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Bleaching of Hemp (*Cannabis Sativa* L.) Fibers with Peracetic Acid for Textiles Industry Purposes

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Abstract: Hemp plant exhibits various eco-friendly properties and hemp fiber processing does not cause environmental damage, however, it is known that most chemical operations have a risk to interrupt a sustainable production. As stated in several studies, peracetic acid is an important environmental friendly bleaching agent when compared to its conventional competitors. In this study, hemp fabric was bleached with peracetic acid with exhaustion and padding methods. The effects of temperature, pH, process time, concentration on whiteness values were determined. The influences of bleaching processes were investigated via instrumental and imaging methods. Physical properties of the treated fibers were also tested. Besides peracetic acid, hydrogen peroxide bleaching was carried out for comparison. COD values of bleaching effluents were analyzed for selected samples. Higher whiteness values were obtained with exhaustion bleachings than pad-batch bleachings. Quite high whiteness values (up to 68.13 Stensby whiteness index) attained in peracetic acid without significant fiber damage.

Keywords: Hemp, Peracetic acid, Bleaching, Hydrogen peroxide, Eco-friendly

Introduction

Textile industry faces with very serious criticisms about environmental pollution, from this point of view; protection of the environment has become one of the most important priorities of this sector. Cotton and synthetics meet a large part of the fiber demand of the world, however, synthetic fiber production is associated with fossil fuels and cotton cultivation requires high water and agricultural chemical consumption [1]. On the other hand, hemp fiber step forwards with its superior eco-friendly properties and organic textile production potential [2-8] Hemp plant which accords a wide range of agro-ecological conditions, is high yielding crop compared to many others. Being a low-input crop, providing natural weed control and low fertilizer requirement are important advantages of hemp plant agriculture [9,10]. Moreover, hemp fiber provides excellent usage performance such as high water permeability, ultraviolet light blocking, anti-static and anti-microbial properties, superior thermal properties and anti-allergic clothing performance [11,12]. European Union funded a project which aimed to support hemp cultivation and fiber production under the thematic program: Quality of life and management of living resources of the 5th Framework [13].

The color properties of bast fibers such as hemp, flax and ramie are usually not suitable for textile applications in their raw form. Due to the non-cellulosic components present in these fibers, the color properties are generally required to be enhanced by a chemical process [14]. However, bast fibers are more resistant to chemical effects than cotton because of their higher crystalline structure [15].

Chlorophyll, xanthophyll, carotene and derivatives of those are the coloring matters in bast fiber nature which are relevant with complex tannin compounds and exist in cortical cells [16]. Also, cambium cells are another source of coloring matters which are relevant with proteins, containing aromatic groups [16]. Besides these natural occurring colorants, textile products might be polluted with external factors (dust, oil, plant particles, water, etc.) and get undesirable colors during processing and storage [17]. The purpose of bleaching is not only removing undesirable colorants but also decompose these compounds [15,17,18].

Hypochlorides and hydrogen peroxide are intensely used in textile industry for bleaching purposes; however, hypochlorite bleaching is being abandoned nowadays due to its harmful effects to the environment [19]. Although hydrogen peroxide has bio-degradable properties itself, there are serious drawbacks of processing with this chemical, since highly alkaline conditions and auxiliary chemical usage is required for the usage of this chemical which results in heavy chemical load in effluents [20]. Moreover, hydrogen peroxide bleaching is performed under high temperature with long process times which causes higher energy consumption. Additionally, there is high water consumption during after-treatment procedures [20]. On the other hand, peracetic acid (PAA) exhibits maximum bleaching performance at mild process conditions and moderate temperature levels. It is known that peracetic acid is highly reactive and a strong oxidization agent [19, 21]. Also, there is no need for neutralization process, only washing is sufficient. So, peracetic acid enables an eco-friendly bleaching with low water, energy and chemical consumption [20]. As the degradation products of PAA are oxygen and acetic acid, it is an environmentally safe bleaching agent [20,22].

Presa and Tavcer [23] investigated the one bath application of bio-scouring and PAA bleaching of cotton. They stated

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that moderate whiteness values were accompanied by good water absorption and low fiber damage. Prabaharan *et al.* [19] studied the optimization of PAA bleaching of cotton. It is reported that optimum bleaching results were obtained at 30 g/*l* PAA (10 %) application in neutral or mildly acidic medium [19]. It is further stated that the most effective application conditions of peracetic acid are pH 6-7 at 50-80 °C for 20-60 minutes processing time depending on the application temperature [20]. Gursoy and Dayıoglu [21] investigated PAA production in bleaching bath and the bleaching performance of synthesized PAA on cotton. Abdel-Halim and Al-Deyab [20] studied on bleaching of cotton with PAA which was prepared through the reaction of hydrogen peroxide and glacial acetic acid in the presence of sulfuric acid catalyst Duan *et. al.* analyzed the structural effects of peracetic acid bleaching on jute fibers. They stated that cellulose content had increased due to the removal of non-cellulosic components such as lignin and hemicellulose [24]. Wang and Postle investigated the color properties of hemp fibers after chemical processing [8].

Recently, hemp fibers have drawn attention for composites production. Since superior mechanical properties and being an environmental-friendly material league together, these fibers become a preferred option for composite designers. Hemp and flax fiber composites exhibited good specific stiffness (higher than glass fiber composites, slightly lower than carbon fiber composite in plate bending) in tension and plate bending. Moreover composites consist of hemp and flax fibers have good vibration damping capacity which makes them operable for musical instrument production [25, 26]. As a renewable source, hemp fiber can be also utilized for composites in building elements [27].

The main scope of this study was to bleach an eco-friendly fiber with an eco-friendly method. For this purpose, PAA and hydrogen peroxide bleaching of hemp fibers were investigated and the results were compared with each other. Bleachings were carried out with exhaustion and pad-batch methods. Whiteness of samples was determined and tenacity loses were measured. In order to comprehend the detailed physical changes on surface morphology of fibers, SEM and florescent microscobe images were evaluated. The bleaching bath effluents of exhaustion processes were analyzed to examine the environmental effects, in respect of chemical oxygen demand (COD), of bleaching operations. Reactive dye uptakes were also measured for selected bleached samples.

Experimental

Fabric

Plain woven greige fabric composed from 20/1 Nm 100 % hemp yarns (16 yarn/cm warp, 12 yarn/cm weft) was used for bleaching applications.

Alkali Scouring

Alkali scouring was performed before bleaching operations in order to improve the hydrophilicity of the fabric and aid for a more effective bleaching effect. Scouring process was designed considering the former studies [28,29], regarding the chemical processing of linen textile materials. Scouring was carried out using 5 g/*l* sodium hydroxide, 3 g/*l* soda ash and 1 g/*l* wetting agent at 95 °C for 60 minutes with 1:20 liquor ratio. Then the fabric was warm washed and subsequently neutralization step was applied using 1 m*l*/*l* acetic acid for 15 minutes at 1:20 liquor ratio. Finally, fabric was cold rinsed and air-dried.

Bleaching

Atac Lab Dye HT (Istanbul, Turkey) and Atac F-350 (Istanbul, Turkey) laboratory type machines were used for exhaustion and padding applications, respectively. Exhaustion bleaching operations were carried out in 1:30 liquor ratio for both PAA (40 %, Sigma Aldrich) and hydrogen peroxide (50 %, Tekkim) applications. Six (2-30 m*l*/*l*) hydrogen peroxide concentrations were applied at 95 °C for 30-90 minutes in company with 1.5 g/*l* NaOH and 3 m*l*/*l* stabilizing agent as bleaching auxiliary chemicals. PAA (40 %) bleachings were performed with seven different concentrations (2.5-30 m*l*/*l*) at pH 5, 7 and 9 at 70 °C. After the evaluation of whiteness values after PAA bleaching at these conditions, PAA bleaching was also carried out at 70 °C with varied pH levels of pH 5-pH 10 for more sensitive optimum pH detection. To investigate the effect of temperature, PAA bleachings were carried out at 50, 70 and 95 °C with 10-30 m*l*/*l* PAA concentrations.

Pad-batch process was carried out with five concentrations (40, 60, 80, 100 and 120 m*l*/*l*) and three waiting times (12, 18 and 24 hours) for both hydrogen peroxide and PAA bleachings. Liquor uptake was 100 %. 40 m*l*/*l* 38°Be NaOH, 1 m*l*/*l* wetting agent, 5 m*l*/*l* stabilizing agent were added to hydrogen peroxide bleaching liquor. pH was adjusted to 7 at pad-batch bleaching with PAA and 1 m*l*/*l* wetting agent was added.

Determination of Whiteness Properties

DataColor 600 spectrophotometer (New Jersey, USA) was used for whiteness measurements. Stensby whiteness indices were determined according to equation (1).

$$WI_{Stensby} = L + 3a - 3b \tag{1}$$

where L^*, a^*, b^* are CIELAB color scale values.

Assessment of Reactive Dye Uptake

Selected hemp fabric samples were dyed with C.I. Reactive Blue 235 with 2 % owf at 60 °C using Atac Lab-Dye HT machine. Exhaustion yields were determined by UV-vis spectrophotometer (Perkin Elmer). The dye uptake was calculated by following equation:

$$E\% \text{ (Exhaustion)} = ((A_0 - A_1)/A_0) \times 100 \quad (2)$$

where, A_0 and A_1 are the absorbance values of dye liquors at λ_{max} before and after dyeing, respectively.

FTIR Spectroscopy

The infrared analysis was performed using a Perkin Elmer Spectrum Two^{TM} Infrared Spectrometer (FT-IR) (Massachusetts, USA) with diamond universal ATR accessory in ATR mode, employing a Diamond crystal giving an effective depth of penetration of 1 micron, and at a resolution of 4 cm^{-1}. The recorded spectrum for each sample was the average of 4 scans.

Fluorescent Microscopy and SEM Images

Fluorescent microscope images were taken by Olympus BX3 model microscope (Tokyo, Japan) with blue filter (460-495 nm) with 4x magnification. SEM images were taken by FEI QUANTA 250 FEG electron microscope (Oregon, United States).

Determination of Redox Potential

Redox potentials of the peracetic acid bleaching liquors (pH 7, room temperature) were determined by Hanna HI 9126 pH/OPR meter (Rhode Island, USA).

Determination of Tenacity, Crease Recovery Angle and Hydrophilicity

Tenacity values of hemp yarns, separated from fabrics, were measured with Tinius Olsen H10KT Benchtop Tester (Redhill, United Kingdom) according to BS EN ISO 2062 1995 (2009) standard. Crease recover angles were determined according to BS EN 22313:1992 standard. DIN54924 standard was utilized for hydrophilicity tests.

Stated tests were carried out on selected following samples which exhibited high whiteness values. For the ease of following, these samples were encoded as follows; A: 90 minutes 20 m*l*/*l* H_2O_2 application at 95 °C, B: 90 minutes 30 m*l*/*l* PAA application at 95 °C, C: 90 minutes 15 m*l*/*l* PAA application at 70 °C, D: Pad-batch application of 120 m*l*/*l* H_2O_2 with 24 hours waiting, E: Pad-batch application of 100 m*l*/*l* PAA with 24 hours waiting.

Chemical Oxygen Demand (COD) Measurement

Chemical Oxygen Demand (COD) values (in mg O_2/*l*) of the effluents of bleaching baths were measured by titration with potassium dichromate ($K_2Cr_2O_7$) according to Chemical Oxygen Demand Method 5220.

Results and Discussion

Exhaustion Bleaching

Hydrogen Peroxide Bleaching

Hydrogen peroxide is commonly used as a bleaching agent for textile industry. Generally, 2-4 m*l*/*l* hydrogen peroxide concentration is sufficient for cotton bleaching in commercial applications in order to achieve required whiteness levels. However, due to the more crystalline structure and high amount of non-cellulosic impurities, hemp fiber is harder to bleach than cotton [15]. As a result, the highest whiteness value was attained by 90 minutes application with 20 m*l*/*l* hydrogen peroxide concentration, which is about ten times greater than that of used for cotton bleaching. The whiteness values of hydrogen peroxide bleached hemp fibers were shown on Figure 1.

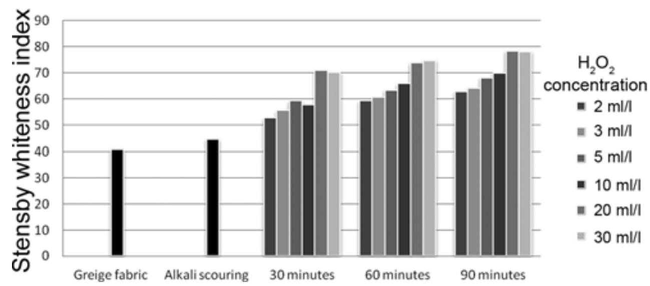

Figure 1. The change on whiteness values of hydrogen peroxide bleached samples depending on concentration and processing time.

The lowest whiteness value, among all hydrogen peroxide bleached samples, was 52.75 Stensby which was obtained following 2 m*l*/*l* hydrogen peroxide bleaching for 30 minutes. It is clear that an increase on hydrogen peroxide concentration and bleaching time resulted in higher whiteness levels (Figure 1). The highest whiteness value of 78.51 Stensby was attained by 20 m*l*/*l* hydrogen peroxide bleaching for 90 minutes. There were very slight and negligible changes between 20 m*l*/*l* and 30 m*l*/*l* hydrogen peroxide bleaching processes for all different bleaching process durations in respect of final whiteness levels (Figure 1). For example, as it can be seen from Figure 1, 20 m*l*/*l* and 30 m*l*/*l* peroxide bleaching processes for 90 minutes led to very similar close whiteness results. This observation was actually in line with the findings of Hou *et al.* who applied cationic activator for hydrogen peroxide bleaching of cotton and stated that whiteness values had not been improved above certain hydrogen peroxide concentration [30].

It is thought that the highest attained whiteness value of 78.51 Stensby was adequate for fabrics which will be used as pure white and/or dyed for light depth of shades. On the other hand, lower whiteness values measured such as 55.62 Stensby (after 3 m*l*/*l* H_2O_2 application for 30 minutes), 59.37 (after 2 m*l*/*l* H_2O_2 application for 60 minutes), 64.21 (after 3 m*l*/*l* H_2O_2 application for 90 minutes) etc. could be sufficient for fabrics which will be dyed for heavy depth of shades to obtain dark colors.

Peracetic Acid Bleaching

Although there are studies available in the literature about the bleaching applications of peracetic acid (PAA), the use of this chemical for hemp fiber bleaching is a novel issue. Therefore, a detailed investigation of peracetic acid (PAA)

Table 1. Whiteness levels of hemp fiber fabrics after peracetic acid (PAA) bleaching at 70 °C under various bleaching time, PAA concentration and bleaching pH conditions

Bleaching pH	Peracetic acid concentration (m*l*/*l*)	Whiteness index (Stensby) Bleaching time (minutes) 30	60	90
5	2.5	49.51	50.69	51.76
	5	50.56	52.96	54.32
	7.5	51.15	53.49	55.21
	10	52.65	54.11	55.87
	15	54.15	56.45	58.14
	20	56.11	55.27	60.31
	30	57.18	57.17	62.81
7	2.5	51.38	52.51	53.45
	5	53.68	54.74	56.49
	7.5	53.47	56.13	57.90
	10	54.62	57.37	58.52
	15	56.86	59.27	61.58
	20	59.79	58.97	62.36
	30	60.26	59.22	60.10
9	2.5	52.36	52.54	54.41
	5	53.26	55.55	56.82
	7.5	56.74	57.17	58.55
	10	57.93	57.13	59.69
	15	59.84	60.55	61.12
	20	62.12	61.06	63.08
	30	61.52	62.28	62.11
Greige fabric			40.90	
Alkali scoured fabric			44.67	

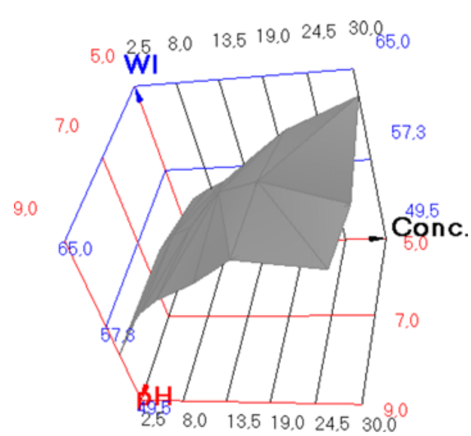

Figure 2. Whiteness changes (by Stensby) of hemp fabrics, bleached at 70 °C for 90 minutes, depending on the bleaching pH and peracetic acid (PAA) concentration.

bleaching process parameters for hemp fiber is essential to acquire the optimum PAA bleaching conditions for this biodegradable, sustainable and renewable bio-fiber. For this reason, in this study, the effects of different bleaching condition parameters such as temperature, concentration, duration and pH were investigated on the final properties of hemp fiber fabric substrate. The effects of various peracetic acid (PAA) bleaching process conditions such as bleaching time, PAA concentration and bleaching pH on the whiteness properties of hemp fiber fabric, bleached at 70 °C, are shown on Table 1 and Figure 2.

Effect of Peracetic Acid Concentration

Seven PAA (40 %) concentrations, ranging between 2.5 m*l*/*l* and 30 m*l*/*l*, were examined with different bleaching process time and pH conditions. The peracetic acid concentration directly affected the whiteness property (Table 1 and Figure 2). Especially at low concentrations, the effect of PAA concentration increase on whiteness property was more obvious.

For instance, 5.7 % whiteness increase was detected between 2.5 m*l*/*l* PAA bleaching and 5 m*l*/*l* PAA bleaching at pH 7 for 90 minutes application, whereas whiteness difference was only 1.3 % for higher PAA concentrations, between 15 m*l*/*l* PAA bleaching and 20 m*l*/*l* PAA bleaching operations, again at pH 7 for 90 minutes application. This situation indicates that whiteness values of hemp fabrics either increase very slightly or reach a plateau leading to similar close whiteness levels at bleaching operations with high PAA concentrations. This can clearly be seen from Figure 3 that whiteness index versus PAA concentration graph is a concave down and exhibit gradual whiteness increase with decreasing slope. This observation was also supported by the redox potentials of PAA bleaching liquors measured at the room temperature (Figure 3). Since akin hyperbolic rise was also measured for the redox potential of blank peracetic acid (PAA) bleaching liquor (without the

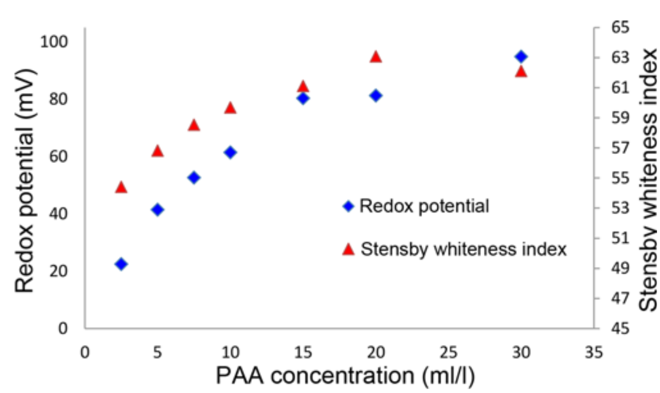

Figure 3. Relation between the redox potential of blank peracetic acid (PAA) bleaching liquors (without hemp fabric presence) and whiteness values attained with 90 minutes application at 70 °C and pH 9.

hemp fabric involvement) with respect to PAA concentration increase. Higher PAA concentration resulted in higher redox potential leading to higher whiteness results on hemp fabrics (Figure 3).

Although the best whiteness performances on hemp fabrics were attained after bleaching with 15-30 m*l*/*l* PAA concentrations, the whiteness levels of hemp fabrics were reaching a plateau and very close after bleaching operations with high PAA concentrations (Table 1 and Figure 3). This means that higher and/or extreme PAA bleaching agent use is not going to result in significantly higher whiteness increase. These high (15-30 m*l*/*l*) peracetic acid concentrations were about ten times greater bleaching agent concentrations than hydrogen peroxide concentration which is generally used for industrial scale cotton bleaching. Therefore, such high PAA concentration usage for hemp bleaching seems to be too high for commercially acceptable limits. Nonetheless on the other hand, it is also important to remind that similar high concentration hydrogen peroxide bleaching processes were needed for higher whiteness levels attainment on hemp fabrics (Figure 1), since, hemp fiber exhibits brownish color with higher amount of natural colorants presence and as well as it contains higher non-cellulosic materials and impurities in comparison to cotton fiber [8,14]. Therefore, hemp fiber needs fairly more aggressive bleaching operation in comparison to cotton fiber. Despite everything, it is important to state that high amount of bleaching agent usage is generally not desirable in the textile industry from the economic and environmental point of views.

Effect of Peracetic Acid Bleaching Process Time

As indicated earlier, the applied peracetic acid bleaching durations were 30, 60 and 90 minutes at 70 ^{o}C. In general, there was an increasing trend on whiteness in relation to an increase on bleaching duration (Table 1). So, higher bleaching application times generally resulted in higher whiteness levels when it compared to the bleaching applications with the same peracetic acid concentration applied at same pH conditions. So, higher amount of peracetic acid should be applied to hemp fiber for 30 minutes bleaching applications in order to attain similar level of whiteness with 90 minutes bleaching applications (Table 1). In some cases such as at pH 7 and pH 9 with high peracetic acid concentration (30 m*l*/*l*) applications, whiteness levels were getting closer and the measured whiteness differences of different processing durations were low (Table 1). For instance, the whiteness values of the hemp fabrics bleached for 30 and 90 minutes at pH 7 with 30 m*l*/*l* PAA were both around 60 Stensby. This means that lower peracetic acid bleaching durations can be chosen at high concentration applications. Bleaching applications with lower durations are obviously advantages for faster production time with lower energy consumption due to lower machinery use durations. On the other hand, one should not forget that high chemical consumption with higher amount of bleaching agent use has some disadvantages such as environmental problems and high cost. So, all these pros and cons of the peracetic acid bleaching conditions should be carefully evaluated in comparison with the level of whiteness achieved and the optimum bleaching conditions should be chosen accordingly.

Effect of Peracetic Acid Bleaching pH

Effect of pH on peracetic acid (PAA) bleaching for hemp fiber was investigated at 70 ^{o}C and with 15 m*l*/*l* peracetic acid concentration. The changes on whiteness values of hemp fibers depending on the pH at 70 ^{o}C bleaching are shown on Figure 4. The bleaching effects of peracetic acid at pH 5, pH 9.5 and pH 10 were significantly lower than those of other pHs studied (Figure 4). After a closer look, the whiteness values of hemp fabrics bleached at pH 5, pH 7 and pH 10 were 58.14, 61.58 and 56.10, respectively. So, bleaching at pH 5 and pH 10 exhibited 5.6 % and 8.9 % less improvement on whiteness when compared to bleaching at pH 7. On the other hand, whiteness values of hemp fibers after the bleaching with pH 5.5-pH 9 range were fairly close to each other. These results are actually in line with the findings of former studies [19,20,31] where stated that neutral or mildly acidic pH conditions were suitable for PAA bleaching for cotton and linen. Yuan [33,34] stated that various peracids reach maximum decomposition rate when pH is equal to peracid's pK_a value, which is 8.2 for peracetic acid. Therefore it was an expected result to obtain higher whiteness values around pH 8-8.5. Prabaharan *et al.* [19] reported two bleaching mechanisms of peracetic acid; nascent oxygen releasing (equation (2)) in the acidic medium and the perhydroxyl radical (HO_2^-) releasing in the neutral or alkali medium. Even though, oxidation potential of atomic oxygen (2.42 V) is higher than perhydroxyl radical (1.70 V) [32], the whiteness indices of mildly acidic, mildly basic and neutral medium bleached hemp fiber samples were very close to each other (Figure 4). It is thought that, the amount of perhydroxyl radical released at the neutral or mildly basic medium might be more than atomic oxygen which is

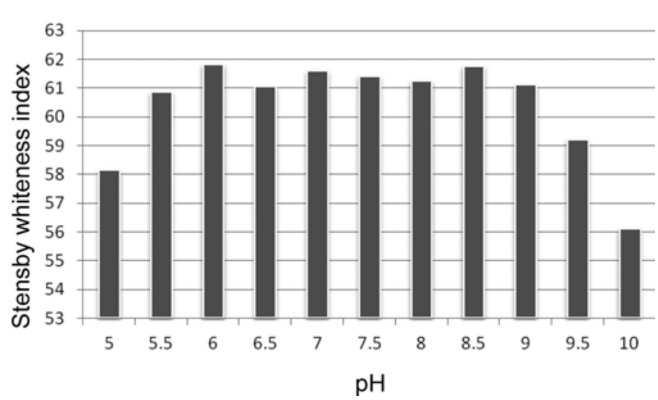

Figure 4. Whiteness property change of hemp fiber depending on peracetic acid bleaching pH condition at 70 ^{o}C.

released at acidic medium leading to similar whiteness performance occurrence

$$CH_3COOOH \rightarrow CH_3COOH + (O) \quad (2)$$

Whiteness values following bleaching at pH 6-9 range were so close to each other, however, bleaching at pH 7 (the whiteness index of 61.58 Stensby) can be recommended, since working at neutral pH will avoid not only the possible cellulose damage which might occur at acidic pH but also the high alkali consumption at basic pH.

Effect of Peracetic Acid Bleaching Temperature

Effect of bleaching temperature (50, 70 and 95 °C) and peracetic acid concentration (10, 15, 20 and 30 m*l*/*l*) on the whiteness values of hemp fibers are shown on Figure 5. The lower bleaching temperatures were applied to investigate the possibility of peracetic acid bleaching at low temperature levels and bleaching at 95 °C was applied to examine the possibility of higher whiteness levels attainment as well as comparison with hydrogen peroxide bleaching process which is usually carried out at this high temperature. As earlier stated, pH 7 can be chosen for hemp fiber bleaching with peracetic acid. Therefore, the effect of bleaching temperature and peracetic acid concentration on hemp fiber bleaching were investigated at pH 7 for 90 minutes.

The results indicate that bleaching temperature is an important parameter on whiteness values of hemp fiber for peracetic acid (PAA) bleaching as well as bleaching pH (Figures 4 and 5). Bleaching at 95 °C resulted in better whiteness values than bleaching at 50 and 70 °C. Hemp fiber fabric bleached with 10 m*l*/*l* PAA at 50 °C exhibited 49.55 Stensby whiteness level, whereas the whiteness levels of greige and scoured hemp fabrics were 40.9 and 44.67, respectively (Figures 5 and 1). 30 m*l*/*l* peracetic acid bleaching at 95 °C led to the highest whiteness level with 68.13 Stensby amongst all peracetic acid bleached hemp samples (Figure 5). There was up to 11 % [between samples bleached at 70 °C (60.1 Stensby) and 95 °C (68.13 Stensby)] difference

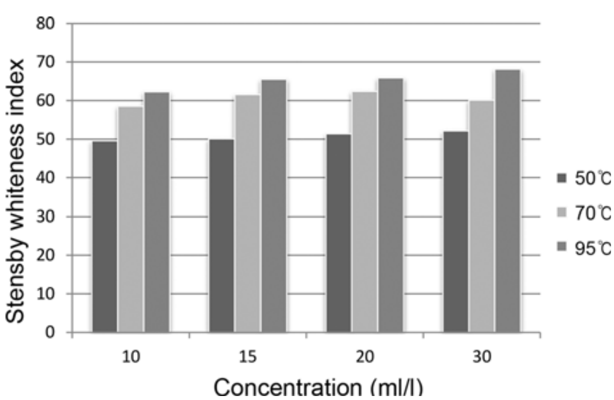

Figure 5. Effect of bleaching temperature and peracetic acid concentration on the whiteness values of hemp fibers.

on whiteness indices for 30 m*l*/*l* peracetic acid applications. It is also notable that, for the same application temperature comparison, whiteness differences between various concentrations were close to each other for 50 °C and 70 °C bleaching processes whereas a more noticeable whiteness increase was observed with bleaching applications at 95 °C. For example, there was only 2.7 % whiteness increase between peracetic acid bleaching applications with 10 and 30 m*l*/*l* at 70 °C; however, 9.4 % whiteness increase was observed between the same bleaching applications with same concentrations at 95 °C (Figure 5). Therefore, it is thought that bleaching temperature is a second-order parameter for low temperature peracedic acid bleaching operations for hemp fiber. Since the degradation of bleaching agent and its bleaching effect gets more aggressive at elevated temperatures, such whiteness increase was an expected result for the same bleaching agent concentration for higher bleaching temperature. In earlier study it was reported that very rapid degradation levels at high application temperatures may lead detachment of oxidizing radicals from the bleaching bath to the atmosphere and end up with whiteness decrease [19]. However, in our study, peracetic acid bleaching was performed in a closed system and no whiteness decrease was observed at 95 °C.

Chemical Oxygen Demand (COD) Values of Bleaching Effluents

Chemical Oxygen Demand (COD) values of the effluents of bleaching baths after bleaching operations are presented in Table 2.

As noticed earlier, peracetic acid is distinguished with its environmental friendly properties.

Higher COD value was measured for hydrogen peroxide bleaching when compared with other two peracetic acid bleaching applications (Table 2). The effluent of 30 m*l*/*l* peracetic acid bleaching bath exhibited less chemical oxygen demand (COD) than that of 20 m*l*/*l* hydrogen peroxide bleaching bath (Table 2). The COD level of 15 m*l*/*l* PAA bleaching effluent was nearly the half of that of 30 m*l*/*l* PAA bleaching effluent (1520 versus 3120 mg O_2/*l*). So it could be said that peracetic acid bleaching is more environmentally-friendly in comparison with hydrogen peroxide bleaching from the chemical oxygen demand (COD) point of view.

Pad-batch Bleaching

The whiteness values of hydrogen peroxide and peracetic

Table 2. Chemical oxygen demand (COD) values of bleaching bath effluents

Bleaching bath effluent type	COD value (mg O_2/*l*)
90 minutes 20 m*l*/*l* H_2O_2 application at 95 °C	5520
90 minutes 15 m*l*/*l* PAA application at 70 °C	1520
90 minutes 30 m*l*/*l* PAA application at 95 °C	3120

acid bleached hemp fabrics with pad-batch method were shown on Figure 6 and Figure 7, respectively. Pad-batch bleaching using peracetic acid and hydrogen peroxide on hemp fiber fabric resulted in low level of whiteness in comparison to previously applied exhaust bleaching method (Figure 1 and Table 1 versus Figures 6 and 7). Especially low bleaching agent concentrations and low waiting times such as 12 hours seem not to be effective for adequate whiteness attainment for both peracetic acid and hydrogen peroxide pad-batch applications.

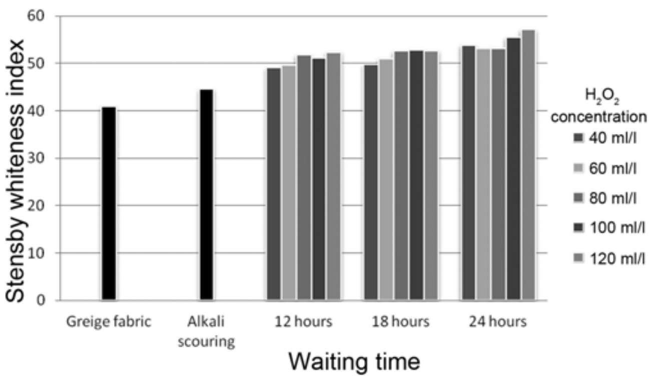

Figure 6. Whiteness indices of hemp fabrics bleached with pad-batch method using hydrogen peroxide.

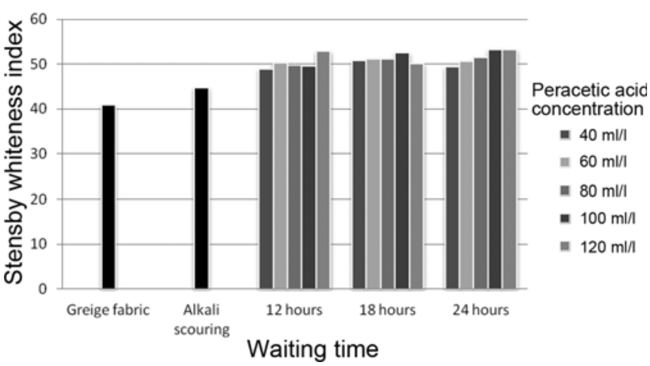

Figure 7. Whiteness indices of hemp fabrics bleached with pad-batch method using peracetic acid.

The best bleaching performance with hydrogen peroxide was achieved with 120 m*l*/*l* concentration and 24 hours waiting time (57.08 Stensby) leading to almost 40 % whiteness improvement considering greige hemp fabric (Figure 6). However, the whiteness values of hydrogen peroxide bleached samples via pad-batch were close to each other. Particularly, whiteness values of the hemp fabrics bleached with different concentrations (40-120 m*l*/*l*) of hydrogen peroxide and waited for 24 hours were very similar. For instance, the lowest whiteness value was 53.86 Stensby (with 40 m*l*/*l* H_2O_2) while the highest whiteness value was 57.08 Stensby (with 120 m*l*/*l* H_2O_2) for 24 hours waiting time. Generally, 40-60 m*l*/*l* hydrogen peroxide is used in the case of pad-batch bleaching of cotton fiber. Although almost double to triple amount of hydrogen peroxide (120 m*l*/*l* H_2O_2) is used for hemp fiber in comparison with the amount used for cotton fiber, the resultant whiteness values of hemp fibers were at low levels.

Similar to pad-batch hydrogen peroxide bleaching, high whiteness values were unable to attain with pad-batch peracetic acid bleaching on hemp fibers for the concentrations and waiting times studied. Whiteness values of PAA bleached samples were close to each other. The lowest whiteness index was 48.88 Stensby (with 40 m*l*/*l* PAA then 12 hours waiting) whereas the highest was 53.21 Stensby (with 100 m*l*/*l* PAA then 24 hours waiting) among PAA pad-batch bleached samples. For the same peracetic acid concentration, there was no drastic increasing trend on the whiteness levels depending on the waiting time. From this point of view, it can be thought that bleaching operation reached a maximum performance then redox reaction slowed down after the bleaching effect culmination and therefore prolonged waiting times did not result in a significant increase on whiteness degrees leading to low whiteness levels.

Table 3. Physical properties of greige, scoured and bleached hemp fiber fabrics

Hemp sample*	Whiteness (Stensby index)	Tensile strength (N)	Elongation (%)	Weight loss (%)	Crease recovery angle	
					Warp	Weft
Greige fabric	40.90	13.26	9.62	-	30	35
Alkali scoured	44.67	12.46	10.19	5.24	53	52
A	78.51	11045	10.70	3.03*	65	70
B	68.13	10.90	7.66	2.37*	64	68
C	61.58	11.26	9.94	1.66*	68	60
D	57.08	12.37	8.27	2.29*	47	56
E	53.21	12.20	7.92	2.80*	59	59

*Weight loss in comparison with alkali scoured fabric, A: 90 minutes 20 m*l*/*l* H_2O_2 exhaustion bleaching application at 95 °C, B: 90 minutes 30 m*l*/*l* peracetic acid exhaustion bleaching application at 95 °C, C: 90 minutes 15 m*l*/*l* peracetic acid exhaustion bleaching application at 70 °C, D: pad-batch bleaching application of 120 m*l*/*l* H_2O_2 with 24 hours waiting, and E: pad-batch application of 100 m*l*/*l* peracetic acid with 24 hours waiting.

Physical Changes on Bleached Hemp Fabrics

In a successful bleaching process, not only the high whiteness values are required but also minimum fiber damage is desired. Measured physical properties of greige, scoured and bleached hemp samples were presented on Table 3. Crease recovery properties of exhaustion bleached samples were improved for both hydrogen peroxide and peracetic acid bleachings. It was thought that the removal of the impurities during scouring and then bleaching process caused better creasing behavior of hemp fabric. On the other hand, the crease recovery angles of pad-batch bleached samples were less than those of exhaustion bleached samples and close to that of scoured hemp fabric.

Weight loss remained limited for all investigated samples which is a preferred result (Table 3). There is no significant decrease on tensile strength properties of hemp fabrics after scouring or respective bleaching operations. The lowest tensile strength and elongation were observed for 90 minutes 30 m*l*/*l* peracetic acid application at 95 °C (Sample B) leading to 17.8 % strength loss in comparison to the greige hemp sample. The measured strength losses after various bleaching operations were not so high and are in the range of 6.7-17.8 % in comparison to the greige hemp sample. Similar strength losses after bleaching processes were up to 12.5 % when compared to scoured hemp sample.

Hydrophilicity of greige, scoured and bleached hemp fabric samples are shown in Figure 8. As a result of higher yarn intensity at warp direction, higher hydrophilicity was observed on warp direction for all studied samples (Figure 8). As expected, the lowest solution heights with the lowest hydrophilic property were detected for greige hemp sample which was related to inherent waxes and other hydrophobic substances of raw hemp fiber (Figure 8). Therefore, all pre-treated hemp fabrics exhibited better hydrophilicity performance than greige hemp fabric due to the removal of such impurities. Although the alkali scoured hemp fabric exhibited the best hydrophilicity performance among all samples, the hydrophilicity level differences between the scoured hemp fabric and other bleached hemp fabrics were not so high. Pejic *et al.* stated that hemicellulose removal of hemp fibers increased the moisture regain whereas lignin removal vice versa [11]. It can be thought that, in parallel with the findings of Pejic *et al.*, possible lignin removal during oxidative bleaching may result in a slight decrease on hydrophilicity capacity. This can be seen from the hydrophilicity degree difference between 90 minutes 30 m*l*/*l* PAA bleaching at 95 °C (Sample B) and 90 minutes 15 m*l*/*l* PAA bleaching at 70 °C (Sample C) (Figure 8). More aggressive peracetic acid bleaching process (30 m*l*/*l* PAA at 95 °C versus 15 m*l*/*l* PAA at 70 °C) led to higher whiteness degree (68.13 Stensby versus 61.58 Stensby) but lower hydrophilicity performance (19, 29, 38 mm and 17, 27, 36 mm rise versus 28, 39, 49 mm and 24, 34, 42 mm rise for weft and warp, respectively) (Figure 8).

According to the SEM images on Figure 9, no dramatic defection was detected on the surface morphologies of treated hemp fibers. The micrographs of Figure 9 show the surfaces of treated hemp fibers with mild longitudinal striations of varying length. These striations were slightly more distinct for exhaustion bleached hemp fibers with peracetic acid and hydrogen peroxide (A, B and C; Figure 9). These slightly more distinct striations might be the

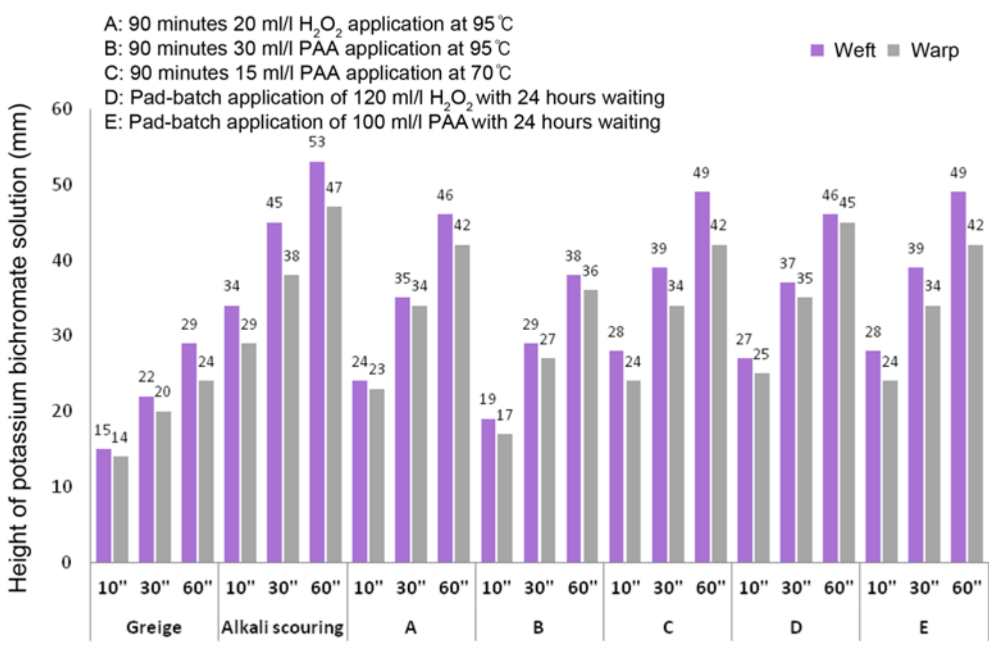

Figure 8. Hydrophilicity of greige, scoured and bleached hemp fabric samples.

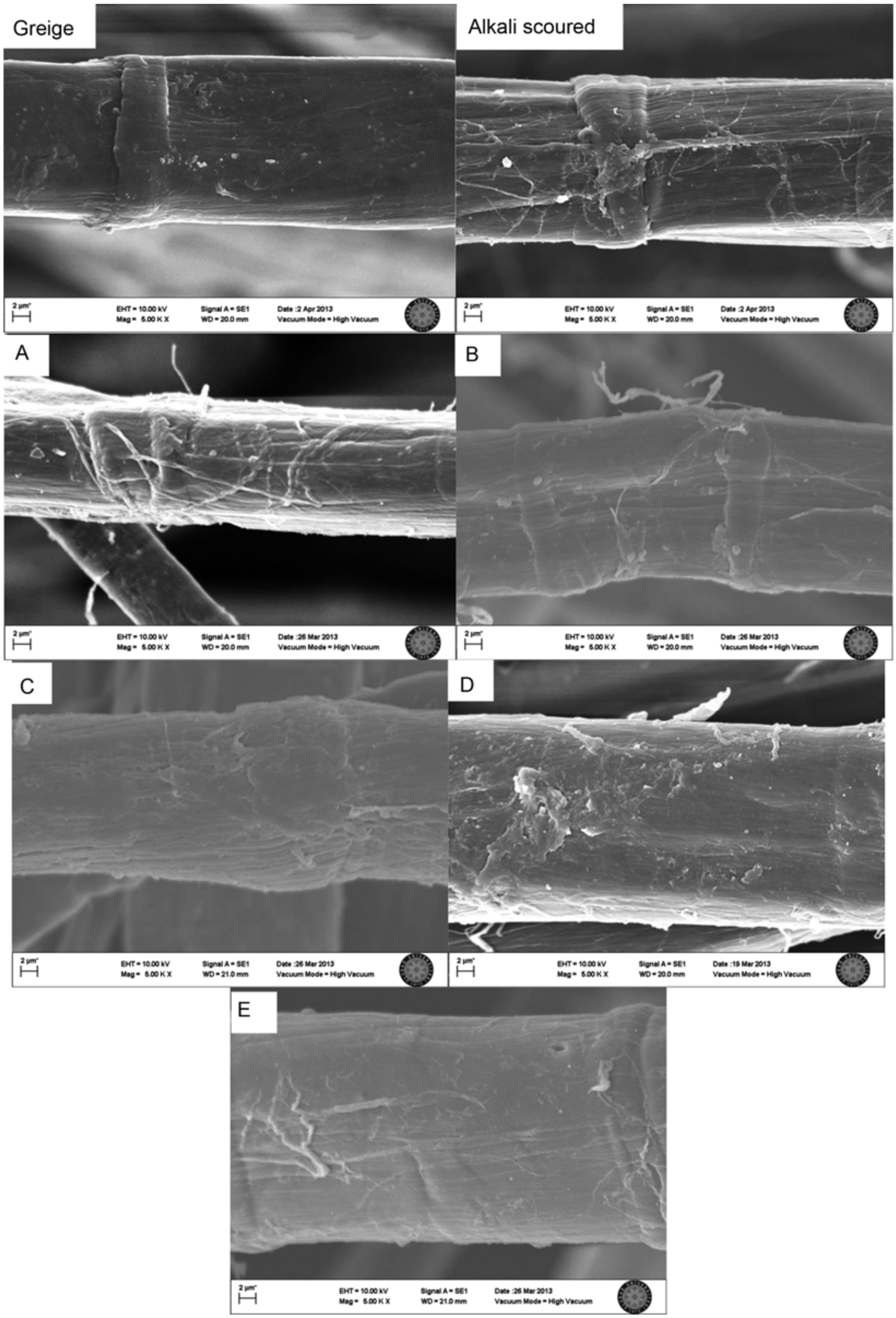

Figure 9. Surface morphologies of greige, scoured and bleached hemp fibers; (A) 90 minutes 20 m*l*/*l* H_2O_2 exhaustion bleaching application at 95 °C, (B) 90 minutes 30 m*l*/*l* peracetic acid exhaustion bleaching application at 95 °C, (C) 90 minutes 15 m*l*/*l* peracetic acid exhaustion bleaching application at 70 °C, (D) pad-batch bleaching application of 120 m*l*/*l* H_2O_2 with 24 hours waiting, and (E) pad-batch application of 100 m*l*/*l* peracetic acid with 24 hours waiting.

Table 4. Reactive dye uptake of greige, alkali scoured and bleached hemp samples

Hemp sample type*	Dye exhaustion (%)
Greige fabric	92.3
Alkali scoured	94.8
A	94.5
B	94.4
C	94.2
D	93.4
E	94.4

*A: 90 minutes 20 m*l*/*l* H_2O_2 exhaustion bleaching application at 95 °C, B: 90 minutes 30 m*l*/*l* peracetic acid exhaustion bleaching application at 95 °C, C: 90 minutes 15 m*l*/*l* peracetic acid exhaustion bleaching application at 70 °C, D: pad-batch bleaching application of 120 m*l*/*l* H_2O_2 with 24 hours waiting, and E: pad-batch application of 100 m*l*/*l* peracetic acid with 24 hours waiting.

reason for slightly lower tensile strength values measured of these fabrics (Table 3). However, it is right spot to mention that these striations are not significantly deep leading to no major significant strength loss (Figure 8 and Table 3). It is also worth commenting that in no case did we observe signs of pitting, cracking or similar features which would normally be associated with degradative damage.

Dye uptake (exhaustions) behaviors of the bleached hemp fabric samples were shown on Table 4.

The bleaching did not cause to exhaustion yield decreasing. Thus, it is thought that the chemical structure of hemp fiber did not deteriorate which allows reactive dyes to bind appropriately to the cellulosic structure, due to the oxidative process. Wax and fats on the hemp fiber were removed with scouring, however, no significant effect on exhaustion properties was observed.

The non-uniform surface of the greige and alkali scoured

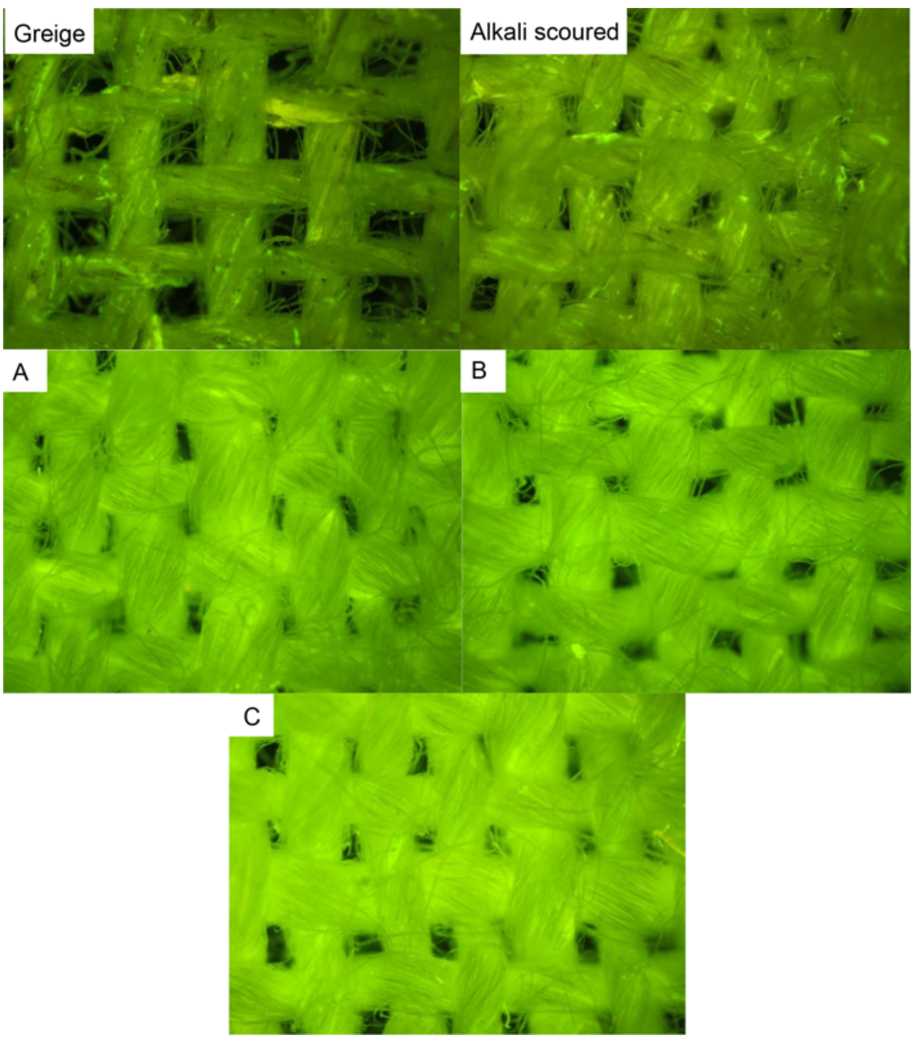

Figure 10. Fluorescent microscopy of untreated and treated hemp fabrics; (A) 90 minutes 20 m*l*/*l* H_2O_2 exhaustion bleaching application at 95 °C, (B) 90 minutes 30 m*l*/*l* peracetic acid exhaustion bleaching application at 95 °C, and (C) 90 minutes 15 m*l*/*l* peracetic acid exhaustion bleaching application at 70 °C.

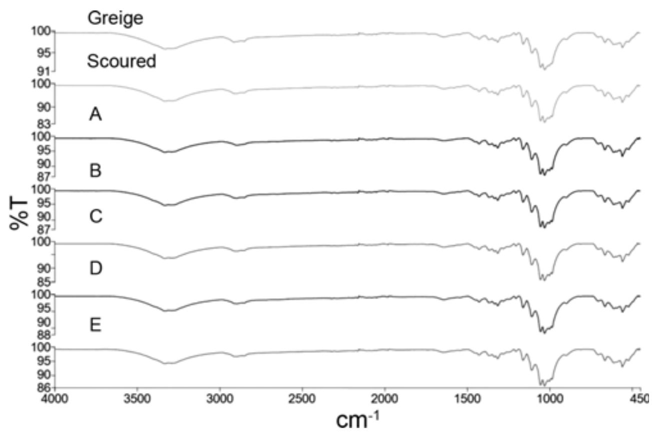

Figure 11. FTIR-ATR spectra of the greige, scoured and bleached hemp fiber fabrics; (A) 90 minutes 20 m*l*/*l* H_2O_2 exhaustion bleaching application at 95 ^oC, (B) 90 minutes 30 m*l*/*l* peracetic acid exhaustion bleaching application at 95 ^oC, (C) 90 minutes 15 m*l*/*l* peracetic acid exhaustion bleaching application at 70 ^oC, (D) pad-batch bleaching application of 120 m*l*/*l* H_2O_2 with 24 hours waiting, and (E) pad-batch application of 100 m*l*/*l* peracetic acid with 24 hours waiting.

fabrics were apparent. Moreover, higher autofluorescent properties were observed for the bleached samples (A, B, C) rather than greige and alkali scoured fabrics. It was associated with the effective removal of the surface impurities such as waxes and fats as well.

Figure 11 shows the FTIR-ATR spectra of the greige, scoured and bleached hemp fiber fabrics. COOH bending peak (664 cm^{-1}), O-H out of plane bending (650-700 cm^{-1}), C-O stretching and ring vibrational modes (895-1125 cm^{-1}), anti-symmetrical deformation of the C-O-C band (1160 cm^{-1}), C-O of acetyl in pectin or hemicelluloses (1240 cm^{-1}), CH_2 wagging of cellulose and hemicelluloses (1315-1335 cm^{-1}), CH bending of cellulose and hemicelluloses (1375 cm^{-1}), carboxylic acid of pectin and COO^- vibration (1425 cm^{-1}), C=C in-plane aromatic vibrations from lignin (1505 and 1595 cm^{-1}), CH_2 stretching and CH stretching of cellulose and hemicelluloses (2862 and 2935 cm^{-1}) and hydrogen bonded of OH stretching in cellulose and/or hemicelluloses (3000-3600 cm^{-1}) are some of the main absorption band assignments of hemp fibres in FTIR(ATR) spectra, using absorbance versus wave number (cm^{-1}) [35-37]. There are not any detectable significant changes on FTIR (ATR) spectra properties of hemp fiber after different bleaching processes.

The constancy of the FTIR-ATR spectra exhibits that scouring and the respective bleaching processing types have no drastic significant effect on the surface morphology of hemp fiber. Actually this is in line with SEM micrographs (Figures 9 and 10) and the results of tensile strength (Table 3) where no significant drastic surface appearance and strength differences were spotted between respective samples.

Conclusion

Similar whiteness values were attained with PAA between pH 5.5-9; however, pH 7 is preferred to avoid the risk of fiber damage at acidic pH and high alkali consumption at basic pH. pH of the bleaching liquor lower than 5.5-6 and higher than 8.5-9 resulted in dramatic decrease on whiteness values. A hyperbolic trend was observed on the redox potential increase for peracetic acid concentrations between 2.5-30 m*l*/*l*, which is consistent with whiteness measurements. For 70 ^oC applications, at the concentrations above 10 m*l*/*l* PAA, the whiteness improvement was limited; Stensby whiteness indices were 61.58, 62.36 and 60.10 for 15, 20 and 30 m*l*/*l* PAA concentrations, respectively. The highest whiteness value attained with PAA was 68.18 (30 m*l*/*l* concentration, 90 minutes process time, 95^{o}C process temperature), however a slight decrease on tensile strength was observed at these conditions. Although higher whiteness properties detected with hydrogen peroxide bleaching, COD analysis indicated the high waste load on the hydrogen peroxide bleaching effluent. PAA caused no dramatic derogation on physical properties of the hemp fiber. Hydrophilicity and crease recovery of peracetic acid bleached fabrics were improved compared with greige fabric. Whiteness values remained limited for bad-batch bleachings of PAA and hydrogen peroxide (highest values were 53.21 and 57.08 for PAA and hydrogen peroxide, respectively) the micrograp, no drastic changes were noted for variable waiting time and concentrations.

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