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# Effect of TAED Activated $H_2O_2$ Bleaching on the Properties and Structure of Jute Fibers

Long WANG[1], Zuoqiang WEN[1], Weiming WANG[1,2*], Jinli ZHOU[1,2]

[1]College of Textile & Garment, Shaoxing University

[2] Key Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province

Shaoxing, China

e-mail: *wangwm@usx.edu.cn

***Abstract*—Both conventional hydrogen peroxide bleaching and tetraacetylethylenediamine/hydrogen peroxide system bleaching were carried out on the scoured jute fiber, and the properties and structures of bleached fibers were compared to estimate the effect of tetraacetylethylenediamine in hydrogen peroxide bleaching. The results shows that tetraacetylethylenediamine/hydrogen peroxide system bleaching could be carried out at lower temperature with a mild alkaline condition, and which is much more effective in removal of noncellulosic materials, especially for color matters and lignin, while causes weaker fiber damage. X-ray diffraction analysis indicates that both conventional hydrogen peroxide bleaching and tetraacetylethylenediamine/hydrogen peroxide system bleaching used in this study does not change the crystalline structure of jute fibers.**

***Keywords-activated bleaching system; crystallinity; morphological structure; degree of polymerization; Jute fibres***

## I. INTRODUCTION

The role of bleaching is to improve the whiteness of cellulosic materials by removing the naturally occurring impurities, including colored matter i.e. pigments [1]. Bleaching agents that are extensively utilized in the conventional bleaching process are chlorine and its derivatives owing to their high efficiency and low cost. However, chlorinated chemicals can produce toxic, mutagenic and carcinogenic compounds during bleaching process [2-3].

For environmental concerns, hydrogen peroxide has become the most common industrial bleaching agent due to its simplicity of use and eco-friendly nature. Unfortunately, conventional peroxide bleaching is typically conducted under conditions of high temperature (e.g. 95℃) and pH 11.5, such a harsh chemical treatment causes not only extensive consumption of energy but also can lead to a significant decrease in the degree of polymerization of cellulose[1,4-5]. For these reasons, activated peroxide systems are desired to save energy and reduce fiber damage. An activated peroxide system is formed by adding a so-called bleach activator into a hydrogen peroxide solution, in which the bleach activator is converted into a peracid by reacting with hydrogen peroxide. The generated peracid has a higher oxidative potential and thereby allows bleaching to be conducted at low temperature [6]. Since the beginning of the 21st century, a variety of bleach activators have been tested for use in activated peroxide systems, such as *N*-[4-(triethylammoniomethyl)benzoyl]-butyrolactam chloride (TBBC) [7], *N*-[4-(triethylammoniomethyl)benzoyl]lactam chlorides (TBLCs) [8], tetraacetylethylenediamine (TAED) [9], *N*-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC) [6], nonanoyloxybenzenesulfonate (NOBS) [10], $[Mn_2O_3(N,N',N''$-trimethyl-1,4,7-triazacyclononane$)_2](PF_6)_2$ (MnTMTACN) [11] and so on. Some reports have confirmed that TAED is one of the most effective activators.

The aim of this paper was to investigate the effect of TAED activated hydrogen peroxide system bleaching on the removal efficiency of noncellulosic materials and structure changes in jute fibers. To understand the effect, the scoured jute fibers were bleached by conventional $H_2O_2$ bleaching and TAED/ $H_2O_2$ system bleaching, and characterized using scanning electron microscopy (SEM), FTIR transmission and X-ray diffraction analysis.

## II. EXPERIMENTAL

### A. Materials

Scoured jute fibers (whiteness value 15.7) were prepared in laboratory, and applied as raw samples for bleaching. Tetraacetylethylenediamine (TAED, purity 92%), hydrogen peroxide ($H_2O_2$, 30%, w/w), sodium silicate ($Na_2SiO_3$), anhydrous sodium carbonate ($Na_2CO_3$), sodium dihydrogen phosphate ($NaH_2PO_4$) and disodium hydrogen phosphate ($Na_2HPO_4$) were purchased from Aladdin Industrial Corporation (Shanghai), China. Penetrant JFC was kindly provided by Tansfar Chemicals (Hangzhou), China.

### B. Methods

#### 1) Conventional $H_2O_2$ bleaching

Conventional $H_2O_2$ bleaching process was carried out in a 250 mL sealed glass container using a vibratile laboratory dyeing machine (Xiamen Rapid, China) with a material-to-liquor ratio of 1:20. Each bleaching bath contained pure $H_2O_2$ 0.09 mol/L, $Na_2SiO_3$ 3g/L, JFC 1g/L, of which the initial pH value was maintained at 11using the anhydrous sodium carbonate. The bath was heated to 95℃, and kept for 60 min. After bleaching, the samples were rinsed thoroughly with distilled water and dried in an oven (Memmert, German).

*2) TAED/$H_2O_2$ System Bleaching*

TAED/$H_2O_2$ system bleaching process was carried out in a 250 mL sealed glass container using a vibratile laboratory dyeing machine (Xiamen Rapid, China) with a material-to-liquor ratio of 1:20. Each bleaching bath contained pure $H_2O_2$ 0.09 mol/L, $Na_2SiO_3$ 3g/L, JFC 1g/L and designed amount of TAED (molar ratio of $H_2O_2$/TAED is 1:0.5), of which the initial pH value was maintained at 8 using the buffer solution of $NaH_2PO_4$- $Na_2HPO_4$. The bath was heated to a target temperature 70℃, and kept for 60 min. After bleaching, the samples were rinsed thoroughly with distilled water and dried in an oven (Memmert, German).

### C. Testing

*1) Whiteness index*

All the whiteness values of the samples were measured on a WSB-3A intelligent digital whiteness tester (Darong, China) according to GB/T 8424.2-2001, P.R. of China. Before testing, the fibers were combed and wrapped around a cardboard until opaque.

*2) Degree of polymerization*

The degree of polymerization (*DP*) of the fibers was calculated from the intrinsic viscosity of the corresponding solutions of the samples in cupriethylenediamine, method according to GB 5888-1986, P.R. of China. And then the retention of degree of polymerization (*RDP*) was calculated to investigate the damage of bleaching on jute fibers, as in (1).

$$RDP(\%)=DP_{bleached}/DP_{unbleached}\times 100\% \quad (1)$$

*3) Cellulose content*

The cellulose content of fibers were tested according to method of quantitative analysis of ramie chemical components (GB 5889-1986, P.R. of China).

*4) Scanning electron microscopy*

The surface appearance of the fibers was analyzed with a SNG 3000 scanning electron microscope (Sec Co. Ltd., South Korea). Prior to analysis the samples were covered with a gold layer.

*5) FTIR transmission*

The FTIR-transmission spectra of the fibers were obtained using Prestigae-21spectrophotometer (Shimadzu, Japan). The mixture of fiber powder and potassium bromide (KBr) was ground in a mortar and pestle and a disc was prepared using a pellet maker. The pallet was scanned from 4000 $cm^{-1}$ to 500 $cm^{-1}$ with 32 scans, a resolution of 4.0 $cm^{-1}$.

*6) X-ray diffraction analysis*

The X-ray diffraction of fiber samples was measured by Empyrean diffractometer, under the following conditions: Cu Kα radiation with graphite monochromator, 40kV and 40 mA. The patterns were obtained in 5~60 ° 2$\theta$ angular interval.

The degree of crystallinity ($I_{CR}$) of the materials was calculated by using (2).

$$I_{CR}(\%)=I_{max}/(I_{max}+I_{min})\times 100\% \quad (2)$$

Where, $I_{max}$ is the diffraction intensity measured at the maximum and represents the crystalline regions; $I_{min}$ is the diffraction intensity measured at the valley and represents the amorphous regions [12].

## III. Results And Discussion

### A. Effect of Bleaching on the Properties of Fiber

The main purpose of bleaching is to remove colored matters and endow the material with a good whiteness [1]. Table I showed that the whiteness of jute could be significantly improved by using bleaching, and the whiteness value of TAED/$H_2O_2$ system bleached jute was much more bigger than that of conventional $H_2O_2$ bleached jute. From the changes in whiteness of jute fiber, it can be concluded that TAED/$H_2O_2$ system bleaching could be conducted at lower temperature with mild alkaline condition (pH 8) and much more effective in removal of colored matters than that of conventional $H_2O_2$ bleaching.

TABLE I. PROPERTIES OF BLEACHED FIBERS

| Samples | Whiteness index | *RDP*(%) | Cellulose content (%) |
|---|---|---|---|
| Scoured jute | 15.7 | - | 75.3 |
| Conventional $H_2O_2$ bleached jute | 37.4 | 75.13 | 83.5 |
| TAED/$H_2O_2$ system bleached jute | 45.9 | 82.59 | 86.9 |

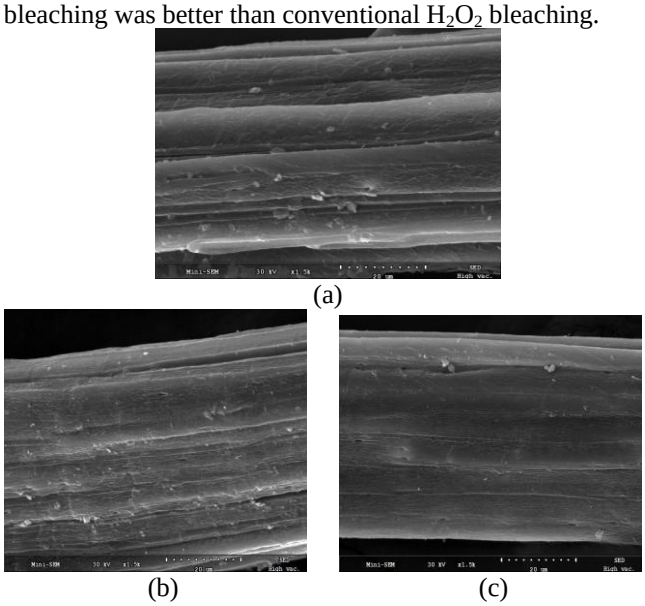
It is well documented in the literature that fiber damage does not reflect through a decrease in tensile strength until a considerable cellulosic chain scission has occurred [13]. Therefore, the degree of polymerization (*DP*) of jute fiber was measured before and after different bleaching treatments to estimate the damage on jute fibers during bleaching, and the results were shown in Table I. The bigger *RDP* value of TAED/$H_2O_2$ system bleached jute indicated little fiber damage. Furthermore, the bigger value of cellulose content demonstrated that TAED/$H_2O_2$ system bleaching was much more effective in removal of noncellulosic materials than that of conventional $H_2O_2$ bleaching.

### B. Scanning Electron Microscopy

In order to clearly estimate the effect of bleaching system on the removal of non-cellulosic materials, the surface structure of scoured jute and different system bleached jute were observed by scanning electron microscope. The results are shown in Fig.1.

As well known, the elementary fibers in jute are associated in bundles by gums (i.e. noncellulosic materials). Those visible grooves along the vertical section of the three observed samples showed that the applied bleaching conditions could not separate the bundles into single elementary fibers. It can be clearly seen from Fig.1 (a) that the scoured jute surface was covered a thick layer of noncellulosic material and adhered some flaky solids. The conventional $H_2O_2$ bleached jute fiber surface (Fig.1(b)) showed some unevenly distributed cavities due to the chemical etching on the surface of noncellullosic materials. TAED/$H_2O_2$ system bleached jute (Fig.1(c)) showed a

relative smooth surface by comparing with the conventional $H_2O_2$ bleached jute. For this, it could be concluded that the residual noncellulosic materials of alkali scoured jute could be further removed by both conventional $H_2O_2$ bleaching and TAED/$H_2O_2$ system bleaching, and TAED/$H_2O_2$ system bleaching was better than conventional $H_2O_2$ bleaching.



(a) (b) (c)

Figure 1. SEM micrographs of (a) scoured jute; (b) conventional $H_2O_2$ bleached jute; (c) TAED/ $H_2O_2$ system bleached jute.

### *C. X-ray Diffraction Analysis*

X-ray diffraction was applied to investigate the crystal structure of the scoured jute and bleached jute, as well as the degrees of crystallinity. The XRD patterns and crystallization parameters of scoured and bleached jute were displayed in Fig. 2 and Table II, respectively.

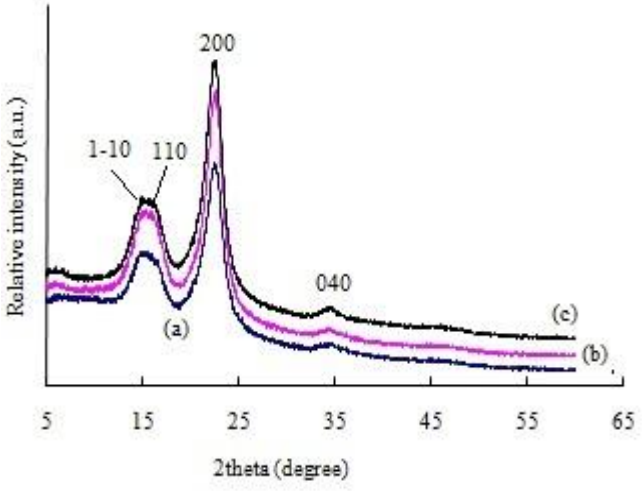



Figure 2. X-ray diffraction patterns of (a) scoured jute; (b) conventional $H_2O_2$ bleached jute; (c) TAED/$H_2O_2$ system bleached jute.

The results in Fig.2 and Table II showed that all the three tested samples showed diffraction peaks at 2$\theta$ angles around 14.6 °, 16.3 °, 22.5 ° and 34.5 °, which are assigned to the reflection from the crystallographic planes (1-10), (110), (200) and (040), those represent the typical XRD pattern for lignocellulosic fibers. In other words, both conventional $H_2O_2$ bleaching and TAED/$H_2O_2$ system bleaching used in this study did not change the crystalline structure.

TABLE II. CRYSTALLIZATION PARAMETERS OF SCOURED JUTE AND BLEACHED JUTE

| Samples | 2theta (degree) | | | | $I_{CR}$ (%) |
|---|---|---|---|---|---|
| | 1-10 | 110 | 200 | 040 | |
| Scoured jute | 14.64 | 16.34 | 22.40 | 34.52 | 65.73 |
| Conventional $H_2O_2$ bleached jute | 14.60 | 16.32 | 22.56 | 34.58 | 71.23 |
| TAED/$H_2O_2$ system bleached jute | 14.62 | 16.32 | 22.38 | 34.60 | 71.52 |

Table II also showed that both the conventional $H_2O_2$ bleaching and TAED/$H_2O_2$ system bleaching could induce a weak decrease in diffraction angles of the crystallographic planes (1-10), (110) and (200), which indicated that there was little increase in lattice spacing ($d_{hkl}$) according to Bragg equation, as in (3). It may be explained that the removal of non-cellulosic polysaccharide chains between exterior cellulose chains could lead to a formation of bigger crystallite [14].

$$\lambda=2d_{hkl}\sin\theta \quad (3)$$

The increase in degree of crystallinity ($I_{CR}$) of bleached samples is due to the removal of amorphous non-cellulosic materials like hemicelluloses, lignin, pectin and so on. It can be also seen from Table II that the degree of crystallinity of TAED/$H_2O_2$ system bleached jute is little bigger than that of conventional $H_2O_2$ bleached jute, which indicated that TAED/$H_2O_2$ system bleaching is more effective in removal of non-cellulose by comparing with conventional $H_2O_2$ bleaching.

### *D. FTIR Analysis*

The FTIR transmission spectra of the scoured jute and bleached jute were shown in Fig. 3. All the spectra were dominated by the adsorption peaks around 3020-3760 $cm^{-1}$ due to O-H stretching group, with the adsorption peaks in footprint regions at 1433 $cm^{-1}$, 1170 $cm^{-1}$ and 1070 $cm^{-1}$. The peaks at 1340 $cm^{-1}$ were ascribed to the C-C and C-O skeletal vibration and the bands at 900 $cm^{-1}$ were associated with the glycosidic linkages between sugars. These absorptions are consistent with thoes of the typical cellulose backbone [15]. In the spectrum of scoured jute, the obvious peaks at 1656 $cm^{-1}$ and small peaks at 1730 $cm^{-1}$ presented carboxylic groups of pectin or the acetyl and uronic ester groups of hemicellulose. The peaks at 1603 $cm^{-1}$, 1508 $cm^{-1}$ and 1465 $cm^{-1}$ related to aromatic rings in lignin. In the spectra of the two bleached jute, the disappearance of the adsorption peak at 1730 $cm^{-1}$ and the reduction in the peak intensity found at 1656 $cm^{-1}$, 1603 $cm^{-1}$, 1508 $cm^{-1}$ and 1465 $cm^{-1}$ indicated that non-cellulosic substances like pectin, hemicellulose and lignin could be effectively removed by both conventional $H_2O_2$ bleaching and TAED/$H_2O_2$ system bleaching. Fig.3 also showed that the reduction values in the

peak intensity at 1603 $cm^{-1}$, 1508 $cm^{-1}$ and 1465 $cm^{-1}$ in the spectrum of TAED/$H_2O_2$ system bleached jute were obvious bigger than those in the spectrum of conventional $H_2O_2$ bleached jute, which demonstrated that TAED/$H_2O_2$ system is much more effective in the removal of lignin by comparing with conventional $H_2O_2$ bleaching. However, the reduction value in the adsorption peak at 1656 $cm^{-1}$ of conventional $H_2O_2$ bleached jute was bigger than that of TAED/$H_2O_2$ system bleached jute.

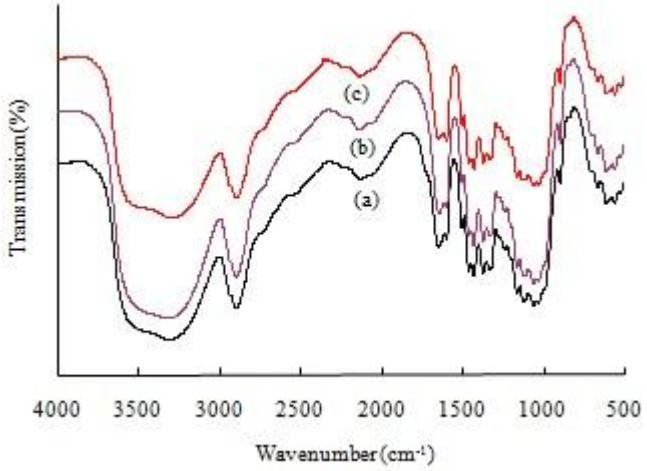



Figure 3. FTIR transmission spectra of (a) scoured jute; (b) conventional $H_2O_2$ bleached jute; (c) TAED/$H_2O_2$ system bleached jute.

## IV. CONCLUSION

In order to estimate the effect of TAED in $H_2O_2$ bleaching, the properties and structures of conventional $H_2O_2$ bleached jute and TAED/$H_2O_2$ system bleached were compared. The results showed that TAED/$H_2O_2$ system bleaching could be carried out at lower temperature with a mild alkaline condition. Comparing with conventional $H_2O_2$ bleached jute, TAED/$H_2O_2$ system bleached jute presented higher values of whiteness, cellulose content and degree of polymerization, which indicated that TAED/$H_2O_2$ system bleaching was much more effective in removal of noncellulosic materials, especially for color matters, while caused weaker fiber damage. FTIR analysis also confirmed that TAED/$H_2O_2$ system bleaching was better for removal of lignin than conventional $H_2O_2$ bleaching. Furthermore, X-ray diffraction analysis showed that both conventional $H_2O_2$ bleaching and TAED/$H_2O_2$ system bleaching used in this study did not change the crystalline structure.

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