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Short communication

A critical reinvestigation of the TAED-activated peroxide system for low-temperature bleaching of cotton

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A B S T R A C T

There exists a misunderstanding on the TAED-activated peroxide system in the textile industry that H_2O_2 used in excess of the stoichiometric amount could produce an addition effect on bleaching of cotton under alkaline conditions. In this study, a critical reinvestigation was carried out on the TAED-activated peroxide system for bleaching of cotton. It was found that the TAED-activated peroxide system achieved its best performance under near-neutral pH conditions. No addition effect was observed when an excessive amount of H_2O_2 was used under alkaline conditions, which is probably due to the base-catalyzed bimolecular decomposition of peracetic acid and the nucleophilic attack by H_2O_2 on peracetic acid. $NaHCO_3$ was shown to be a desired alkaline agent for maintaining near-neutral pH for the TAED-activated peroxide system. This study provides new insight into the application of the TAED-activated peroxide system for low-temperature bleaching of cotton under more environmentally benign conditions.

1. Introduction

Cotton contains natural yellowish impurities which detract from the inherent white appearance of cotton cellulose (Wakelyn et al., 2007). Bleaching is often required to remove these impurities for the preparation of cotton-based textiles unless they are dyed in deep or dark shades. Hydrogen peroxide (H_2O_2) is the most widely used bleaching agent for industrial bleaching of cotton (Zeronian & Inglesby, 1995). However, bleaching of cotton with H_2O_2 is conventionally carried out under alkaline conditions (pH 11–12) at temperatures close to the boil, leading to high energy consumption as well as severe fiber damage. Hence, there is a strong demand for developing a low-temperature bleaching system to overcome the drawbacks of the conventional hot H_2O_2 bleaching system.

Bleach activators can react with H_2O_2 to form peracids *in situ* (Hofmann, Just, Pritzkow, & Schmidt, 1992). This reaction is also called perhydrolysis. Peracids are more kinetically active species and enable bleaching at low temperatures. Tetraacetylethylenediamine (TAED) is commonly used as a bleach activator for industrial bleaching of cellulosic fibers (El-Shafie, Fouda, & Hashem, 2009; Hebeish et al., 2009; Huang, Jan, & Lu, 2007; Ismal, Ozguney, & Arabau, 2007; Scarborough & Mathews, 2000; Shao, Huang, Wang, & Liu, 2010). As shown in Scheme 1, TAED reacts with H_2O_2 to consecutively form triacetylethylenediamine (TriAED) and diacetylethylenediamine (DAED) with the release of two molecules of peracetic acid (PAA) (Davies & Deary, 1991). PAA plays a main role in low-temperature bleaching. While many other bleach activators have been recently reported for bleaching of cotton (Cai & Evans, 2007; Hashem, El-Bisi, Sharaf, & Refaie, 2010; Lim, Gursoy, Hauser, & Hinks, 2004; Wang & Washington, 2002; Xu, Shamey, & Hinks, 2010), TAED continues to be of high interest due to its commercial application in the textile industry.

It has been taken for granted in almost all studies on the TAED-activated peroxide system that H_2O_2 used in excess of the stoichiometric amount could produce an addition effect on bleaching of cotton under alkaline conditions. However, it will be demonstrated in this study that the TAED-activated peroxide system is most effective using stoichiometric amounts of H_2O_2 and TAED under near-neutral pH conditions.

2. Experimental

2.1. Materials

Single jersey circular-knitted cotton greige fabric (100%) was used in experiments. TAED (purity 92%) was kindly provided by Zhejiang Jinke Chemicals Co. Ltd., China. Penetrant JFC was used as a wetting agent for bleaching of cotton, and purchased from Dynamic Chemicals Ltd., China. H_2O_2 (30% w/w), disodium

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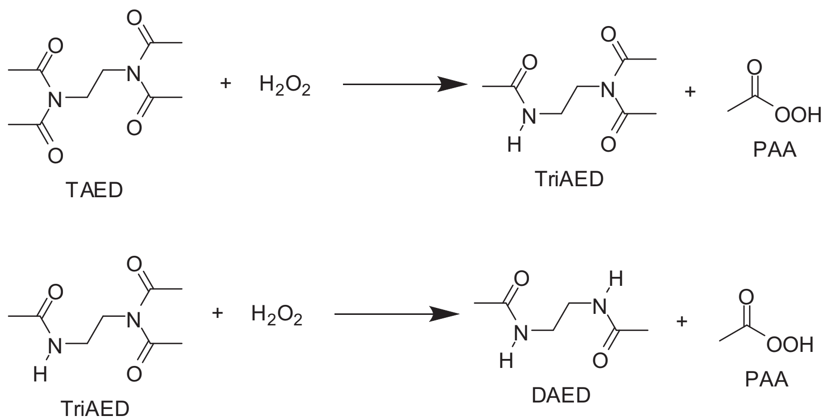


Scheme 1. Chemical reaction of TAED and H_2O_2.

ethylenediaminetetraacetate (EDTA), and all buffer substances were purchased from Sinopharm Group Co. Ltd., China.

2.2. Bleaching method

Bleaching was carried out in a reciprocating shaker bath with a liquor-to-goods ratio of 20:1. A solution was prepared by adding Penetrant JFC (1 g L^{-1}), disodium EDTA (1 g L^{-1}), and buffer substances (0.1–0.5 M) or an alkaline agent (30 or 60 mmol L^{-1}). Cotton fabric (5 g) was added to the above solution at 70 °C, followed by adding TAED (15 mmol L^{-1}) and H_2O_2 (0–300 mmol L^{-1}). The bleaching was maintained for 60 min. After that, cotton fabric was rinsed with copious amounts of water and dried under ambient conditions. Each individual experiment was performed in three replicates.

2.3. Whiteness measurement

Cotton fabric was measured on an X-Rite 8400 spectrophotometer with the settings of illuminant D_{65} and the CIE 1964 standard observer. The CIE whiteness index (WI) was calculated by Eq. (1) (AATCC, 2010),

$$\mathrm{WI} = Y + 800(0.3138 - x) + 1700(0.3310 - y) \quad (1)$$

where Y, x, y are the chromaticity coordinates of the cotton fabric. Each sample was measured four times with 90° rotation between measurements to give an average value.

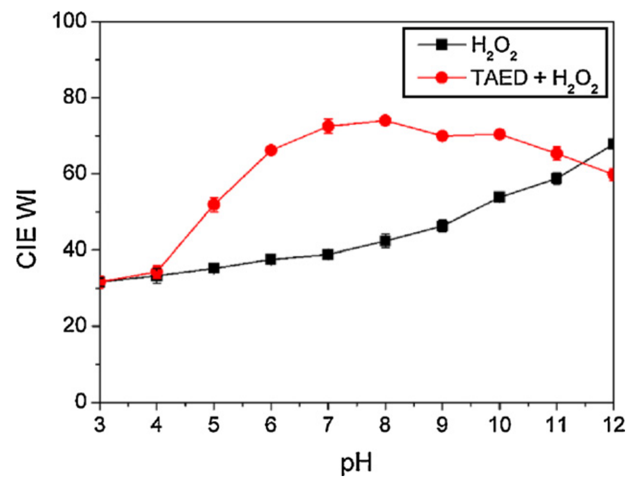


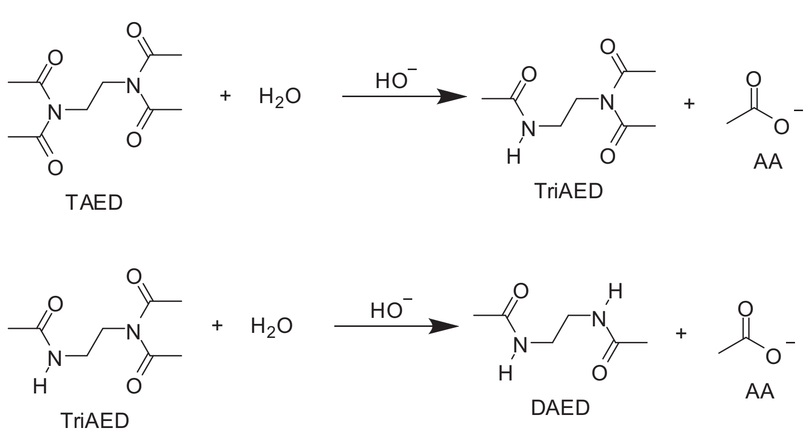
Fig. 1. Effect of pH on whiteness of cotton fabric bleached using 30 mmol L^{-1} H_2O_2 with and without the addition of 15 mmol L^{-1} TAED at 70 °C. (*Note*: bleaching was performed in a 0.1 M pH buffer system.)

$$H_2O_2 \rightleftharpoons H^+ + HOO^-$$

Scheme 2. H_2O_2 dissociation.

3. Results and discussion

Fig. 1 shows the effect of pH on whiteness of cotton fabric bleached using 30 mmol L^{-1} H_2O_2 with and without the addition



Scheme 3. Alkaline hydrolysis of TAED.

of 15 mmol L^{-1} TAED at 70 °C. It can be seen that the whiteness of cotton fabric is improved as pH increased when TAED is not added to H_2O_2 solution. This is due to the fact that H_2O_2 easily dissociates into perhydroxyl anion (HOO^-) under more alkaline conditions (Scheme 2), and HOO^- is believed to be the active bleaching species (Zeronian & Inglesby, 1995). However, H_2O_2 is not active enough for bleaching of cotton unless it is applied under extremely alkaline conditions (for example, pH 12). The TAED-activated peroxide system is formed to generate PAA (Scheme 1) when TAED is added to H_2O_2 solution. As can be seen from Fig. 1, the TAED-activated peroxide system provides an optimal level of whiteness at pH 7–8. This indicates that the perhydrolysis of TAED is well conducted for bleaching of cotton. The loss of bleaching performance over the pH range of 7–3 is most likely due to the fact that the perhydrolysis of TAED is decelerated under more acidic conditions. However, the loss of bleaching performance over the pH range of 8–12 is often ascribed to the alkaline hydrolysis of TAED as shown in Scheme 3 (Cai, Evans, & Smith, 2001; Davies & Deary, 1991; Scarborough & Mathews, 2000; Shao et al., 2010). Considering that the rate of perhydrolysis is far greater than that of hydrolysis (Edwards & Pearson, 1962; Jencks & Carriuolo, 1960; Klopman, Tsuda, Louis, & Davis, 1970; Pearson & Edgington, 1962; Wiberg, 1955), the hydrolysis of TAED should not be the key reason to cause the significant loss of bleaching performance. There is considerable research to show that peracids may undergo base-catalyzed bimolecular decomposition (Ball, Edwards, Haggett, & Jones, 1967; Goodman, Robson, & Wilson, 1962; Koubek et al., 1963). Therefore, it is thought that the base-catalyzed bimolecular decomposition of PAA should be the most possible reason to cause the significant loss of bleaching performance under alkaline conditions. As indicated in Fig. 1, the decomposition of PAA tends to be more severe as pH increases from 8 to 12.

An excessive amount of H_2O_2 is often used in the TAED-activated peroxide system for the purposes of driving the perhydrolysis of TAED to completion as well as producing an addition effect on bleaching (H_2O_2 plus PAA). Considering the higher cost of TAED compared to H_2O_2, it is understandable to use the excessive amount of H_2O_2 to completely convert TAED to PAA. However, it is necessary to reexamine the addition effect of H_2O_2 and PAA on bleaching because H_2O_2 exhibits its best bleaching performance at pH 12 but PAA at near-neutral pH (Fig. 1). To provide new evidence for the effect of H_2O_2 on the bleaching performance of the TAED-activated peroxide system, a certain amount of TAED (15 mmol L^{-1}) was used with various amounts of H_2O_2 (0–300 mmol L^{-1}) for bleaching of cotton at three typical pH values (7, 10 and 12), and the whiteness of cotton fabric is shown in Fig. 2.

As shown in Fig. 2a, the whiteness of cotton fabric is significantly improved as the concentration of H_2O_2 increases in the range of 0–30 mmol L^{-1}. This is because TAED is in excess of the stoichiometric amount and thus PAA is generated in the amount depending on the concentration of H_2O_2. In the range of 30–300 mmol L^{-1} H_2O_2, however, H_2O_2 is in excess of the stoichiometric amount. As a result, PAA is generated in a constant amount (*i.e.* 30 mmol L^{-1}), assuming complete conversion of TAED to PAA. Since the excess H_2O_2 is not active enough for bleaching of cotton at pH 7, it is not surprising that an optimal level of whiteness is achieved at 30 mmol L^{-1} H_2O_2, and is maintained relatively constant over the range of 30–300 mmol L^{-1} H_2O_2.

The TAED-activated peroxide system provides the whiteness of cotton fabric at relatively lower levels at pH 10 in the range of 0–30 mmol L^{-1} H_2O_2, as shown in Fig. 2b, compared with the data shown in Fig. 2a. This confirms the base-catalyzed bimolecular decomposition of PAA which takes place at pH 10, resulting in a loss of bleaching performance. However, unlike the relatively constant bleaching performance through the range of 30–300 mmol L^{-1} H_2O_2 at pH 7, it is observed that the TAED-activated peroxide system loses its bleaching performance at pH 10 when an excessive amount of H_2O_2 is used. It is supposed that PAA most likely undergoes nucleophilic attack by the excess H_2O_2 under alkaline conditions as shown in Scheme 5. Unfortunately, the decomposition of PAA caused by the excess H_2O_2 has not attracted enough attention in the textile industry. It can be seen From Fig. 2c that the TAED-activated peroxide system completely loses its

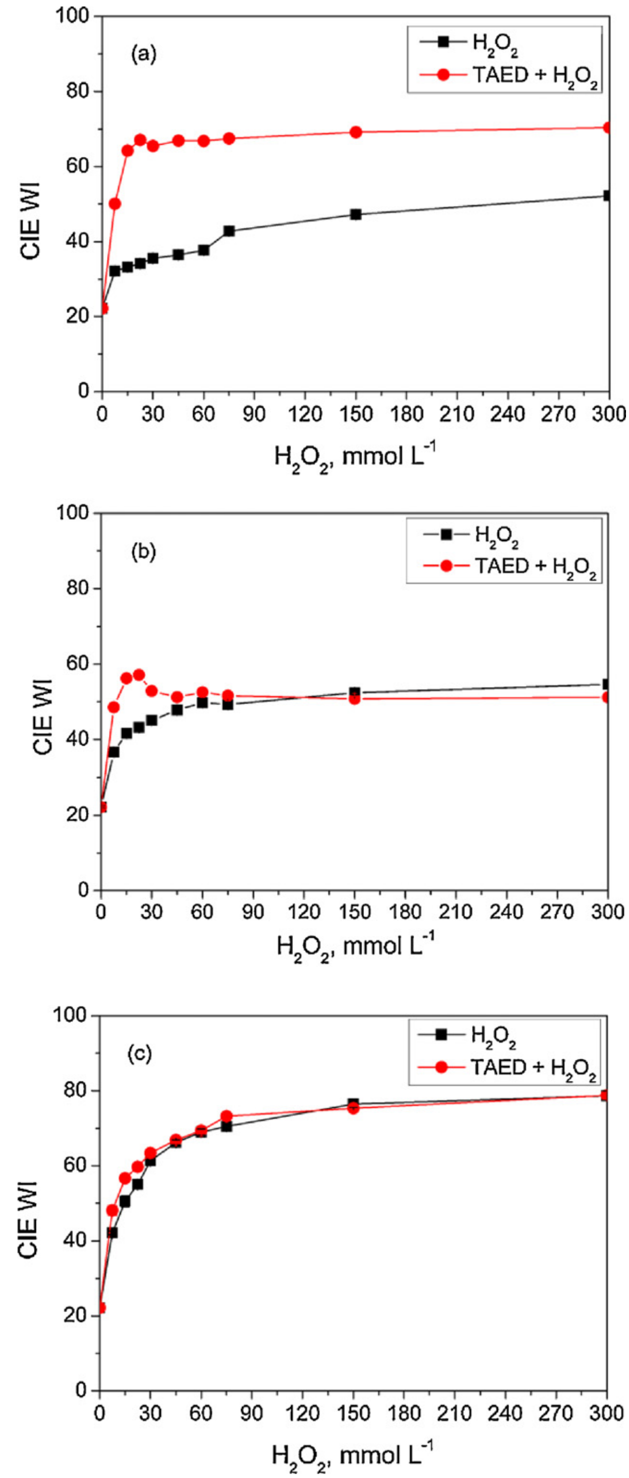
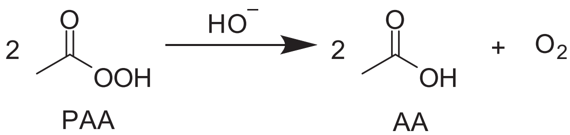
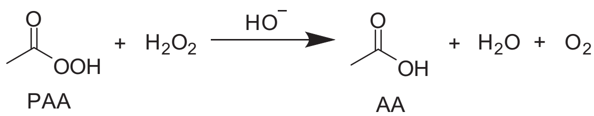


Fig. 2. Effect of H_2O_2 concentration on whiteness of cotton fabric bleached using 0–300 mmol L^{-1} H_2O_2 with and without the addition of 15 mmol L^{-1} TAED at (a) pH 7, (b) pH 10, and (c) pH 12. (*Note*: bleaching was performed in a 0.5 M phosphate buffer system.)



Scheme 4. Base-catalyzed bimolecular decomposition of PAA.



Scheme 5. Nucleophilic attack by H_2O_2 on PAA.

superiority compared to H_2O_2 for bleaching of cotton fabric at pH 12. This is because both two types of decomposition of PAA (shown in Schemes 4 and 5, respectively) take place under extremely alkaline conditions to reduce the bleaching performance, but, on the other hand, H_2O_2 becomes more active at high pH to enhance the bleaching performance.

Since the TAED-activated peroxide system releases acetic acid (AA) after bleaching of cotton, pH of the bleaching solution will drop as the bleaching process is going. As a result, the perhydrolysis of TAED (Scheme 1) will be decelerated or eventually terminated. Hence, it is essential to add an alkaline agent for neutralizing the released AA and maintain pH in a desired range. Fig. 3 shows the performance of three common alkaline agents (namely $NaHCO_3$, Na_2CO_3 and NaOH) on bleaching of cotton fabric. In Fig. 3a, $NaHCO_3$ is shown to provide a higher level of whiteness than Na_2CO_3 and NaOH. It should be pointed out that an increase in the amount of $NaHCO_3$ has no apparent effect on the whiteness of cotton fabric while an increase in the amount of Na_2CO_3 or NaOH causes significant reduction in the whiteness of cotton fabric. This is ascribed to the excellent ability of $NaHCO_3$ for maintaining pH in a near-neutral range before and after bleaching compared to Na_2CO_3 and NaOH (as shown in Fig. 3b).

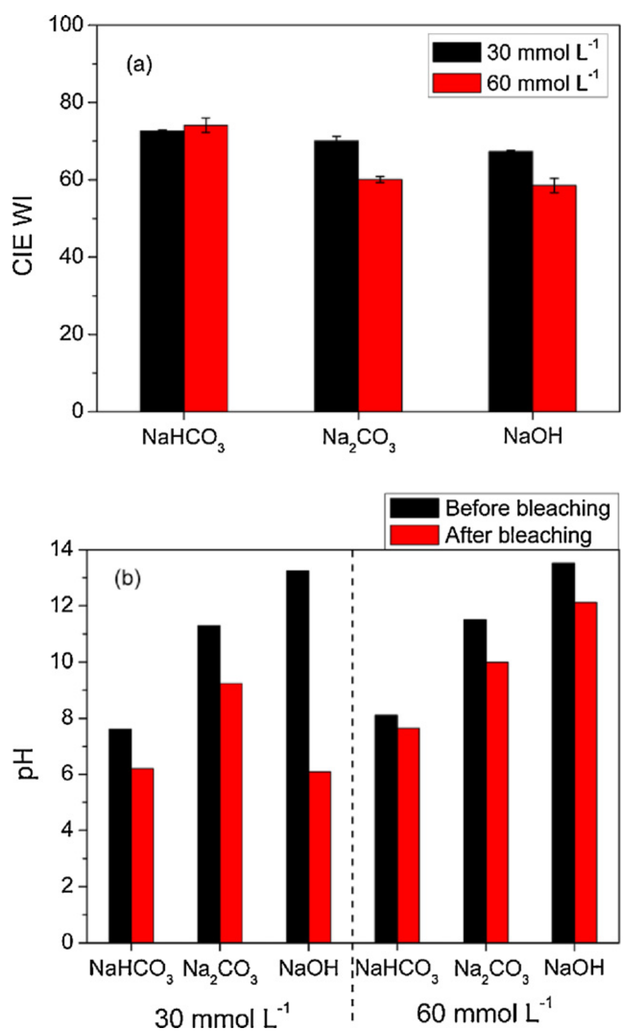


Fig. 3. Performance of different alkaline agents for use in the TAED-activated peroxide system: (a) whiteness of cotton fabric, and (b) pH before and after bleaching. (*Note*: bleaching was performed at 70 °C using 15 mmol L^{-1} TAED and 30 mmol L^{-1} H_2O_2.)

4. Conclusions

The TAED-activated peroxide system provided the best performance on bleaching of cotton fabric under near-neutral pH conditions. The bleaching performance was impaired probably due to the incomplete perhydrolysis of TAED under acidic conditions ($pH < 7$) or the base-catalyzed bimolecular decomposition of PAA under alkaline conditions ($pH > 8$). Additionally, the use of H_2O_2 in the TAED-activated peroxide system in excess of the stoichiometric amount produced no addition effect on the bleaching performance because H_2O_2 was not active enough for bleaching of cotton at pH lower than 10, and, on the other hand, PAA might undergo nucleophilic attack by H_2O_2 at pH higher than 10. $NaHCO_3$ was more applicable than Na_2CO_3 and NaOH to the TAED-activated peroxide system for bleaching of cotton due to its excellent ability of maintaining pH in a near-neutral range.

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