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Novel Approach to Dye Polyethylene Terephthalate (PET) Fabric in Supercritical Carbon Dioxide with Natural Curcuminoid Dyes

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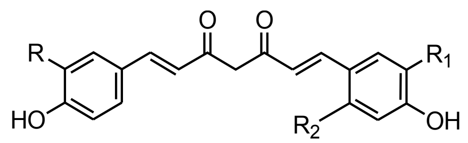
Abstract
The use of natural dyes has increased in the last few decades due to the eco-friendly approach of dyeing. There are still some limitations that are associated with natural dyes, such as dyeing efficiency, reproducibility of shades, process complexity, availability etc. The main problem associated with the dyeing property of natural dyes is "low exhaustion". In this study, natural dyestuff from Curcuma longa L. was extracted and polyethylene terephthalate fabric was dyed with it in the same bath by employing the supercritical carbon dioxide method. The method was developed to improve the dye-ability of natural dyes and reduce the process time and effluent. Curcuminoid dye exhaustion on PET fabric showed almost 80% by using supercritical carbon dioxide dyeing methods, and the highest colour strength (K/S = 12) was obtained. Coloured polyethylene terephthalate fabric treated with supercritical carbon dioxide showed deeper shades (L^* = 72.92) and better fastness properties as compared with high temperature exhaust dyeing methods.

Key words: *supercritical carbon dioxide, exhaust dyeing method, polyethylene terephthalate fabric, Curcuma longa L.*

Introduction

For thousands of years, people have been using textile materials dyed from natural sources. A natural dye consists of colourants obtained from animal or vegetable sources without any chemical processing, widely used for body painting and making food during ancient times [1-2]. Since that period of time, people have been using these dyes in cosmetics, food, and leather as well as in the medicine industry [3]. The greatest use of natural dyes was found when the art of weaving was developed [4]. In 1856, the invention of the first synthetic dye by William Henry Perkin [5] changed the situation, and afterwards the use of synthetic dyes gained faster acceptability due to a wide range of applications in various fields like food [6] and cosmetics [7], and more widely in the field of textiles [8] due to the easier process of colouration. These dyes also offer greater variety and stability of colour as compared with natural dyes. Hence most dyers prefer using synthetic dyestuff. However, synthetic dyes may cause problems like allergic reactions, skin diseases and may even prove to be carcinogenic as well [9-10]. They also pose a significant threat towards the environment, which is all because synthetic colourants are synthesised from petrochemical sources, which may cause serious environmental problems [11]. Nowadays a great awareness regarding the impacts of toxic chemicals on the environment and human health has led to the rejection of the use of synthetic dyes. In these circumstances, greater emphasis is being put on thinking about greener alternatives [12]. Most researchers consider the use of natural colourants because they pose no risk to human health and are environmental friendly as well. Thus the application of natural dyes should be considered as a better alternative to synthetic ones [13] because of their good antibacterial, deodorising, and UV protection properties [14-17]. The dyeing of poly (ethylene terephthalate) fabrics with an aqueous extract of *Caesalpinia sappan L.* wood showed excellent colouring properties in a plasma treatment [18]. Dyeing synthetic fabrics with natural dyes using UV/ozone pretreatment improved dye ability in terms of colour strength and fastness properties [19]. Curcuminoid dye has been proven to act as an antioxidant, showing anti-inflammatory, wound healing, anticancer, antifungal and antibacterial activity [20- 21]. Modified cotton fabrics with enzymes and chitosan influenced the dye uptake and washing fastness of cotton fabrics dyed with curcuminoid [22]. Curcumin structures (Scheme 1) consist of two phenolic groups and one active methylene group, which has been used for chemical variations [23]. The double bonds in curcumin provide definite conformational flexibility to the molecules. An extraction process for different natural colourants was carried out by aqueous extraction,



R	R_1	R_2	Structure
H	H	H	Bis-demethoxycurcumin
OCH_3	H	H	Demethoxycurcumin
OCH_3	OCH_3	OCH_3	5'-Methoxycurcumin

Scheme 1. *Chemical structure of curcumin analogues [21].*

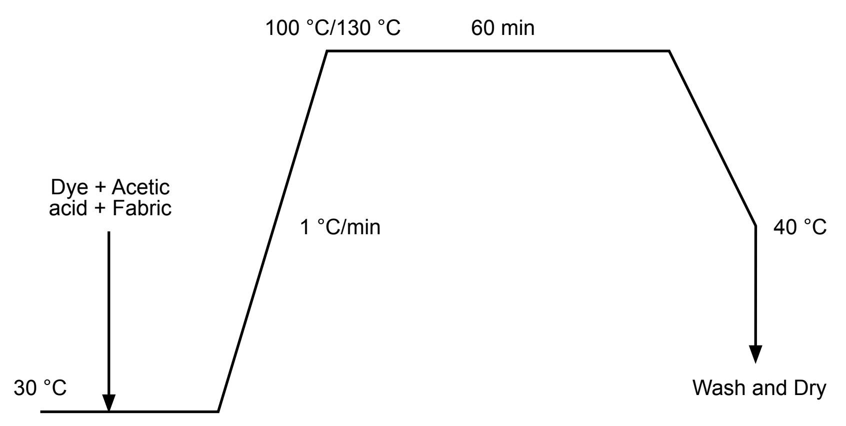


Figure 1. *Dyeing profile of PET dyeing with curcuminoid dyes.*

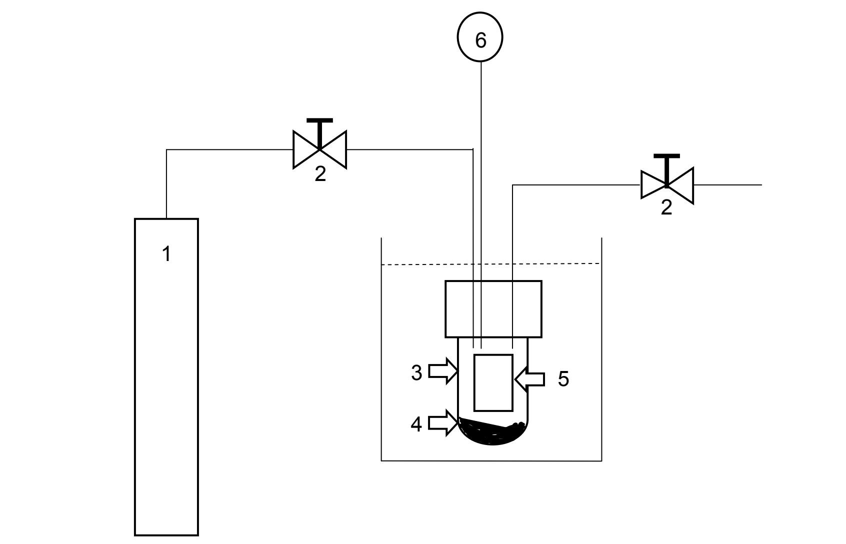
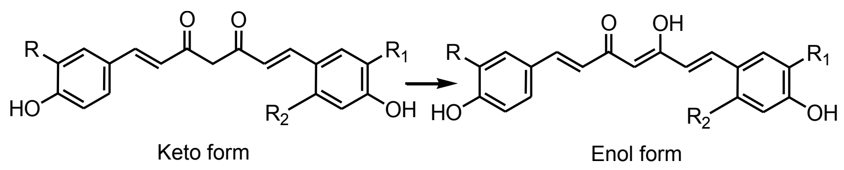


Figure 2. *Schematic diagram of the process for extracting & dyeing of PET fabric in the supercritical carbon dioxide technique. Note: 1 – CO_2 cylinder, 2 – valve, 3 – reactor vessel, 4 – raw turmeric, 5 – fabric, 6 – pressure gauge.*



Scheme 2. *Solvatochromic effect of curcuminoid.*

organic solvent extraction, super critical fluid extraction and enzyme assisted extraction [24-25].

In this study, we focused on the development of optimum extraction conditions of the colouring component from curcuminoid dyes and their application on polyethylene terephthalate (PET) fabric in a supercritical carbon dioxide dyeing bath. The dyeing properties of curcuminoid dye were compared with unset and heat set PET fabrics. The colour strength and fastness properties of PET fabric dyed using the high temperature and supercritical carbon dioxide methods were compared.

Experimental

Materials

Scoured 100% Polyethylene terephthalate (PET) fabric of plain weave construction with an areal density of 70 ± 5 g/m^2 (both warp and weft yarn of 75 denier) obtained from WFK, GmbH, Germany was used for the experiment. The PET fabric was pre-set by the dry heat setting for 30 sec at 180 °C in a laboratory tenter Tex-dryer (made in South Korea) machine. All chemicals and solvents (ethanol, chloroform, acetone and n-hexane) used in the extraction of dyestuff were obtained from Merck (Germany). Turmeric (*Curcuma longa L*) was chosen to extract the curcumin dyes (***Scheme 1***), which was purchased from a local market in Dhaka, Bangladesh.

Extraction of dyestuff and dyeing of PET fabric by the HT method in separate baths

Fresh rhizomes of turmeric were washed and then sliced into small pieces. Then they were dried at 90 °C in a hot air oven (Made in China) for one hour. After grinding the pieces, 10 g of the powder was put into Soxhlet apparatus and mixed individually with 200 ml of each of the solvents, such as ethanol (b.p. 78 °C), methanol (b.p. 65 °C), acetone (b.p. 56.5 °C) and water. Afterwards the solutions were heated according to the boiling points (b.p.) of the solvents for 8 hours. Finally dark brown curcuminoid dyes were obtained by filtration. The λ_{max} of the extracted dyes in different solvents was measured by UV-Vis spectroscopy (Agilent 8453, made in USA).

PET fabrics were dyed in a laboratory dyeing machine (Mathis labomat, Switzerland) at a liquor ratio of 40:1. After adjusting the pH level to 3, 4.5, 7 & 9, the PET fabric was immersed in a dye bath containing ethanol based dyestuff for four different shade % (2%, 4%, 6% and 8%), and the temperature was raised to 100 °C at a rate of 1 °C/min. Dyeing was carried out at this temperature for 60 min. The same process was carried out for the dyeing of PET fabric, where the dyeing temperature was maintained at 130 °C (***Figure 1***).

Extraction of dyestuff and dyeing of PET fabric by the supercritical carbon dioxide method in the same bath

Supercritical fluid extraction is an advanced separation technique because of the enhanced solvating power of CO_2 gas above its critical point. Carbon dioxide is an ideal solvent for dye extraction with a high degree of purity [26]. In this study, we applied this technique to extract and purify natural colourant from *Curcuma longa L*.

The turmeric powder was poured into the dyeing autoclave according to the various shade % (2%, 4%, 6% and 8%), where the magnetic stirrer ensured proper circulation and solubility of the dyestuff (***Figure 2***). PET fabric was suspended in the autoclave by means of a clamping system, and then the machine was sealed properly. Carbon dioxide was added into the autoclave through a valve, and the temperature was cooled down to -17 °C for 30 minutes; thus the pressure inside the autoclave increased up to 60 bar. Afterwards the autoclave was placed in an oil bath, the temperature raised to 150 °C for 60 min, and 200 bar pressure was maintained by the ventilating valve. Dyeing was carried out for 1hr in this condition. After dyeing, the samples were rinsed and washed with a soaping agent and finally dried in a dryer.

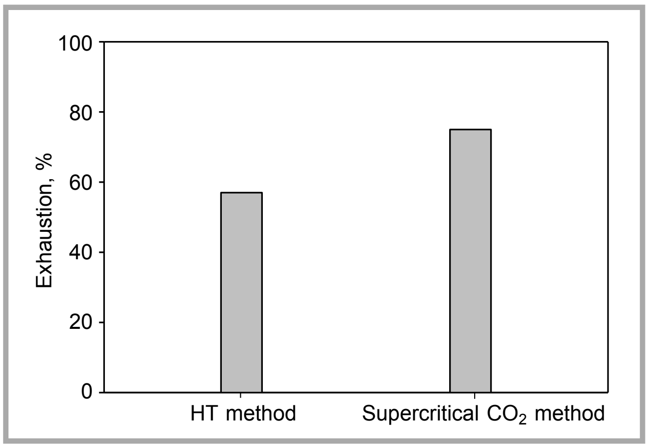
Measurement of dye exhaustion

After dyeing, a 3 ml sample of the residual dye bath was removed to measure the absorbance value using a UV-Vis spectrophotometer (Agilent 8453, USA), and the percentage of dye bath exhaustion (%E) was calculated using the following ***Equation (1)***:

$$\%E = \frac{A_1 - A_2}{A_1} \times 100 \qquad (1)$$

Where, A_1 and A_2 are the absorbance of the dye bath before and after dyeing, respectively.

Figure 3. *Exhaustion of curcuminoid dye in PET fabric in different techniques.*



Measurement of colour strength

The color strength (K/S) of the dyed fabrics was measured using a spectrophotometer (X-rite 8000 Series, standard light D_{65}, 10° standard observer, specular component included; X-rite, USA) which was interfaced with a personal computer. K/S values were obtained directly from the instrument, which followed the Kubelka-Munk theory, as in ***Equation (2)***:

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

Where, K is the absorption coefficient and S the scattering coefficient of the sample. R is the absolute reflectance.

Measurement of colour fastness

In order to measure the colour fastness, the PET fabrics were dyed (1/1 standard depth) by the HT and supercritical carbon dioxide methods. The colour fastness was determined according to international standards, and the fastness to washing (ISO 105-C06 A2S:2010), fastness to rubbing (ISO 105-X12:2016) and fastness to light (ISO 105-B02: 2014) were measured. For light fastness measurements, the dyed fabrics were exposed to a xenon lamp (TruFade colour fastness tester, UK) for 24 hours at standard testing conditions. Changes in the shade and staining of the adjacent Multifibre (Multifibre DW, adjacent fabric, BS ISO 105-F10:1989 were assessed using grey scales.

Measurement of tensile strength

For measurement of the tensile strength of the dyed PET fabrics, an Instron tensile tester: model-5565 (made in USA) (DIN EN ISO 13934-1) was used. The tensile strength of the dyed fabrics was tested both in the warp and weft directionss.

Results and discussion

Spectral analysis of extracted dyes

Spectral analysis (λ_{max}) shifts of the extracted dyes in various solvents are shown in (***Table 1***). The solvatochromic effect of the extracted dyes in various solvents indicated that the differences in the values of λ_{max} for ethanol, acetone and water from that of methanol were 5.2 nm, 15.4 nm and 30.1 nm, respectively. From the solvatochromic effect, it can be said that with an increase in the polarity of the solvent, curcuminoid dyes get converted from a keto into an enol form (***Scheme 2***). Hence the excitation of the solvent shifts to a $\pi \rightarrow \pi^*$ transition [27]. However, the maximum amount of curcuminoid dyes was obtained using methanol and ethanol in the form of a dark orange colour.

Dye exhaustion

Dye exhaustion is directly related to the dyeing cost and effluent control. It is also an indicator of the colour fastness. The exhaustion of curcuminoid dyes in PET fabric (***Figure 3***) employing the supercritical CO_2 method was higher than that of the high temperature exhaust dyeing method at pH 4.5. This was because of the temperature and pressure in the supercritical CO_2 method being higher than that in the high temperature exhaust dyeing method. The higher temperature and pressure in the supercritical CO_2 method

Table 1. *λmax of extracted dyes in various solvents.*

Solvent	λ_{max}, nm	Extraction (%) based on weight
Methanol	420.3	5.15
Ethanol	425.5	5.25
Acetone	435.7	4.10
Water	450.4	2.60

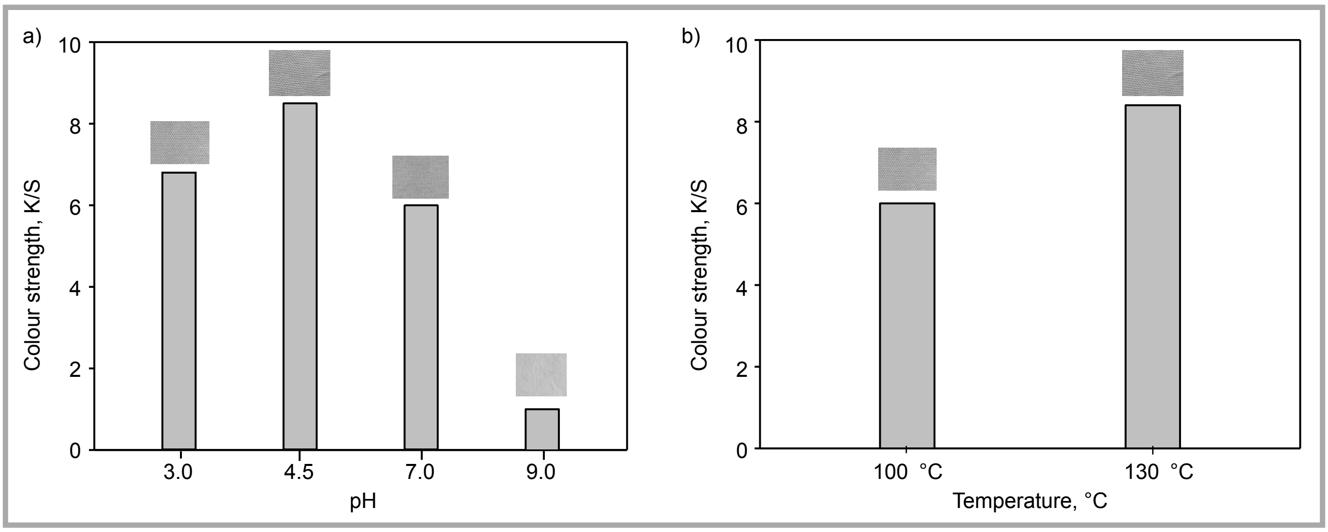


Figure 4. *Effect of pH a) and temperature b) on the colour strength of PET fabric dyed with curcuminoid dyes in the HT method.*

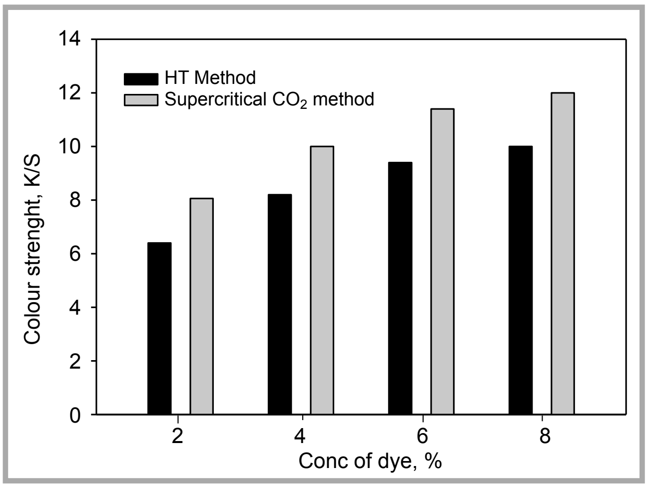


Figure 5. *Effect of different dyeing techniques on the colour strength of PET fabric dyed with curcuminoid dyes.*

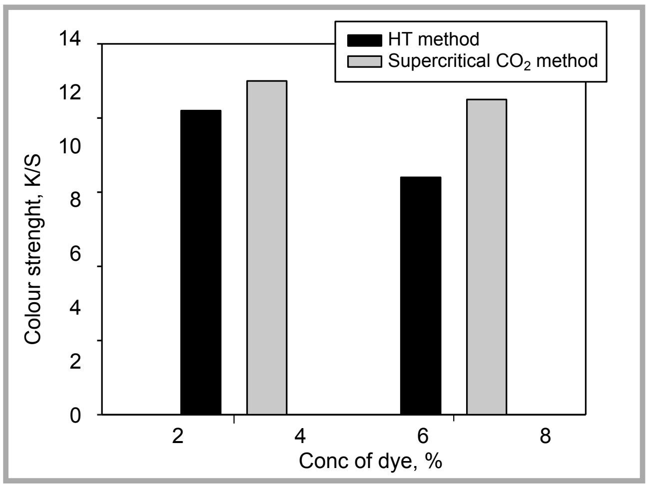


Figure 6. *Effect of heat setting on PET fabrics dyed by different methods (4% shades).*

facilitated a higher degree of diffusion of dye molecules into the polymer chain of the PET fibre.

Colour strength

Curcuminoid dyes showed a halochromic effect because their color changed with different pH [28]. ***Figure 4*** shows that the effect of pH influenced the colour strength of PET fabrics dyed by the HT method. A higher colour strength of dyed PET fabrics was obtained at pH 4.5, and keep the higher acidic media at pH 3 the color strength slightly decreased. In addition, in neutral pH conditions the colour strength of the dyed PET fabrics gradually decreased. However, in alkaline conditions at pH 9, ester groups of PET fibres were hydrolysed. Therefore curcuminoid dye molecules could easily move out from the fabric surface, significantly reducing the colour strength.

In ***Figure 4***, it is shown that higher temperature imparted higher colour strength to the PET fabrics when dyed with curcuminoid dyes by the HT method. It was because higher temperature increased the mobility of polymer chains in the amorphous regions of the fibre. Hence curcuminoid dye molecules diffused easily into the polymer chains of the fibre.

The colour strength of dyed PET fabrics was dependent on the concentration of the curcuminoid dye, as shown in ***Figure 5***, in both the high temperature exhaust and supercritical CO_2 dyeing methods. Thus it can be stated that the colour strength (K/S) increased with the increasing concentration of the natural colour curcuminoid in both methods up to a certain limit. Moreover it was clearly demonstrated that by using the supercritical carbon dioxide method, curcuminoid dye molecules can easily penetrate into polyester fabric. The colour strength of the PET fabrics increased as the concentration of the dyestuff increased. In ***Table 3*** the colour depth and shade are compared between high temperature dyeing at pH 4.5 and the supercritical CO_2 method used for dyeing PET fabric with curcuminoid dye. It is obvious that the HT method imparted deeper shades to PET fabrics in comparison with those dyed with the supercritical carbondixode method. Moreover the positive a^* and b^* values indicate red and yellow tones, resulting in the yellowing colour of the dyed fabric sample. It can be concluded from the results that the PET fabric dyed by the supercritical CO_2 method showed less reddishness and more bluishness than HT dyed PET fabrics.

Polyester dye uptake is dependent on the number of crystals present and the orientation of the amorphous phase. Dye diffusion depends on the segmental mobility of the amorphous region and on the size distribution of the crystallites [29]. ***Figure 6*** shows that the colour strength of the pre-heat set PET fabric was found to be higher in the supercritical carbon dioxide dyeing method than that obtained in the HT dyeing method. A significant change in colour strength was observed in the HT dyeing method for pre-heat set and un-set PET fabrics. The pre-heat setting enhanced the distance between the crystalline structures and increased the amorphousness of the polymer chain, hence the dyes could easily penetrate into the fabric. The heat setting of PET fibre formed separate crystalline and non-crystalline regions. In addition, small crystallites in the matrix decreased and big ones were formed; thus the free volume enhanced the dye uptake [30]. Generally it can be said that the pre-heat setting did not affect much the colour strength of the fabric dyed by the super critical CO_2 method, because crystallites were formed during dyeing at supercritical conditions.

Colour fastness properties

In order to study the colour fastness properties of polyethylene terephthalate (PET) fabrics dyed by the two different methods, we measured the colour fastness to washing, rubbing and light, which are presented in ***Table 4***. It was observed that the curcuminoid dyes showed very good fastness ratings for both the supercritical CO_2 and high temperature exhaust dyeing methods. From the experiment, it can be stated that the high crystallinity of polymer chains of the polyethylene terephthalate (PET) got converted into an amorphous state under the influence of the high temperature and super critical CO_2 methods. Therefore the curcuminoid dye molecules could penetrate into the polymer chain and got strongly entrapped as well. Fabrics dyed by both methods demonstrated very good wash and rubbing fastness ratings. However, light fastness ratings appeared to be fair to moderate when the dye concentration increased on the fabric surface. It can be concluded that under the influence of light, curcuminoid dyes got converted from a keto to an enol form, and thus the dyes could get sublimated from the fabric surface.

Tensile strength

The tensile strength of the PET fabrics dyed with curcuminoid dyes is shown in ***Table 5***. It was observed that after dyeing the fabrics under the different dyeing conditions, there was no significant amount of strength loss in both directions.

Table 2. Effect of different p^H and apparent colour of curcuminoid dyed PET fabric.

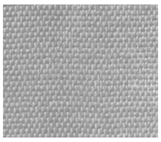
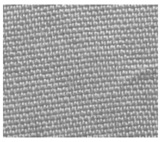
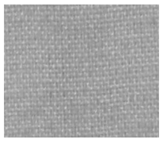
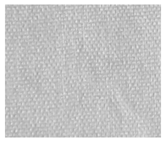
	p^H = 3	p^H = 4.5	p^H = 7	p^H = 9.0
HT dyeing method				

Table 3. Colourimetric data of PET fabric dyed with curcuminoid dye using different dyeing methods.

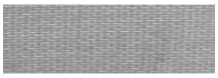
	Dyed sample	L^*	a^*	b^*	C	h
HT method		70.18	+13.88	+91.53	92.58	81.38
Supercritical CO_2 method		72.92	+7.06	+92.62	92.89	85.64

Table 4. Colour fastness properties of PET fabric dyed with curcuminoid dyes.

Dyeing technique	Shade % (owf)	Fastness rating					
		Wash fastness			Rubbing fastness		Light fastness (24 hours)
		Colour change	Staining (cotton)	Staining (wool/silk)	Dry rubbing	Wet rubbing	
Supercritical CO_2 dyeing method	2	5	4-5	4-5	5	4-5	2
	4	5	4-5	4-5	5	4-5	2-3
	6	4-5	4-5	4-5	4-5	4-5	3
	8	4-5	4-5	4-5	4-5	4-5	3-4
HT dyeing method	2	4-5	4-5	4-5	4-5	4-5	2
	4	4-5	4-5	4-5	4-5	4-5	2-3
	6	4-5	4-5	4	4-5	4	2-3
	8	4-5	4-5	4	4	4	3

Table 5. Tensile strength of PET fabrics dyed with curcuminoid dyes.

Dyeing method	Strength of fabric, N	
	Warp direction	Weft direction
PET fabric (without treated)	504	256
PET fabric dyed by HT method	452	242
PET fabric dyed by supercritical CO_2 method	463	249

Economical aspects of the supercritical carbon dioxide method

The approach to the extraction of curcuminoid dyes and dyeing of fabric in the supercritical carbon dioxide method using the same bath is mostly profitable. Not only is the cost of the process lower but also the time of the process is also reduced in this method. Moreover no effluent is produced after the extraction and the dyeing process. Therefore this technique can be applied commercially for the dyeing of polyethylene terephthalate (PET) fabric. Nevertheless whether these techniques can be commercially and successfully applied in the case of other synthetic fabrics requires more investigation to be done.

Conclusions

The ultimate goal of this study was to find a suitable eco-friendly dyeing technique for the dyeing of PET fabric with natural curcuminoid dyes. The extraction of the dyestuff and dyeing of PET fabric by the supercritical carbon dioxide method were carried out in the same dye bath. While in the case of the HT method, the extraction and dyeing were carried out in separate dye baths. The results showed that all the properties of the PET fabric dyed by the supercritical carbon dioxide method examined were far better than those obtained by the high temperature exhaust dyeing method. The colour strength of the curcuminoid dyed fabric increased with increasing dye concentration. However, the colour strength of curcuminoid dyed PET fabrics was enhanced more by using the super critical CO_2 method than by the HT dyeing method. The pre-setting of polyester fibres plays an important role in right-first-time dyeing. The differences between with or without the pre-heat setting could little affect supercritical CO_2 dyeing on PET fabric using curcuminoid dye.

Acknowledgements

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