Facile Bifunctional Dyeing of Polyester under Supercritical Carbon Dioxide Medium with New Antibacterial Hydrazono Propanenitrile Dyes

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ABSTRACT: In this work, new hydrazonopropanenitrile dyes with potential antibacterial activity were applied for dyeing polyester fabrics with supercritical carbon dioxide as a dyeing medium. The experimental conditions were optimized to obtain both visibly and spectrophotometrically uniform dye uptakes in the fabric. Raman microspectroscopy firmly indicated the dye uptake through all layers of the fabric. The color strength of the fabric was evaluated by K/S measurements and proved to be higher than those of conventional dyeing. The fastness properties of the dyed fabric were evaluated and found to give excellent results. The antibacterial test was performed according to the AA-TCC method, and the results were recorded.

1. INTRODUCTION

With the increasing awareness of environmental pollution and ever more stringent regulations, the textile industry is continuously looking for environmentally benign processes to replace the existing water dyeing method. Disperse dyes are commonly used in conventional dyeing processes, which require a large amount of water and disperse agents. Dispersing agents are surfactants that increase the dye solubility in water. Treatment of wastewater containing dye and surfactant is a big concern due to its hard-to-destroy characteristics, large volume, and color problems.

An alternative to conventional dyeing is the supercritical fluid dyeing (SFD) process.1−3 One of the most frequently used supercritical fluids is carbon dioxide. scCO2 has easily attainable critical conditions (Tc = 304.34 K, Pc = 7.38 MPa) and shows adequate solubility for organic dyes, low toxicity, low viscosity, and high diffusivity.6 Studies on the solubility of azodyes in scCO2 have been reported and may be used as additional information on dyeing in scCO2.7−13 scCO2 has also been reported to reduce considerably glass transition temperature Tg for many polymeric matrix.14−16

Disperse dyes are very popular and are an important class of dyes for dyeing polyester fabric owing to their brilliance, wide range of hue, and excellent fastness properties. Especially useful in this respect are azodyes derived from coupling of diazonium salts with nitrogen heterocyclic compounds as coupling components. These heterocyclic azodyes provide bright strong shades that range from yellow, orange, red, and blue to green colors.17−20

Moreover, the aminopyrazole compounds are very useful as precursors for the synthesis of fused heterocyclic ring systems which play an important role in biological and pharmacological activities,21,22 and they can also be used as intermediates in the dyestuff industry.23,24

In view of these findings and in continuation of our studies on the synthesis of a variety of functional disperse dyes from the readily obtainable cheapest starting materials,25 we now report on the application of azopropenitrile dyes for dyeing polyester in scCO2 medium.

2. EXPERIMENTAL SECTION

2.1. Materials. The dyes used in this study shown in Scheme 1 were prepared according to the method described in the literature.26 100% woven polyester fabric (109 g/m2) was kindly supplied by Shikisin-sha company-Japan.

2.2. Dyeing Apparatus. Figure 1 is a diagram of the whole apparatus. The liquefied CO2 leaving from the cylinder passed through a cooling unit and was injected into a high-pressure syringe pump (model Jasco PII-2880 plus). High pressure CO2 eventually flowed into a dyeing autoclave. The dyeing autoclave (Jasco EV-3) as schematized in Figure 1 is a 50 cm3 stainless steel autoclave equipped with a steel screw-tube, a pressure sealed magnetic stirrer, and a quick release cap.

2.3. Procedures. Polyester fabric (usually 3 × 10 cm) was wrapped around a stainless steel cylinder coil bearing punched holes (0.5 cm diameter) and being mounted inside the autoclave. The purified dye was loaded on the bottom of the surface of the vessel, and the amount of dye used varied from 2 to 6% (on weight of fabric). The autoclave was then sealed and heated to the desired temperature. At the same time, CO2 was pumped into the vessel and kept at a working pressure with stirring. The head of the pump was kept at −5 °C using a cooler. The circulation system was activated as the pressure reaches 10 MPa. The stream of the fluid was injected using the magnetic drive under the column at 750 rpm. The fluid flowed from the inside to the outside of the cylinder. After a definite reaction time (1−3 h), the shut-off valve was slowly opened to release CO2 until the pressure of the dyeing vessel reached

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atmospheric pressure. After dyeing the fiber was removed, soaped at a temperature of 60 °C for 15 min, and then washed with water.

2.4. Measurements. Fastness properties to washing, rubbing, and light of the dyed polyester fabrics were determined according to JIS L 0844, JIS L 0849, and JIS L 0842:2004 test methods, respectively. Antibacterial activity assessment against G +ve bacteria (*Staphylococcus aureus*) and G −ve bacteria (*Escherichia coli*) was evaluated qualitatively according to the AATCC Test Method (147-1988) and expressed as zone of growth inhibition ZI (mm).

The color parameters of the dyed polyester fabric were measured using the (Konica Minolta spectrophotometer CM-3600 d) spectrophotometer. The following CIELAB coordinates were measured: lightness (L*), chroma (C*), hue (h°), the degree of redness (+ve) and greenness (−ve) (a*), and the degree of yellowness (+ve) and blueness (−ve) (b*). The color strength (K/S) values were obtained using the (Konica Minolta spectrophotometer CM-3600 d) spectrophotometer. The Raman spectra were collected using a LabRAM HR Evolution systems (Horiba Sientific, Japan).

**Statistical Analysis.** All tests have been made by taking the average of three (samples) readings. The standard error of the mean was calculated according to the equation given below and found to be +(-)0.1

\[
SE_x = \frac{S}{\sqrt{n}}
\]

where S = sample standard deviation, and n = the number of observations of the sample.

3. RESULTS AND DISCUSSION

The main task of the current work is to introduce a facile one-step procedure for producing polyester fabric with demanded functional performance via dyeing with antibacterial dyes. The results obtained and their interpretations are as follows.
3.1. Factors Affecting Dyeing Properties of Polyester (PES) Fabrics. Effect of Dye Concentration. Figure 2a shows that, within the range examined, increasing the dyestuff concentration up to 6% resulted in a significant improvement in the color strength (K/S) of the obtained samples. This holds true for dyestuff No. 1, 3, and 4, while for dyestuffs No. 2 and 5, the K/S reached their maximum at 4% of concentration and then leveled off.

Effect of Time. The effect of dyeing time on the amount of the dye adsorbed on PES fiber is shown in Figure 2b. It is evident that increasing the dyeing time from 1 h to 3 h resulted in an increase in the K/S value, and this behavior was consistent with all the dyestuffs under our study.

Effect of Pressure. The effect of pressure on color yield was also studied at pressures ranging from 5 to 15 MPa (Figure 2c). The solubility of the dye increased with an increase in pressure due to an increase in the density of scCO2 at certain temperatures. As the intermolecular distance decreases, the interaction between solute and solvent increases, and this in turn leads to an increase in solubility. As a result, the dissolved dye molecules can be diffused relatively easily into the amorphous region of the swelled fiber and adsorbed on to the fabric. This resulted in a higher adsorption of dye on the fabric.

Effect of Temperature. The effect of temperature on color yield was also studied at temperatures ranging from 80 to 120 °C at a concentration of 2% and a pressure of 15 MPa (Figure 2d). It was shown that the best temperature to achieve the equilibrium capacity of dye adsorption was the highest in the temperature range under our study (120 °C). The main reason for this phenomenon is that, at a higher temperature, the diffusion of dye molecules is more rapid, and the probability of dye adsorption on the surface of PES fabric increases.

Effect of Solvent. The solubility of dyes in scCO2 is one of the most important parameters for dye selection as well as for process temperature and pressure optimization. The research carried out by Ciba Specialty Chemicals Inc., Basel Switzerland on the dye uptake of PES fabric dyed in scCO2 with all kinds of disperse dyes on the market indicated that those disperse dyes with a higher degree of exhaustion in conventional aqueous dyeing did not give a higher degree of exhaustion in scCO2 at all. However, for the dyes under our study, good exhaustion was shown in both conventional water dyeing and the super critical method. Table 1 exhibits the type of solvent used for each dye of the series. It is obvious that increasing molecular weight not only resulted in decreasing solubility but also increased the need for a cosolvent which is methanol (1.2 mL). For dyes 1, 2, and 3 there was no exhaustion using scCO2 alone.

### Table 1. Solvent Used for Dyeing

<table>
<thead>
<tr>
<th>dye</th>
<th>mol wt</th>
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<tr>
<td>1</td>
<td>373.41</td>
<td>MeOH/scCO2</td>
</tr>
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<td>2</td>
<td>389.15</td>
<td>MeOH/scCO2</td>
</tr>
<tr>
<td>3</td>
<td>373.41</td>
<td>MeOH/scCO2</td>
</tr>
<tr>
<td>4</td>
<td>311.77</td>
<td>scCO2</td>
</tr>
<tr>
<td>5</td>
<td>297.07</td>
<td>scCO2</td>
</tr>
</tbody>
</table>

3.2. Study of Fastness Properties. The fastness data of the dyed polyester fabrics was summarized in Table 2, and the dyed fabrics showed an excellent fastness to washing (5) according to the international geometric grayscale. All dyes proved to have excellent (4−5 to 5) rubbing fastness. The light fastness of the majority of the synthesized dyes on polyester was excellent (5) according to the grayscale.

The results are superior compared to those of the samples dyed in water which ranged from 1 to 4 on the grayscale.

### Table 2. Fastness Properties of Dyed PES Samples

<table>
<thead>
<tr>
<th>dye</th>
<th>WF</th>
<th>RF</th>
<th>CC</th>
<th>St.</th>
<th>LF</th>
<th>WF</th>
<th>RF</th>
<th>CC</th>
<th>St.</th>
<th>LF</th>
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<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>1-2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>3-4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
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<td>5</td>
<td>5</td>
<td>5</td>
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</tbody>
</table>

WF: wash fastness; RF: rubbing fastness; LF: light fastness; CC: color Change; St.: Staining in color with cotton.

3.3. Study of Antimicrobial Activity. As shown in Table 3, the results obtained were found to be excellent especially with samples dyed with dyes number 1, 2, and 3 due to the presence of antipyrine moiety in the structure. The results can
be interpreted in terms of nonspecific action, i.e., antibacterial activity can be achieved either by causing damage to bacterial cells or by means of inhibition of a specific bacterial target. On the other hand, the antibacterial activity was found to be more effective against the examined G +ve bacteria than the G −ve bacteria, which reflect the difference between them in membrane structure and amenability to disruption and destruction. The effect of dyeing in scCO₂ also became more obvious when comparing the results with those of the samples dyed in water. Dyeing in scCO₂ was always shown to be more effective than dyeing in water.

3.4. Color Assessment. The color of the supercritical dyed polyester fabrics was evaluated using the CIELAB system in terms of L*, a*, and b*. The color coordinated listed in Table 4 indicates that the dye has good affinity to polyester fabric and tends to give the following:

i. The dyes under our study showed good affinity to polyester fabrics at the given temperature and gave generally bright and intense hues ranging from yellow to orange.

ii. The color hues of the dyes on polyester fabrics were shifted to the yellowish direction on the yellow-blue axis according to the positive values of b* except for dye number 3 which shifted to the bluish direction according to the negative value of b*.

iii. The color hues of the dyes on polyester fabric were shifted to the greenish direction on the red-green axis as indicated from the negative value of a* except for dye number 3 which shifted to the reddish direction on the red-green axis as indicated from the positive value of a*.

The measured K/S value given by the reflectance spectrophotometer is directly related to the dye concentration on the dye substrate.

3.4. Raman Spectra for the PES Dyed Samples. Spectra were collected in the range of 0 to 4000 cm⁻¹. The spectra were acquired using scan time settings of 50 s for fiber analysis. Raman data acquisition and data processing were achieved using Lab Spec 6 spectroscopy suit software.

Samples dyed with dye 1 showed signals for δ (CH₃) at 1380 cm⁻¹; CC-aromatic ring chain vibrations at 1460 cm⁻¹; C==N at 1610 cm⁻¹; aromatic C==C stretching at 1624 cm⁻¹; C==O stretching at 1700 cm⁻¹; CN at 2220 cm⁻¹; CH at 2800 cm⁻¹; =CH at 3000 cm⁻¹; and NH at 3250 cm⁻¹.

Samples dyed with dye 2 showed signals for C−O−C at 800 cm⁻¹; δ (CH₃) at 1380 cm⁻¹; CC-aromatic ring chain vibrations at 1460 cm⁻¹; C==N at 1610 cm⁻¹; aromatic C==C stretching at 1624 cm⁻¹; C==O stretching at 1700 cm⁻¹; CN at 2220 cm⁻¹; CH at 2800 cm⁻¹; =CH at 3000 cm⁻¹; and NH at 3250 cm⁻¹.

Samples dyed with dye 3 showed signals for δ (CH₃) at 1400 cm⁻¹; CC-aromatic ring chain vibrations at 1460 cm⁻¹; C==N at 1610 cm⁻¹; aromatic C==C stretching at 1624 cm⁻¹; C==O stretching at 1700 cm⁻¹; CN at 2220 cm⁻¹; CH at 2800 cm⁻¹; =CH at 3000 cm⁻¹; and NH at 3250 cm⁻¹.

Samples dyed with dye 4 showed signals for δ (CH₃) at 1380 cm⁻¹; CC-aromatic ring chain vibrations at 1450 cm⁻¹; C==N at 1610 cm⁻¹; aromatic C==C stretching at 1624 cm⁻¹; C==O stretching at 1737 cm⁻¹; CN at 2220 cm⁻¹; CH at 2800 cm⁻¹; =CH at 3000 cm⁻¹; and NH at 3250 cm⁻¹.

Samples dyed with dye 5 showed signals for C−Cl at 550 cm⁻¹; CC-aromatic ring chain vibrations at 1450 cm⁻¹; C==N at 1610 cm⁻¹; aromatic C==C stretching at 1624 cm⁻¹; C==O stretching at 1737 cm⁻¹; CN at 2220 cm⁻¹; CH at 2800 cm⁻¹; =CH at 3000 cm⁻¹; and NH at 3250 cm⁻¹.

It is clear from the above data that compared to Raman spectrum of pure polyester from the literature, dyed PES samples used in this work had the same peaks from 600 to 1900 cm⁻¹; however, the PES samples did not show any peaks from 2000 to 4000 cm⁻¹. The peaks in this range were attributed to the function groups of the dyestuff under study, mainly CN, CH, and NH, respectively.

4. CONCLUSIONS

In our experiment, there was no wastewater produced as a result of the dyeing procedures as compared to the conventional water dyeing. The dyeing was much more efficient than the conventional procedure. Without doubt, the scCO₂ dyeing has certain advantages. The optimum dyeing temperature and pressure are 120 °C and 15 MPa, respectively, and the optimum dye concentration ranges from 2−6% owf. The color yield and water-wash, rubbing, and light fastness were excellent as shown in our results. All dyed samples also exhibited excellent antibacterial efficiency against G +ve and G −ve bacteria. The results obtained prompted us to study the dyeing efficiency of these dyes on other fabrics such as Nylon and Polypropylene, the results of which will be reported in our future work.

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Table 4. Color Coordinates and K/S of the Dyed PES Samples

<table>
<thead>
<tr>
<th>dye</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h</th>
<th>K/S</th>
<th>K/S</th>
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<td>1</td>
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<td>100.96</td>
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<td>15.24917</td>
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xCO₂ dyeing | conventional dyeing

Table 3. Antibacterial Activity of the Dyes and Dyed Samples

<table>
<thead>
<tr>
<th>dye</th>
<th>ZI of the dyed PES in water</th>
<th>ZI of the dyed PES in scCO₂</th>
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<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>12</td>
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<td>15.5</td>
<td>17</td>
<td>G +ve</td>
</tr>
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<td>21</td>
<td>24.5</td>
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</tr>
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<table>
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<td>18</td>
</tr>
<tr>
<td>5</td>
<td>21</td>
</tr>
</tbody>
</table>

**ZI**: zone of inhibition; G +ve: (S. aureas); G −ve (E. coli).

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Notes
The authors declare no competing financial interest.

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