



Establishment of an activated peroxide system for low-temperature cotton bleaching using N-[4-(triethylammoniomethyl)benzoyl]butyrolactam chloride



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ABSTRACT

Cotton bleaching is traditionally carried out in strongly alkaline solution of hydrogen peroxide (H_2O_2) at temperatures close to the boil. Such harsh processing conditions can result in extensive water and energy consumptions as well as severe chemical damage to textiles. In this study, an activated peroxide system was established for low-temperature cotton bleaching by incorporating a bleach activator, namely N-[4-(triethylammoniomethyl)benzoyl]butyrolactam chloride (TBBC) into an aqueous H_2O_2 solution. Experimental results showed that the TBBC-activated peroxide system exhibited the most effective bleaching performance in a pH range of 6–8 which could be approximated by adding sodium bicarbonate (NaHCO_3). The TBBC/ H_2O_2 / NaHCO_3 system led to rapid bleaching of cotton at a temperature as low as 50 °C. In comparison with the hot alkaline peroxide bleaching system, the TBBC/ H_2O_2 / NaHCO_3 system provided cotton fabric with an equivalent degree of whiteness, higher degree of polymerization, and slightly lower water absorbency. The new activated peroxide system may provide a more environmentally benign approach to cotton bleaching.

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1. Introduction

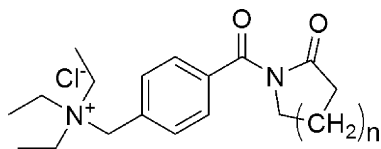
Raw cotton contains natural yellowish impurities which can significantly detract from the inherent whiteness of cotton cellulose. Bleaching is therefore required in preparation of cotton-based textiles to remove these impurities. Hydrogen peroxide (H_2O_2) is the most widely used oxidant for cotton bleaching in the textile industry due to its environmental friendliness and low costs (Zeronian & Inglesby, 1995). However, cotton bleaching with H_2O_2 is often carried out under extremely alkaline conditions at the boiling temperature. Such harsh processing conditions not only cause extensive energy consumption, but also severe chemical damage to cotton fibers. Additionally, when the bleaching process is completed, a neutralization process is required to remove the residual alkali by adding acetic acid, and a large amount of water is also required for washing to remove the residual H_2O_2 from the

bleached cotton fibers. Hence, there is currently a strong demand for establishing an alternative approach to cotton bleaching.

A low-temperature bleaching process can be achieved with an activated peroxide system which is established by incorporating a so-called bleach activator into an aqueous H_2O_2 solution (Hofmann, Just, Pritzkow, & Schmidt, 1992). A peracid is in situ generated by reaction of bleach activator with H_2O_2 (this reaction is also called perhydrolysis), which has an oxidative potential higher than H_2O_2 and is responsible for cotton bleaching at lower temperatures. Activated peroxide systems nowadays have been widely applied for domestic laundering for removal of coloring contaminants from textiles (Milne, 1998). Since the beginning of the 21st century, activated peroxide systems have been increasingly considered in the textile industry as a promising approach to low-temperature cotton bleaching, in which tetraacetylenediamine (TAED) is mostly used as a bleach activator because of its commercial availability and environmental benignity (El-Shafie, Fouda, & Hashem, 2009; Hebeish et al., 2009; Long, Xu, Du, & Fu, 2013; Scarborough & Mathews, 2000; Shao, Huang, Wang, & Liu, 2010; Xu, Long, Du, & Fu, 2013). However, TAED has poor water solubility which limits its application in industrial textile bleaching. In addition, the TAED-activated peroxide system is not very effective at temperatures below 70 °C. Therefore, much effort has been dedicated to finding a

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Scheme 1. Chemical structure of TBLCs ($n = 1-5$).

new bleach activator capable of establishing a more effective activated peroxide system (Abdel-Halim & Al-Deyab, 2013; Cai & Evans, 2007; Cai, Evans, & Smith, 2001; Hashem, El-Bisi, Sharaf, & Refaie, 2010; Ibrahim, Sharaf, & Hashem, 2010; Wang & Washington, 2002; Wang, Li, Zhu, & Yang, 2014).

N-[4-(Triethylammoniomethyl)benzoyl]lactam chlorides (TBLCs) are a novel class of quaternary ammonium compounds as given in Scheme 1, which are designed and tailored for use as bleach activators (Lee, Hinks, Lim, & Hauser, 2010). It is assumed that the cationic group provides a good water solubility of TBLCs, and the lactam group be cleaved by H_2O_2 to generate a peracid, namely *N*-(4-carboxybenzyl)-*N,N*-diethylethanaminium chloride (CPBDC) as demonstrated in Scheme 2. *N*-[4-(Triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC) is a prototype of TBLCs which was firstly applied for low-temperature bleaching of cotton fabric (Gursoy, El-Shafei, Hauser, & Hinks, 2004; Gursoy, Lim, Hinks, & Hauser, 2004; Lim, Gursoy, Hauser, & Hinks, 2004; Lim, Lee, Hinks, & Hauser, 2005). In these early investigations, however, the TBCC-activated peroxide system was established and applied deliberately under alkaline conditions using a large excess amount of H_2O_2 , and the resultant bleaching performance was not as satisfactory as expected. TBCC was found to have a poor stability to hydrolysis which was thought to be a barrier to developing an effective activated peroxide system (Lee, Lim, Hauser, & Hinks, 2005). There was no breakthrough until *N*-[4-(triethylammoniomethyl)benzoyl]butyrolactam chloride (TBBC) was synthesized with an enhanced hydrolytic stability and found to be effective under near-neutral pH conditions (Lee et al., 2010; Xu, Shamey, & Hinks, 2010). Though work has been carried out on testing the performance of the TBBC-activated peroxide system on cotton bleaching (Xu, Shamey, Hinks, & El-Shafei, 2012; Xu, Hinks, & Shamey, 2011), the mechanism that controls the reaction pathways of TBBC in the system is unclear. In this study, experimental data are generated from cotton bleaching with the TBBC-activated peroxide system, by which the involved mechanism can be elucidated and a proposal is inspired to establish a new activated peroxide system based on TBBC.

2. Experimental

2.1. Materials

Cotton greige knitted fabric was kindly provided by Cotton Incorporated (USA), and used as the model fabric for bleaching. TBBC was synthesized and purified to $\geq 97\%$ using the method reported previously (Lee et al., 2010). H_2O_2 (35% w/w) was purchased from Sigma-Aldrich (USA). Triton X-100 was used as a wetting agent in bleaching, and purchased from Fisher Scientific (USA). A peroxide stabilizer commercially named Prestogen N-D was purchased from BASF (USA). Cupriethylenediamine (0.1 M) was used for preparing cellulose dispersions from bleached cotton fabrics, and purchased from the Fisher Scientific Company, USA. All other chemicals were of analytical grade unless otherwise stated.

2.2. Preparation of the TBBC-activated peroxide system

A quantity of buffer substances (citrate, phosphate or carbonate) or an alkaline agent ($NaHCO_3$, Na_2CO_3 or $NaOH$) was dissolved in

100 mL of DI water. Triton X-100 (0.1 g) and Prestogen N-D (0.1 g) were also added to the solution as bleaching auxiliaries. A combination of TBBC and H_2O_2 in a molar ratio of 1:0 to 1:10 was added to the solution under stirring to form the TBBC-activated peroxide system for use as a bleach bath.

2.3. Cotton bleaching

A sample of cotton fabric (10 g) was immersed in the bleach bath. Bleaching was heated to and maintained at a target temperature (e.g. 25, 50, 75 and 100 °C) for various time periods from 0 to 60 min. When bleaching was completed, the bleached cotton fabric was rinsed thoroughly in water and dried under ambient conditions. Three replicates were run for each bleaching experiment.

2.4. Measurements of cotton fabrics

2.4.1. Degree of whiteness

The degree of whiteness of bleached cotton fabric was measured using the CIE whiteness index (WI) according to the AATCC Test Method 110-2010. The measurement was performed on a Datacolor SF 600× spectrophotometer (Datacolor International, USA) with the following settings: illuminant D65, large area view, specular included and CIE 1964 Supplemental Standard Observer. Each sample was folded twice to give an opaque sample with four plies, and measured four times with 90° rotation between measurements to give an average value.

2.4.2. Degree of polymerization

Cellulose dispersions were prepared from bleached cotton fabrics using cupriethylenediamine solution as a solvent, and the fluidity (*F*) of cellulose dispersions was determined according to the AATCC Test Method 82-2007. The degree of polymerization (DP) of cotton fabrics was calculated from the fluidity by Eq. (1). The DP value is correlated with chemical damage of cotton fibers resulting from oxidative bleaching. A higher DP value indicates a lower fiber damage.

$$DP = 2032 \log_{10} \left(\frac{74.35 + F}{F} \right) - 573 \quad (1)$$

2.4.3. Water absorbency

The water absorbency (WA) of cotton fabric was evaluated by measuring the elapsed time of a water drop on the cotton fabric according to the AATCC Test Method 79-2010. A shorter elapsed time of water drop on cotton fabric indicates a better water absorbency.

3. Results and discussion

3.1. Key factors affecting bleaching performance

3.1.1. pH value

The TBBC-activated peroxide system was prepared in 0.1 M buffer solutions at various pH values with the addition of 30 mmol/L TBBC and 36 mmol/L H_2O_2 , in which H_2O_2 was used in a slight excess over the stoichiometric amount for driving reactions to completion. The effect of pH values on the bleaching performance was estimated by the degree of whiteness of bleached cotton fabric. As can be seen in Fig. 1, a maximum degree of whiteness was achieved when cotton fabric was bleached at a pH value in the range of 6 to 8 which is hereby denoted by pH_M . This indicates that the perhydrolysis of TBBC was optimally conducted for generation of CPBDC (Scheme 1) which was most effective at pH_M for cotton bleaching. The degree of whiteness decreased as the pH value decreased from pH_M to 3. This was most likely due to the fact that the perhydrolysis

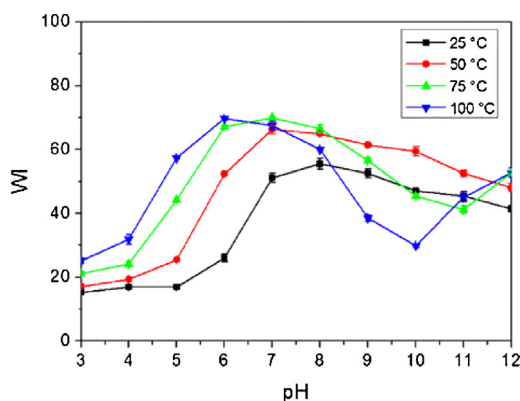


Fig. 1. Effect of pH on the degree of whiteness of cotton fabric for bleaching with the TBBC-activated peroxide system. Note: bleaching was carried out in 0.1 M buffer solution for 60 min by adding 30 mmol/L TBBC and 36 mmol/L H_2O_2 .

of TBBC was decelerated or eventually terminated under such low pH conditions that CPBDC could not be generated in an adequate amount for cotton bleaching. The degree of whiteness decreased as the pH value increased from pH_M to 12 for bleaching at 25 and 50 °C, 11 for bleaching at 75 °C, and 10 for bleaching at 100 °C. In previous investigations (Lee et al., 2005, 2010), such a decrease in the degree of whiteness with increase in pH was often ascribed to the hydrolysis of TBBC as demonstrated in Scheme 3. Since the perhydrolysis rate is at least two orders of magnitude faster than the hydrolysis rate (Jencks & Carriuolo, 1960; Pearson & Edgington, 1962; Wiberg, 1955), however, the hydrolysis of TBBC would not be responsible for the decrease in the degree of whiteness. It has been known that peracids readily undergo alkali-catalyzed bimolecular decomposition in an aqueous solution (Ball, Edwards, Haggett, & Jones, 1967; Goodman, Robson, & Wilson, 1962; Koubek et al., 1963). It thus deemed reasonable in this work that the decrease in the degree of whiteness with increase in pH should be ascribed to the alkali-catalyzed bimolecular decomposition of CPBDC as demonstrated in Scheme 4, especially under more alkaline conditions.

It is interesting to find in Fig. 1 that the degree of whiteness increased as pH increased from 11 to pH 12 at 75 °C and from 10

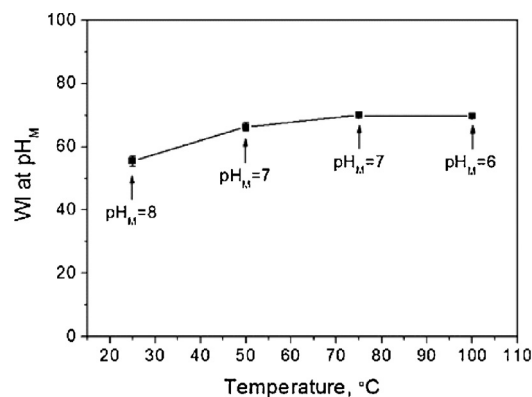
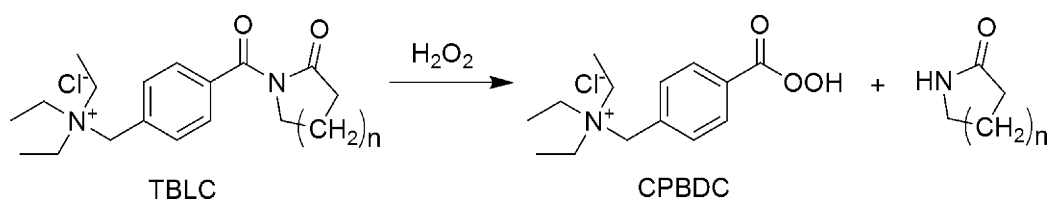


Fig. 2. Effect of temperature on the degree of whiteness of cotton fabric for bleaching with the TBBC-activated peroxide system at pH_M . Note: bleaching was carried out in 0.1 M buffer solution for 60 min by adding 30 mmol/L TBBC and 36 mmol/L H_2O_2 .

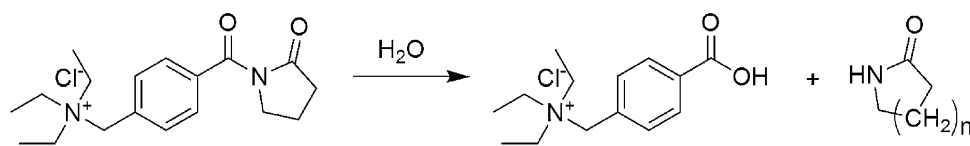
to 12 at 100 °C, respectively. This was actually due to the use of a 1:1.2 molar ratio of TBBC to H_2O_2 , of which the slightly excessive amount of H_2O_2 was proposed to drive the perhydrolysis of TBBC to completion but became more active for cotton bleaching with increasing alkalinity and temperature.

3.1.2. Temperature

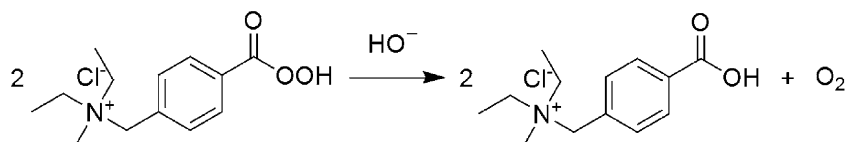
It appears in Fig. 1 that the effect of pH on the degree of whiteness varies with temperature. For a clearer understanding of the effect of temperature on the bleaching performance, the degree of whiteness at pH_M is plotted against temperature as shown in Fig. 2. The effect of temperature on the degree of whiteness at pH_M is more apparent within the range of 25–50 °C than within the range of 50–100 °C. This is because a higher temperature accelerated the rates of the TBBC perhydrolysis and the subsequent cotton bleaching with CPBDC, and the TBBC-activated peroxide system provided an adequate bleaching performance at a temperature above 50 °C. It is noted that the value of pH_M decreased from 8 to 6 as temperature increased from 25 °C to 100 °C, for which a possible reason may be that an increase in temperature promoted the dissociation of H_2O_2 at a lower pH and as such the TBBC perhydrolysis. As indicated in



Scheme 2. Perhydrolysis of TBLCs.



Scheme 3. Hydrolysis of TBBC.



Scheme 4. Possible alkali-catalyzed bimolecular decomposition of CPBDC.

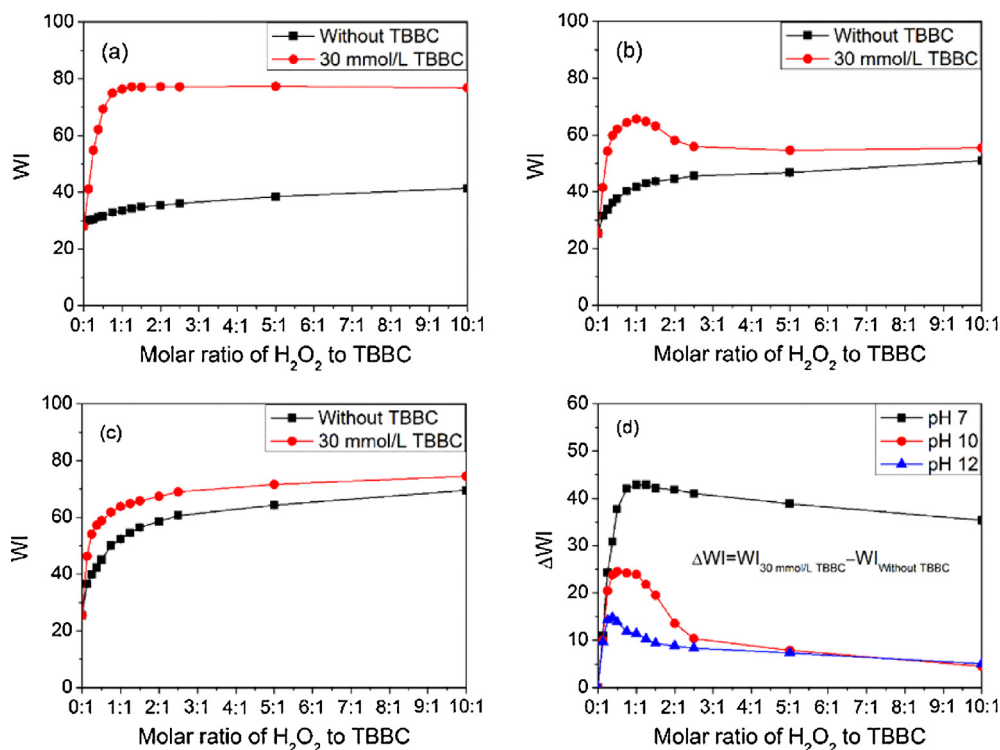


Fig. 3. Effect of molar ratio of H_2O_2 to TBBC on the degree of whiteness of cotton fabric for bleaching at pH 7 (a), pH 10 (b), pH 12 (c), and on the difference in the degree of whiteness between cotton fabrics for bleaching with and without adding TBBC (d). Note: bleaching was carried out in 0.5 M buffer solution at 50 °C for 60 min.

Fig. 2, it is very possible to establish an effective TBBC-activated peroxide system at a temperature as low as 50 °C.

3.1.3. Molar ratio of H_2O_2 to TBBC

Various molar ratio of H_2O_2 to TBBC was used in the activated peroxide system for bleaching at pH 7, 10 and 12, respectively. The plots of the degree of whiteness against the molar ratio of H_2O_2 to TBBC are shown in Fig. 3. As can be seen, the molar ratio of H_2O_2 to TBBC had a great effect on the degree of whiteness which, however, is related to pH.

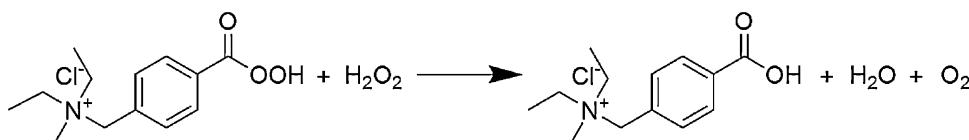
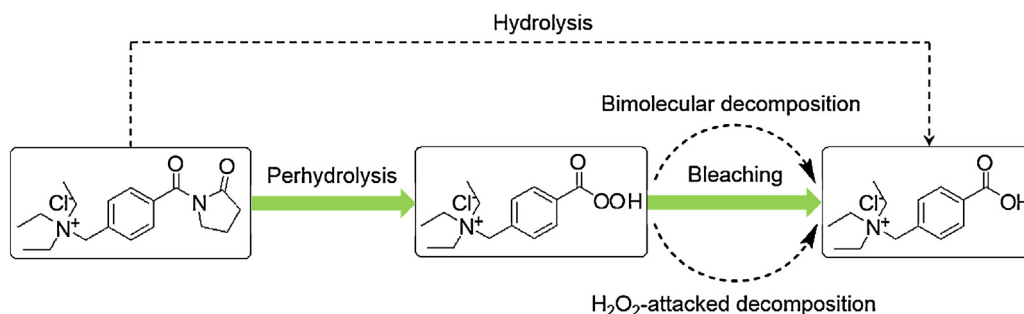
When the TBBC-activated peroxide system was established and applied for bleaching at pH 7 (Fig. 3a), the degree of whiteness of cotton fabric was greatly increased as the molar ratio of H_2O_2 to TBBC increased from 0:1 to 1:1 and stayed relatively constant over the molar ratio range of 1:1 to 10:1. It is indicated from Fig. 1 that the perhydrolysis of TBBC was optimally established for generation of CPBDC which was responsible for bleaching at pH 7. When the molar ratio of H_2O_2 to TBBC was less than the stoichiometric ratio (e.g. 1:1), the amount of CPBDC generated from perhydrolysis would depend on the amount of H_2O_2 used in the system. As the molar ratio of H_2O_2 to TBBC was increased above the stoichiometric ratio, the amount of CPBDC generated from perhydrolysis would be stoichiometrically equal to the amount of TBBC. An excessive amount of H_2O_2 may drive the perhydrolysis of TBBC to completion, but was ineffective for bleaching at pH 7.

When the TBBC-activated peroxide system was established and applied for bleaching at pH 10 (Fig. 3b), however, the molar ratio of H_2O_2 to TBBC exhibited profoundly different effect on the degree of whiteness of cotton fabric. As the molar ratio of H_2O_2 to TBBC increased from 0:1 to 1:1, the degree of whiteness of cotton fabric increased similarly but relatively lower as compared with that resulting from bleaching at pH 7. The lower degree of whiteness was ascribed to the alkali-catalyzed bimolecular decomposition of CPBDC (Scheme 4). However, it is interesting to note in Fig. 3b that the degree of whiteness of cotton fabric greatly decreased as the

molar ratio of H_2O_2 to TBBC increased from 1:1 to 10:1, especially from 1:1 to 2:1. This was most likely caused by the nucleophilic attack of H_2O_2 on CPBDC as demonstrated in Scheme 5 because the excessive amount of H_2O_2 used in the system more readily dissociated under alkaline conditions (e.g. pH 10) to perhydroxyl anions (HOO^-) which are very strong nucleophilic reagent.

When a large excess amount of H_2O_2 was applied in the TBBC-activated peroxide system for bleaching of cotton under extremely alkaline conditions (pH 12) as shown in Fig. 3c, it is difficult to observe the effect of the nucleophilic attack to CPBDC by H_2O_2 on the degree of whiteness because of a joint effect of the hydrolysis of TBBC (Scheme 2), the bimolecular decomposition of CPBDC (Scheme 3) and the enhanced H_2O_2 bleaching. In order to clearly recognize the effect of the excessive amount of H_2O_2 on the bleaching performance, the data shown in Fig. 3a–c were mathematically treated by subtracting the degree of whiteness that was achieved using the H_2O_2 system (without adding any TBBC) from the degree of whiteness that was achieved using the TBBC-activated peroxide system (with adding 30 mmol/L TBBC), and the results were plotted in Fig. 3d. It is noted that the excessive amount of H_2O_2 caused more negative effect on the bleaching performance at higher pH values.

It has been widely accepted that a large excessive amount of H_2O_2 should be used in activated peroxide systems under alkaline conditions for providing an additive effect on the bleaching performance (Gursoy et al., 2004a,b; Lim et al., 2004, 2005). It seems plausible that such an additive effect existed because the TBBC-activated peroxide system provided a little better bleaching performance than the H_2O_2 system as observed in Fig. 3c. However, the fact is disclosed in Fig. 3d that the TBBC-activated peroxide system lost most of its bleaching performance in the presence of an excessive amount of H_2O_2 under alkaline conditions due to the nucleophilic attack of H_2O_2 on CPBDC (Scheme 5). This finding is very valuable for establishing an effective activated peroxide system for cotton bleaching.

Scheme 5. Nucleophilic attack of H_2O_2 on CPBDC.

Scheme 6. Possible reactions in the TBBC-activated peroxide system.

3.2. Establishment of the TBBC/ H_2O_2 / NaHCO_3 system

Based on the above results and discussion, it can be concluded that there may exist several possible reactions in the TBBC-activated peroxide system as demonstrated in Scheme 6. The perhydrolysis of TBBC and the cotton bleaching with CPBDC are desired reactions while the hydrolysis of TBBC, alkali-catalyzed bimolecular and H_2O_2 -attacked decompositions of CPBDC are undesired side-reactions. pH is a key factor affecting the proceeding of these reactions and, at pH_M , the desired reactions are optimally established but the undesired side-reactions are prevented. Hence, the bleaching performance can be maximized by maintaining the TBBC-activated peroxide system at pH_M .

In practical cotton bleaching, it is advisable to use a common alkali as an approach to approximating pH_M in the TBBC-activated peroxide system. NaHCO_3 , Na_2CO_3 and NaOH were primarily examined in this work. As can be seen from Fig. 4a, NaHCO_3 was more applicable than Na_2CO_3 and NaOH for maintaining pH within the desired range before and after bleaching, e.g. $\text{pH}_M \pm 1$. As is known, NaHCO_3 is a weaker alkali than Na_2CO_3 and NaOH . An aqueous solution of NaHCO_3 has a pH value of less than 9 while aqueous solutions of NaHCO_3 and NaOH may have pH values of greater than 10. Hence, NaHCO_3 had an advantage over Na_2CO_3 and NaOH for use as an alkali in suppressing the undesired side reactions in the TBCC-activated peroxide system. Accordingly, NaHCO_3 was superior to Na_2CO_3 and NaOH , actually equivalent to pH_M for improving the degree of whiteness as shown in Fig. 4b. NaHCO_3 was not only effective for neutralizing the acid produced in the TBBC-activated peroxide system, but also resulted in no apparent increase in pH with an excessive amount. As shown in Fig. 5, a 1:1 molar ratio of NaHCO_3 to TBBC was adequate for use in the TBBC-activated peroxide system which provided cotton fabric a maximum degree of whiteness, and an excessive amount of NaHCO_3 had no apparent effect on bleaching performance.

The TBBC-activated peroxide system could thus be established by incorporating TBBC, H_2O_2 and NaHCO_3 , of which a molar ratio of 1:1.2:1.25 was suggested for the purpose of ensuring a complete conversion of TBBC into CPBDC for cotton bleaching at low temperatures. As shown in Fig. 6, such an established TBBC/ H_2O_2 / NaHCO_3 system exhibited a rapid bleaching performance at a temperature as low as 50°C .

The TBBC/ H_2O_2 / NaHCO_3 system was compared with the hot alkaline H_2O_2 / NaOH system in terms of the degree of whiteness, degree of polymerization and water absorbency of bleached

cotton fabrics as shown in Table 1. It can be seen that the TBBC/ H_2O_2 / NaHCO_3 system was equivalent to the H_2O_2 / NaOH system in improving the degree of whiteness of cotton fabric. It is interesting to note that, unlike the H_2O_2 / NaOH system which resulted in a remarkable reduction in the degree of polymerization of cotton fabric, the TBBC/ H_2O_2 / NaHCO_3 system resulted in no apparent reduction in the degree of polymerization of cotton fabric. This indicates that the TBBC/ H_2O_2 / NaHCO_3 system had advantage over the H_2O_2 / NaOH system in protecting cotton fibers from chemical damage during the bleaching process. The TBBC/ H_2O_2 / NaHCO_3 system was found to be slightly inferior to the H_2O_2 / NaOH system in improving the water absorbency of cotton fabric, but it is

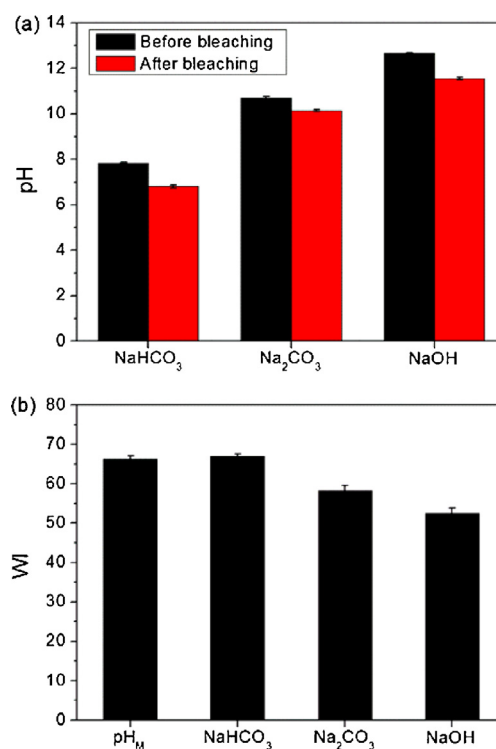


Fig. 4. Performance of various alkaline agents for use in the TBBC-activated peroxide system: (a) pH before and after bleaching and (b) degree of whiteness of cotton fabric after bleaching. Note: bleaching was carried out at 50°C for 60 min by adding 30 mmol/L TBBC, 36 mmol/L H_2O_2 and 50 mmol/L alkaline agent.

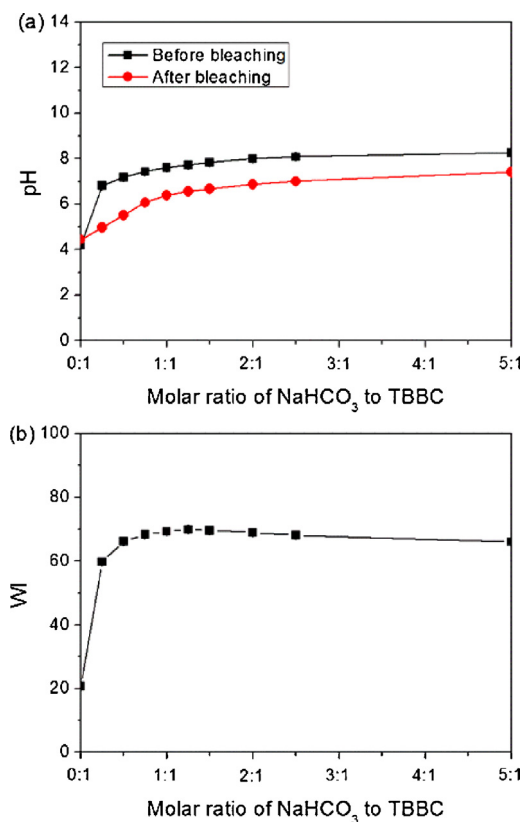


Fig. 5. Effects of the molar ratio of NaHCO₃ to TBBC on pH before and after bleaching (a), and on degree of whiteness of cotton fabric after bleaching (b). Note: bleaching was carried out at 50 °C for 60 min by adding 30 mmol/L TBBC and 36 mmol/L H₂O₂.

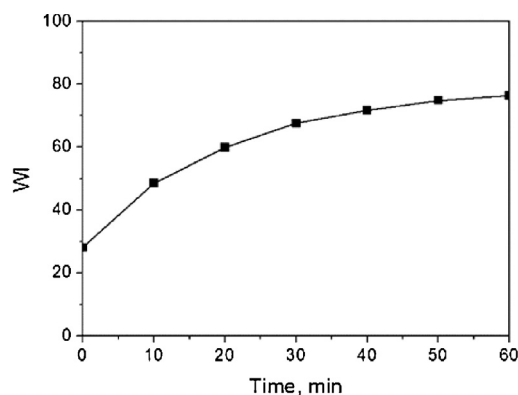


Fig. 6. Degree of whiteness of cotton fabric bleached with the TBBC/H₂O₂/NaHCO₃ system at 50 °C for various time periods using 30 mmol/L TBBC, 36 mmol/L H₂O₂ and 37.5 mmol/L NaHCO₃.

Table 1
Performance comparison of the TBBC/H₂O₂/NaHCO₃ system and the H₂O₂/NaOH system for bleaching of cotton fabric.

Bleaching system	WI	DP	WA (s)
Control (greige fabric)	8.89 ± 1.40	4147 ± 86	>60
TBBC/H ₂ O ₂ /NaHCO ₃ ^a	78.38 ± 1.23	4192 ± 103	3–5
H ₂ O ₂ /NaOH ^b	79.98 ± 0.94	3271 ± 115	<1

^a Cotton fabric was bleached using 30 mmol/L TBBC, 36 mmol/L H₂O₂ and 37.5 mmol/L NaHCO₃ at 50 °C for 40 min.

^b Cotton fabric was bleached using 4 g/L H₂O₂ (35% w/w) and 2 g/L NaOH at 95 °C for 40 min.

considered that the water absorbency of cotton fabric bleached with the TBBC/H₂O₂/NaHCO₃ system would be adequate for further dyeing.

4. Conclusions

An activated peroxide system was established by using TBBC as a bleach activator for cotton bleaching at a low temperature. Experimental results showed that the TBBC-activated peroxide system was most effective for bleaching in a pH range of 6–8 which was slightly affected by temperature. The bleaching performance was reduced either below this pH range where the perhydrolysis of TBBC and the cotton bleaching with CPBDC were most likely decelerated or eventually terminated, or above this pH range where CPBDC could undergo extensive alkali-catalyzed bimolecular and H₂O₂-attacked decompositions. NaHCO₃ was preferably selected as an alkaline agent for use in the TBBC-activated peroxide system for its capacity of maintaining pH in the desired range of 6–8. An effective activated peroxide system was resulted from a combination of TBBC, H₂O₂ and NaHCO₃, of which a molar ratio of 1:1.2:1.25 was applicable for rapid cotton bleaching at a temperature as low as 50 °C. In compared to the hot alkaline H₂O₂/NaOH system, the TBBC/H₂O₂/NaHCO₃ system provided cotton fabric with an equivalent degree of whiteness, higher degree of polymerization and slightly lower water absorbency. The new activated peroxide system may provide an alternative approach to cotton bleaching that can be carried out under much mild conditions such as near-neutral pH, low temperature and rapid time period.

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