Application of TAED/H$_2$O$_2$ system for low temperature bleaching of crude cellulose extracted from jute fiber

Zuoqiang Wen$^1$, Linbo Zou$^1$ and Weiming Wang$^{1,2,\ast}$

$^1$College of Textile & Garment, Shaoxing University, Shaoxing, China
$^2$Key Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province, Shaoxing, China

$\ast$Corresponding author e-mail: wangwm@usx.edu.cn

Abstract. Tetraacetylethlenediamine (TAED) activated hydrogen peroxide system had been applied for bleaching of crude cellulose extracted from jute fiber. Comparing with conventional hydrogen peroxide bleaching system, those results showed that bleaching temperature and time could be effectively reduced, and a preferable whiteness could be produced under faint alkaline condition. And the optimum conditions for activated bleaching system could be summarized as molar ratio of H$_2$O$_2$/TAED 1:0.7, pH 8, pure hydrogen peroxide 0.09 mol/L, temperature 70 °C and time 60min.

1. Introduction
In recent years, as the most abundant natural resource around the word, cellulose becomes one of the most important biomass resources because it has some advantages including reproducible, non-toxic and biodegradable. As well known, cellulose is mainly prepared from wood, vegetable fibers (e.g., cotton, flax, hemp and jute), and agricultural residuals [1]. For extraction processes, bleaching is one of the most important steps for removing non-cellulosic materials (e.g., color matters, lignin, hemicelluloses, and so on).

As an efficient extraction of cellulose mostly depends on the removal of lignin except for cotton, therefore, chlorine and its derivatives are the common bleaching chemicals. However, chlorinated chemicals can produce toxic, mutagenic and carcinogenic compounds during bleaching process. For environmental concerns, developing or looking for chlorine-free or total chlorine-free bleaching technologies has become a research hot spot. Some previous researches have revealed that hydrogen peroxide is the most potential chlorine-free bleaching agent [2-3]. Unfortunately, conventional H$_2$O$_2$ bleaching is typically carried out at high temperature (e.g. 95°C) and high alkaline condition of pH 11.5, such a serious chemical treatment not only consume a larger amount of energy, but also lead to a significant decrease in cellulose polymerization degree [4-5]. To overcome the disadvantages of the conventional H$_2$O$_2$ bleaching method, activated H$_2$O$_2$ bleaching systems are developed to decrease bleaching temperature. From the beginning of 21th century, many activators have been utilized in the activated H$_2$O$_2$ bleaching systems, in which tetraacetylethlenediamine (TAED) is one of the most effective activators.

In order to increase whiteness and reduce energy consumption during the hydrogen peroxide bleaching process of crude cellulose extracted from jute fiber, the feasibility of using TAED as a bleaching activator was has been investigated.
2. Experimental

2.1. Materials

Crude cellulose extracted from jute fiber (whiteness value 15.7) was used as experimental samples. Tetraacetylethlenediamine (TAED, purity 92%), hydrogen peroxide (H₂O₂, 30%, w/w), sodium silicate (Na₂SiO₃), anhydrous sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃), sodium dihydrogen phosphate (NaH₂PO₄), disodium hydrogen phosphate (Na₂HPO₄) were purchased from Aladdin Industrial Corporation (Shanghai), China. Penetrant JFC was kindly provided by Tansfar Chemicals (Hangzhou), China.

2.2. Methods

2.2.1. Activated H₂O₂ bleaching method

All bleaching experiments were conducted in a 250 mL sealed glass conical flask using a vibratile laboratory dyeing machine (Xiamen Rapid, China) with a fiber-to-liquor ratio of 1:20. Each bleaching bath contained pure H₂O₂ (viz. 0.03-0.15 mol/L), Na₂SiO₃ 3g/L, JFC 1g/L and designed amount of TAED (molar ratio of H₂O₂/TAED is 1:0.1-1.1), and the pH value was adjusted to 7-11 by using corresponding buffer solution. The treatment solution was heated to a 50-90°C, and kept for a desired time (viz. 30-180 min). After bleaching, the samples were rinsed thoroughly with distilled water, and then dried in an oven (Memmert, German).

2.2.2. Whiteness Testing

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. Before testing, the samples was loosened and put on a flat carrier until opaque.

3. Results and Discussion

3.1. Effect of molar ratio of H₂O₂/TAED on whiteness

In order to drive the perhydrolysis of TAED to completion and provide a good bleaching effect, the best molar ratio of H₂O₂ and TAED should be 1:0.5 (Scheme 1). However, it is shown in Figure 1 that an optimal whiteness value arrived at a 1:0.9 molar ratio of H₂O₂ and TAED. It may be explained that the peracids could react with the excessive H₂O₂ (Scheme 2) when the molar ratio changed in the range of 1:0.1~1:0.5. In addition, the hydrolysis of excessive TAED accompanied with perhydrolysis (Scheme 3) will lead to decrease in the pH of the bleaching medium, which will result in decrease in the rate of TAED perhydrolysis reaction (Scheme 1) because perhydrolysis reaction needs faint alkaline[6]. To avoid such undesired drop in the bleaching medium pH, the molar ratio of H₂O₂ and TAED should be controlled in the range of 1:0.7~1:0.9. And the results in figure 1 also show that there was no obvious difference in whiteness value with the molar ratio changed from 1:0.7 to 1:0.9. Therefore, our conclusion is that the optimal molar ratio should be kept at 1:0.7.

Scheme 1 Perhydrolysis of TAED
Figure 1  Effect of molar ratio of H₂O₂ and TAED on whiteness

\[
\begin{align*}
\text{OOH} & \quad \xrightarrow{\text{H}_2\text{O}_2} \quad \text{OOH} + \text{HO}_2 + \text{O}_2
\end{align*}
\]

Scheme 2 Possible reaction between peracids and hydrogen peroxide

3.2. Effect of pH on Whiteness

Figure 2  Effect of pH value on cellulose whiteness
The effect of bleaching solution pH on the bleached samples’ whiteness are shown in Figure 2, which indicated that the whiteness of bleached samples arrived at an optimum value of 30.8 at pH 8. It is considerate that perhydrolysis could be catalyzed because the alkaline could11 generated peracids. However, hydrolysis of TAED and biomolecular decomposition of peracids also could be accelerated by strong alkaline. Furthermore, the invalid decomposition rate of hydrogen peroxide will increase by increasing the bleaching medium pH[7].

3.3. Effect of $H_2O_2$ concentration on whiteness

Figure 3 showed that the whiteness of bleached samples increased with hydrogen peroxide concentration increased up to 0.09 mol/L, and then almost levelled off with hydrogen peroxide concentration further increased. It is speculated that lower dosage of hydrogen peroxide could not completely destroy the existed colored matters i.e. pigments. Meanwhile, it is well known that the TAED/$H_2O_2$ bleaching system is coexistence system of hydrogen peroxide, TAED and peracids, and all the three components’ concentration increased with increasing of initial hydrogen peroxide concentration, which is favored by perhydrolysis, TAED hydrolysis and reaction between peracids and hydrogen peroxide. Thus, it is clear that 0.09 mol/L hydrogen peroxide is the optimum concentration to obtain a reasonable whiteness.

![Figure 3](image1.png)

*Figure 3* Effect of $H_2O_2$ concentration on cellulose whiteness

3.4. Effect of temperature on cellulose whiteness

![Figure 4](image2.png)

*Figure 4* Effect of temperature on cellulose whiteness
It is shown in figure 4 that whiteness value of the bleached samples gradually increased when the bleaching temperature increased in the range of 50 °C and 70 °C, and then significantly decreased with further increasing of temperature. This is mainly because the perhydrolysis and oxidative bleaching were accelerated by increasing the treatment temperature. And it is speculated that excessive high temperature is much more benefit for invalid reaction (scheme 2, scheme 3 and so on) than perhydrolysis of TAED. Therefore, using TAED as bleaching activator for hydrogen peroxide bleaching could effectively decrease the bleaching system temperature.

3.5 Effect of time on whiteness
It can be seen from figure 5 that 60 min was sufficient to produce a reasonable whiteness value, and there could be a reverse effect on the samples whiteness when bleaching time was further prolonged. It is maybe explained that the decolorizing process have being completed in 60 min.

![Figure 5: Effect of time on whiteness](image)

4. Conclusion
In this study, TAED had been utilized as a bleaching activator for H$_2$O$_2$ bleaching of crude cellulose extracted from jute fiber. The designed experiments showed that TAED could effectively reduce bleaching temperature and time by comparing with conventional hydrogen peroxide bleaching, and the activated bleaching system could produce preferable whiteness at faint alkaline medium.

References
[1] P. Shahbazi, T. Behzad, and P. Heidarian, Isolation of cellulose nanofibers from poplar wood and wheat straw: optimization of bleaching step parameters in a chemo-mechanical process by experimental design, Wood Sci. Technol., 51(2017), 1173-1187
[2] J.M. Fang, R.C. Sun, and J. Tomkinson, Isolation and characterization of hemicelluloses and cellulose from rye straw by alkaline peroxyde extraction, Cellulose, 7(2000), 87-107
[3] S.I. Mussatto, G.J.M. Rocha and I.C. Roberto, Hydrogen peroxide bleaching cellulose pulps obtained from brewer’s spent grain, Cellulose, 15(2008), 641-649
[4] C.H. Xu, R. Shamey and D. Hinks, Activated peroxyde bleaching of regenerated bamboo fiber using a butyrolactam-based cationic bleaching activator, cellulose, 17(2010), 339-347
[5] M.M. Ibrahim, W.K. Ei-zawawy, Y. Juttke, et al., Cellulose and microcrystalline cellulose from rice straw and banana plant washer: preparation and characterization, cellulose, 20(2013), 2403-2416
[6] X.Z. Fei, J.L. Yao, J. Du, et al, Analysis of factors affecting the performance of activated peroxyde systems on bleaching of cotton fabric, Cellulose, 22(2015), 1379-1388
[7] M. A. Salam, Effect of hydrogen peroxide bleaching onto sulfonated jute fiber, J. Appl. Polym. Sci., 99(2006), 3606-3607