PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Prog. Color Colorants Coat. 15 (2022), 143-156

Ministry of Science, Research and Technology
Institute for Color Science and Technology

A Comparative Study on the Environmental Friendly Bleaching Processes of Poly(lactic acid) Substrate: Application of Ultraviolet/O_3/H_2O_2 System

F. S. Fattahi
Department of Textile Engineering, Isfahan University of Technology, P.O. Box: 84156-83111, Isfahan, Iran.

ARTICLE INFO

Article history:
Received: 06 Mar 2021
Final Revised: 10 Jun 2021
Accepted: 14 Jun 2021
Available online: 06 Oct 2021

Keywords:
Poly(lactic acid)
Bleaching
Ultraviolet/O_3
Whiteness Index
Eco-friendly.

ABSTRACT

Recently, there has been an increasing interest towards the finishing of textiles (fibers, yarns, fabrics and nonwovens) using eco-friendly technology, which can achieve a wide range of functional properties and environmental benefits. This study is related to a modern eco-friendly bleaching technology that relies on Ultraviolet/O_3 radiation of poly(lactic acid) fabric through simple technique. The effects of Ultraviolet/O_3 radiation along with the pretreatments with distilled water, hydrogen peroxide, and hydrogen peroxide/sodium silicate solutions on the bleaching of the poly(lactic acid) fabrics were examined using UV-Visible and reflectance spectral method and the results were compared with that of virgin untreated samples. Ultraviolet/O_3 bleaching routes were screened to obtain desired whiteness index (WI), tint factor (T_w), lightness/darkness (L), redness/greenness (a*), yellowness/ blueness (b*), chroma (c*) and hue (h°) of the bleached poly(lactic acid) fabrics. The optimal properties of the bleached poly(lactic acid) knitted fabric could be obtained at Ultraviolet/O_3 irradiation for 80 min on the fabrics which pre-impregnated in a hydrogen peroxide solution with a wet pick up of 70 %, pressure of 1.1 bar and speed of 2 m/min. (Ultraviolet/O_3/H_2O_2 bleaching system). The Ultraviolet/O_3/H_2O_2 bleached fabric showed the best colorimetric properties (WI: 87.7, T_W: -0.1, L*:94.227, a*:-0.106, b*:0.294, c*:0.2512, h°: 98.6551). Moreover, the reflectance of this sample has increased significantly in the range of 400-450 nm which leads to a glossy withe shade on the fibers. The SEM images presented that after Ultraviolet/O_3/H_2O_2 bleaching process, some fractures with nano scale size (about 130 nm) are formed on the poly(lactic acid) fabric surface. The ATR-IR spectrum of Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fibers displays more intense C–C–O absorption bands (1161 cm^{-1}). Prog. Color Colorants Coat. 15 (2022), 143-156© Institute for Color Science and Technology.*

1. Introduction

Textile industry puts heavy strain on worldwide resources as it uses huge quantities of energy, water, and hazardous chemicals [1]. This condition has raised issues about the sustainability of textiles because of severe burden on environment [2]. Consequently, other methods have become essential to ensure the sustainability of textile wet processing [3]. This main stage (wet processing) includes a huge quantity of water for washing and dissolution media [4]. Thus, it gets

*Corresponding author: f.fattahi@tx.iut.ac.ir
fattahi_farnaz@yahoo.com

loaded with auxiliary chemicals and unfixed dyes as wastewater wastes [5]. Similarly, a number of chemicals used as washing and finishing agents pollute the water used during wet processing operations [6, 7]. This wastewater contaminates the ecosystem if discharged untreated [8, 9]. The toxic effluent of chemical axillaries used throughout the wet process could severely damage the ground water and aquatic life [5, 10, 11]. Consequently, *green chemistry* has emerged as an operative tool to make textile wet processing sustainable [12-14]. In fact, *green chemistry* has helped in the development of alternative green and biodegradable chemicals usable as wetting, washing, bleaching and finishing agents [15-17]. A number of different techniques can be used to in textile wet processing optimize the interfacial properties of a fabric, such as bleaching process [2, 4]. Due to the focus of various industries on pollution-free technologies [18], the novel methods should be designed instead of the traditional methods [19, 20].

Bleaching process has the ability to decolorize the fiber through removing lignin, hemicellulose and surface impurities [21-23]. Producing white fabrics by destroying the coloring matter with the help of bleaching chemicals with minimum degradation of the fiber is the main purpose of the bleaching process [24, 25]. Poly(lactic acid) fiber is widely used in apparel and consumer textile products due to its excellent properties of hygroscopicity, air permeability, biodegradability, and mechanical performance [26, 27]. Treatments on poly(lactic acid) fabric to remove its impurities are important and necessary, determining qualities of the poly (lactic acid) fabrics make it an attractive option as an alternative to conventional polymers [28, 29]. These treatments are mainly implemented in two pretreatment processes of scouring and bleaching [30]. Because of the poor alkali resistance of poly (lactic acid) fibers, strong alkalis can cause strength loss via hydrolysis in conventional bleaching processing. Scouring and bleaching must all therefore be carried out according to this sensitivity. Bleaching process can have an influence on the physical strength of poly(lactic acid) fiber. With this in mind, suitable conditions should be designed for bleach processing of 100 % poly(lactic acid) that do not degrade the polymer [31].

It is reported that the poly(lactic acid) fabric was bleached with various oxidative bleaching agents (hydrogen peroxide, sodium chlorite and sodium hypochlorite) [32]. In another research, The poly(lactic acid) fabrics were bleached with different bleaching agents (Belox® 35 (a stabilized aqueous solution with approximately 35% H_2O_2) ,Clarite® LTC (a combination product with wetting, detergent and dispersing properties), Invatex® LTA (an agent to assist and boost the peroxide reaction), and Invazyme ® LTE (an arylesterase to catalyze the peroxide bleaching combined with Invatex® LTA) for 1 hour [33]. A one-bath scouring/bleaching procedure with 7 % owf hydrogen peroxide (100 °C, 60 min) was found to be an appropriate pretreatment for pale-shade poly(lactic acid)/cotton blended fabrics to achieve acceptable absorbency and whiteness [34]. A research stated that the alkaline scouring in a bath holding 2 g/L soda ash and non-ionic surfactant at 60 ºC for 20 min. was applied for poly (lactic acid)/cotton fabrics [35]. In this study, the application of Ultraviolet/O_3 bleaching process for poly (lactic acid) fabrics will be investigated experimentally in a lab-scale study. A Ultraviolet/O_3 system will be employed to bleach raw poly(lactic acid) knitted fabric under mild conditions. This process is an environmentally friendly method which can improve the "green technology" in the textile industry [36, 37].

The bleaching process in textiles can be assayed by term of *Whiteness.* Color results from an interaction between light, object, and the viewer. Color is usually described by three attributes or dimensions such as hue, saturation and lightness. A color space can be used to describe the range of visible or reproducible colors or gamut of a viewer or device. The CIE developed more uniform color space called CIELAB or CIE L*a*b*. *Whiteness* is defined as an attribute by which an abject is judged to depart from a standard white towards yellow. In this paper, it is tried to state the spectral and colorimetric behaviors of the Ultraviolet/O_3 poly (lactic acid) bleached fabrics under different conditions and selecting the optimum rout based on the whiteness index (WI), tint factor (T_w), lightness/darkness (L*), redness/greenness (a*), yellowness/blueness (b*), chroma (c*) and hue (hº) values.

2. Experimental

2.1. Materials

The following fabrics are applied throughout this exploration: Pure poly(lactic acid) fabrics (100 %): weight 18.45 g/m^2, thickness 0.781 mm and Yarn linear density is 150/144 dtex/filament. These fabrics were kindly supplied by Nature Works LLC Company,

USA.

2.2. Scouring process

The poly(lactic acid) fabrics was scoured with 2 g/L anionic/non-ionic detergent, 1 g/L Kieralon Jet B conc. (non-ionic surfactant, BASF) and 1 g/L sodium carbonate ('soda ash') at 60 ºC for 15 min. at a liquor ratio of 10: 1, washed thoroughly. After scouring, the fabrics were rinsed with cold water for 10 min and dried in ambient conditions to remove mill dirt and lubricants.

2.3. Bleaching process

To obtain an optimal Ultraviolet/O_3 bleaching procedure for pretreatment of the poly(lactic acid) knitted fabric, various processing routines were designed including Ultraviolet/O_3/H_2O, Ultraviolet/O_3/H_2O_2 , Ultraviolet/O_3/(H_2O_2 + Na_2SiO_3), and scouring + Ultraviolet/O_3. The Ultraviolet/O_3 bleaching process is shown in Figure 1.

A piece of the knitted fabric (around 5.5 g) was immersed in the pre-impregnation bleach solution and padded twice through a laboratory padder with a wet pick up of 70 %, pressure of 1.1 bar and speed of 2 m/min.

2.3.1. Scouring +Ultraviolet/O_3 bleaching

There is no bleaching solution. The poly(lactic acid) fabrics was radiated in an Ultraviolet/O_3 chamber after scouring.

2.3.2. Ultraviolet/O_3/H_2O bleaching

A bleach solution was prepared by distilled water (1 L). After pre-impregnation process, the poly(lactic acid) fabrics was radiated in Ultraviolet/O_3 chamber.

2.3.3. Ultraviolet/O_3/H_2O_2 bleaching

A bleach solution was prepared by dissolving certain amounts of concentrated H_2O_2 35 % (4 mL) in water (1 L). After pre-impregnation process, the poly(lactic acid) fabrics was radiated in Ultraviolet/O_3 chamber.

2.3.4. Ultraviolet/O_3/(H_2O_2 + Na_2SiO_3) bleaching

A bleach solution prepared by dissolving certain amounts of concentrated H_2O_2 35 % (4 mL) in water (1 L) with addition of Na_2SiO_3 at 7 g/L, respectively. After pre-impregnation process, the poly(lactic acid) fabrics was radiated in Ultraviolet/O_3 chamber.

2.3.5. Ultraviolet/O_3 radiation

The poly(lactic acid) fabrics was irradiated in a Ultraviolet/O_3 irradiation cabinet for 80 min (40 min face up and 40 min face down), respectively. (Ultraviolet/O_3 radiation cabinet: 11 mW/cm^2 intensity UV lamps without outer envelope (6 Lamps, made in Poland) is placed in a cubic box with side length 60 cm. Strips of samples are placed around the source at a suitable distance (~2 cm). Atomic oxygen is generated both when molecular oxygen is subjected to the 184.9 nm radiation and when ozone is irradiated at 253.7 nm. The radiation at 253.7 nm is absorbed by most hydrocarbons and also by ozone.).

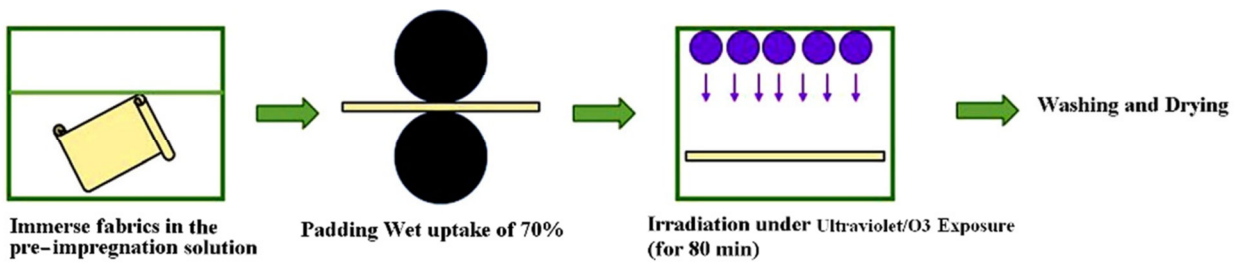

Figure 1: Scheme of the bleaching process.

2.3.6. Scouring

When the irradiation was completed, the sample was rinsed adequately with cold water (30-40 ºC) room temperature for 10 min in a liquor to goods ratio of 20:1, and then oven dried under 60 ºC for 30 min.

2.4. Fabric properties

The whiteness (WI) of the poly(lactic acid) knitted fabrics was measured with a 0/d Tex-flash spectrophotometer according to AATCC test method 110-2015 based on a procedure of measuring CIE whiteness index (WI) [17, 38].

2.5. Colorimetric assay

The poly(lactic acid) fabrics were subjected to 0/d Tex-flash spectrophotometer under illuminant D65 light at 10˚ observation angle to measure the color coordinates in terms of CIE Lab and CIE Lch (L*, a*, b*, c*, and h˚) system in visible spectrum region (400-470 nm). The chroma (c*) and hue angle (h˚) of the samples was measured by the following equations (Eq. 1 and 2)[39].

$$Chroma\ (C^*) = \sqrt{a^2 + b^2} \quad (1)$$

$$Hue\ angle\ (h^\circ) = \tan^{-1}\left(\frac{b}{a}\right) \quad (2)$$

Where, L*= lightness/darkness, a*= redness/greenness and b*= yellowness/blueness.

2.6. Fourier transforms infrared spectroscopy (FTIR-ATR)

FTIR spectra were collected by a Bomem-MB FTIR-ATR spectrometer instrument (Model 100) in an absorbance mode at a wavenumber range of 4000–400 cm^{-1}. The sample pellets were prepared by mixing 2.0 mg of fabric powder with 200.0 mg of potassium bromide. The specimens were analyzed at 4 cm^{-1} resolution, and the recorded spectrum for each was the average of 100 scans.

2.7. Scanning Electron Microscopy

Scanning Electron Microscopy examination of the fibers was carried out in order to assess whether the various treatments had caused any visible degradation to the fiber surfaces. A XL30 MODEL/PHYLIPS Company/Netherland instrument was used for this purpose. In order to avoid problems due to charge build up, the poly (lactic acid) fabrics were previously sputter coated with gold palladium for two minutes in a SCDOOS MODEL/Bal-Tech Company/Switzerland sputter coating unit. The images were captured with magnifications of 2500, 15000 and 30000.

2.8. Reflection spectra

The reflection spectra in the visible range 400-700 nm of all of examined samples, obtained using a 0/d Tex-flash spectrophotometer from Data Color in the visible region under illuminant D65, employing a 10º standard observer with UV component included and specular component excluded. In order to measure the spectral reflectance of the fabrics, the fabric folded four times and the measurement was done twice. In the second time the measurement was done after the 90 degrees rotation of the fabric, and then the average of these measurements were considered as the reflectance of the sample.

3. Results and Discussion

3.1. Colorimetric assays of poly(lactic acid) bleached fabrics

Bleaching processing of poly (lactic acid) fabrics is usually carried out to improve luster, handling, dye-ability and water absorbency. Alkaline peroxide bleaching at 80 ºC is a popular way to remove the impurities, but in this work, a novel eco-friendly technology (Ultraviolet/O_3 bleaching process) is used for bleaching of poly(lactic acid) fabrics. The five white poly(lactic acid) fabrics applied as substrates had been treated differently. Substrate 2,3,4 and 5 bleached with Ultraviolet/O_3, Ultraviolet/O_3/H_2O, Ultraviolet/O_3 /H_2O_2 and Ultraviolet/O_3/(H_2O_2 + Na_2SiO_3) radiation correspondingly. The other poly(lactic acid) fabric (substrate 1) was just normally scoured (Figure 2).

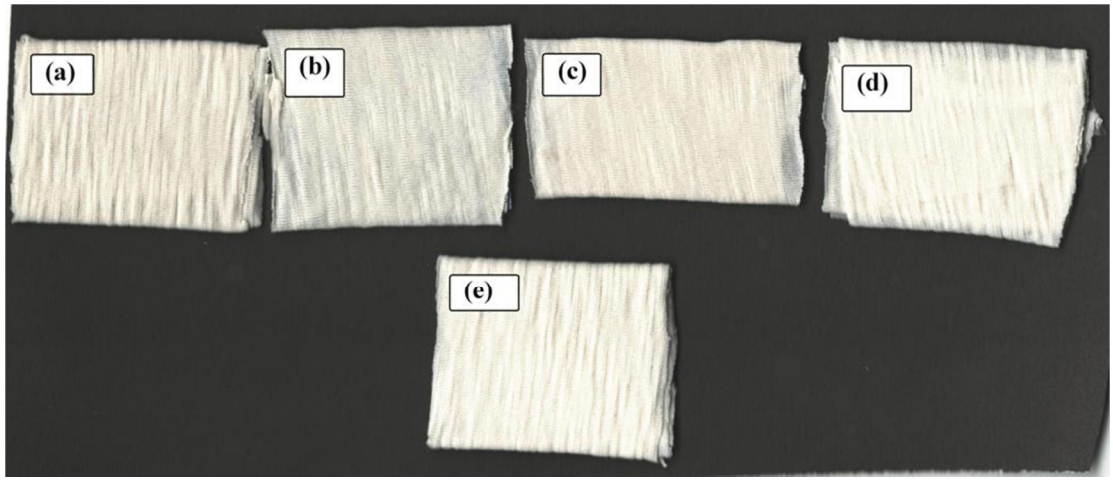

Figure 2: (a) Unbleached poly(lactic acid) fabric, (b) Ultraviolet/O_3 bleached poly(lactic acid) fabric, (c) Ultraviolet/O_3/(H_2O_2 + Na_2SiO_3) bleached poly(lactic acid) fabric, (d) Ultraviolet/O_3/H_2O bleached poly(lactic acid) fabric and (e) Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fabric.

To compare the whiteness characteristics of the bleached poly(lactic acid) fabrics, their whiteness indexes as well as their tint factor were calculated by using the common CIE whiteness formula (Eq. 3 and 4) [40]:

$$WI = Y + 800(x_n - x) + 1700(y_n - y) \quad (3)$$

$$T_W = 900(x_n - x) - 650(y_n - y) \quad (4)$$

Where, Y indicates the lightness attribute of bleached white fabrics and (x, y) and (x_n, y_n) show the chromaticity coordinates of bleached white substrate and light source under CIE1964 standard observer, respectively. Based on the CIE whiteness formula, samples are defined as whites if their whiteness index (WI) and tint factor (T_w) obey from limitations determined by Equations 5 and 6 [41].

$$40 < WI < (5Y - 280) \quad (5)$$

$$-4 < T_W < +2 \quad (6)$$

Where, samples with Tw=0 are defined as bluish whites and those with positive (Tw>0) and negative (Tw<0) tint factors represent the greenish and reddish whites, correspondingly [42].

Table 1 displays the specifications of bleached poly(lactic acid) fabrics applied as substrates in this research. According to Table 1, the poly(lactic acid) fabrics have different whiteness and tint attributes. In addition, based on limitations determined by equations 5 and 6, Ultraviolet/O_3 bleached PLA fabrics are defined as white. While, the whiteness index (WI) and tint factor (Tw) of virgin PLA fabric are out of boundaries determined by CIE whiteness formula.

Table 1 : Effect of processing routine on the whiteness index and tint factor of poly(lactic acid) bleached fabrics.

Bleached poly(lactic acid) fabric	Bleaching Technique	WI(%)	T_w
Substrate 1	Scouring	38.8	-4.2
Substrate 2	Ultraviolet/O_3 [a]	79.2	-0.2
Substrate 3	Ultraviolet/O_3/H_2O	87.2	-0.2
Substrate 4	Ultraviolet/O_3/H_2O_2	87.7	-0.1
Substrate 5	Ultraviolet/O_3/(H_2O_2 + Na_2SiO_3)	86.1	-0.5

[a] Ultraviolet/O_3 exposure: 11 mW/cm^2 254 nm lamps for 80 min.

On the other hand, based on Table 1, all the bleached poly(lactic acid) fabrics have negative value of tint factor. Meanwhile, Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fabric with the highest whiteness index (WI=87.7) and lowest tint factor (Tw= -0.1) could be defined as the whitest substrate among the four bleached fabrics. Clearly, the special whitening treatment of poly(lactic acid) fabrics with Ultraviolet/ O_3/H_2O_2 radiation leads to its superior whiteness attribute in comparison with other white substrates.

Table 2 presents the results of various bleaching treatment routines on the colorimetric attributes of the poly(lactic acid) fabrics. White are identified by low chroma values and distributions around opposite poles of lightness coordinate in different color order system [41]. In CIE L*a*b* space, L* indicates the lightness; the perfect white sample has L* = 100 [42, 43]. As seen from the Table 2, the Ultraviolet/O_3/H_2O_2 bleached fabric, has the highest L* value (94.227 %) and the lowest C* value (0.2512). The b* value defines the yellowness/blueness coordinate in certain color space, for example Hunter L, a, b and CIELAB [44]. The b* value is used as the difference between a specimen and a standard reference color. If b* value is positive, there is more yellowness than blueness where although b or b* value is negative, more blueness is observe (The samples with b* > 0 means yellowness and b* < 0 blueness [45]). According to Table 2, the minimum value of b* is belonged to Ultraviolet/ O_3/H_2O_2 bleached fabric, this means that this sample has lowest yellow shade because of the lower b* value [46].

The hue angle (h˚) depending on which quadrant the color is located. In Figure 3, it seems that the tint attribute of poly(lactic acid) bleached fabrics shifts from the first quarter of hue area to the second quarter. It means that the tint effect of bleached fabrics changes from reddish white shade to the yellowish and greenish white shade.

Table 2: The colorimetric attributes of poly(lactic acid) bleached fabrics.

Bleached PLA fabric	Bleaching Technique	L*	a*	b*	C*	h˚
Substrate 1	Scouring	65.212	0.757	4.242	4.3665	59.3494
Substrate 2	Ultraviolet/O_3 [a]	92.251	-0.026	0.974	1.9743	91.2510
Substrate 3	Ultraviolet/O_3/H_2O	93.715	-0.022	0.647	0.7025	91.9827
Substrate 4	Ultraviolet/O_3/H_2O_2	94.227	-0.106	0.294	0.2512	98.6551
Substrate 5	Ultraviolet/O_3/(H_2O_2 + Na_2SiO_3)	93.172	-0.038	1.543	1.5461	91.4077

[a] Ultraviolet/O_3 exposure: 11 mW/cm^2 254 nm lamps for 80 min.

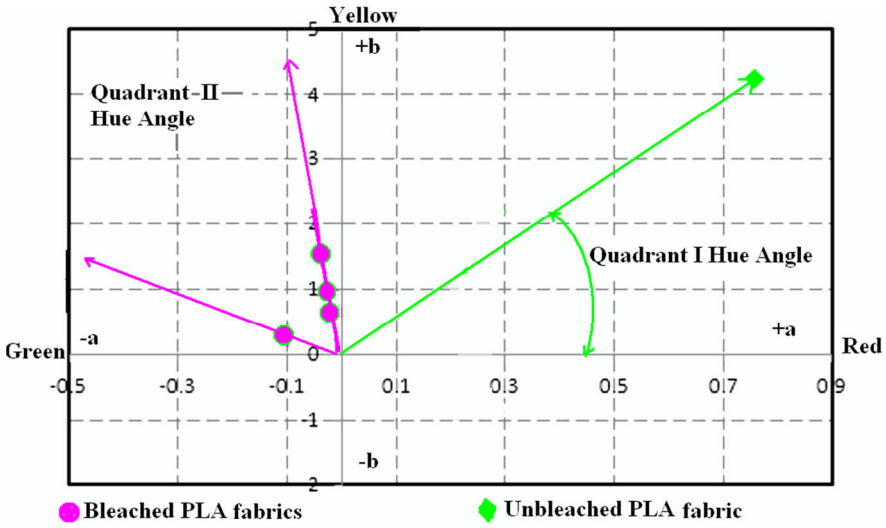

Figure 3: The a*b* scatter plot of poly(lactic acid) bleached fabrics over the CIELAB color space.

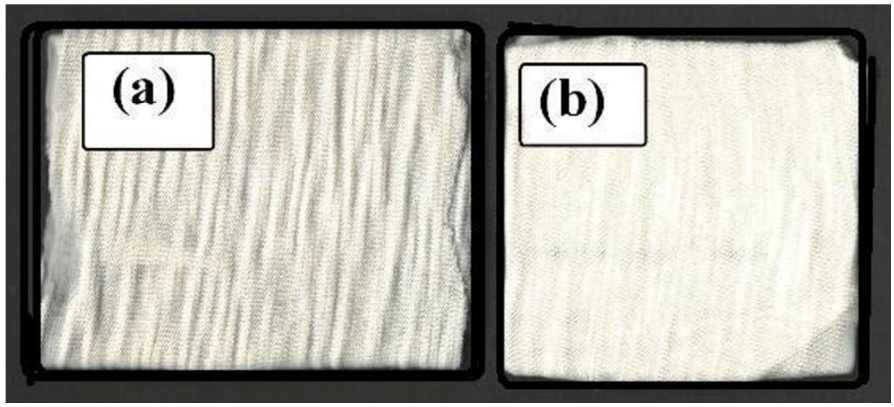

Figure 4: (a) Unbleached poly(lactic acid) fabric and (b) Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fabric.

The Ultraviolet/O_3/H_2O_2 bleached fabric showed the best colorimetric properties among these five substrates (WI: 87.7, T_W: -0.1, L*:94.227, a*:-0.106, b*:0.294, c*:0.2512, h°: 98.6551) (Figure 4).

3.2. Reflecting spectrum of bleached poly(lactic acid) fabrics

Figure 5 displays the reflecting spectrum of the poly(lactic acid) samples (virgin fabrics and bleached fabrics). In the physic science, objects which can reflect 100% of the emitted light are called perfect white. In other words, the samples with the uniform and complete reflection in the whole visible spectrum are called ideal white. But this capability (not completely) is only present in a few objects such as magnesium oxides, lead and barium sulfate [47]. Therefore a white surface is said to reflection more than 70 % of the emitted visible light (a realistic definition) [48].

As seen in Figure 3, Ultraviolet/O_3/H_2O and Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fabrics have the higher level reflection (about 86 %) especially in 470-570 nm. Moreover the reflectance spectrum of these samples became more uniform along the visible spectrum specifically in 470-700 nm. On the other hand, the reflecting spectrum of most fibers is reduced in the purple to blue region (400-450 nm) due to the higher absorption of visible light [40, 49].

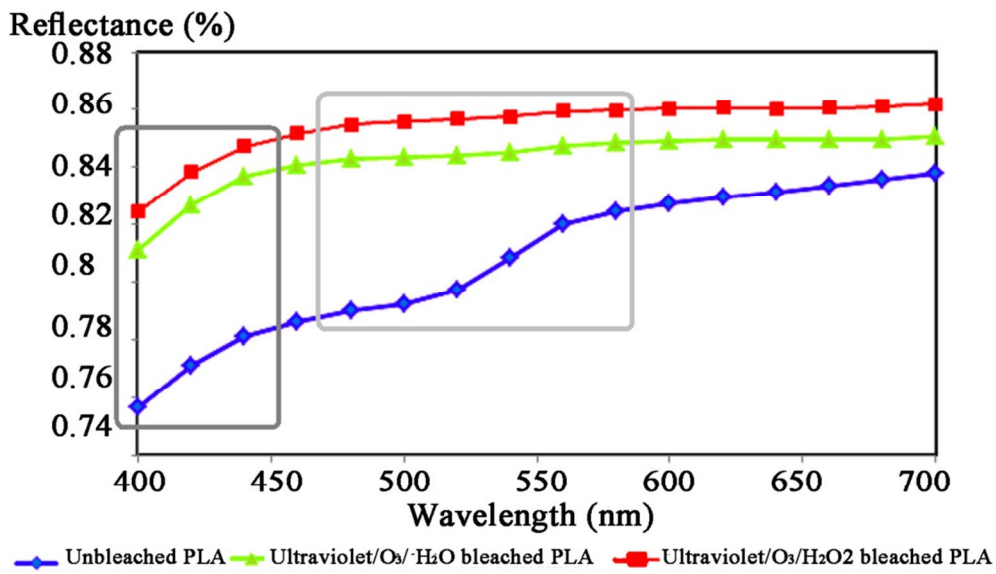

Figure 5: Reflecting spectrum of bleached and virgin unbleached poly(lactic acid) fabrics.

This leads to a yellowish white shade on the fibers. It can be observed from the Figure 3 that the reflectance of the poly (lactic acid) fabrics has increased considerably in the range of 400-450 nm after Ultraviolet/O_3 treatment which leads to a glossy white.

3.4. Bleaching chemistry: Structural analysis by ATR-IR spectroscopy

In order to study the structural properties of fabrics, the samples are considered using ATR-IR spectroscopy. The ATR-IR spectroscopy provides information regarding changes in the bonding in the top 0.5-1 mm. Figure 6 show the ATR-IR spectrum of the bleached and unbleached poly (lactic acid) fabrics. The ATR-IR spectrum of poly(lactic acid) fiber which bleached with Ultraviolet/O_3/H_2O_2 system shows significant oxidation of the poly(lactic acid) fabrics. There is a considerably more intense absorption bands ascribed to O–H stretching (3390 cm^{-1}). Also it can see that, the ATR-IR spectrum of Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fibers shows more intense C–C–O absorption bands (1161 cm^{-1}), indicating that the formation of alcohol groups is dominant. However, bleaching of poly(lactic acid) fibers with Ultraviolet/O_3/H_2O_2 system also generates CH_3C=O moieties (absorption band at 1324 cm^{-1}). This indicates the oxidation process of the poly(lactic acid) fabrics after Ultraviolet/O_3/H_2O_2 bleaching process [50]. The formation of free radicals on the fiber surface (due to photochemical interactions) is an important factor for chemical modification of materials with this method [51].

Irradiation of fibers by a radiation source changes the physical and chemical properties (based on the radiation conditions and the chemical nature of the fiber). Ultraviolet/O_3 radiation is an oxidation process that can excite the surface molecules. Ultraviolet radiations have significant potential for photochemical modification of polymers. The photon energy of ultraviolet radiation is sufficient to cause chemical changes in the structure of polymers. Ultraviolet radiation (184-365 nm) is produced by xenon lamps or mercury vapor lamps at low pressure [52]. The Ultraviolet/O_3 process uses a low-pressure mercury lamp in a chamber containing atmospheric pressure air.

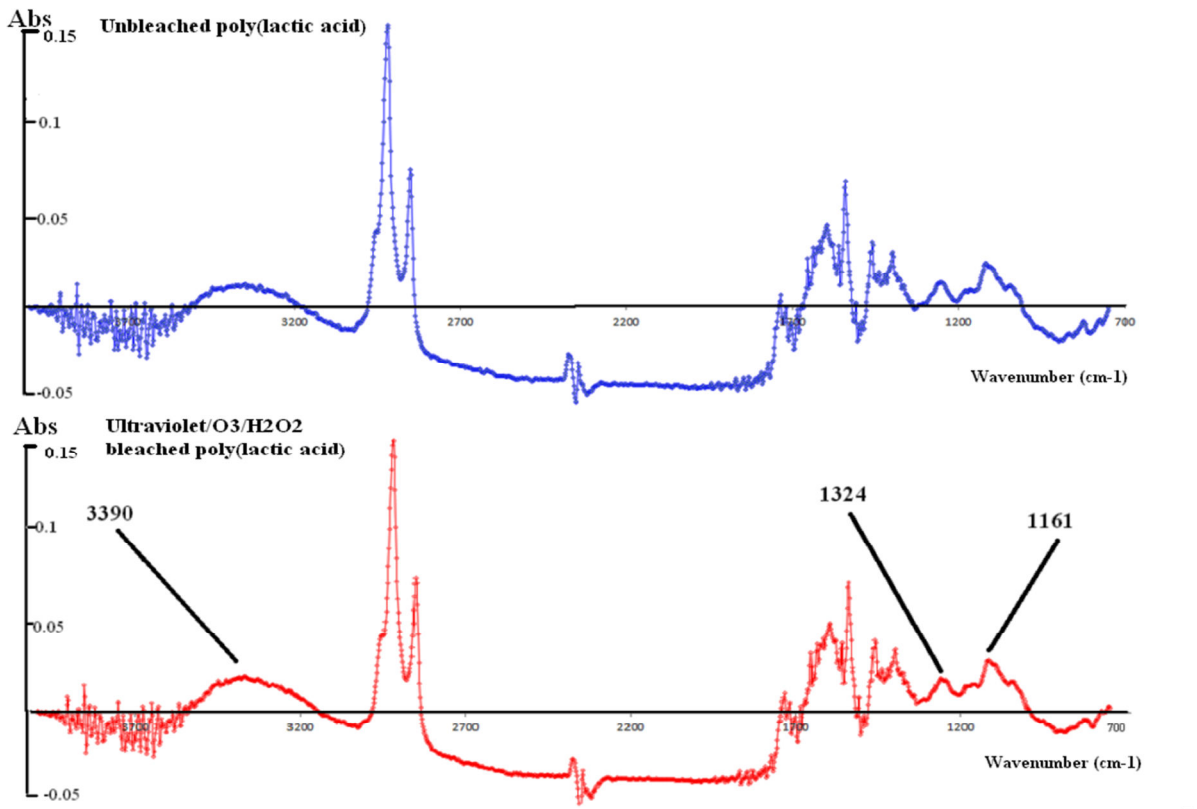

Figure 6: ATR-IR spectra of the spectra of unbleached and Ultraviolet/O_3/H_2O_2 bleached poly (lactic acid) fabrics.

The light emitted from the mercury lamp is absorbed by the oxygen molecules in the air at a wavelength of 184.9 nm. These dissociated molecules produce atomic oxygen [53]. Oxygen radicals will react easily with the oxygen molecules to produce the ozone molecule. Simultaneously, the light emitted from the mercury lamp is absorbed by ozone molecules at a wavelength of 253.7 nm. This process causes the photolysis of ozone molecules to oxygen radicals with very high reactivity with short life [54]. As ozone molecules is continuously produced and degraded, a constant concentration of oxygen atoms is formed inside the chamber, which acts as a strong oxidizer [55, 56].

On the other hand, the formation of free radicals on the surface of fibers is recognized as a key factor in the oxidation process by Ultraviolet/O_3 radiation. When fibers are exposed to the ultraviolet radiation, firstly the surface molecules are excited. Covalent bond breakage (like carbon-carbon, carbon-hydrogen and carbon-oxygen bonds) occurs in the polymeric chains, so that some radicals are formed on the surface of the fibers [57, 58]. On the other hand, atomic oxygen and ozone molecules are highly reactive excited components [59, 60]. These oxidizing agents react with excited molecules and radicals and form the reactive oxygenated groups (such as carbonyl, carboxylic acid and hydroxyl) [61]. Effects of Ultraviolet/O_3 radiation on poly (lactic acid) fabrics was showed in Figure 7.

3.5. Bleaching physics: Morphology analysis by scanning electron micrographs

Scanning electron microscopy (SEM) has been used to observe the morphology and topography changes in the surface of poly (lactic acid) fibers because of Ultraviolet/O_3 bleaching. The SEM of poly (lactic acid) fibers before and after Ultraviolet/O_3 bleaching treatment are shown in Figure 8. As seen in the picture, after the Ultraviolet/O_3 bleaching process, some fractures with nano scale size (about 130 nm) are produced on the fiber surface. These alterations in the morphology of the fibers are due to physical etching effect of Ultraviolet/O_3 irradiation [62]. The formation of surface roughness (due to the physical etching effects) is a key factor in the surface engineering of polymeric fibers and films via Ultraviolet/O_3 irradiation [51].

$a)\ Hydrogen\ abstraction$

$$PH \xrightarrow{Ultraviolet/O3} P\cdot + H\cdot \qquad PH: Poly(lactic\ acid)$$

$$P\cdot + O_2 \rightarrow POO\cdot$$

$$POO\cdot + PH\cdot \rightarrow POOH + P\cdot$$

$b) Decomposition\ of\ hydroperoxide$

$$POOH\cdot \xrightarrow{Ultraviolet/O3} PO\cdot + HO\cdot$$

$$HO\cdot \xrightarrow{PH} P\cdot + H_2O$$

$$PO\cdot \xrightarrow{PH} POH + P\cdot$$

Figure 7: Formation of radicals.

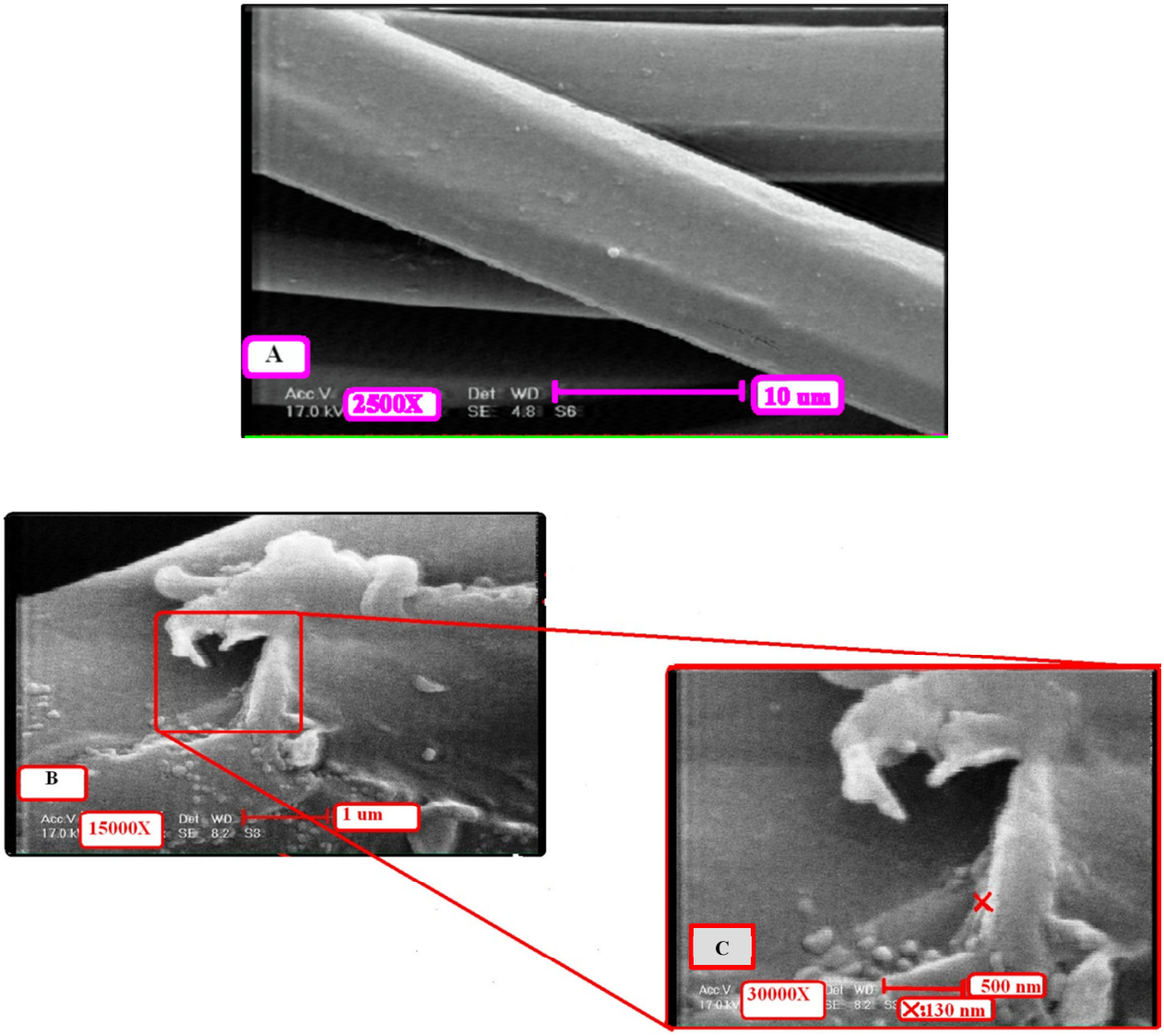

Figure 8: SEM photographs of the poly (lactic acid) fabrics: (A) unbleached fabric (2500 x), (B) Ultraviolet/O_3/H_2O_2 bleached fabric (15000 x) and (C) Ultraviolet/O_3/H_2O_2 bleached fabric (30000 x).

The morphology of the fibers treated with Ultraviolet/O_3 radiation under different conditions show a significant change in the fiber surface (The fiber surface is destroyed) [63, 64]. Grooves, cavities and ruggedness form on their surface [65, 66]. This surface ruggedness is due to the effect of physical corrosion caused by bombardment of ions inside the chamber [67, 68]. The type of physical changes on the fiber surface are different under various processing conditions with Ultraviolet/O_3 radiation [69]. This is due to the differences in ions that produce different corrosion effects. These physical changes are mostly in the form of cavities, and pores [70, 71]. In some cases, the surface layer of fibers is broken up heterogeneously, creating peaks and valleys. In some cases, the surface changes of the samples are by creating horizontal channels that have a diameter of nanometers and are evenly distributed on the surface [27, 72].

4. Conclusions

In recent years, the textile industry has focused on the application of novel pollution-free and environmentally friendly technologies called “green technology”. Ultraviolet/O_3 radiation is one of the best ecofriendly methods for these purposes. In this work a novel

Ultraviolet/O_3/H_2O_2 bleaching process is used for remove the impurities of poly (lactic acid) fabrics under mild conditions. The main results are as follows:

- Ultraviolet/O_3/H_2O_2 bleaching process is defined for the Ultraviolet/O_3 irradiation (80 min.) on the poly (lactic acid) fabrics which pre-impregnated in a hydrogen peroxide solution.
- The reflectance spectrum of Ultraviolet/O_3/H_2O_2 bleached poly (lactic acid) fabrics became more uniform along the visible spectrum specifically in 470-700 nm with higher level reflection (about 86 %) especially in 470-570 nm which leads to a shiny white.
- White is identified by low chroma values and distributions around opposite poles of lightness coordinate in different color order system. The Ultraviolet/O_3/H_2O_2 bleached poly(lactic acid) fabric exhibited the highest L* value and the lowest C* value.
- After Ultraviolet/O_3/H_2O_2 bleaching process, some fractures with nano scale size (about 130 nm) are produced on the poly (lactic acid) fabric surface due to ions bombardment in the radiation chamber.
- The ATR-IR spectrum of Ultraviolet/O_3/H_2O_2 bleached poly (lactic acid) fibers displays more intense C–C–O absorption bands (1161 cm^{-1}), representing that the formation of alcohol groups is dominant. Though, bleaching of poly (lactic acid) fibers with Ultraviolet/O_3/H_2O_2 system also produces CH_3C=O moieties (absorption band at 1324 cm^{-1}) on the fabric surface.

Acknowledgments

The author is grateful to scientific research fund of Textile Engineering Department at Isfahan University of Technology for the financial support.

5. References

1. P. Cesar da Silva, G. Cardoso de Oliveira Neto, J.M. Ferreira Correia, H.N. Pujol Tucci, Evaluation of economic, environmental and operational performance of the adoption of cleaner production: Survey in large textile industries, *J. Clean. Prod*., 278(2021), 123855-12372.
2. A. K. Roy Choudhury, Green chemistry and the textile industry, *Text. Progress*., 45(2013) 3-143.
3. R. A. Sheldon, M. Norton, Green chemistry and the plastic pollution challenge: towards a circular economy, *Green Chem*., 22(2020), 6310-6322.
4. S. Madhav, A. Ahamad, P. Singh, P.K. Mishra, A review of textile industry: Wet processing, environmental impacts, and effluent treatment methods, *J. Environ. Qual.,* 27(2018), 31-41.
5. M. Gopalakrishnan, V. Punitha, D. Saravanan, Water conservation in textile wet processing, In: Water in Textiles and Fashion(S.S. Muthu), Woodhead Publishing, Sawston, USA, 8(2019), 135-153.
6. S. Managi, R. Lindner, C.C. Stevens, Technology policy for the sustainable development goals: From the global to the local level, *Technol. Forecast. Soc. Change.*, 162(2021), 120410-120414.
7. S. B. Moore, L.W. Ausley, Systems thinking and green chemistry in the textile industry: concepts, technologies and benefits, *J. Clean. Prod*., 12(2004), 585-601.
8. A. Singh, A. Kaur, A. K. Patra, R. Mahajan, A sustainable and green process for scouring of cotton fabrics using xylano-pectinolytic synergism: switching from noxious chemicals to eco-friendly catalysts, 3 *Biotech*., 8(2018), 184-193.
9. A. Kaur, L. M. Varghese, B. Battan, A.K. Patra, R.P. Mandhan, R. Mahajan, Bio-degumming of banana fibers using eco-friendly crude xylano-pectinolytic enzymes, *Prep. Biochem. Biotech.*, 50(2020), 521-528.
10. J. Chen, Q. Wang, Z. Hua, G. Du, Research and application of biotechnology in textile industries in China, *Enzyme Microb. Technol*., 40(2007), 1651-1655.
11. A. Singh, L.M. Varghese, B. Battan, A.K. Patra, R.P. Mandhan, R. Mahajan, Eco-friendly scouring of ramie fibers using crude xylano-pectinolytic enzymes for textile purpose, *Environ. Sci. Pollut. Res*., 27(2020), 6701-6710.
12. M. Hosseinnezhad, K. Gharanjig, R. Jafari, H. Imani, Green dyeing of woolen yarns with weld and madder natural dyes in the presences of biomordant, *Prog. Color Colorants Coat*., 14(2021), 35-45.
13. H. Dave, L. Ledwani, S.K. Nema, Nonthermal plasma: A promising green technology to improve environmental performance of textile industries, in: The Impact and Prospects of Green Chemistry for Textile Technology(I. Shahid, B.S. Butola), Woodhead Publishing, Sawston, USA, (2019), 199-249.
14. M. Hosseinnezhad, K. Gharanjig, S. Belbasi, S.H. Seied Saadati, Green dyeing of Silk Fabrics in the Presence of Pomegranate Extract as Natural mordant, *Prog. Color Colorants Coat.,* 10(2017), 129-133.
15. T. Hussain, A. Wahab, A critical review of the current water conservation practices in textile wet processing, *J. Clean. Prod*., 198(2018), 806-819.

16. I. Shahid ul, B.S. Butola, A. Kumar, Green chemistry based in-situ synthesis of silver nanoparticles for multifunctional finishing of chitosan polysaccharide modified cellulosic textile substrate, Inter. *J. Biolog. Macromol*., 152(2020), 1135-1145.
17. N. Wang, P. Tang, C. Zhao, Z. Zhang, G. Sun, An environmentally friendly bleaching process for cotton fabrics: mechanism and application of UV/H_2O_2 system, *Cellul*., 27(2020), 1071-1083.
18. S. Yousef, M. Tatariants, M. Tichonovas, L. Kliucininkas, S.-I. Lukošiūtė, L. Yan, Sustainable green technology for recovery of cotton fibers and polyester from textile waste, *J. Clean. Prod*., 254(2020), 120078-120090.
19. R. F. Nascimento, A. O. d. Silva, R. P. Weber, S. N. Monteiro, Influence of UV radiation and moisten associated with natural weathering on the ballistic performance of aramid fabric armor, *J. Mater. Res. Technol*., 9(2020), 10334-10345.
20. S. Ben Hmida, N. Ladhari, Study of parameters affecting dry and wet ozone bleaching of denim fabric, *Oz: Sci. Eng*., 38(2016), 175-180.
21. M. Rayung, N. A. Ibrahim, N. Zainuddin, W. Z. Saad, N. I. Razak, B. W. Chieng, The effect of fiber bleaching treatment on the properties of poly(lactic acid)/oil palm empty fruit bunch fiber composites, *Inter. J. Molecul. Sci*., 15 2014), 14728-14742.
22. T. Wang, Y. Zhao, Optimization of bleaching process for cellulose extraction from apple and kale pomace and evaluation of their potentials as film forming materials, *Carbohydr. Polym*., 253(2021) 117225.
23. P. Golkar Taft, S. Jafarnia, E. Tabatabee Ghomshe, N. Chiniforush, L. Ranjbar Omrani, Effect of conventional in-office bleaching and laser assisted bleaching at two different wavelengths on Color stability of glass-Ionomers, *J. Islam. Dent. Assoc. Iran*., 29(2017), 7-14.
24. L. Xia, L. L. Lu, Y. X. Liang, Preparation and characterization of poly(lactic acid) micro- and nanofibers fabricated by centrifugal spinning, *Fiber. Polym.*, 21(2020), 1422-1429.
25. F. S. Fattahi, A. khoddami, O. Avinc, Sustainable, renewable, and biodegradable poly(lactic acid) fibers and their latest developments in the last decade, sustainability in the textile and apparel industries, In: Sustainability in the textile and apparel industries (S. S. Muthu, M. A. Gardetti), Springer International Publishing, Switzerland, 2020, 8.
26. F. S. Fattahi, Quantitative analyze of fourier transform Infrared spectroscopy (FTIR) of Poly (Lactic Acid) after UV/Ozone Irradiation, *J. Text. Sci. Technol.*, 8(2019), 47-55.
27. F. S. Fattahi, A. Khoddami, J. Rahmatinejad, Nanoscale roughness on the surface of polyester fibers through ultraviolet/ozone treatment, *Iran. J. Polym. Sci. Technol.*, 32(2020), 457-473.
28. F. Fattahi, H. Izadan, A. Khoddami, Investigation into the effect of UV/Ozone irradiation on dyeing behaviour of poly(lactic acid) and poly(ethylene terephthalate) substrates, *Prog. Color Colorants Coat.,* 5(2012), 15-22
29. F. S. Fattahi, A. Khoddami, H. Izadan, Review on production, properties, and applications of poly(lactic acid) fibers, *J. Text. Sci. Technol*, 14(2015), 11-17.
30. G. Jacucci, L. Schertel, Y. Zhang, H. Yang, S. Vignolini, Light management with natural materials: from whiteness to transparency, *Adv. Mater.*, 23(2020), 2001215.
31. F. Fattahi, H. Izadan, A. Khoddami, Deep dyeing of poly(lactic acid) and poly(ethylene terephthalate) fabrics using UV/Ozone irradiation, in 4th International color and coatings congress (ICCC), Iran, 2011.
32. N. I. Razak, N. A. Ibrahim, N. Zainuddin, M. Rayung, W.Z. Saad, The influence of chemical surface modification of kenaf fiber using hydrogen peroxide on the mechanical properties of biodegradable kenaf fiber/poly(Lactic Acid) composites, *Molecul*., 19(2014).
33. N. Špička, Ž. Zupin, J. Kovač, P.E. Forte Tavčer, Enzymatic scouring and low-temperature bleaching of fabrics constructed from cotton, regenerated bamboo, poly(lactic acid), and soy protein fibers, *Fiber. Polym.*, 16(2015), 1723-1733.
34. D. Battegazzore, T. Abt, M.L. Maspoch, A. Frache, Multilayer cotton fabric bio-composites based on PLA and PHB copolymer for industrial load carrying applications, *Compos: B. Eng.*, 163(2019), 761-768.
35. D. Phillips, J. Suesat, M. Wilding, D. Farrington, S. Sandukas, D. Sawyer, J. Bone, S. Dervan, Influence of different preparation and dyeing processes on the physical strength of the Ingeo fibre component in an Ingeo fibre/cotton blend. Part 2; Bleaching followed by dyeing with disperse and reactive dyes, *Color. Technol*., 120(2004), 41-45.
36. M. Sadeghi-Kiakhani, S. Safapour, F. Sabzi, A.R. Tehrani-Bagha, Effect of ultra violet (UV) irradiation as an environmentally friendly pre-treatment on dyeing characteristic and colorimetric analysis of wool, *Fiber. Polym*., 21(2020), 179-187.
37. Y. Yang, S. Kim, W.Y. Kim, Effect of ozone treatment on ferroelectric polymer film, *Mol. Cryst. Liq. Cryst.,* 704(2020), 119-124.
38. J. W. Gooch, Whiteness Index, In: Encyclopedic Dictionary of Polymers, Springer, New York, US, 2011, 811-811.
39. M. M. Mahdi, F. Tuj-Zohra, S. Ahmed, Dyeing of shoe upper leather with extracted dye from acacia nilotica plant bark-An eco-friendly initiative, *Prog. Color Colorants Coat.,* 14(2020), 241-258.
40. R. Jafari, M. Shahmohammadi, Evaluation of performance of uchida whiteness formula in CIE modified tinting region, *J. Color Sci. Technol*., 11(2017), 23-34.
41. R. Jafari, The dependency of colorimetric characteristics of black fabrics to the whiteness attribute of substrate, *Prog. Color Colorant Coat.*, 11(2018), 113-122.

42. M. Safi, N. Khalili, Effect of measurement geometry on the colorimetry of glossy white samples, *J. Color Sci. Technol*., 14(2020), 237-246.
43. M. Safi, N. Khalili, A.M. Arabi, Effect of various opacifiers on color parameters and gloss of glazed tiles, *J. Color Sci. Technol.*, 5(2011), 253-261.
44. R. Jafari, S.H. Amirshahi, Spectral reconstruction of blacks and whites by using the statistical *colorants, Prog. Color Colorants Coat.,* 8(2015), 135-144.
45. M. İ. Bahtiyari, H. Benli, Ozone bleaching of cotton fabrics with the aid of ultrasonic humidifier, *Cellul.*, 23(2016), 2715-2725.
46. H. Benli, M. İ. Bahtiyari, Combination of ozone and ultrasound in pretreatment of cotton fabrics prior to natural dyeing, *J. Clean. Prod*., 89(2015), 116-124.
47. R. Jafari, A Review on Blackness, *J. stud. Color World.*, 4(2014), 21-32.
48. R. Jafari, Achromatics: Definitions, Concepts and Indices (Part I: Whiteness), *J. stud. Color World.*, 4(2014), 49-56.
49. F. Taheri, M. Safi, R. Jafari, A review on the application of optical brightener agents in textile industry, *J. Stud. Color World.*, 9(2019), 65-78.
50. F. S. Fattahi, Quantitative analyze of fourier transform infrared spectroscopy (FTIR) of poly (lactic acid) after UV/Ozone irradiation, *J. Text. Sci. Technol.*, 8(2019), 47-55.
51. F. S. Fattahi, S. A. mousavi shoushtari, An introduction to UV/Ozone treatment and its applications in the surface engineering of polymeric fibers and films, *J. Stud. Color World.*, 10(2020), 65-76.
52. D. Hetemi, J. Pinson, Surface functionalisation of polymers, *Chem. Soc. Rev.,* 46(2017) 5701-5713.
53. A. Prasetyaningrum, W. Widayat, B. Jos, Y. Dharmawan, R. Ratnawati, UV irradiation and ozone treatment of κ-carrageenan: kinetics and products characteristics, *Bull. Chem. React. Eng. Catal., 15*(2020), 319-330.
54. E. Najafi, J. Y. Kim, S.-H. Han, K. Shin, UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion, *Colloids Surf :A Physicochem. Eng. Asp.*, 284-285(2006), 373-378.
55. C. V. Rekhate, J. K. Srivastava, Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review, *Chem. Eng. J. Adv.*, 3(2020), 100031.
56. Y. Pan, Y. Wu, H.A. Hsain, R. Su, C. Cazorla, D. Chu, Synergetic modulation of the electronic structure and hydrophilicity of nickel–iron hydroxide for efficient oxygen evolution by UV/ozone treatment, *J. Mater. Chem: A*, 8(2020), 13437-13442.
57. A. Muhammad Nur Amir, Y. Ahmad Nor, N. Samsudin, A. Ma'an Fahmi Rashid, Y. Tshai Kim, Surface functionalization of mesoporous hollow carbon nanoparticles using UV/Oozne treatment, *Biolog. Nat. Resour. Eng. J.*, 3(2020), 35-45.
58. W. Xu, J. Jiang, L. Han, X. Feng, Highly efficient UV-Ozone treatment for IAZO active layer to facilitate the low temperature fabrication of high performance thin film transistors, *Ceram. Int.,* 46(2020), 17295-17299.
59. J. Li, J. K. Kim, M. Lung Sham, Conductive graphite nanoplatelet/epoxy nanocomposites: Effects of exfoliation and UV/ozone treatment of graphite, *Scr. Mater.*, 53(2005), 235-240.
60. W. Qin, Z. Lin, H. Dong, X. Yuan, Z. Qiang, S. Liu, D. Xia, Kinetic and mechanistic insights into the abatement of clofibric acid by integrated UV/ozone/peroxydisulfate process: A modeling and theoretical study, *Water Res.*, 186(2020), 116336.
61. K. Jung, D.H. Kim, J. Kim, S. Ko, J.W. Choi, K.C. Kim, S.-G. Lee, M.-J. Lee, Influence of a UV-ozone treatment on amorphous SnO_2 electron selective layers for highly efficient planar MAPbI3 perovskite solar cells, *J. Mater. Sci. Technol.*, 59(2020), 195-202.
62. F. Fattahi, H. Izadan, A. Khodami, Investigation into the effect of UV/Ozone irradiation on the dyeing behaviour of poly(lactic acid) and poly(ethylene terephthalate) substrates, *Prog. Color Colorants Coat.,* 5(2012), 15-22.
63. Y. J. Kang, H. Chung, M.-S. Kim, W. Kim, Enhancement of CNT/PET film adhesion by nano-scale modification for flexible all-solid-state supercapacitors, *Appl. Surf. Sci.*, 355(2015), 160-165.
64. C. Urata, B. Masheder, D.F. Cheng, A. Hozumi, How to reduce resistance to movement of alkane liquid drops across tilted surfaces without relying on surface roughening and perfluorination, *Langmuir.*, 28(2012), 17681-17689.
65. J. Liu, L. He, L. Wang, Y. Man, L. Huang, Z. Xu, D. Ge, J. Li, C. Liu, L. Wang, Significant enhancement of the Adhesion between metal films and polymer substrates by UV–Ozone surface modification in Nanoscale, *ACS Appl. Mater. Interf.*, 8(2016), 30576-30582.
66. S. Periyasamy, D. Gupta, M.L. Gulrajani, Nanoscale surface roughening of mulberry silk by monochromatic VUV excimer lamp, *J. Appl. Polym. Sci.*, 103 (2007), 4102-4106.
67. F. Fattahi, A. Khodami, O. Avinc, Nano-structure roughening on poly(lactic acid)PLA substrates: scanning electron microscopy (SEM) surface morphology characterization, *J. Nanostruct.*, 10(2020), 206-216.
68. E. M. Kim, J. Jang, Surface modification of meta-aramid films by UV/ozone irradiation, *Fiber. Polym.*, 11(2010), 677-682.
69. B. Dudem, L.K. Bharat, J.W. Leem, D.H. Kim, J.S. Yu, Hierarchical Ag/TiO_2/Si forest-like nano/micro-architectures as antireflective, plasmonic photocatalytic, and self-cleaning coatings, *ACS Sustain. Chem. Eng.*, 6(2018), 1580-1591.
70. J. Jang, Y. Jeong, Nano roughening of PET and PTT fabrics via continuous UV/O3 irradiation, *Dyes Pigm.,* 69(2006), 137-143.

71. G. H. Koo, J. Jang, Surface modification of poly(lactic acid) by UV/Ozone irradiation, *Fiber. Polym.*, 9(2008), 674-678.

72. D. W. Yun, J. Jang, Surface modification of ultra high molecular weight polyethylene films by UV/ozone Irradiation, *Text. Color. Finish*., 23(2011), 76-82.

How to cite this article:
F.S. Fattahi, A Comparative Study on the Environmental Friendly Bleaching Processes of Poly(lactic acid) Substrate: Application of Ultraviolet/O_3/H_2O_2 System. Prog. Color Colorants Coat., 15 (2022), 143-156.