

Supercritical CO₂ dyeing of polyester fabric with photochromic dyes to fabricate UV sensing smart textiles

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ARTICLE INFO

Keywords:

Supercritical carbon dioxide (scCO₂) dyeing
Polyester
Photochromic dye
Spirooxazine
Naphthopyran

ABSTRACT

Photochromic molecules are well-established colourants in the manufacturing of niche products, providing reversible colour change effects when irradiated with ultraviolet (UV) light. The high material cost of such speciality dyes along with the general high carbon footprint and extensive water consumption of textile products necessitates resource-efficient production processes. The use of supercritical CO₂ (scCO₂) dyeing technique enables the economic production of textile high-end products, where a uniform through colouration is desired. This study investigates the potential application of two commercial photochromic dyes based on spirooxazine (Sea Green – SO-SG) and naphthopyran (Ruby Red – NP-RR) to polyester fabric using scCO₂ dyeing technique and examines their photochromic behaviour. The dyeing was carried out at 120 °C and 25 MPa for 1 h. The photochromic performance was evaluated using a specially designed online colour measurement system capable of simultaneous UV irradiation and continuous measurement of photochromic colour change even after the shutdown of the UV source. The colour yields (K/S values), photoswitching rates and durability against washing were the main parameters examined. The results showed that scCO₂ dyed photochromic polyester fabrics exhibited reversible colour changing properties upon UV exposure and removal. The samples dyed with SO-SG demonstrated a comparable degree of photo-colouration, lower background colour, faster colouration and decolouration speeds, but inferior wash fastness compared with NP-RR dyed samples. Particularly, the same class of dyes applied by scCO₂ dyeing showed faster fading rates compared with conventionally dyed and screen printed samples. This study shows that scCO₂ dyeing method is a potential alternative to develop uniformly coloured photochromic textiles providing excellent photochromic performance with additional economic and environmental benefits.

1. Introduction

Photochromic colourants change their colour from colourless to a coloured state when irradiated by UV light and revert to their original colourless state when exposed to visible light or increased temperature. Photochromic materials have been used in different application areas including ophthalmic lenses, optical data recording and storage, memories, light control filters, security printing, sensors and displays [1,2], but their use in textiles has been limited. Nowadays, however, the interest in using photochromic textiles has risen especially due to their important and potentially fun applications in smart and functional

textiles [3]. Applications in textiles range from everyday clothing to high-tech smart and functional textiles such as in fashion and intelligent design, security and brand protection, anti-counterfeit, camouflage, textile UV sensors, and active protective clothes [4]. Photochromic textiles have the advantage of quickly changing colour in response to light while maintaining general textile properties. For example, UV sensing textiles show higher flexibility, are easily customizable and require low maintenance compared to conventional sensor systems [5]. Despite the availability of significant interest, commercial development of photochromic textiles is limited mainly due to technical issues associated with application methods and performance [1]. Several

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<https://doi.org/10.1016/j.dyepig.2020.108671>

Received 27 January 2020; Received in revised form 13 June 2020; Accepted 26 June 2020

Available online 15 July 2020

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techniques have been reported for the preparation of photochromic textiles, including screen-printing [6–11], digital inkjet printing [12–16], exhaust dyeing [15,17–20], sol-gel coating [21,22], pad-dry method [23,24], electro-spinning [25,26], and mass colouration [27, 28]. Details about the different methods of production of photochromic textiles, their properties, and applications in the textile field were reviewed by Periyasami et al. [29]. Among the methods, screen-printing and conventional exhaust dyeing are the most widely used techniques. Screen-printing has been successfully used to apply photochromic dyes to textiles. While good photochromic effects have been obtained, the binder used usually imparts a relatively harsh handle to the fabrics, which affects their comfort characteristics. It also has relatively poor fastness and photostability properties compared with the exhaust dyeing method [3]. Exhaust dyeing of photochromic dyes as disperse dyes to various textile substrates has also been widely investigated. Exhaust dyeing is commonly considered as the most convenient and easy technique compared with mass colouration and printing methods [15,18, 19]. However, many inevitable problems are connected to the dyeing method such as the requirement of long dyeing time at high temperature, a large amount of water and auxiliary chemicals, incomplete exhaustion and fixation even with salts and alkalis, and the discharge of the contaminated wastewater, which makes it ecologically and environmentally less safe. During exhaust dyeing of textiles, approximately 5–10% of the dyes are not used and end up in wastewater [30]. Specifically, the exhaustion and colour build-up properties of photochromic dyes were reported rather low [18,19], which makes the process even more costly given the high cost of photochromic colourants. Attempts to replace water with organic solvents was also challenged by issues such as toxicity, recoverability, and cost [24]. Recently, application of photochromic colourants using digital inkjet printing has presented promising results for one-sided patterned applications [12,16,31]. Despite its advantages over conventional screen-printing in regards to resource efficiency and process flexibility, the requirement of inks, which meet the stringent physical, chemical, and environmental criteria along with the associated print qualities remain a challenge. Overall, most of the conventional techniques currently used to produce photochromic textiles have common issues such as higher cost of production, lower level of colour development, and insufficient durability, that still need to be addressed for successful commercial application [4]. Therefore, appropriate production techniques, which meet the necessary commercial requirements, are still needed.

For uniformly through-coloured applications, the dyeing process in scCO_2 is an attractive alternative to aqueous and solvent-based processes offering significant environmental and economic benefits [32]. Environmental advantages include avoiding the use of freshwater and associated wastewater, use a small amount of dye without auxiliaries (dispersing agents, levelling agents, and pH buffers), and all leftover dye can be reused resulting almost zero hazardous effluent. Moreover, the CO_2 used is a waste product from industrial emissions and almost no air pollution is generated as 95% of the CO_2 can be recycled. The economic analysis showed that, although the initial investment cost for a scCO_2 dyeing machine is higher than the aqueous dyeing machine, the operation cost is lower (0.35 € instead of 0.99 € per kg of polyester) with an overall 50% lower process cost for scCO_2 dyeing. This is due to the higher rate of dyeing, simpler dye formulation, and requirement of less energy by the scCO_2 dyeing method compared with aqueous dyeing methods [33].

The dyeing process in scCO_2 is simple and faster than aqueous processes mainly due to its low viscosity and high diffusivity properties. Briefly, the dye is dissolved in supercritical medium, transported to the fibre, and penetrates the fibre relatively fast as the CO_2 can also swell and plasticize the polymer facilitating the diffusion of dye molecules. At the end of the process, the system is depressurized, the CO_2 and excess dye can be recycled, and no drying is required. Overall, the dyeing of polyester in scCO_2 instead of water is both economically and environmentally superior [34,35]. The simpler dye formulation with a small

amount of dyestuff is particularly advantageous in the case of expensive materials such as photochromic dyes. The use of scCO_2 as a solvent can also avoid any undesirable solvent effect on the photochromic properties as the CO_2 can be easily removed from the polymer during pressure release after completion of the dyeing procedure.

Photochromic dyes are suitable colourants to be applied in scCO_2 medium owing to similar molecular structure as the conventional disperse dyes in that they are small to medium-sized neutral molecules with a balance of hydrophilic and hydrophobic character [36]. They displayed the same dyeing behaviour as disperse dyes when applied to polyester fabric using exhaust dyeing method [19]. Application of some photochromic dyes in polymeric matrixes using scCO_2 has been proven to be feasible. Glagolev and his research group [37–40] investigated the potential of scCO_2 impregnation to produce different photochromic polymeric materials using various photoactive compounds. Lima et al. [41] also studied the impregnation of polycarbonate and silica gel composite film into a photochromic dye Reversacol Graphite in scCO_2 medium to fabricate photochromic lenses. To the best of our knowledge, however, the application of photochromic dyes to polyester fabrics using scCO_2 dyeing method has not yet been investigated.

This study investigates the potential application of selected commercial photochromic dyes, i.e. spirooxazine and naphthopyran based dyes, to polyester fabric using the scCO_2 dyeing technique to produce UV sensing smart textiles. The photo-colouration and fading properties of the photochromic dyed samples were performed using an online colour measurement system. The colour yield and switching rates and their durability against washing were examined. Results showed that both photochromic dyes were successfully incorporated into the polyester fabric using scCO_2 technique displaying comparable performance in terms of colour yield but a distinct rate of colour build-up and wash fastness properties. This study provides an insight into the behaviour of photochromic dyes applied directly as disperse dyes to the polyester fabric from scCO_2 media with a large potential to facilitate the development of uniformly coloured photochromic textiles in an eco-friendly and resource-efficient way.

2. Experimental

2.1. Materials

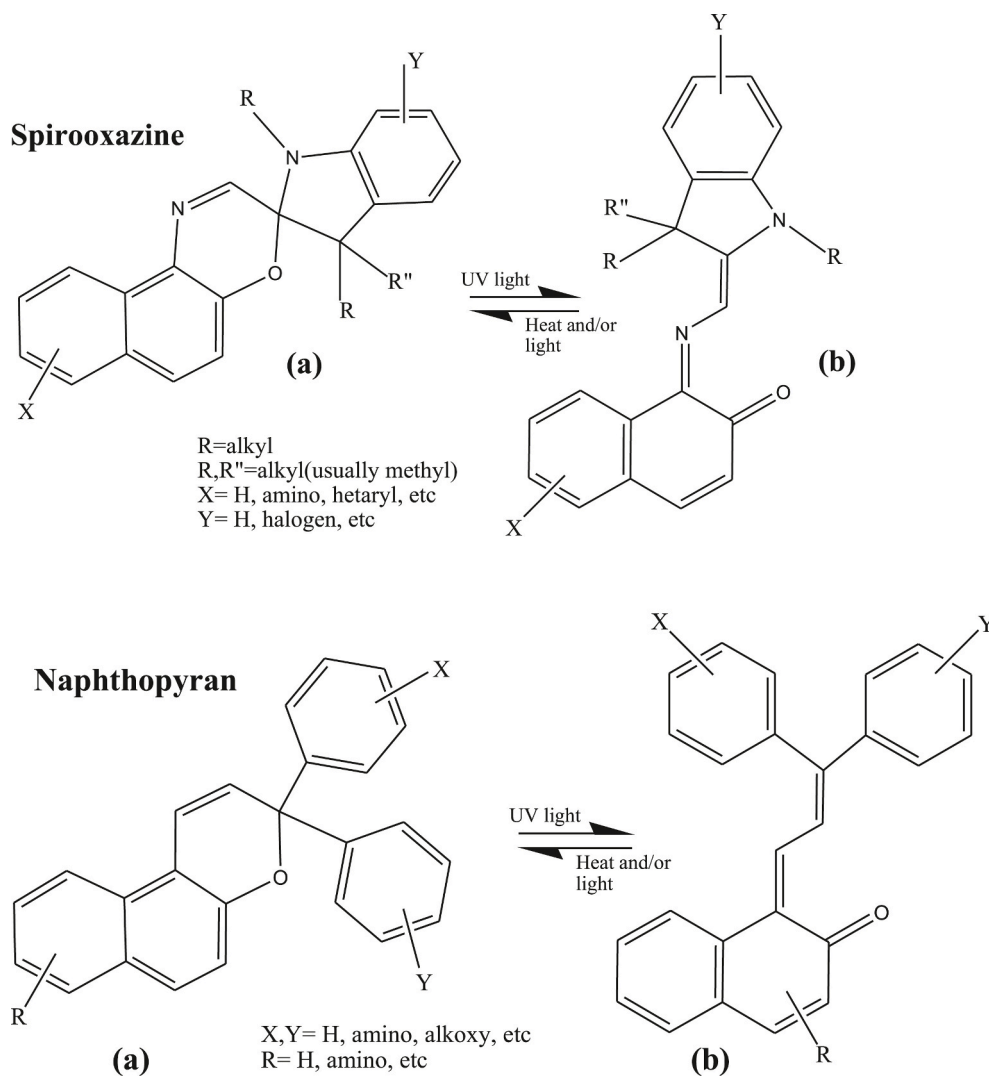
The substrate used in this study was a heat-set plain-woven polyester fabric (147 g/m^2) supplied by FOV Fabrics (Sweden). Two commercial photochromic dyes; Reversacol Ruby Red and Reversacol Sea Green (Vivimed Labs, UK) were selected (Table 1) and their generalized structures are illustrated in Scheme 1. The CO_2 used in all experiments was supplied by AGA industrial gases (Sweden) and has 99.5% purity.

2.2. Dyeing procedure

Dyeing was performed using a batch type scCO_2 dyeing apparatus (Fig. 1) equipped with a high-temperature oil (glycerine) bath, a rotary wheel where the vessels are mounted, a motor, temperature and time controller, a heater, and cooling element. The apparatus is a beam type dyeing machine, where the polyester fabric (21 × 30 cm, ca. 10 g) was wrapped around a Teflon mesh, suspended inside the dyeing vessel (with internal volume = 290 mL, $P_{\text{max}} = 30$ MPa, and $T_{\text{max}} = 130$ °C) and the photochromic dye (0.027% owf ~ 2.56 mg) was placed below the fabric at the bottom of the vessel. The amount of colourant was selected on the basis to compare results of photochromic textiles

Table 1
Commercial photochromic dyes used and their notations.

Notation	Colour	Chemical class
SO-SG	Sea Green	Spirooxazine
NP-RR	Ruby Red	Naphthopyran



Scheme 1. General dye structure of spirooxazine and naphthopyran and their photochromic transformation from (a) ring-closed to (b) ring-opened forms.

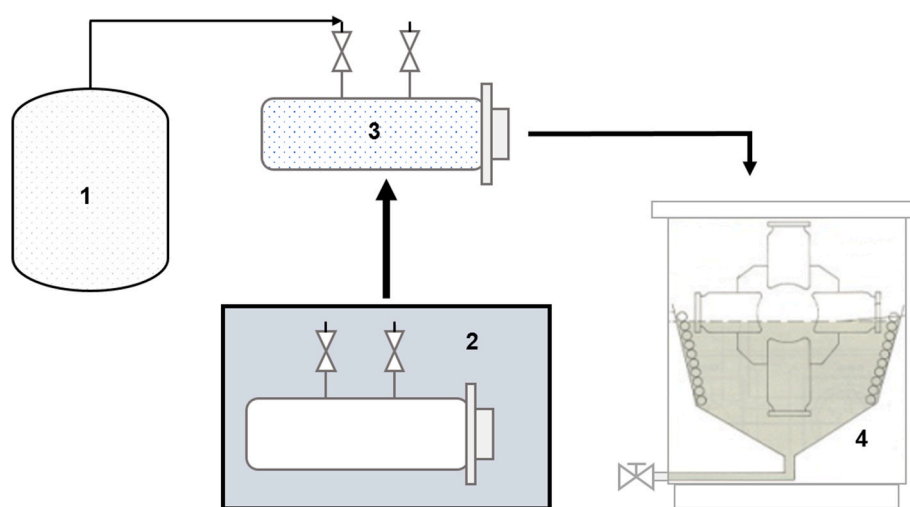


Fig. 1. Scheme of sCO₂ lab dyeing procedure (1) CO₂ tank, (2) Freezer, (3) Dyeing vessel, (4) High-temperature oil bath.

produced with digital inkjet printing [16].

As illustrated in Fig. 1, the dyeing vessel (3) was pre-cooled in a separate freezer (2) and afterwards filled with the required amount of

CO₂. Then, the vessels were mounted on the shaft rotating inside the pre-heated oil bath (4) and the temperature rose at a rate of 3 °C per minute to the working temperature. For all samples, dyeing was carried out

using the same dyeing condition of 120 °C and 25 MPa for 1 h. After dyeing, the vessels were removed from the oil bath and the CO₂ was vented slowly and the samples were taken out for further analysis without reduction cleaning procedure.

2.3. Dynamic colour measurement

The colouration and decolouration properties of the photochromic textiles were measured using an LCAM Photochrom 3 spectrophotometer (Technical University of Liberec, Czech Republic), which can measure the colour development and fading performance continuously over various cycles of UV- exposure and relaxation. The LCAM Photochrom 3 is equipped with LED Engine LZ1-00UV00 LED as an activation light source with a radiometric power 1680 mW and an emission peak with a wavelength of 365 nm. The measuring light source is a dual system of combined high-power white LEDs with CCTs of 4000, 5000 and 7000 K. Upon measurement, samples are illuminated with 60 klx, which constitutes an illuminance between brightest sunlight intensity (120 klx) and daylight intensity without direct sunlight at noon (20 klx). The temperature of the samples was controlled to around 21 °C and reflectance values were recorded in intervals of 2 s during continuous UV irradiation and shutdown. Colour analysis of each dye is made at their dominant wavelength, which is 500 nm for NP-RR and 620 nm for SO-SG. The colour values (K/S) were calculated from the reflectance spectra using the Kubelka-Munk function, Equation (1).

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

where: R is reflectance percentage at maximum absorption wavelength, K is the absorption coefficient, and S is the scattering coefficient of the dyed samples.

The colouration and fading kinetics, determined from the K/S-time datasets, were fitted to an extension of the first-order kinetic model, Equation (2). This model is generally used to describe the behaviour of photochromic dyes incorporated into the textile matrix during colouration and decolouration [42].

$$\Delta \frac{K}{S} = \left(\frac{K}{S_0} - \frac{K}{S_\infty} \right) * e^{(-kt)} + \frac{K}{S_\infty} \quad (2)$$

where: K/S₀ and K/S_∞ are the initial and final (saturated) colour intensity values respectively attained upon exposure or relaxation of UV light, k is the rate constant and t is the time of exposure. The subscripts define the time relationships: (0) = time in the beginning and (∞) = time at infinity. From this equation, the half-time of colour change (t_{1/2}) was calculated using Equation (3) [43].

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

Thus, the photochromic performance of scCO₂ dyed photochromic polyester fabrics was evaluated in terms of the colour yield ΔK/S upon activation with UV-light, rate constants of colour increase (k_{col}) to achieve maximum colouration (K/S_∞), and rate constant of colour decrease (k_{decol}) to revert to the ring-closed colourless state (K/S₀), and half-lives (t_{1/2}) of colouration and decolouration.

2.4. Background colour measurement

The conventional colour measurement system was conducted to evaluate the background colour of photochromic fabric samples to estimate the permanent shade developed in their inactive state due to the high-temperature dyeing process. The background colour is expressed as the colour difference ΔE between the non-dyed polyester fabric and the photochromic dyed samples without UV irradiation. Datacolor Check Pro spectrophotometer (USA) was used under the condition of D65 illuminant and 10° standard observer. Three measurements were read at

different sites of the same sample and average values are reported. All measurements were performed at room temperature (approx. 22 °C) without UV irradiation.

2.5. Durability towards washing

To evaluate the durability property, samples were subjected to one (1W) and ten (10W) washing cycles according to ISO 6330:2012, domestic washing and drying procedure (at 40 ± 3 °C, using 20 ± 1 g reference detergent for 30 min) using a domestic laundry machine. Sufficient ballasts of 100% polyester fabric were added to achieve the specified weight in the reference washing machine. A comparative study on the photochromic properties of samples before and after washing was performed to evaluate their performance against washing. The decrease in colour yield (K/S) after washing can be used to express the washing fastness of the photochromic effect. The fastness is evaluated according to a relative loss in percentage using Equation (4), which measures the magnitude of the residual photochromic performance after washing.

$$\text{Fastness (\%)} = \frac{K/S(2)}{K/S(1)} \times 100 \quad (4)$$

where: K/S₍₁₎ and K/S₍₂₎ are the colour yield of the photochromic fabric before and after the standard washing respectively, upon UV exposure.

2.6. Statistical analysis

Two replicate samples were produced, and three measurements were taken for each sample where each measurement contains three cycles of continuous colouration and two cycles of decolouration. The obtained data were fitted to the first-order kinetic model, Equation (2) using Origin Lab software. The factor effects such as the type of the photochromic dye, washing condition, and the number of UV exposure and fading cycles on the colour yield and rate of colouration and decolouration were analysed using Minitab 17 software according to the criteria p ≤ 0.05.

3. Results and discussion

The photochromic behaviour of the scCO₂ dyed polyester samples was evaluated by continuous measurement of the photo-colouration during UV irradiation and the decolouration after UV light is removed. For each sample, three cycles of colouration and two cycles of decolouration were measured continuously and the experimental data were fitted using the first-order kinetic model, Equation (2). According to the results, all photochromic samples developed in scCO₂ changed their colour when exposed to UV light and reverted to their original colour when UV light was removed. The samples produced using the two dye types generally showed comparable performance in terms of colour yield but distinct kinetics and durability towards washing were observed as discussed in this section.

3.1. Data fitting

The experimental data fitting procedure is presented here to show how the data was analysed. The experimental data sets contain reflectance values (converted into K/S values) collected at intervals of 2 s. For SO-SG dyed samples, the photochromic textile is activated upon 300 s (150 data points) and deactivated upon 400 s (200 data points). For NP-RR dyed samples 500 s activation and 1000 s deactivation intervals were used, which account for 250 and 500 data points, respectively. The experimental data sets contain three replicates for each sample type and three cycles of colouration and two cycles of decolouration were collected for each replicate. Therefore, each sample has nine colouration and six decolouration data sets and these data sets were fitted to the first-order kinetic model (Equation (3)) for comprehensive analysis. Here, the

experimental data of the colouration and fading of the second cycle measurement of the second replicate samples are shown as a representative sample (Fig. 2). According to the obtained R^2 values, the model could describe more than 90% of the variability in the response variable (K/S) which is fair enough to analyse the kinetics of the photochromic dyes applied to polyester fabric.

3.2. Effect of repeated UV exposure and relaxation on the photochromic behaviour

To evaluate the durability and life time of photochromic materials repeatability of the photochromic colour switching is important to measure. Although a low number of colouration and decolouration cycles, with three and two, respectively, were applied in this study, a trend to evaluate the behaviour of SO-SG and NP-RR dyes can be seen. Results of the degree of photocoloration and rate kinetics of each sample after repeated UV exposure and fading cycles is shown in Fig. 3. Results showed that after three cycles of UV irradiation, SO-SG retained 73% and NP-RR retained 77% of its original colour strength measured upon the first UV exposure (Fig. 3a). Also, the speed of colouration has decreased by 27% and 11% for SO-SG and NP-RR, respectively after three cycles of UV exposure in comparison to upon the first UV exposure (Fig. 3c). The fading cycles have less significant effect on the decolouration rates for both dyes (Fig. 3d). After one washing cycle (Fig. 3b), the degree of colouration was not affected much by the repeated UV exposure. Among the two dyes, NP-RR demonstrated better resistance towards the repeated UV exposure compared to SO-SG suggesting good fatigue resistance. From the trend, it can be concluded that both the degree of photo colouration and colour switching speeds decreased to some extent due to repeated exposure of UV light and relaxation. This trend suggests low fatigue resistance although more cycles are required for a deepened understanding of the fatigue behaviour.

3.3. Colour yield ($\Delta K/S$)

The collected reflectance values during continuous UV exposure and relaxation were converted into K/S values using the Kubelka-Munk function. Generally, the K/S value corresponds to the intensity of the developed colour; the higher the value the deeper the developed colour. From the results displayed in Table 2, samples dyed with NP-RR exhibited a slightly lower colour yield with $\Delta K/S$ of 0.088 compared with SO-SG dyed samples with $\Delta K/S$ of 0.096. These colour intensities exhibited by both dyes were not statistically different suggesting similar colourability. According to previous reports, differences in the degree of colouration between dye classes were observed. However, there was no obvious correlation between the degree of photo colouration and the chemical class of the dyes. The difference is mostly related to the particular chemical nature of individual dye structures [19]. Accordingly, it can be concluded that these specific dye structures used in this study have a similar degree of colouration when applied to polyester fabric in $scCO_2$ medium. Using the same types and amount of dye, inkjet printed samples with UV-curable photochromic inks resulted in an initial $\Delta K/S$ of 0.107 and 0.103 for samples printed with SO-SG and NP-RR, respectively [16]. A similar trend but slightly higher colour strength was achieved by inkjet printed samples compared to $scCO_2$ dyed samples. In both methods, SO-SG displayed a slightly higher degree of photocoloration compared with NP-RR in which the value is a little higher in the case of SO-SG prints although the difference was not statistically significant. This marginal improvement in the degree of photo colouration, when applied by inkjet printing, could be due to the relatively lower penetration of the dyes into the polyester fabric when they are applied by inkjet printing which facilitates the conversion to coloured form. In $scCO_2$ dyeing method, however, the dyes are deeply penetrated into the fibre, which may be in a more restricted environment inhibiting the photochromic conversion and hence decrease the

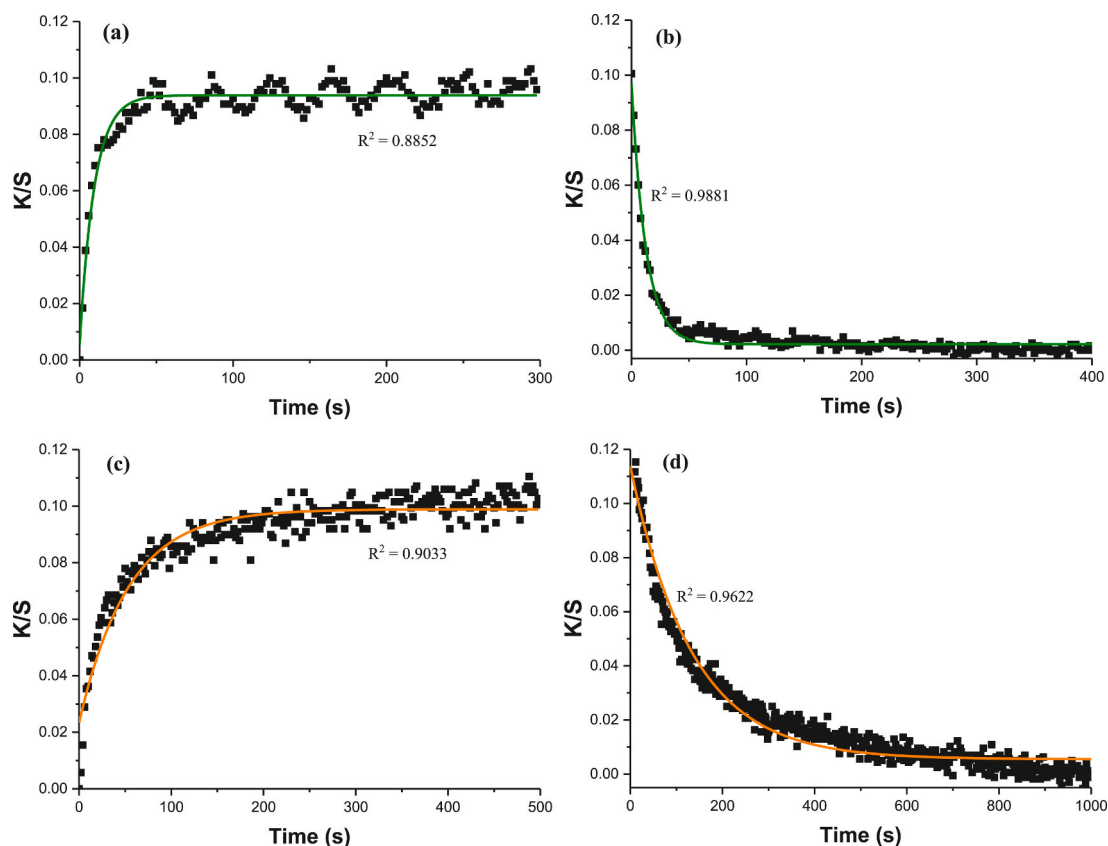


Fig. 2. Fitting of the experimental data of photochromic dyed polyester fabrics measured upon UV exposure and removal. (a) SO-SG colouration, (b) SO-SG decolouration, (c) NP-RR colouration (b) NP-RR decolouration. Measured K/S data (■) and fitted curve using the first-order kinetic model (—).

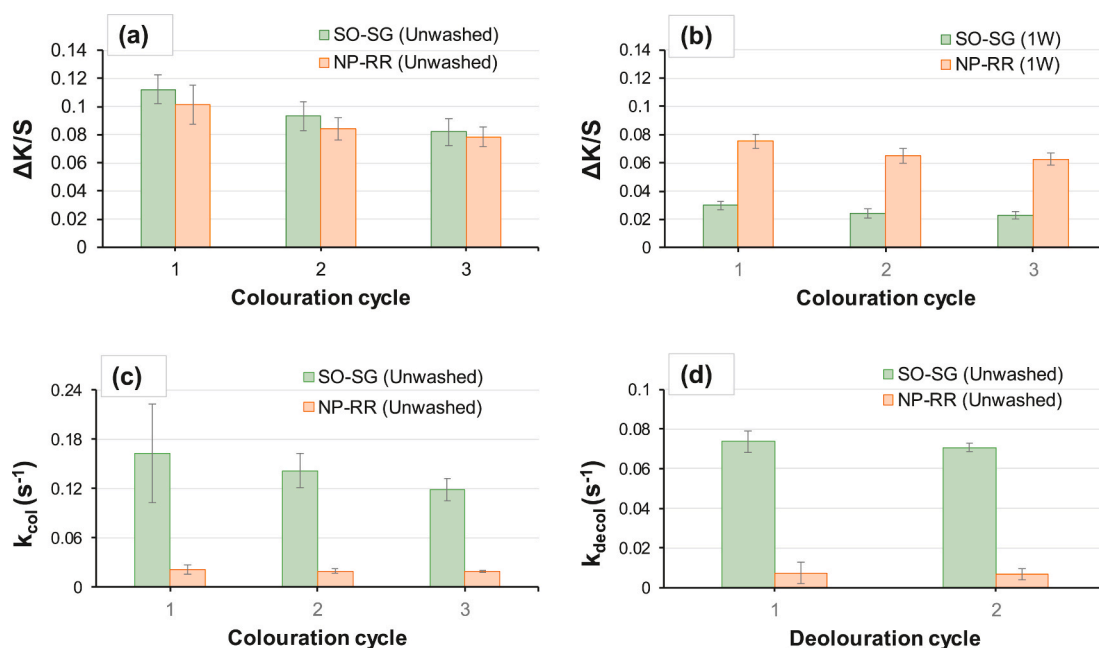


Fig. 3. Effect of the colouration and decolouration cycles on the degree of colouration ($\Delta K/S$) and kinetic rate constants ($k_{col/decol}$) of photochromic dyed samples. (a) $\Delta K/S_{col}$ of unwashed samples, (b) $\Delta K/S_{col}$ of samples after one wash cycle, (c) k_{col} of unwashed samples, (d) k_{decol} of unwashed samples.

Table 2

Average colour yield (K/S) of photochromic dyed polyester samples upon UV exposure.

Sample	Unwashed	1W	10W
SO-SG	0.096 ± 0.016	0.026 ± 0.013	0.020 ± 0.004
NP-RR	0.088 ± 0.004	0.068 ± 0.007	0.071 ± 0.006

degree of photo colouration. Other factors of influence on the fibre-matrix interaction are differences in polarity and dipole interactions [44–47]. Thus, the results of the colour yields in both methods showed that the dyes have almost similar colourability property but different fastness properties to washing.

3.4. The rates of colouration and decolouration

The rate of colouration and decolouration of a photochromic material is an index of colour change speed which have important practical implication. Before the actual measurement, representative samples

were exposed to UV light to estimate the time required to reach their saturation colouration and fading back to their uncoloured states. From the results, samples dyed with NP-RR took a relatively long time to reach their maximum colouration (500 s) and to revert to their uncoloured state (1000 s) while samples dyed with SO-SG needed only 300 s and 400 s for complete colouration and decolouration, respectively. Thus, all further investigations and measurements were carried out based on these time intervals.

3.4.1. Kinetic rate constants

The fitted colouration and fading curves of photochromic fabric samples measured upon UV exposure and relaxation are shown in Fig. 4 and the rate constant values are presented in Fig. 5. The results showed that SO-SG showed a significantly higher rate of colour development and faded more rapidly than NP-RR. As illustrated from the figures, an average rate of colourations (k_{col}) of 0.141 s^{-1} and 0.020 s^{-1} was obtained for unwashed SO-SG and NP-RR dyed samples, respectively. This means SO-SG had more than seven-fold faster colour development compared with NP-RR. Furthermore, unwashed SO-SG dyed samples

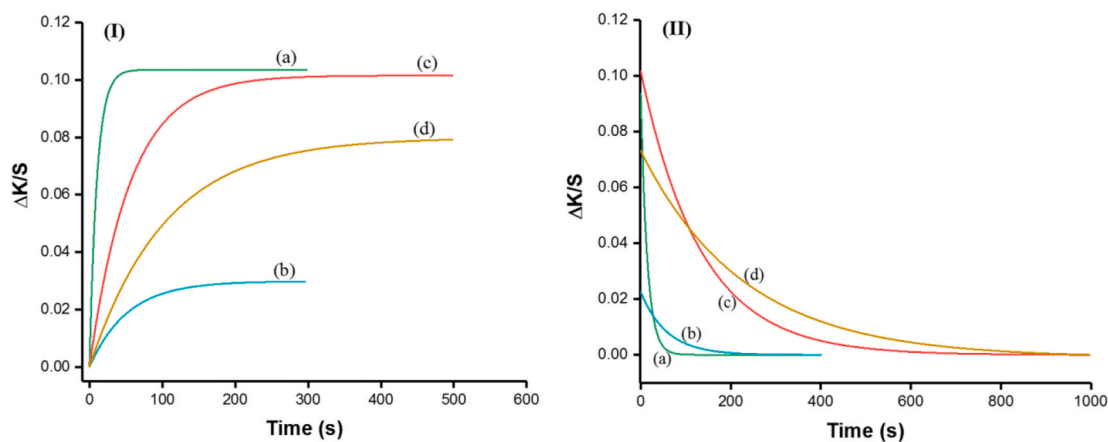


Fig. 4. Average fitted plots for colouration (I) and decolouration (II) curves of photochromic dyed samples (a) SO-SG (unwashed), (b) SO-SG (1W), (c) NP-RR (unwashed), and (d) NP-RR (1W). The values are normalized to have the same initial and final values for the colouration and decolouration curves, respectively.

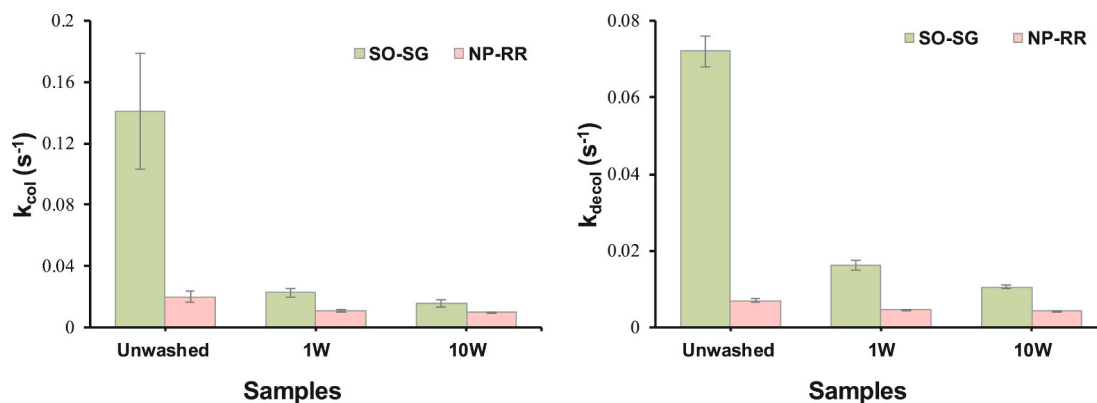


Fig. 5. Average rate constants (a) k_{col} and (b) k_{decol} of $scCO_2$ dyed photochromic fabric samples before and after repeated washing cycles.

demonstrated more than ten times faster fading speed (k_{decol} of $0.072 s^{-1}$) compared with NP-RR (k_{decol} of $0.007 s^{-1}$) dyed samples. For both dyes and all washing conditions, the fading rate is slower than the rate of colour build-up, which is a common behaviour of photochromic dyes. For example, unwashed SO-SG dyed samples have a two-fold slower and NP-RR an approx. Three-fold slower decolouration reaction than colouration reactions. For both dyes, fading started immediately upon the removal of the UV-light source.

This difference in rate kinetics between the two dyes could arise from the intrinsic difference between the two dye classes. Spirooxazines are inherently faster-switching and more temperature-sensitive dyes, whereas naphthopyrans are more durable, but slow-switching [8,48]. A similar faster colour development by spirooxazine dyes printed on the polyester fabric was also reported compared with naphthopyrans [6]. Naphthopyran based dyes applied to polyester using the inkjet printing method also showed lower fading rates compared with spirooxazine based dyes [12]. Thus, the results obtained in the current study are consistent with previously reported ones. In addition to the inherent characteristics of the dyes, the polymer matrix and the relative position of the dye molecules in the polymer matrix could affect the reaction kinetics. The weak wash fastness properties displayed by SO-SG dyed samples (Section 3.6) suggests limited dye penetration. This promotes fast response upon isomerization, as the dye concentration used was small and the dye molecules located near the surface provide free space, which facilitates faster ring opening and closing. In contrast, samples dyed with NP-RR displayed better wash fastness property, indicative of the presence of more number of dye molecules which are deeply penetrated and locked within the polymer matrix. Owing to the semi-crystalline and hydrophobic nature of polyester, these deeply penetrated NP-RR dye molecules are more constrained with limited space taking a relatively long time for the photo transformation to occur.

This observation was also made when inkjet printing SO-SG and NP-RR dyes in UV-curable ink onto polyester fabric [16]. Here, the inherently faster switching SO-SG dye showed a slower rate constant than NP-RR dyes. However, SO-SG was more affected by changes in the matrix rigidity of the dye-carrying ink, with a higher relative increase of reaction kinetics compared with NP-RR dyes. A less rigid matrix resulted in a five-fold increase of k_{col} of SO-SG prints compared to a two-fold increase of NP-RR prints. In conclusion, matrix rigidity influences the behaviour of photochromic dyes significantly, which has been discussed in prior studies [16,31,49–52]. The assumed location of the dye in the fibre structure affects the dye kinetics and does not interfere with the inherent properties of the different photochromic dyes. As mentioned earlier, spirooxazines are generally faster-switching dyes, but naphthopyrans are more durable.

3.4.2. Half-lives

The half-life ($t_{1/2}$) of colouration/fading is a common measure to express the colour switching speeds of photochromic materials. Unlike

the overall rate behaviour described above, the half-life values give information about the kinetic behaviour of dyes during their initial colouration and decolouration phases. Generally, the initial colouration and decolouration rates are faster compared with the rates near to saturation and towards the end of decolouration. This phenomenon is related to the half-life of the photochromic reaction which has important practical implications. The half-life of colouration ($t_{1/2col}$) is the time required to reach half of the total photochromic response upon exposure to UV irradiation and similarly, the half-life of fading ($t_{1/2decol}$) is the time taken to revert half of the developed colour (K/S_{∞}) [22]. This means that smaller numerical values of $t_{1/2}$ indicate faster colouration and decolouration speeds and vice versa. As can be seen from the results in Table 3, SO-SG dyed samples showed relatively higher colouration and fading rates, expressed by lower half-lives of colouration and fading, compared with NP-RR dyed samples regardless of the washing condition. These results are expected and consistent with the results of the reaction rates presented in the previous section. The same trend has also been observed in previous studies of the same classes of photochromic dyes applied to polyester fabric using exhaust dyeing and screen-printing methods [6,19]. A higher rate of colouration and fading by spirooxazine-based dyes compared with naphthopyrans was consistently reported in agreement with this study.

One notable observation was that the half-life of fading of the same class of dyes applied by $scCO_2$ dyeing are significantly lower than those obtained when applied by aqueous or solvent-based dyeing methods [19,24] and comparable with digital inkjet printing as presented in Table 4 [12,16,31].

The shortest time ($t_{1/2decol} = 0.15$ min) was achieved for $scCO_2$ dyed samples with spirooxazine (SO-SG) followed by inkjet printing of spirooxazine in a UV-curable ink and solvent-based ink. This is an additional advantage by $scCO_2$ dyeing since a minimum half-life of fading is commercially useful. Generally, faster reaction rates upon activation and deactivation can be preferable for improved product reliability depending on the application. Other advantages of $scCO_2$ dyeing over the conventional dyeing techniques include the simplicity of the process and the absence of auxiliary chemicals. As only CO_2 is used as dyeing medium and photochromic dyes are involved in the process, kinetic

Table 3

Half-lives ($t_{1/2}$) of colouration and decolouration of $scCO_2$ dyed photochromic polyester fabric samples.

Sample	$t_{1/2}$ (s)					
	Colouration			Decolouration		
	Unwashed	1W	10W	Unwashed	1W	10W
SO-SG	5.2 ± 1.3	31.5 ± 4.3	44.9 ± 6.3	9.6 ± 0.5	43.2 ± 3.2	66.3 ± 3.0
NP-RR	35.6 ± 4.9	65.3 ± 4.2	69.8 ± 1.3	100.2 ± 6.2	155.3 ± 8.6	163.7 ± 3.3

Table 4

Comparison of half-lives of fading of photochromic dyes applied to the polyester fabric by using different application methods.

Application method	Dye class	$t_{1/2\text{decol}}$ (min)	Reference
Exhaust dyeing	Spirooxazine	3.1 ^a	[19]
	Naphthopyran	18.1 ^a	
Solvent dyeing	Spirooxazine	3.1 ^a	[24]
	Naphthopyran	11.5 ^a	
Digital inkjet printing	Spirooxazine	1.0, 0.9 ^a	[12,16]
	Naphthopyran	5.1, 0.8 ^a	
scCO ₂ dyeing	Spirooxazine	0.15	Current work
	Naphthopyran	1.8	

^a Minimum half-life values selected to show the fastest achievable fading rates.

switching is not disturbed by the solvent or other chemical agents and hence is faster than the exhaust and solvent dyeing methods involving a solvent and auxiliary agents.

3.5. Background colour

Background colour measurement was performed to evaluate the permanent shade of the photochromic textiles in their inactive state influenced by the dyeing process. During the dyeing process, high temperatures may thermally influence isomerization of photochromic dyes that could develop a permanent background colour. This permanent background colour is considered as a common drawback of photochromic textiles due to its possible negative effect on the degree of photocoloration and which may also be an undesirable feature for certain application requiring a white background [12]. The colour strength expressed by K/S (Fig. 6) and ΔE values (Table 5) were used to evaluate the background colour of photochromic dyed fabric samples. The ΔE refers to the colour difference between the undyed fabric and the fabric after dyeing, without UV irradiation. From the background K/S results, it was evident that samples dyed with NP-RR have relatively higher K/S value (deeper background colour) compared with SO-SG dyed samples which was also confirmed during visual observations.

A similar trend was also observed according to the ΔE values as presented in Table 5. Higher ΔE values displayed by NP-RR dyed samples with a ΔE value of 2.81 imply higher background colour compared with those dyed with SO-SG with $\Delta E = 1.47$. Generally, the ring-closed form of photochromic dyes is usually uncoloured. However, because of the textile application process, a characteristic background colour is often observed. The presence of thermochromism and thermal instability of the dyes under application conditions were mentioned as the two main factors for the development of background colour. Among

Table 5

Average ΔE values of the background colour of photochromic dyed polyester fabrics and their washed counterparts.

Samples	Treatment		
	Unwashed	1W	10W
SO-SG	1.47 ± 0.12	1.35 ± 0.13	1.28 ± 0.08
NP-RR	2.81 ± 0.15	2.69 ± 0.08	2.62 ± 0.07

these factors, the degree of thermochromism is believed to be the dominant one [19,24]. At a higher treatment temperature, the ring-closed form of some photochromic dye molecules is converted thermally to their coloured open-form (merocyanine) and subsequently locked in this form into the fibre structure, resulting in a permanent colour [6]. Thus, the difference in the level of background colour between the two dyes could be due to a difference in their thermal sensitivity as well as the penetration level of the dyes in their ring-opened form. Generally, spirooxazines are more sensitive to temperature than naphthopyrans [1]. On the other hand, NP-RR dye molecules seem to be deeper penetrated in the fibre bulk compared to SO-SG dyes as established from the wash fastness result. Deeper penetration into the bulk compared to if the dyes are predominantly situated on the fibre surface, results in more restricted space for the dyes to move and thus locks them in their coloured form. However, next to free volume, polarity, rigidity and direct interactions also influence dye-matrix behaviour [44–47,53]. A further explanation for the distinct interaction between the dyes and the fibre is through van der Waals forces, dipolar forces, and hydrogen bonding which could stabilize the open form of photochromic dyes during application [20]. In the case of disperse dyeing of polyester, the dye molecules are believed to be diffused into the free volumes of the fibre (the amorphous region of the polymer system) and bound physically to the polyester molecules via dispersion forces and induced dipole interactions. Thus, this could stabilize the ring-opened form of the photochromic dye restricting the re-formation of the original uncoloured ring-closed form of the dye.

3.6. Durability towards washing

The washing test was used as a measure of the durability of the photochromic behaviour and to gain knowledge about the penetration level of the dye molecules into the polyester fibre. To assess the durability of photochromic dyed samples, a comparative study on the photochromic colour build-up and fading properties of the samples before and after standard washing cycles were used. According to the results presented in the previous sections (section 3.3 to 3.5), almost all samples generally displayed a decrease in photochromic performances

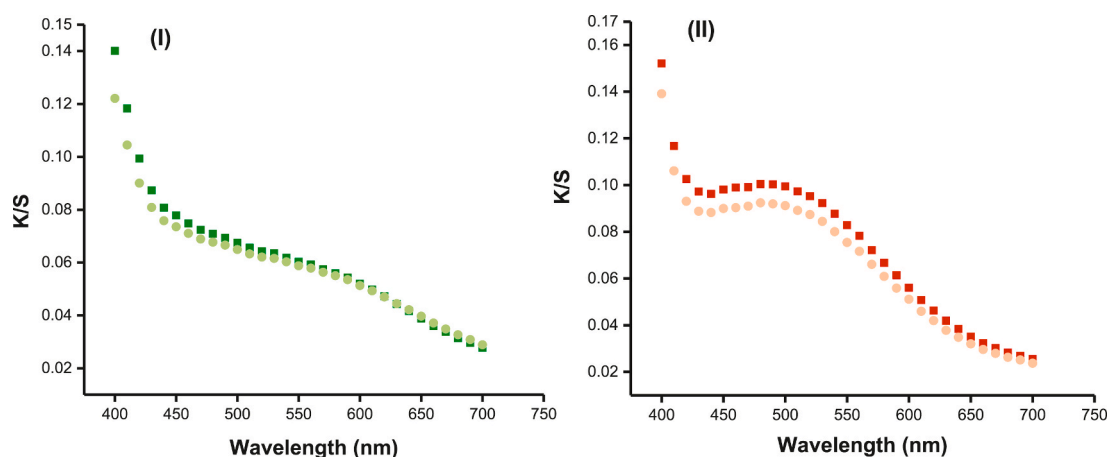


Fig. 6. Background colour strength of (I) SO-SG and (II) NP-RR dyed samples before (■) and after (●) washing measured without UV-irradiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

after washing irrespective of the type of photochromic dye used. As presented in Table 2, the mean $\Delta K/S$ of the two dyes before and after washing, expressed as fastness percentage was significantly different. Samples dyed with NP-RR exhibited better fastness percentage (77%) compared with SO-SG dyed samples with a significantly lower fastness percentage of 27% after the first washing cycle. After ten washing cycles, SO-SG dyed samples showed a marginal decrease in the fastness percentage (20%) while a slight improvement in fastness percentage was observed for samples dyed with NP-RR (80%). This result is in line with the general behaviour of the two dye classes applied to textile in which naphthopyrans are more stable than spirooxazines. The relatively better wash fastness behaviour by NP-RR dyed samples suggests enhanced penetration or better affinity towards polyester compared to SO-SG.

The background colour of samples before and after washing was also compared to evaluate the wash fastness properties of the two dyes in their permanently ring-opened form. According to the results (Fig. 6 and Table 5), washing had a minor influence on the background colour of both dyes with a slight reduction in colour strength for both dyes after washing cycles (Fig. 6). As seen from the ΔE values, the background colour of SO-SG samples reduces to 92% from 1.47 to 1.35 compared to 96% from 2.81 to 2.69 for NP-RR samples after one washing cycle. After ten washing cycles, the background colour of SO-SG samples reduces to 87% from 1.47 to 1.28 compared to 93% from 2.81 to 2.62 for NP-RR samples. Thus, much of the colour was lost during the first washing cycle while the colour lost after ten washing cycles was small compared with the colour loss during the first wash (see Table 5). The slightly higher reduction in the background colour of spirooxazine dyed polyester is likely to result from the removal of more dyestuff due to that SO-SG dyes are located more on the fibre surface.

The effect of washing on the rates of colouration and decolouration of photochromic fabric samples was also evaluated. The results showed that the washing has a significant effect on the reaction kinetics of photochromic samples developed with both dye types. Samples dyed with SO-SG showed a dramatic decrease in fading rates after washing while the washing effect was less significant on the kinetics of NP-RR dyed samples. As presented in Fig. 4, for SO-SG dyed samples, the first washing cycle lowers the colouration rate by 84% and the decolouration rate by 77%. On the other hand, for NP-RR dyed samples, the reduction was less significant in which k_{col} decreased by 46%, and k_{decol} by 35% during the first washing cycle. Nevertheless, samples dyed with SO-SG still displayed a significantly higher rate of colouration ($k_{col} = 0.022 \text{ s}^{-1}$) and fading ($k_{decol} = 0.016 \text{ s}^{-1}$) after the first washing cycle compared with NP-RR dyed samples, which is a two-fold lower rate of colouration and three times lower decolouration speed. After ten washing cycles, there was still a reduction in both the colouration and fading rates, but the extent of the reduction was smaller compared with the reduction happened during the first washing cycle (see Fig. 4). Similarly, the half-lives of colouration and decolouration increased (decrease in the colour switching rates) after both washing cycles for both dyes. Among them, SO-SG displayed a relatively slower kinetics after both washing cycles compared with NP-RR (Table 3). Overall, a progressive reduction in colour yield, background colour, and rate of photoisomerization was observed after both washing cycles but the effect after ten washing cycles was less significant compared with the first washing cycle. The obtained result correlates well with the inherent property of the specific dye classes with a more durable character of naphthopyrans and faster kinetics of spirooxazines. According to previous reports and which is in line with the current results, spirooxazines showed higher thermal sensitivity, which causes faster thermally driven decolouration than naphthopyrans [6,54].

The durability towards washing of $scCO_2$ dyed and inkjet printed samples (printed with UV-curable photochromic inks incorporated in an ink resin with high crosslinking density) with the same types and amounts of dye has also been compared. Results showed that ink-jetted and UV-cured prints of NP-RR having an initial $\Delta K/S$ of 0.103 was reduced to $\Delta K/S$ of 0.062 after one washing cycle, which is a 60%

fastness percentage. For SO-SG prints with the same crosslinking density, the initial colour strength obtained after printing ($\Delta K/S$ of 0.107) was decreased to $\Delta K/S$ of 0.086 after one wash (80% fastness percentage) [16]. Thus, samples dyed with NP-RR in $scCO_2$ exhibited better fastness percentage compared with NP-RR ink-jet prints while SO-SG printed samples showed better fastness percentage compared with those produced using $scCO_2$ dyeing method. When the durability against washing of the same class of dyes applied by exhaust dyeing and screen-printing methods is compared with $scCO_2$ dyeing, generally, a similar trend of reduction in photochromic performance was observed. However, there are not enough data reported so far to make complete and quantitative comparisons of the durability of samples against repeated washings using these methods. One notable observation, however, was that spirooxazine dyes exhibited an increase in the degree of photo colouration after the first washing and decreased with subsequent washings when applied to the polyester fabric by screen printing. While for naphthopyran dyes, a consistent but marginal decrease in the degree of photo colouration was observed with repeated washing in most of the cases [8].

4. Conclusions

This paper presents a novelty of water-free dyeing of UV sensing smart textiles using photochromic dyes with superior colour performance compared to conventional dyeing techniques. Two photochromic dyes belonging to the spirooxazine and naphthopyran dye classes were successfully applied to the polyester fabric using $scCO_2$ dyeing. The uniformly coloured photochromic polyester fabrics prepared using $scCO_2$ dyeing technique exhibit significant reversible colour changing properties when exposed to UV light. The two photochromic dyes on polyester fabrics showed comparable performance in terms of colour yield and distinct characteristics in terms of reaction kinetics, background colour, and wash fastness properties. Sea green from the spirooxazine family had faster reaction kinetics, lower background colour, and reduced wash fastness properties compared with the ruby red from the naphthopyran dye class. Notably, the photochromic fabric produced by $scCO_2$ dyeing exhibited faster dye kinetics compared to photochromic textiles produced with conventional exhaust and solvent dyeing techniques. Improving the durability properties could be of interest in future research for effective utilization of this technique. Overall, the experimental findings suggest that $scCO_2$ dyeing technique is a promising alternative to conventional processes for uniform colouration, not only because of its economic importance but also due to its environmental advantages such as avoiding the use of water, organic solvents, auxiliary chemicals, and requiring small amounts of dye and short dyeing time. The obtained photochromic textiles can be used for applications such as UV sensing smart textile.

CRediT authorship contribution statement

Molla Tadesse Abate: Conceptualization, Funding acquisition, Formal analysis, Writing - original draft. **Sina Seipel:** Conceptualization, Funding acquisition, Formal analysis, Writing - original draft. **Junchun Yu:** Formal analysis. **Martina Visková:** Funding acquisition, Formal analysis. **Michal Vik:** Funding acquisition, Formal analysis. **Vincent Nierstrasz:** Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the European Union under the

framework of the Erasmus Mundus program; Sustainable Management and Design for Textile (SMDTex) grant number 2016–1353/001-001-EMJD. All the Universities collaborating on the program are gratefully acknowledged. The authors are grateful for the support from Borås stad, TEKO (The Swedish Textile and Clothing Industries Association) and Sparbanksstiftelsen Sjuhärad for enabling this research.

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