

CHEMICAL MODIFICATION FOR RESISTANCE TO PHOTO-OXIDATIVE DEGRADATION AND IMPROVED BLEACHING AND COLOR FASTNESS PROPERTIES OF HEMP FIBER

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The objective of the research has been to overcome some inherent drawbacks of hemp fiber via chemical modification, which is a vital issue in using it as a textile fiber like cotton. Hemp fiber was modified with treatment liquor (mixture of sulfurous acid and sodium hydroxide) in aqueous medium to remove lignin. The effects of the treatment liquor concentration, fiber to liquor ratio, reaction time and temperature on the percent lignin extracted from hemp fiber were studied. Modified hemp fibers (MHF) were bleached in an alkaline pH aqueous medium with hydrogen peroxide. The process significantly improved lignin removal, bleaching and color fastness. In fact, the whiteness index of bleached MHF was significantly higher than that of bleached raw hemp, but its tensile strength was slightly affected. The photo-oxidative degradation of hemp fiber was 70% lower than that of unmodified (raw) hemp fiber and almost like that of cotton yarn. The color fastness properties of dyed bleached modified hemp fiber were significantly better than those of dyed bleached unmodified hemp fiber and close to those of dyed bleached cotton yarn.

Keywords: hemp fiber, chemical modification, delignification, photo-oxidative degradation, bleaching and color fastness

INTRODUCTION

Hemp is a lignocellulosic plant bast fiber, but it does not have a valuable commercial market in the textile sector in the production of cloth like cotton because of some fundamental weaknesses, such as coarseness, rigidity, photo-yellowing, poor bleaching and color fastness.¹ Hemp fiber is composed of cellulose, hemicelluloses, lignin, waxy materials, pectic substances, and coloring matter.² Partial removal of non-cellulosic materials from hemp fiber to improve its textile characteristics has recently been a subject of much interest. A few efforts have shown microbial processing only removed waxy, pectic substances and a small amount of lignin from hemp fibers.^{3,5} Degumming of hemp fibers was found efficient using combined microwave energy and deep eutectic solvent treatment.⁴ The effects of chemical and physical pretreatment processes on hemp fibers have been investigated.⁶ Alkali-treated hemp fibers have shown improved mechanical properties,⁷ bleaching may remove pectin and lignin of bast fiber,⁸⁻⁹ and surface modification of hemp fiber improved its spinning properties.¹⁰ To remove the lignin and hemicellu-

loses either partially or entirely from the lignocellulosic fiber, it needs to have at least two stages of treatment, involving chlorite and alkaline charges, which may cause accelerated degradation of the fiber structure.¹¹

To improve the inherent properties of hemp fiber, we have developed a chemical modification method to make it suitable for textile application. The modifying agent, such as sulfurous acid, produced a salt of sulfites (SO_3) or bisulfites (HSO_3) in the presence of sodium hydroxide. These sulfite (SO_3) or bisulfite (HSO_3) ions (groups) cleavage most lignin carbohydrate complex bonds (ester and ether) in hemp fiber during modification of hemp fiber; as a result, most of the lignin will be isolated into the modification liquor. On the other hand, sulfite (SO_3) or bisulfite (HSO_3) groups are easily chemically attached to the phenolic and alcoholic groups in lignin molecules.¹² Therefore, the rest of the phenolic and alcoholic groups in the lignin molecules of modified hemp fiber will be blocked by the sulfite (SO_3) or bisulfite (HSO_3) groups,

which will avoid the photo-yellowing/oxidation of modified hemp fiber.

In the present investigation, efforts have been made to find out the optimum conditions of a modification treatment of hemp fiber with treatment liquor (sulfurous acid and sodium hydroxide) in an aqueous medium, such as treatment liquor concentration, fiber to liquor ratio, reaction time and temperature. The mechanical properties of modified hemp fiber have also been studied and compared with those of raw hemp fiber. Raw and modified hemp fibers will be photolyzed by UV light to ascertain the photo-oxidative degradation resistance of modified hemp fibers and compare them with raw hemp fiber. The bleaching and color fastness properties of modified bleached hemp fiber will be compared with those of raw bleached hemp fiber.

EXPERIMENTAL

Materials

Mechanically processed hemp fiber was obtained from Greene Natural Fibers, Snowhill, NC. Chemicals of reagent grade utilized were sulfurous acid, sodium carbonate, diethylenetriamine, sodium hydroxide, potassium permanganate, thiosulfate, and reactive

dyestuffs obtained from Sigma (Sigma-Aldrich Corporation, St. Louis, Missouri, USA).

Modification of hemp fiber

Hemp fiber modification was carried out in a stainless steel high-pressure pulping digester. The treatment liquor was prepared from 16% sulfurous acid and 5% sodium hydroxide. The chemical modification digester was prepared with 10-50% treatment liquor based on the oven-dried weight of the hemp fiber. The fiber to liquor ratio was adjusted between 1:2-1:6. The modification reaction was carried out at temperatures in the range of 130-170 °C for 0.5-2.5 h. After the modification, the fiber was thoroughly washed with water and then dried in an air oven for further characterization.¹²⁻¹³ The reaction scheme is shown in Figure 1.

Determination of lignin

The kappa number was determined according to TAPPI Standard Method T 236. The lignin content was calculated according to Equation 1:

$$\text{Lignin level (\%)} = \text{Kappa number} \times 0.13 \quad (1)$$

Testing method

Tensile strength, bending length and weather resistance of the modified hemp fiber were tested according to ASTM method D 2524-94, ASTM method D1388-96 and AATCC test methods RA64 186-2001, respectively.

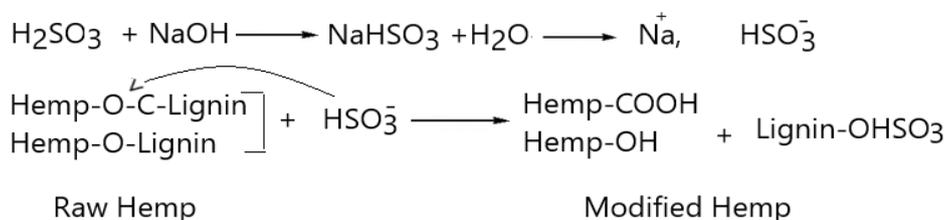


Figure 1: Modification reaction of hemp fiber with sulfurous acid and sodium hydroxide

Fourier transform infrared spectroscopy (FTIR)

Infrared spectra (FTIR-ATR) were recorded by a Perkin Elmer Spectrum 100 FTIR Spectrometer on raw and modified hemp with a Perkin Elmer 100 FTIR spectrophotometer. All the spectra were obtained in the range of 650–4000 cm^{-1} .¹⁴

Bleaching of modified hemp fiber

Modified hemp fiber was bleached with 3% hydrogen peroxide in the presence of sodium carbonate in an aqueous medium in a beaker. The fiber to liquor ratio was adjusted to 1:10 at pH 11, and bleaching was carried out at 95 °C for 90 min. The bleached fiber was rinsed thoroughly in water and then dried in an air oven.¹⁵

Dyeing of modified hemp fiber

The modified hemp fiber was dyed with 3% Reactive Red 1 and 3% Reactive Blue 5 in an aqueous medium, separately. The dyeing bath was prepared with 10% sodium chloride (by mass of oven-dried hemp fiber) with 1:20 fiber-to-liquor ratio. The dyeing was carried out at 70 °C for 60 min. The dyed sample was rinsed thoroughly in water and distilled water and then dried in an air oven.¹⁶

Photolysis

A xenon lamp weatherometer was used to study the photolysis of the modified hemp fiber according to AATCC TM169-2020.

Color fastness

The light and wash fastness of dyed modified hemp fibers was assessed according to AATCC 16 and AATCC 61, respectively.

RESULTS AND DISCUSSION

Characterization of modified hemp fibers

Hemp fiber was modified with treatment liquor ($\text{H}_2\text{SO}_3/\text{NaOH}$) in an aqueous medium. The average results obtained under optimum modification conditions are shown in Table 1. During modification, while all other variables remained constant, comparatively lower lignin content of modified hemp fibers was obtained at 40% treatment liquor, 1:4 fiber to liquor ratio, reaction time of 2 hours, and temperature of 150 °C. Table 1 shows that above the optimum conditions, the decrease in the lignin content of hemp fiber was very low. Perhaps, this happens

because lignin in the middle lamella of hemp fiber can be accessible to the treatment liquor, the fiber being swiftly delignified, whereas lignin contained in the secondary wall and linked with hemicelluloses is not easily attainable; as a result, hemp fiber delignified slowly by treatment liquor. A similar trend was found for modification time and temperature. This may be due to the fact that prolonged treatment above 150 °C causes degradation of the hemp fiber composition, resulting in gradual dissolution of the lignin content from the solid fiber walls into the treatment liquor.¹³

Modified hemp fiber was characterized by FTIR-ATR analysis to confirm its modification. The ATR spectra of the raw hemp fiber (A) and modified hemp fiber (B) are shown in Figure 2.

Table 1
Optimization of modification reaction parameters

| Modifying agent concentration | | Time | | Temperature | | Fiber to liquor ratio | |
|-------------------------------|-------------------|-------------------|-------------------|---------------------|-------------------|-----------------------|-------------------|
| Treatment liquor (%) | % Delignification | Reaction time (h) | % Delignification | Reaction temp. (°C) | % Delignification | S:R | % Delignification |
| 10 | 5.4 | 0.5 | 5.0 | 120 | 5.5 | 1:2 | 3.7 |
| 20 | 4.2 | 1.0 | 4.2 | 130 | 4.8 | 1:3 | 2.9 |
| 30 | 3.1 | 1.5 | 3.2 | 140 | 3.6 | 1:4 | 2.5 |
| 40 | 2.5 | 2.0 | 2.6 | 150 | 2.7 | 1:5 | 2.4 |
| 50 | 2.4 | 2.5 | 2.6 | 160 | 2.6 | 1:6 | 2.5 |

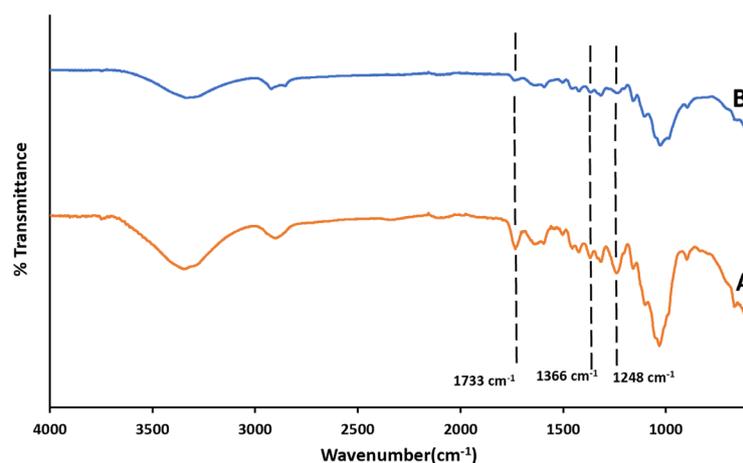


Figure 2: ATR spectra of (A) raw hemp fiber and (B) modified hemp fiber

As may be noted, the raw hemp fiber shows a band at 3309 cm^{-1} attributed to the O–H, a wide range sharp peak observed at 1733 cm^{-1} corresponds to the ester bond between lignin and carbohydrates in hemp fiber, the peak at 1248 cm^{-1} corresponds to the ether bond between lignin

and carbohydrates in hemp fiber, and a band observed at 1366 cm^{-1} attributed to the phenolic O–H in lignin. However, the modified hemp fiber shows minimal peaks at 1733 cm^{-1} and 1248 cm^{-1} , compared to the raw hemp fiber, indicating that modified hemp significantly decreased the lignin

content due to cleavage of the ester and ether linkage between lignin and carbohydrates in hemp fiber, and lignin was isolated during the

modification. Besides, a tiny peak also observed for modified hemp at 1366 cm^{-1} corresponds to the phenolic-OHSO₃ in lignin.¹²

Table 2
Physical properties of raw and modified hemp fiber

| Sample | Tensile strength (Kgf) | Breaking extension (%) | Tensile modulus (g/tex) | Bending length (cm) | Lignin content (%) |
|---------------------|------------------------|------------------------|-------------------------|---------------------|--------------------|
| Raw hemp fiber | 28.5 | 1.0 | 2810 | 6.0 | 6.0 |
| Modified hemp fiber | 26.40 | 3.5 | 950 | 2.4 | 2.5 |

Table 3
Loss in tensile strength of raw and modified hemp fiber after exposure of UV light

| Exposure period (AFU) | Loss in tensile strength (%) | | |
|-----------------------|------------------------------|---------------------|-------------|
| | Raw hemp fiber | Modified hemp fiber | Cotton yarn |
| 10 | 3.0 | 1.3 | 0.2 |
| 20 | 5.1 | 1.7 | 0.8 |
| 30 | 8.5 | 2.5 | 1.3 |
| 40 | 13.7 | 3.2 | 2.5 |
| 60 | 18.2 | 4.9 | 3.8 |
| 70 | 25.8 | 7.1 | 6.0 |
| 80 | 29.0 | 8.0 | 7.5 |

Physical properties of modified hemp fiber

Lignocellulosic fiber suffers from inherent defects, such as low elongation, high modulus, and bending length, which limit its spinning to yarn for producing cloth. Table 2 shows that chemical modification significantly (3 times) increased the elongation and decreased the lignin content, modulus (toughness), and bending length of hemp fiber, which is more than 60%. These results prove that the modified hemp fiber is more flexible and can be used as a textile fiber for spinning yarn.

Loss in tensile strength of raw and modified hemp fiber after exposure of UV light

A summary of loss in tensile strength of raw and modified hemp fiber after exposure to UV light is presented in Table 3. It is observed from Table 3 that the percent loss in tensile strength of both raw and modified hemp fiber decreases with the increase in exposure time. At the end of 80 AFU, the tensile strength loss of modified hemp fiber (8%) was considerably lower than that of raw hemp fiber (29%) and almost similar to that of cotton yarn. This may be explained by the fact that the large reactive groups present in lignin, which are phenolic and alcoholic hydroxyl

groups, are highly sensitive to the action of light. When hemp fiber is exposed to UV light, the photo-oxidative degradation occurs in lignin, as a result, the lignin-carbohydrate complexes bonding is cleaved and hence, the tensile strength is lost.¹⁷⁻¹⁸ Since modified hemp fiber has a low amount of lignin, compared to the raw hemp fiber, and most of the phenolic and alcoholic hydroxyl groups in the remaining lignin were blocked by SO₃ groups due to chemical modification with treatment liquor (mixture of sulfurous acid and sodium hydroxide), this may have played a vital role in significantly decreasing the photo-oxidative degradation of modified hemp fiber.¹⁹

Bleaching properties of raw and modified hemp fiber

The bleaching properties of modified hemp fibers are shown in Table 4. Modification significantly increased the whiteness index of bleached modified hemp fibers, but decreased the tensile strength and lignin content. The whiteness index (CIE) of bleached raw hemp fiber and bleached modified hemp fibers was found to be 58 and 80, respectively. Images of raw and bleached hemp fibers are shown in Figure 3.

Table 4
Bleaching properties of raw and modified hemp fiber

| Sample | Whiteness index (CIE) | Tensile strength (g/den) | Elongation (g/den) | Lignin content (%) |
|------------------------------|-----------------------|--------------------------|--------------------|--------------------|
| Bleached raw hemp fiber | 58 | 1.7 | 1.4 | 5.0 |
| Bleached modified hemp fiber | 80 | 1.6 | 3.6 | 1.2 |



Figure 3: Raw hemp fiber (left), bleached raw hemp fiber (middle) and bleached modified hemp fiber (right)

Table 5
Color fastness properties of dyed raw and modified hemp fiber

| Sample | Light fastness rating | | Wash fastness rating | |
|------------------------------|-----------------------|-----------------|----------------------|-----------------|
| | Reactive Red 1 | Reactive Blue 5 | Reactive Red 1 | Reactive Blue 5 |
| Bleached raw hemp fiber | 3 | 2-5 | 2-5 | 2 |
| Bleached modified hemp fiber | 5 | 4-5 | 4 | 3-4 |
| Bleached cotton yarns | 5 | 4-5 | 4-5 | 4 |

Color fastness properties of raw and modified hemp fiber

Colorfastness (light and washing) test results of bleached raw and modified hemp fibers are shown in Table 5. In all cases, bleached modified hemp fiber showed significantly better light and wash fastness, compared to bleached raw hemp fiber, and similar values to those of bleached cotton yarn (Table 5). This may be explained by the much higher van der Waals forces of attraction between the dyestuff and the bleached modified hemp fiber, compared to bleached raw hemp fiber, due to the low content of lignin. As a result, dyed bleached modified hemp fiber washes out a lower amount of dyes. For color fastness, about 2.5% lignin in fiber is enough to start photo-yellowing of lignocellulosic fiber. When dyed beached raw hemp fiber is exposed to UV light, its lignin phenolic hydroxyl groups create free radicals and transform into quinoid structures. This leads to yellowing on the fiber surface, thus causing significant fading of dyed raw hemp fiber.¹⁷

CONCLUSION

Hemp fibers were modified with treatment liquor (mixture of sulfuric acid and sodium hydroxide) in an aqueous medium. Optimum modification conditions were determined to be 40% treatment liquor, treatment time of 2 h, temperature of 150 °C, and fiber to liquor ratio of 1:4. The photo-oxidative degradation of modified hemp fiber was characterized after UV light exposure at 80 AFU. The modified hemp fiber showed significantly lower photo-oxidative degradation. In fact, it was 70% lower than that of raw hemp fiber and similar to that of cotton yarn. The whiteness index of bleached modified hemp fiber was significantly higher than that of bleached raw hemp fiber, but its tensile strength was slightly affected. The color fastness *e.g.*, light and wash fastness, of bleached modified hemp fiber dyed with reactive dyes provided excellent results, superior to those of bleached raw hemp fiber.

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REFERENCES

- ¹ S. M. M. Kabir, R. Karim and K. Islam, *Eur. Sci. J.*, **13**, 378 (2017), <https://doi.org/10.19044/esj.2017.v13n33p378>
- ² M. Zimniewska, *Materials*, **15**, 5 (2022), <https://doi.org/10.3390/ma15051901>
- ³ A. Thygesen, M. Liu, A. S. Meyer and G. Daniel, *Procs. 34th Risøe International Symposium on Materials Science*, Roskilde, Denmark, 2013, p. 373, https://backend.orbit.dtu.dk/ws/portalfiles/portal/58196496/HEMP_FIBRES.pdf
- ⁴ B. Ahmed, Q. Wu, H. Lin, J. Gwon, I. Negulescu *et al.*, *Ind. Crop. Prod.*, **184**, 115046 (2022), <https://doi.org/10.1016/j.indcrop.2022.115046>
- ⁵ M. D. Stanescu, *Cellulose Chem. Technol.*, **57**, 1 (2023), <https://doi.org/10.35812/CelluloseChemTechnol.2023.57.01>
- ⁶ A. B. Thomsen, A. Thygesen, V. Bohn, K. V. Nielsen, B. Pallesen *et al.*, *Ind. Crop. Prod.*, **24**, 113 (2006), <https://doi.org/10.1016/j.indcrop.2005.10.003>
- ⁷ W. Fracz, G. Janowski and L. Bak, *Polymers*, **13**, 12 (2021), <https://doi.org/10.3390/polym13121965>
- ⁸ L. Duan, W. Yu and Z. Li, *J. Eng. Fibers Fab.*, **12**, 1 (2017), <https://journals.sagepub.com/doi/pdf/10.1177/155892501701200104>
- ⁹ H. M. Wang, R. Postle, R. W. Kessler and W. Kessler, *Text. Res. J.*, **73**, 8 (2003), <https://doi.org/10.1177/004051750307300802>
- ¹⁰ A. Arshad, M.Sc. thesis, University of Manitoba, Canada, 2013, https://mspace.lib.umanitoba.ca/bitstream/handle/1993/22053/Ali_Arshad.pdf?sequence=3
- ¹¹ P. B. Sarker and H. Chatterjee, *J. Text. Inst.*, **39**, 8 (1948), <https://doi.org/10.1080/19447024808659428>
- ¹² S. Lagergren and S. A. Rydholm, *Svensk Papperstidn.*, **62**, 103 (1959)
- ¹³ S. Hanhikoski, E. Warsta, A. Varhmo and K. T. Niemela, *Holzforschung*, **70**, 7 (2016), <https://doi.org/10.1515/hf-2015-0099>
- ¹⁴ C. Marcello and A. Salam, *ACS Sustain. Chem. Eng.*, **43**, 14262 (2022)
- ¹⁵ M. A. Salam, *J. Appl. Polym. Sci.* **99**, 6 (2006), <https://doi.org/10.1002/app.22954>
- ¹⁶ M. A. Salam, S. K. Sheik and F. I. Farouqui, *JTATM*, **6**, 2 (2009), <https://ojs.cnr.ncsu.edu/index.php/JTATM/article/view/File/488/460>
- ¹⁷ S. M. Chatterjee, *Ind. Text. J.* **8**, 149 (1975)
- ¹⁸ G. S. Egerton, *JSDC*, **65**, 12 (1949), <https://doi.org/10.1111/j.1478-4408.1949.tb02558.x>
- ¹⁹ A. R. Procter, W. Q. Yean and D. A. I. Goring, *PPM Canada*, **68**, 9 (1967)