A COMPARATIVE STUDY ON PHYSICO-CHEMICAL CHARACTERISTICS OF SCOURED AND BLEACHED HEMP FABRIC THROUGH SEM, FTIR AND XRD

RASHI KUSHWAHA, PRIYANKA KESARWANI and ANJU KUSHWAHA

University of Allahabad, Prayagraj, 211002, Uttar Pradesh, India
✉ *Corresponding author: P. Kesarwani, kpriyanka1208@gmail.com*

Received May 2, 2024

Hemp (*Cannabis sativa* L.) is an annual plant and one of the most widely used crops cultivated for obtaining long and strong bast fibers. The resulting fibers contain cellulose, hemicelluloses, lignin, and other impurities. The presence of lignin and impurities makes the hemp fibers stiffer and brittle. These disadvantages challenge the direct application of fabric in the apparel industry. Therefore, a pretreatment is important for tuning the properties of hemp fabric for successful use in the apparel industry. The aim of this study has been to examine the effect of scouring and bleaching on the surface morphology, chemical structure, and crystallinity of the hemp fabrics by using instrumental techniques, such as SEM, FTIR, and XRD. SEM analysis of the samples showed slight changes in the properties of scoured, and scoured and bleached hemp fabric. The surface of the scoured fibers became smooth due to removal of non-cellulosic material (lignin, hemicelluloses and wax) and the thickness of the fiber slightly increased. Further, after bleaching, the surface of the fibres became very rough and the thickness of the fiber was reduced. FTIR analysis showed that the absorbance peak of -OH stretching decreased after the bleaching process. XRD analysis showed a slight increase in crystallinity index (%) of scoured, and scoured and bleached fabrics due to the removal of non-cellulosic materials after chemical treatments.

Keywords: bleaching, cellulosic material, hemp fabric, pre-treatment, scouring

INTRODUCTION

Hemp is an annual plant obtained from the *Cannabis sativa* L. of the family of Moraceae. This plant is similar to flax and is grown in many countries, including Canada, the USA, France, Egypt, Austria, China, South Korea and India. It can be grown organically in all tropical countries of the world[1] without the use of pesticides, herbicides, or fertilizers.[2] It can grow fast, and in 100 days, the plant can reach 3.5–4 m in height.

Hemp fibers are extracted from its bast by various types of retting processes, such as dew retting, water retting, and chemical retting *etc*. The resulting fibers are much lower in cellulose content than cotton, and, unlike cotton, they contain hemicelluloses and lignin. These two compounds often occur together in the cell walls of plants to give them strength.[3] Due to the presence of lignin on the fiber surface, the fabric made from hemp fibers is very stiff, brittle, and has a harsher handle than cotton.[4] These disadvantages challenge the direct application of hemp fabric in the apparel industry. Therefore, a pretreatment is important for tuning the properties of hemp fabric for successful use in the textile and apparel industries.

Pretreatments, especially scouring and bleaching, prior to dyeing and printing are crucial for the desired effects.[5] Scouring is performed to enhance the absorbency of textile fibers through the removal of non-cellulosic impurities, such as oil, fat, wax, and pectin, which are responsible for the hydrophobic characteristic,[6,7] and bleaching is the whitening process of fibers by the elimination of flavone pigments that cause yellowness using certain oxidants.[8] Bleaching happens either when the unsaturated or conjugated chromophoric sites undergo transformation or destruction, or when colored matter becomes solubilized and removed.[9] The pretreatment process can alter the surface structure and crystallinity of the cellulosic fabric, and reduce the content of amorphous materials, such as hemicelluloses, lignin, and some other impurities, which, in turn, improves the quality of hemp fabric for the production of apparel, upholstery, bags, *etc*. in the textile industry.[10]

In this paper, the scouring and bleaching of natural greige hemp fabrics was done by using sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), and sodium metasilicate (Na_2SiO_3). The aim of this study was to examine the effect of scouring and bleaching on the surface morphology, chemical composition, and crystallinity of the hemp fabrics by using instrumental techniques, such as scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

Greige 100% hemp fabric was purchased from Hemp Affair Pvt. Ltd., Noida, Uttar Pradesh, India. A non-ionic surface active agent (Felosan HLDN) was purchased from CHT India Pvt. Ltd., Maharastra. Sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), sodium metasilicate (Na_2SiO_3), sodium chloride (NaCl) and glacial acetic acid with 60.05 g/mol ($C_2H_4O_2$) were purchased from Science Corporation, Johnsen Ganj, Prayagraj, India.

Scouring

The greige hemp fabric was scoured by the recipe given by Hassan and Zaghlol.[11] In this process, hemp fabric was treated in a dye bath with sodium hydroxide (2 g/L) and a non-ionic surface wetting agent (1 g/L) at 90 °C for 1 hour at pH 10–11, keeping the material-to-liquid ratio at 1:20. The pH was maintained using sodium chloride. After scouring, the fabric was washed thoroughly with tap water and then neutralized with 1 g/L concentration of acetic acid for 10 minutes at room temperature to remove the alkali substances present in the fabric. Thereafter, the fabric was washed in tap water and dried at room temperature.

Bleaching

Bleaching of hemp fabric was carried out after scouring according to the recipe given by Karaca.[7] It was done in a dye bath by using H_2O_2 (5 g/L), NaOH (1 g/L), and Na_2SiO_3 (1 mL/L) for 1 hour at 80 °C. After bleaching, the fabric was washed thoroughly with tap water and then neutralized with 1 g/L concentration of glacial acetic acid for 10 minutes at room temperature to remove the alkali substances present in the fabric. The treated fabric was then rinsed with cold water, washed with hot water for 5 minutes, and finally dried at room temperature.

It is essential to neutralize the fabric after bleaching and rinse it well with water[12] because after bleaching, if peroxide (residual peroxide) remains on the fabric, it will cause incorrect dyeing in the subsequent dyeing processes.[13] A flow diagram of the pretreatment of hemp fabric (scouring and bleaching) is shown in Figure 1.

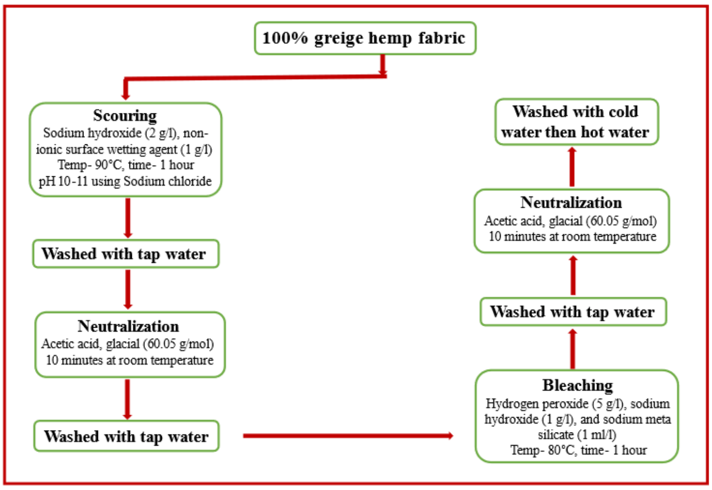

Figure 1: Flow diagram of the pretreatments of hemp fabric

Scanning electron microscopy (SEM)

The morphological structure of the greige, scoured, and scoured and bleached hemp fabric was observed with JSM-6490LV (JEOL, Japan) scanning electron microscopy at the USIC Lab of Babasaheb Bhimrao Ambedkar University, Lucknow. For this, the fabric sample was mounted on a mounting stand with the help of carbon tape, to keep it fixed during scanning. After mounting, the samples were coated with platinum (Pt) to reduce the charging effect and ensure that they could respond to an incident electron beam. Micrographs of the samples were recorded using magnifications of 30× to 1000× to study the surface characteristics of all the fabric samples.

Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was studied to determine the presence of different functional groups of cellulose and non-cellulosic material in the greige, scoured, and scoured and bleached hemp fabric samples. It was also used to analyze the changes that occur in the functional groups after scouring and bleaching of the fabric samples. The FTIR spectra of these fabric samples were recorded using a Nicolet 6700 (Thermo Scientific, USA) at the USIC Lab of Babasaheb Bhimrao Ambedkar University, Lucknow. The samples were placed with KBr into ultra-thin pallets for scanning at the spectrum range of 4000-400 cm^{-1}. 32 scans were taken of the samples, with a resolution of 4 cm^{-1}.

X-ray diffraction (XRD)

The X-ray diffraction was used to characterize the degree of crystallinity of greige, scoured, and scoured and bleached hemp fabric samples because scouring and bleaching may affect the crystalline and amorphous regions in the fabric. The diffraction of the samples was recorded using Rigaku Smartlab equipment at the Centre of Material Sciences, University of Allahabad. Scattered radiation was detected in the range of 2θ at a scan rate of 5º per minute.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

The morphology of greige, scoured, and scoured and bleached hemp fabric was studied by scanning electron microscopy to investigate the modifications that occurred on the surface of the fabric after scouring and bleaching treatments. The SEM images of greige, scoured, and scoured and bleached fabric samples are shown in Figure 2 (a, b and c). The SEM image at 20 µm depicts the surface morphology and thickness of the fibers present in the fabric.

Figure 2 (a) clearly shows the fibers present in the greige hemp fabric. It depicts that the surface of the fibers has a slightly rougher texture than the scoured hemp fiber in Figure 2 (b). It may be due to the presence of non-cellulosic impurities, such as lignin, wax, hemicelluloses, *etc*. on the surface of the fiber. Impurities might have made the fabric surface rougher. Other researchers[14,4] have also reported that the presence of lignin on the hemp fiber surface makes the fiber harsher. Further, they also reported that the presence of impurities makes fabrics stiffer and brittle. When the SEM image of scoured hemp fibers (Fig. 2 (b)) is observed, it can be noted that the fiber sample had a smoother surface than greige hemp fibers. The surface of the fiber became smoother due to the removal of non-cellulosic impurities from the fiber surface. Similar results were observed by Gohl and Vilensky, and Mather and Wardman.[15,4] They reported in their studies that the surface of the fiber becomes smooth after the removal of impurities. It can be seen in Figure 2 (c) that, after the bleaching process, the outer surface of the fiber became very rough and fuzzy. This may be due to the acidic nature of the H_2O_2 used in the bleaching process. The findings are in accordance with the results described by Vatsala R.,[16] who reported that longer contacts of hydrogen peroxide with cellulosic material makes the fabric weak or gives a tendering effect on the surface of the fabric due to its acidic composition.

In addition, the average thickness of the hemp fiber was also identified by scanning electron microscopy, and the results are shown in Table 1. It was observed that the thickness of the fiber in greige hemp fabric was 13.32 µm. There was a slight increase (15.47 µm) in the thickness of the fiber after scouring. The increase in thickness may be due to the alkali treatment in the scouring process. The alkali (NaOH) used in the scouring process might have increased the thickness of the fiber. Alkali enters the amorphous region of the fiber polymer system, forcing the polymer to move apart and form additional hydrogen bonds. Gohl and Vilensky also stated that alkali molecules swell the fiber by entering the amorphous region of the fiber polymer system.[15]

It can be observed from Table 1 that the average thickness of the fiber decreases to 14.05 µm after the bleaching process. This may be due to the breakdown of the bonds present on the fiber surface. The hydrogen peroxide used in the bleaching process might have degraded the fiber surface, which resulted in a decrement in the fiber thickness. The result is also confirmed by the SEM images in Figure 2 (b and c). The image in Figure 2 (c) confirms that the surface of the fiber is degraded, which results in a rough and fuzzy fabric surface.

Furthermore, Figure 2 (b and c) depicts that the structure of the fabric became compact after scouring and bleaching, when compared with the greige hemp fabric because the removal of non-cellulosic impurities from the fabric during scouring and bleaching might have caused closer interaction among the fibers.

Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy is one of the most commonly used methods for the identification of different functional groups. It also provides information about the presence or absence of both major (cellulose, hemicelluloses, lignin, *etc.*) and minor (mineral, pectin, waxes, *etc.*) constituents of natural fibers.[17] Identification of the absorption bands of the greige, scoured, and scoured and bleached hemp fabric is shown in Figure 3 and Table 2. The FTIR spectra show noticeable peaks in the range of 4000 to 400 cm^{-1} for greige, scoured, and scoured and bleached fabric samples. The peaks in the range of 3400 to 3200 cm^{-1} are characteristic of the stretching vibration of -OH bonds.

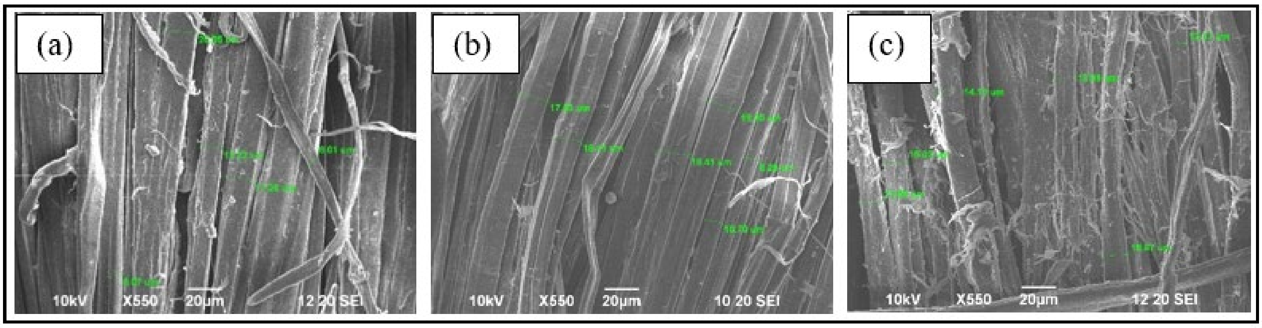

Figure 2: SEM images of (a) greige, (b) scoured, and (c) scoured and bleached hemp fabrics

Table 1
Average thickness of greige, scoured and scoured and bleached hemp fabrics

No.	Samples	Average thickness of fibres (μm)
1.	Greige hemp	13.32
2.	Scoured hemp	15.47
3.	Scoured and bleached hemp	14.05

This peak also includes inter and intra-molecular hydrogen bond vibrations in cellulose molecules.[18,19] It can be observed from Figure 3 that the peak at 3307 cm^{-1} is due to the hydroxyl group (-OH) of cellulose, the peak at 1151 cm^{-1} in the spectra is due to C-O-C stretching, and the peak at 1420 cm^{-1} is due to C-H stretching in the spectrum of greige hemp fabric. Duan, Vanitjinda, Arik, El-Gaoudy, and Hannan[20–24] reported almost similar peaks of -OH, C-O-C, and C-H stretching in their studies. Wang[22] confirmed that -OH, C-O-C, and C-H stretching are the backbones of typical cellulose.

It was observed on the scoured sample, the absorbance peak of -OH stretching shifted from 3307 cm^{-1} to 3353 cm^{-1}. Further, after bleaching, there was a slight shift of -OH bond peak from 3353 cm^{-1} to 3278 cm^{-1}. This may be due to the breakdown of hydrogen bonds on the fiber surface by the use of H_2O_2 in the bleaching process, which is also confirmed by the SEM results shown in Figure 2 (c). It can be seen in Table 2 that the absorbance peak of the C-H stretching band slightly increases from 1420 cm^{-1} to 1431 cm^{-1} in scoured fabric. Furthermore, after bleaching, the band of C-H stretching shifts from 1431 cm^{-1} to 1422 cm^{-1}. Also, it can be noted in Table 2 that the absorbance peak of C-O-C stretching for the greige hemp fabric was 1151 cm^{-1} and it shifted to 1160 cm^{-1} after the scouring process. Further, after bleaching, the band of C-O-C stretching moved from 1160 cm^{-1} to 1150 cm^{-1}. Almost similar peaks were observed for the C-O-C stretching of greige, scoured, and scoured and bleached hemp fabric because C-O-C (ether linkages) are chemically quite inactive, extremely resilient, and impermeable to weakening agents. Gohl & Vilensky[15] also stated that the cellulosic fibers contain ether linkages, but due to the irreversible carbon-oxygen bonds present in every ether molecule, they are chemically quite inactive.

X-ray diffraction (XRD)

X-ray diffraction is an effective tool to investigate the chemical composition and the crystal structure of natural fibers, with the crystalline and amorphous domains of cellulose.[17] Alkali treatment of hemp fabric may change the crystallinity of the fibers. Nishikawa and Ono[26] first revealed the crystalline nature of cellulose with X-ray diffraction. X-ray diffraction spectra were used to measure and compare the crystalline and amorphous arrangements of the greige, scoured, and scoured and bleached hemp fabrics, as shown in Figure 4.

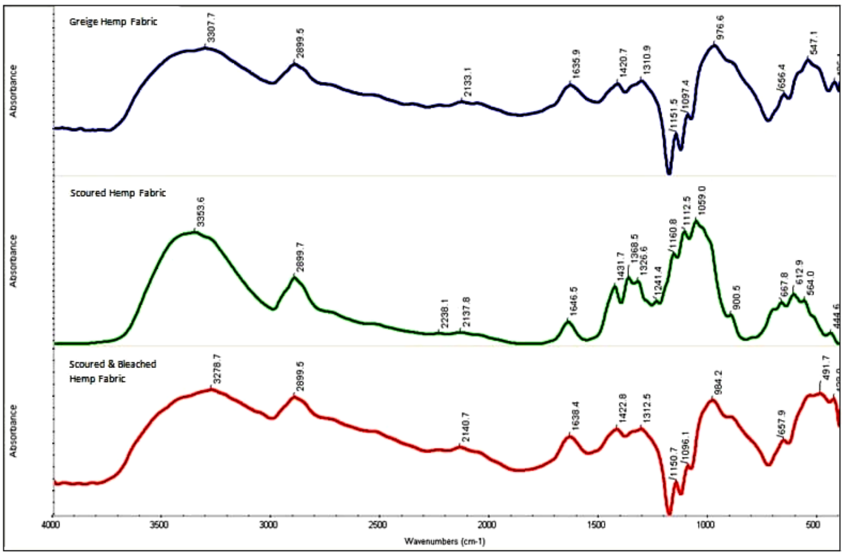

Figure 3: FTIR spectra of greige, scoured, and scoured and bleached hemp fabrics

Table 2
Infrared band assignments for greige, scoured, and scoured and bleached hemp fabrics

Sample	Griege fabric	Scoured fabric	Scoured and bleached fabric	Possible assignments
Absorption band wavelength (cm^{-1})	3307	3353	3278	-OH bond
	1420	1431	1422	C-H stretching bond
	1151	1160	1150	C-O-C bond of ethers group

The XRD patterns in Figure 4 depict sharp peaks at 2θ = 22.6° and 34.6°, which signifies the presence of a crystalline structure, and a short and broad peak at 2θ = 15.0°, which signifies the amorphous area of the hemp fabric. Slight differences are observed in the peaks of greige, scoured, and scoured and bleached hemp fabric. This means that there was a slight transformation in the crystalline structure of treated and untreated fabric due to very slight changes in the diffraction angle (2θ). These findings are in accordance with the results published by Wang, Ouajai, and Shanks, Duan.[25,27,20] They reported in their study that the diffraction intensity of the relative diffraction angle slightly increased after chemical treatments, which indicated an increase in crystallinity index. Segal's empirical expression was used to calculate the crystallinity index, CI (%).[28]

$$CI\ (\%) = \left[\frac{I_{002} - I_{AM}}{I_{002}}\right] \times 100 \quad (1)$$

where I_{002} is the maximum intensity counter reading of the crystalline phase peak and I_{AM} is the counter reading of the amorphous phase peak.

The calculated crystallinity index values of greige, scoured, and scoured and bleached hemp fabric are 80.13%, 81.06%, and 81.14%, respectively. A slight increase in crystallinity index is noted in scoured, and scoured and bleached fabrics when compared with the greige fabric, as depicted in Table 3. The increase in the crystallinity index after scouring and bleaching may be due to the removal of non-cellulosic materials, such as hemicelluloses and lignin, which were present in the amorphous regions of the fabric. These results agree with the findings of Vanitjinda, Chen, and Kumar and Singh,[21,30,31] who stated that the removal of amorphous materials, such as hemicelluloses, lignin, waxes *etc*. during the chemical treatments increases the crystallinity index (Cl) of the fabric. They also reported that the bleaching process increases the Cl of the fibers.

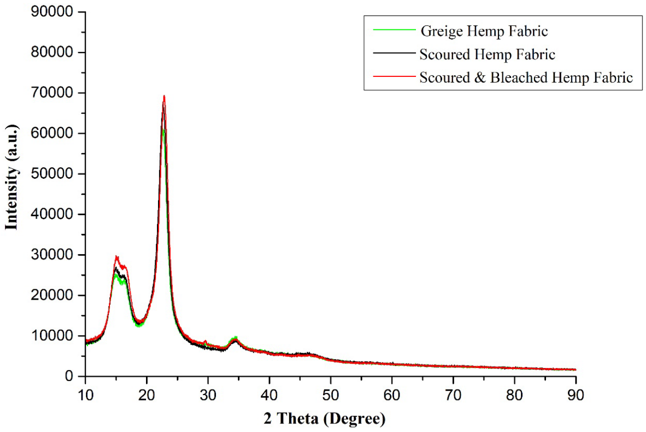

Figure 4: XRD diffraction patterns of greige, scoured, and scoured and bleached hemp fabrics

Table 3
Crystallinity index (%) of greige, scoured, and scoured and bleached hemp fabrics

S. No.	Sample	Crystallinity index (%)
1.	Greige hemp fabric	80.13
2.	Scoured hemp fabric	81.06
3.	Scoured and bleached hemp fabric	81.14

CONCLUSION

The purpose of this study was to examine the effect of scouring and bleaching on the morphological properties of hemp fabrics. SEM analysis of the samples showed slight changes in the properties of scoured, and scoured and bleached hemp fabrics, when compared to the greige hemp fabric. It was found that the surface of scoured fibers became smooth due to the removal of non-cellulosic material (lignin, hemicelluloses, and wax), and the thickness of the fiber slightly increased after scouring due to alkali treatment. After bleaching, the fibers became very rough and the thickness of the fiber was reduced; this may be due to the acidic nature of H_2O_2 used in the bleaching process. Further, FTIR results confirmed that the -OH bond peak shifted from 3307 cm^{-1} to 3353 cm^{-1} after scouring. It was observed in the spectrum of the bleached sample that the absorbance peak of -OH stretching moved from 3353 cm^{-1} to 3278 cm^{-1}. The XRD analysis showed a slight increase in the crystallinity index (%) of scoured, and scoured and bleached fabric due to the removal of non-cellulosic materials by the chemical treatments. Thus, it can be concluded that scouring of the hemp fabric with NaOH has enhanced the properties of the fabric, whereas bleaching with 5% H_2O_2 at concentration has degraded the surface of the fabric to some extent.

ACKNOWLEDGEMENT: The authors wish to thank the Babasaheb Bhimrao Ambedkar University (BBAU) Lucknow and the Department of Material Science (UoA) Prayagraj for their support and cooperation in testing surface morphology, chemical composition, and crystallinity of the hemp fabrics through instrumental techniques, such as SEM, FTIR, and XRD in their lab.

REFERENCES

[1] T. Today, Textile News, Fashion Trends (2018).
[2] V. Jonaitienė, Z. Jankauskienė and I. Stuogė, in "Natural Fibres: Advances in Science and Technology Towards Industrial Applications", edited by R. Fangueiro, S. Rana, RILEM Bookseries, vol 12. Springer, Dordrecht, 2016, p. 407, https://doi.org/10.1007/978-94-017-7515-1_32
[3] S. Asim, *Trends in Textiles & Fashion Designing*, **3** (2018)
[4] R. R. Mather and R. H. Wardman, "The Chemistry of Textile Fibres", Royal Society of Chemistry, 2011
[5] H. Benli and M. Bahtiyari, *J. Clean. Prod.*, **89**, 116 (2015), https://doi.org/10.1016/j.jclepro.2014.11.007
[6] M. Nerurkar, J. Manasi, and A. Ravindra, *Appl. Biochem. Biotechnol.*, **175**, 253 (2015), https://doi.org/10.1007/s12010-014-1259-6

[7] B. Karaca, E. Bozacı, A. Demir, E. Ozdogan and N. Seventekin, *J. Appl. Polym. Sci.*, **125**, 793 (2012), https://doi.org/10.1002/app.35359
[8] S. F. Kabir, M. I. Iqbal, P. P. Sikdar, M. M. Rahman and S. Akhter, *Eur. Sci. J.*, **10**, 200 (2014)
[9] E. S. Abdel-Halim and S. S. Al-Deyab, *Carbohyd. Polym.*, **86**, 988 (2011), https://doi.org/10.1016/j.carbpol.2011.05.051
[10] M. D. Teli and A. C. Jadhav, *Int. Res. J. Eng. Technol.*, **3**, 2754 (2016)
[11] T. M. Hassan and T. M. Zaghlol, *Int. Design J.*, **9**, 183 (2019), https://doi.org/10.21608/IDJ.2019.83439
[12] C. Xu, D. Hinks, A. El-Shafei, P. Hauser, M. Li, M. Ankeny and K. Lee, *J. Fiber Bioeng. Inform.*, **4**, 209 (2011)
[13] D. Yürüten, G. G. Bülbül, H. N. Cantürk, İ. Kasapoğlu, M. K. Digilli et al., "Textile Pretreatment", Akedom, Denge Corporate Academy, https://dengekimya.com/media/uwfnb3d4/akedom_textile-pretreatment-booklet_a5.pdf
[14] J. G. Cook, "Handbook of Textile Fibres: Natural Fibres", Woodhead Publishing Ltd., 2001
[15] E. P. G. Gohl and L. D. Vilensky, "Textile Science – An Explanation of Fibre Properties", 2nd ed., CBC Publication Ltd., 2005
[16] R. Vatsala, "Textbook of Textiles and Clothing", ICAR Publication, 2003, pp.1-448
[17] M. Fan, D. Dai and B. Huang, in "Fourier Transform – Materials Analysis", edited by S. M. Salih, IntechOpen, 2012, Chapter 3, p. 45, https://doi.org/10.5772/2659
[18] D. L. Pavia, G. M. Lampman, and G. S. Kriz, "Introduction to Spectroscopy", Thomson Learning, Boston, 2001
[19] V. Senapitakkul, G. Vanitjinda, S. Torgbo, P. Pinmanee, T. Nimchua *et al.*, *Acs Omega*, **5**, 28168 (2020), https://doi.org/10.1021/acsomega.0c03837
[20] L. Duan, W. Yu and Z. Li, *J. Eng. Fiber. Fabr.*, **12**, 33 (2017), https://doi.org/10.1177/155892501701200104
[21] G. Vanitjinda, T. Nimchua, P. Sukya, *Int. J. Biol. Macromol.*, **122**, 503 (2019). https://doi.org/10.1016/j.ijbiomac.2018.10.191
[22] B. Arik, *Fibers Polym.*, **21**, 82 (2020), https://doi.org/10.1007/s12221-020-9329-6
[23] H. El-Gaoudy, N. Kourkoumelis, E. Varella and D. Kovala-Demertzi, *Appl. Phys. A*, **105**, 497 (2011), https://doi.org/10.1007/s00339-011-6507-9
[24] M. A. Hannan, P. Haque, S. F. Kabir and M. M. Rahman, *J. Nat. Fibers*, **17**, 623 (2018), https://doi.org/10.1080/15440478.2018.1518742
[25] W. M. Wang, Z. S. Cai, J. Y. Yu and Z. P. Xia, *Fibers Polym.*, **10**, 776 (2009), https://doi.org/10.1007/s12221-009-0776-3
[26] S. Nishikawa and S. Ono, *Procs. Tokyo Mathemat.-Phys. Soc.*, **7**, 131 (1913), https://doi.org/10.11429/ptmps1907.7.8_131
[27] S. Ouajai and R. A. Shanks, *Macromol. Biosci.*, 5, 124 (2005), https://doi.org/10.1002/mabi.200400151
[28] L. Segal, J. J. Creely, A. E. Martin Jr. and C. M. Conrad, *Text. Res. J.*, **29**, 786 (1959), https://doi.org/10.1177/004051755902901003
[29] V. J. Aneetta, S. Amsamani and C. Naveena Shri, *Indian J. Home Sci.*, **35**, 1 (2023)
[30] W. Chen, H. Yu, Y. Liu, Y. Hai, M. Zhang *et al.*, *Cellulose*, **18**, 433 (2011), http://dx.doi.org/10.1007/s10570-011-9497-z
[31] S. V. Kumar and H. Singh, *Indian J. Fibre Text. Res.*, **48**, 326 (2023), https://doi.org/10.56042/ijftr.v48i3.6057