropylene] in supercritical dyeing condition. The corresponding results will be reported in our future work.

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Highlights

- Two series of anthraquinone dye derivatives were prepared and characterized.
- Dyeing experiments were performed on PET fabric using supercritical carbon dioxide.
- Four compounds, CNU-2, CNU-3, CNU-5 and CNU-7, exhibited more than 80% dye fixation.
- Based on fastness results our molecules are more sustainable and ecofriendly for textile dyeing companies.