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Supercritical Carbon Dioxide Dyeing for PET and Cotton Fabric with Synthesized Dyes by a Modified Apparatus

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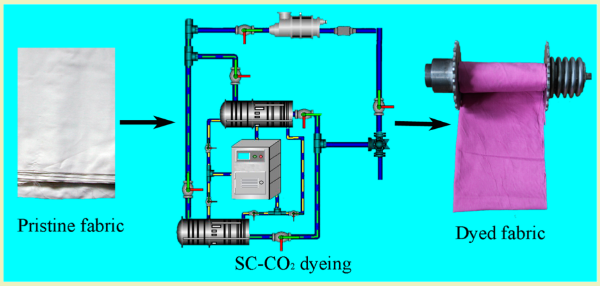
Supporting Information

ABSTRACT: Supercritical carbon dioxide (SC-CO_2) dyeing for the polyethylene terephthalate (PET) and cotton fabric was implemented by a modified dynamic-recirculation apparatus that was successfully designed and constructed in our laboratory. This energy-efficient apparatus contains two horizontal dyeing vessels and equips the rotating warp beam. The circulating SC-CO_2 fluid and revolving fabrics facilitate the uniform adsorption and quick uptake of dye molecules to the fabrics. Moreover, three dyes were synthesized and applied for dyeing fabric samples performed in mild conditions of 353.2 K and 18.0 MPa for 60 min in SC-CO_2. Satisfactory and commercially acceptable products with reasonably good color uniformity, color strength and color fastness were obtained in dyeing experiments with this SC-CO_2 apparatus. Color characteristics of the dyed PET and cotton fabrics such as the absorption and reflectance spectra were determined, and their surface morphologies were investigated by scanning electron microscopy.



KEYWORDS: *Supercritical carbon dioxide, dyeing, PET fabric, cotton fabric, synthesized dye, dynamic-recirculation apparatus*

INTRODUCTION

With increasing awareness of environmental protection and proposing more stringent regulations, the textile industry is continuously looking for environmentally benign processes to replace the traditional water-based dyeing methods that inevitably use large amounts of water and excessively employ various chemical additives.[1] Recently, supercritical carbon dioxide (SC-CO_2) dyeing has become an alternative benign solvent in the textile industry for waterless dyeing methods, because SC-CO_2, in which organic dyes show adequate solubility, has easily accessible critical conditions (T_c = 304.34 K, P_c = 7.38 MPa), low toxicity, low viscosity, and high diffusivity.[2] The water-saving, energy-efficient, and environment-friendly procedures make it a promising method in using SC-CO_2 for textile dyeing.

The dissolving power toward disperse dyes, as well as the swelling and plasticization action toward hydrophobic polymers, make SC-CO_2 suitable for the coloration of polyethylene terephthalate (PET) and other synthetic textiles.[3] Regarding the success of dyeing of PET with disperse dyes in SC-CO_2,[4−9] attempts have been made in applying this technique to dye natural fibers like cotton and wool. So far, different dyeing methods have been documented in the literature to adapt the SC-CO_2 dyeing process to the coloration of natural fibers.[10−20] Along with the developments of various dyeing processes and approaches for different kinds of fibers, the SC-CO_2 dyeing apparatus or machines also play an important role in the applications of this technology in the textile industry, on which considerable attention has been paid by researchers in recent decades. The progress about SC-CO_2 dyeing apparatus or machines has been well summarized by the research group of Long et al. in 2014.[21]

This study provided a dynamic-recirculation SC-CO_2 apparatus with two horizontal dyeing vessels equipped with a rotating warp beam. The horizontal dyeing vessel is designed to overcome the influence of gravity on the dyeing effect, to achieve high uniformity and production efficiency. A single-vessel device needs gas venting to anew loading fabrics and repetitive heating that leads to low production efficiency, increased cost, and considerable CO_2 gas consumption. Here, a high-efficiency two dyeing vessel apparatus has been designed that can dye two batches of fabrics simultaneously and independently. We also reported a one-step dyeing method for PET and cotton fabrics in SC-CO_2 with synthesized dyes at our laboratory, and the fabrics were colored without any pretreatment. The color fastness, color strength, and fixation efficiency of dyed fabrics were also investigated.

MATERIALS AND METHODS

Materials. All chemicals used for dye synthesis were purchased from the Energy chemical company (Shanghai, China). The carbon dioxide gas (99.6 vol %) obtained from Huaxinda Industrial Gases Co., Ltd. (Fuzhou, China) was used for SC-CO_2 dyeing. PET and cotton fabric (300 g of the fabric sample with a dimensions of about 0.3 × 10 m) used in this study were obtained from Weiqiao Pioneering Group Co., Ltd. (Shandong, China). The synthesized dyes were carefully purified and characterized by ^1H NMR (Bruker-Biospin 400

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spectrometer) and MS (Thermo-Finnigan ion trap mass spectrometry).

The procedure of dye synthesis is shown in Scheme 1, and the properties of these dyes are summarized in Table 1.

Scheme 1. Synthesis Scheme of the Dyes

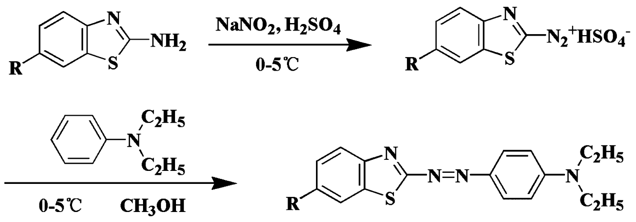

Table 1. Properties of Three Dyes Prepared in This Study

dyes	R	M_w (g mol^{-1})	λ_{max} (nm)
1	$-OCH_3$	340.14	510
2	$-COOCH_2CH_3$	382.15	515
3	$-NO_2$	355.11	535

SC-CO_2 Dyeing Apparatus. A dynamic-recirculation apparatus for dyeing PET and cotton fabrics in SC-CO_2 was designed and constructed by our group composed of refrigeration, pressurization, circulation dyeing, separation, and recycling systems, together with pressure and temperature control. A schematic diagram of the whole apparatus was depicted in Figure 1 with all subsystems and especial devices (in Figures 2 and 3) enumerated with numbers, and described in the following.

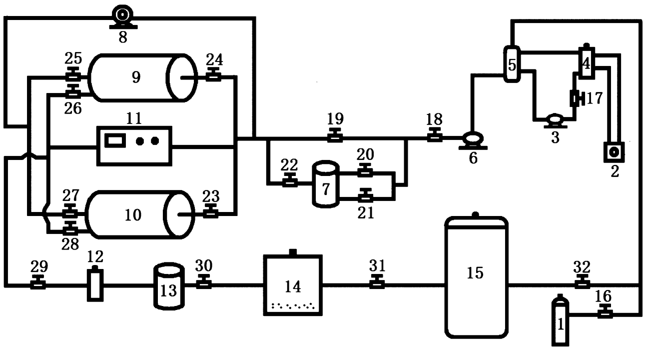

Figure 1. SC-CO_2 apparatus: (1) CO_2 cylinder, (2) refrigerating machine, (3) carrying pump, (4, 12) heat exchanger, (5) condenser, (6) pressurization pump, (7) dyestuff vessel, (8) circulation pump, (9, 10) dyeing vessel, (11) mould temperature control unit, (13) separator, (14) CO_2 gas purifier, (15) CO_2 gas recycling container, and (16−32) valves.

The first subsystem of the dyeing experiment is a refrigeration section for liquefaction of CO_2 gas, made up of a refrigerating machine (2), a heat exchanger (4), a carrying pump (3), and a condenser (5). The refrigerating machine (2) has two separated cooling groups with a total power of 2.5 kW, a refrigerating capacity of 5060 W, and a wind capacity of 3600 m^3/h. The CO_2 gas passed heat exchanger (4) was delivered by carrying pump (3) to the condenser (5) for cooling CO_2 gas. The cooled medium in the condenser (5) is the mixture of water and ethylene glycol with a temperature ranged from −10 to +5 °C. The second subsystem is a pressurization section mainly composed of the pressurization pump (6), which is a plunger electric reciprocating pump equipped with a motor of 2.2 kW. The maximum flow rate is 0.05 m^3 and the rated pressure is 32 MPa.

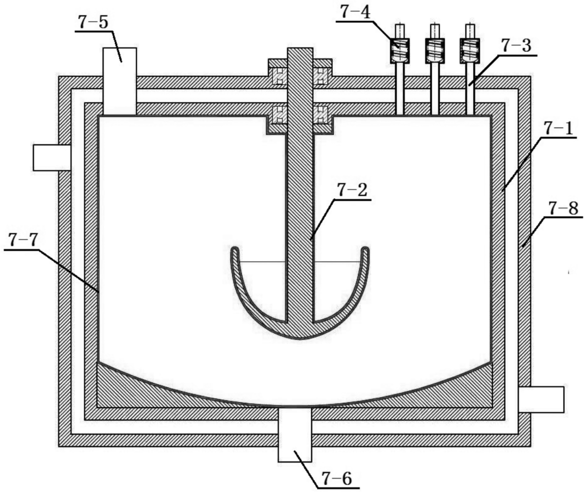

Figure 2. Profile of the dyestuff vessel for SC-CO_2 apparatus: (7-1) dyestuff vessel body, (7-2) stirring unit, (7-3) dyestuff sprue, (7-4) attemperator, (7-5) fluid inlet, (7-6) fluid outlet, (7-7) nonstick coating, and (7-8) electrically aided heating jacket.

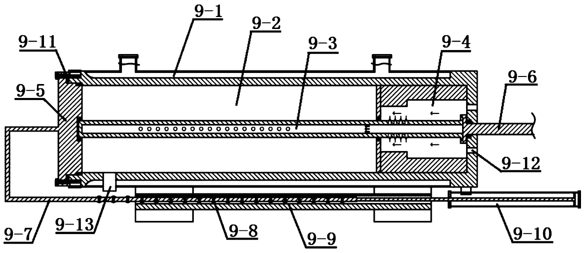

Figure 3. Profile of the dyeing vessel for SC-CO_2 apparatus: (9-1) dyeing vessel body, (9-2) dyeing cavity, (9-3) rotating warp beam, (9-4) fluid intake cavity, (9-5) dyeing vessel cover, (9-6) rotational drive shaft, (9-7) driveshaft, (9-8) pulley, (9-9) slide way, (9-10) hydraulic actuate cylinder, (9-11) hydraulic lock devices, (9-12) fluid inlet, and (9-13) fluid outlet.

The third subsystem is about the circulation dyeing section, made up of a dyestuff vessel (7), a circulation pump (8), dyeing vessels (9, 10), and a mould temperature control unit (MTCU) (11). The dyestuff vessel (7) is a stainless steel autoclave with a volume of 2 L, of which the detailed profile and structure are described in Figure 2. The dyestuff vessel device includes dyestuff vessel body (7-1), stirring unit (7-2), dyestuff sprue (7-3) for dyestuff injecting, attemperator (7-4), and inlet (7-5) and outlet (7-6) used for CO_2 circulation. Moreover, the body (7-1) inwall was coated with nonstick coating (7-7) as well as an electrically aided heating jacket (7-8) around its outside. The circulation pump (8) is a magnetic drive pump with a head of 30 m, worked at a flow rate of 10 m^3/h, a maximum speed of 3000 r/min and a power of 2 kW, and controlled by a magnetic coupling with a standard power of 10 kW. The characteristic dyeing vessels (9, 10) with a cubage of 7 L were designed and constructed as a cylindrical shape stainless steel autoclave, and equipped with a rotating warp beam. A detailed profile and configuration are shown in Figure 3. The dyeing vessel was made up of dyeing vessel body (9-1), dyeing cavity (9-2), fluid intake cavity (9-4), rotating warp beam (9-3) with the perforations, dyeing vessel cover (9-5), fluid inlet (9-12), and fluid outlet (9-13). During dyeing process, the fabric wrapped around this rotating warp shaft (9-3) was placed into this dyeing vessel, and then the rotating warp shaft was driven by a rotational drive shaft (9-6) with a cyclical circulation. The dyeing vessel on the outside equips the mobile driver section to actuate the dyeing vessel cover movement, composed of driveshaft (9-7), pulley (9-8), slide way (9-9) and hydraulic actuate cylinder (9-10). A hydraulic lock device (9-11) is set between dyeing vessel cover and dyeing body to fast lock or unlock the dyeing vessel cover. Dyeing vessel was heated by the MTCU (11) with a temperature range between 40 and 300 °C, with a heating power of 24 kW, a pump power of 2.2 kW, and at a pump pressure of 10 MPa.

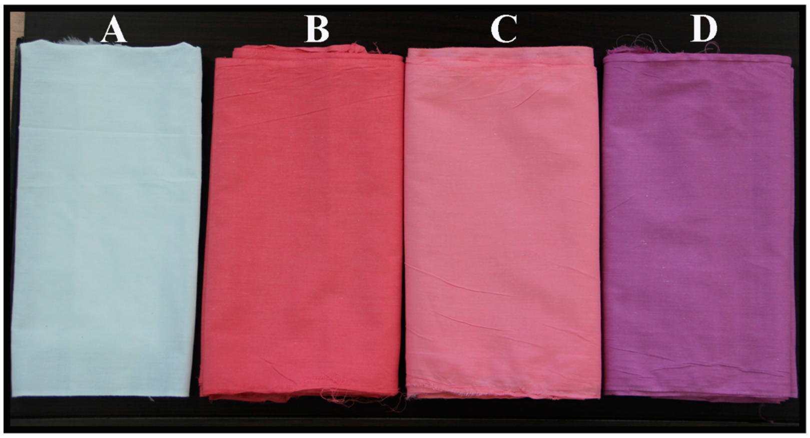

Figure 4. Photograph of pristine PET fabric (A), dyed PET fabrics with dye 1 (B), dye 2 (C), and dye 3 (D) in SC-CO_2.

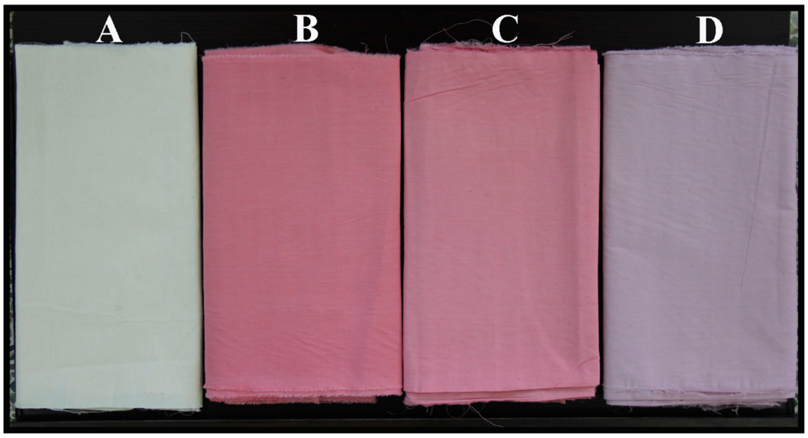

Figure 5. Photograph of pristine cotton fabric (A), dyed cotton fabrics with dye 1-3 (B–D) in SC-CO_2.

After the dyeing procedure, it is essential to separate and recycle residual dyestuffs and carbon dioxide. Accordingly, the fourth subsystem for separating and recycling dyestuffs and CO_2 gas was designed and fabricated in the fabric dyeing, mainly composed of a heat exchanger (12), a separator (13), a CO_2 gas purifier (14), and a CO_2 gas recycling container (15). The heat exchanger (12) having the same structure and configuration as that of (4) was employed for depressurizing supercritical fluid to keep favorable separation temperatures in the separator (13) with a volume of 2 L. The CO_2 gas purifier (14) was designed with a chamber of 5 L and filled with molecular sieves for further purification of the CO_2 gas released from the separator (13). Finally the purified CO_2 gas was recycled in a gas recycling container (15) of 10 L. To accurately control and implement the dyeing process, an automatic parameter control subsystem was designed and equipped which was composed of a central control interface, a programmable logic controller (PLC) control cabinets, and the indicators of pressure and temperature. All the parameters like the pressure and temperature could be set and were automatically controlled in the dyeing process.

SC-CO_2 Dyeing Experiments. First, fabrics (300 g) were wrapped around the rotating warp beam, and then placed in the dyeing vessel, and synthesized dyes (0.65 g) were put into the groove of stirring unit in the dyestuff vessel. Next, all the vessels in the whole system were well sealed. The CO_2 leaving from a cylinder passed through the heat exchanger and cooled in the condenser. Subsequently, the cooled CO_2 liquid was pumped by the pressurization pump into the dyeing subsystem. The introduced dyes were simultaneously predissolved by SC-CO_2 fluid in the dyestuff vessel before being preheated by the heating jacket. About 20 min later, the dyeing vessel was filled with SC-CO_2, and then the CO_2 circulation pump was opened to let the CO_2 fluid circulate in the subsystem. When the pressure and temperature of SC-CO_2 attained set points (18.0 MPa, 353.2 K), the dyeing process started and lasted for 60 min. After dyeing, the temperature of the supercritical dyeing fluid was reduced to about 303.2 K, and then the separation and recycling subsystem got to work. Consequently, the SC-CO_2 and dyestuff were separated in the separator and remaining dyestuff was recycled. The CO_2 gas was further purified in the CO_2 gas purifier and collected in gas recycling container for reuse. When the CO_2 gas was sufficiently recycled and the pressure dropped to atmospheric pressure, the dyeing vessel was opened and the colored fabrics were removed from the vessel to measure the color fastness and color strength.

The pressure and temperature of experiments were monitored by the central control subsystem equipped with a digital indicator and a red indication alarm for any values that run out of set ranges, with estimated errors of ±0.05 K and ±0.02 MPa for the temperature and pressure measurements, respectively. Figures 4 and 5 are the photograph of the colored fabrics with our synthesized dyes in SC-CO_2.

Color Strength and Color Fastness Test. The color strength (K/S) of the dyed cotton fabric was determined by the Kubelka–Munk equation (eq 1), where R_{min} is the minimum value of the reflectance curve, which was determined by measuring the dyed cotton fabric with a Lambda 900 UV–vis spectrophotometer. The reflectance (R) was obtained at 10 nm intervals in the range of 300–650 nm.

$$K/S = \frac{(1 - R_{min})^2}{2R_{min}} \quad (1)$$

The K/S value of the extracted cotton fabric ($(K/S)_{extracted}$) was determined and used to calculate the percentage of dye molecules that was fixed to cotton fabric (F). The dyed fabric was extracted for 1 h

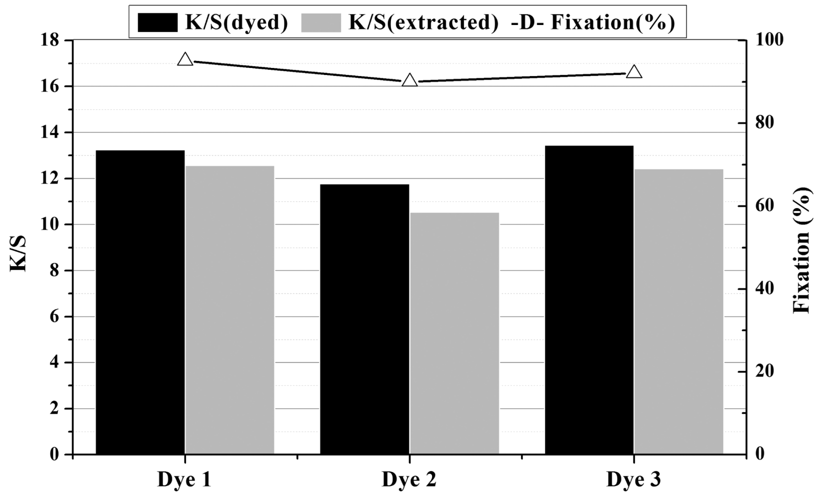

Figure 6. $(K/S)_{\text{dyed}}$, $(K/S)_{\text{extracted}}$, and F values of dyed PET fabrics with three dyes at a constant dyeing temperature of 353.2 K and pressure of 18.0 MPa for 60 min.

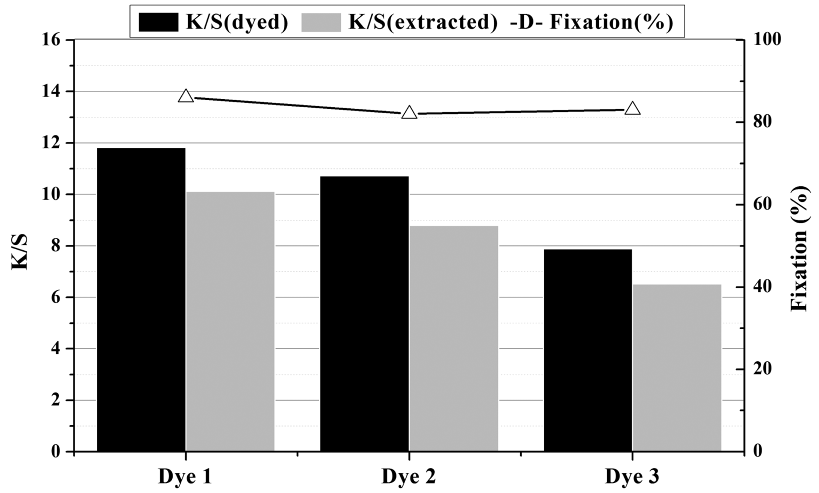

Figure 7. $(K/S)_{\text{dyed}}$, $(K/S)_{\text{extracted}}$ and F values of dyed cotton fabrics with three dyes at a constant dyeing temperature of 353.2 K and pressure 18.0 MPa for time 60 min.

with acetone at 80 °C by a Soxhlet extraction method for the removal of unfixed reactive disperse dyes. The $(K/S)_{\text{dyed}}$ (after dyeing) and $(K/S)_{\text{extracted}}$ (after extraction) of the dyed cotton fabric were measured, and then put into eq 2 to calculate the F value.

$$F = \frac{(K/S)_{\text{extracted}}}{(K/S)_{\text{dyed}}} \times 100\% \qquad (2)$$

The washing fastness of dyed fabric was examined by a washing-fastness apparatus (SW-12A II), and multifiber adjacent fabrics (acetate, cotton, polyamide, polyester, acrylic, and wool) were used for staining fastness assessment according to China textile criteria GB/T 3921-2008 (method C). The rubbing fastness of dyed fabric was performed at a rubbing tester (11219) with dry and wet samples according to China textile criteria GB/T 3920-2008. Color fastness of China textile is rated at nine levels (1, 1-2, 2, 2-3, 3, 3-4, 4, 4-5, 5); the best level is 5, and the worst is 1. Generally, the dry rub fastness reaches the 4-5 level; wet rub fastness, 4; staining fastness, 4; fading fastness, 3-4, respectively, conforming to the standards of garment dyes.

■ RESULTS AND DISCUSSION

Color Strength and Color Fastness. A satisfactory and commercialization dyed products were obtained by employing the horizontal dyeing vessel with a rotating warp beam. Colors ranged from scarlet to pink to purple for dyed PET fabrics, and from pink to baby pink to lilac for dyed cotton fabrics. The shades with different color strength were further discussed in the following.

As shown in Figure 6, $(K/S)_{\text{dyed}}$, $(K/S)_{\text{extracted}}$, and F values of dyed PET fabrics with the synthesized dyes were investigated at a dyeing temperature of 353.2 K, pressure of 18.0 MPa, and time of 60 min. Dye 3 and dye 1 had comparative $(K/S)_{\text{dyed}}$ values that were significantly greater than that of dye 2. Meanwhile, dye 1 possessed a higher $(K/S)_{\text{extracted}}$ value (12.57) than that of dye 2 (10.54). The $(K/S)_{\text{dyed}}$, $(K/S)_{\text{extracted}}$, and F values for dyed cotton fabrics are illustrated in Figure 7. The $(K/S)_{\text{dyed}}$ values for the three dyes ranked in the following order: dye1 > dye 2 > dye 3. In addition, a higher $(K/S)_{\text{extracted}}$ value (10.12) was shown by dye 1 and a lower $(K/S)_{\text{extracted}}$ (6.52) value by dye 3. The F values of these dyes in dyeing PET and cotton fabrics both ranked in the following order: dye 1 > dye 3 > dye 2, which could be attribute to the dye molecule structure and dye solubility in SC-CO_2. One explanation for this result could be that dye molecule of lower polarity and smaller molecular weight generally had higher solubility in SC-

Table 2. Fastness Data of Dyed PET and Cotton Fabrics with Three Dyes at Our Dyeing Conditions (353.2 K, 18.0 MPa, 60 min) in SC-CO_2

		staining								
	fading	acetate	cotton	nylon	polyester	acrylic	wool		dry	wet
dyed PET fabric with dye 1	4-5	5	5	5	5	5	5		5	4-5
dyed PET fabric with dye 2	4-5	4-5	5	5	4-5	5	5		5	4-5
dyed PET fabric with dye 3	4-5	5	5	5	5	5	5		5	4-5
dyed cotton fabric with dye 1	3-4	4-5	4-5	4-5	4-5	4-5	4-5		4-5	4
dyed cotton fabric with dye 2	3-4	4-5	4-5	4-5	4-5	4-5	4-5		4-5	4
dyed cotton fabric with dye 3	3-4	4-5	4-5	4	4	4-5	4-5		4-5	4

CO_2, and high dye solubility improved the *F* value of the dyed fabric. On the other hand, the *F* value of dyed PET fabric was higher than that of cotton that is because adsorption of dye on the PET fiber was higher than that on the cotton fiber. Higher dye adsorption on the PET fabric could be due to structural features of PET fiber. The PET fiber was hydrophobic and possessed close structure and high crystallinity. In addition, the CO_2 molecules easily broke into the dense area of the fibers to swell and plastify PET, and increased the activity of the fiber molecular chain and the diffusion of free volume, which may play a dominant role in dye adsorption. In contrast, the weaker van der Waals and hydrogen bonding forces were responsible for dye adsorption in cotton dyeing, thus, adsorption of dye on the cotton fiber was lower than that on the PET fiber. Therefore, the highest *F* value of dyed PET fabric with dye 1 was 95%, which was higher than that of cotton (86%).

The results of color fastness exhibited that a better grade for dyed PET product than cotton product. As summarized in Table 2, all color fastness grades of dyed PET products were very good. The fading fastness reached a grade of 4-5 and staining fastness of 4-5 or 5, and the rubbing fastness was 4-5 (wet) or 5 (dry), which met the requirements for industrial use. The ratings for color fastness of dyed cotton products were slightly lower than that of PET. The fading fastness was 3-4 and the staining fastness reached 4 or 4-5. The rubbing fastness for wet and dry were 4 and 4-5, respectively.

Color Characteristics. The synthesized dyes of different colors (crimson, mauve, black violet) successfully dyed PET and cotton fabrics. Absorption and reflectance spectra were recorded using a Lambda 900 UV−vis spectrophotometer in the wavelength range of 350−700 nm. The absorption spectra of dyes were recorded in acetone solvent, which showed a single absorbance with maximum values at 510 nm for dye 1, 515 nm for dye 2, and 535 nm for dye 3 (Figure 8). The reflectance spectra of dyed PET and cotton fabrics were recorded adopting white standard $BaSO_4$, and the minimum value of the reflectance curve were centered around 510 nm for dye 1, 515 nm for dye 2, and 535 nm for dye 3 (Figure 9). Under the above spectroscopic characterization, the peak wavelength of absorption and reflectance spectra with dye 3 were slightly greater than those of dye 1 and dye 2. It is speculated that an electron-acceptor group ($-NO_2$) substituted on the chromophore core caused slight bathochromic shift of dye 3 relative to dyes 1 and 2.

Microscopic Studies. The surface morphology of PET and cotton fibers took on remarkable alterations before and after dyeing with dye 1, as recorded using scanning electron microscopy (SEM). Although the surfaces of pristine PET and cotton fibers were smooth and clean, there was some stripe on the cotton fiber (Figure 10A,B). In contrast, amounts of extraneous substance was observed, which was dye molecule deposited on the surface of fibers dyed with dye 1 (Figure 10C,D). Moreover, more extraneous substance was found on the surface of the dyed PET fiber (Figure 10 C) than that of the dyed cotton fiber (Figure 10D), which may result from a better dyeing effect between dye 1 and PET fabric than that of cotton.

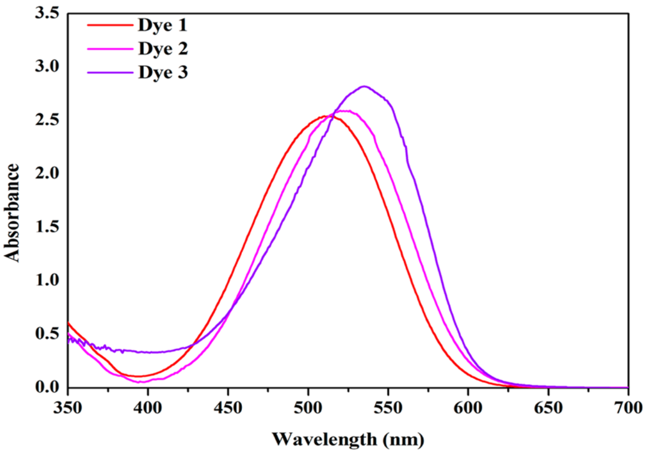

Figure 8. Absorption spectra of three dyes at short wavelengths.

Practical Application of SC-CO_2 Dyeing. With a higher mass transfer rate between the rotary fabric and the circulating SC-CO_2 fluid, our dynamic-recirculation SC-CO_2 apparatus is instrumental to achieve a uniform adsorption and quick uptake of dye molecules on the fabrics. In addition, the fabric sample is swelled by impregnating in the SC-CO_2 fluid, which accelerates the dye molecules adsorption, diffusion and penetration into the amorphous regions of fiber and shortens the dyeing time. On account of the above merits, the modified SC-CO_2 apparatus was used for dyeing zipper (chain and tape) of which the main ingredients was PET in practical industrial production. As shown in Figure 11, commercially acceptable zipper products dyed with the three dyes were obtained with good color uniformity, excellent color strength, high washing fastness and rubbing fastness (rating at 4-5 to 5).

■ CONCLUSIONS

In summary, a modified SC-CO_2 apparatus has been successfully designed and constructed for the first time to dye PET and cotton fabrics with three synthesized dyes, which achieved a green and environmentally friendly dyeing process and acquired a remarkable dyeing effect. The apparatus contains two horizontal dyeing vessels and equips the rotating warp beam, which makes the simultaneous dyeing of both PET and cotton fabrics possible. The subsystems and special devices of the SC-CO_2 apparatus were described, and the SC-CO_2 dyeing experiments were operated at a temperature of 353.2 K and pressure of 18.0 MPa for 60 min. The color strength and

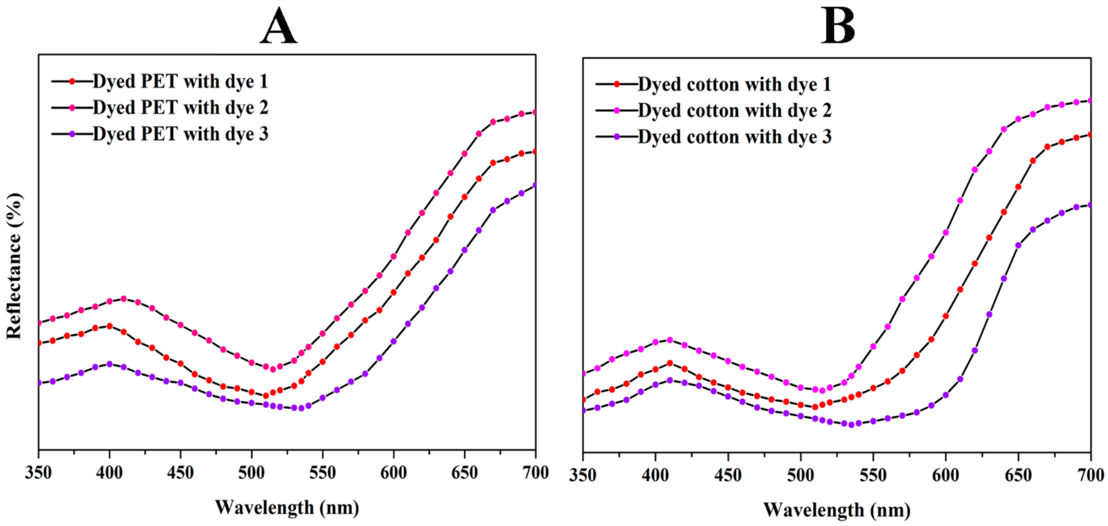

Figure 9. Reflectance spectra of dyed (A) PET and (B) cotton fabrics with three dyes at short wavelengths.

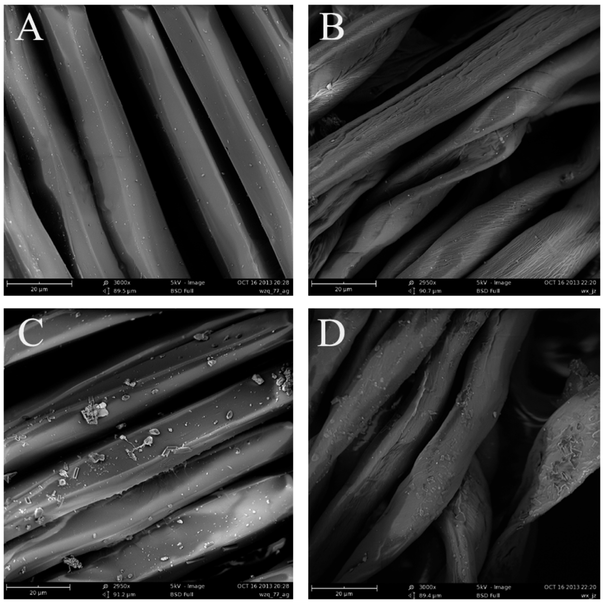

Figure 10. SEM images of fiber samples: pristine PET fiber (A), pristine cotton fiber (B), dyed PET fiber with dye 1 (C), and dyed cotton fiber with dye 1 (D).

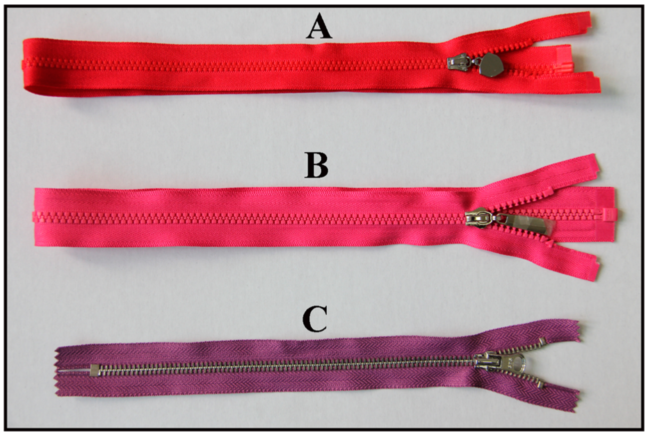

Figure 11. Photograph of the colored zippers with dye 1 (A), dye 2 (B), and dye 3 (C) in SC-CO_2.

color fastness of dyed fabric samples have been measured. The $(K/S)_{\mathrm{dyed}}$ and $(K/S)_{\mathrm{extracted}}$ values at the above dyeing conditions reach up to 13.45 and 12.57 for dyed PET, and to 11.82 and 10.12 for dyed cotton, respectively. The highest F value of dyed PET is 95% and of cotton, 86%. Higher color strength and deeper color have been recorded for dyed PET than that for dyed cotton. The color fastness is also acceptable with high ratings for rubbing (wet and dry), fading and staining fastness for PET fabric samples, and slightly lower ratings for cotton fabric samples. The dyeing method of natural fiber requires further improvement in the future. In this work, color characteristics of dyed fabrics such as the absorption and reflectance spectra have also been investigated, and their surface morphologies have been analyzed by SEM.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General details of experimental procedure, characterization data and copies of ^{1}H NMR spectra and mass spectra of synthesized dyes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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