



The TAED/H₂O₂/NaHCO₃ system as an approach to low-temperature and near-neutral pH bleaching of cotton



Xiaoxia Long, Changhai Xu*, Jinmei Du, Shaohai Fu*

Key Laboratory of Eco-textiles, Ministry of Education, Jiangnan University, 1800 Lihu Avenue, Wuxi, Jiangsu 214122, China

ARTICLE INFO

Article history:

Received 29 December 2012

Accepted 26 February 2013

Available online 5 March 2013

Keywords:

Cotton

Low-temperature bleaching

Hydrogen peroxide

TAED

Peracetic acid

Activated peroxide system

ABSTRACT

A low-temperature and near-neutral pH bleaching system was conceived for cotton by incorporating TAED, H₂O₂ and NaHCO₃. The TAED/H₂O₂/NaHCO₃ system was investigated and optimized for bleaching of cotton using a central composite design (CCD) combined with response surface methodology (RSM). CCD experimental data were fitted to create a response surface quadratic model (RSQM) describing the degree of whiteness of bleached cotton fabric. Analysis of variance for the RSQM revealed that temperature was the most significant variable, followed by [TAED] and time, while [NaHCO₃] was insignificant. An effective system was conducted by adding 5.75 g L⁻¹ TAED together with H₂O₂ and NaHCO₃ at a molar ratio of 1:2.4:2.8 and applied to bleaching of cotton at 70 °C for 40 min. Compared to a commercial bleaching method, the TAED/H₂O₂/NaHCO₃ system provided cotton with comparable degree of whiteness, slightly inferior water absorbency and acceptable dyeability, but had competitive advantage in protecting cotton from severe chemical damage in bleaching.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

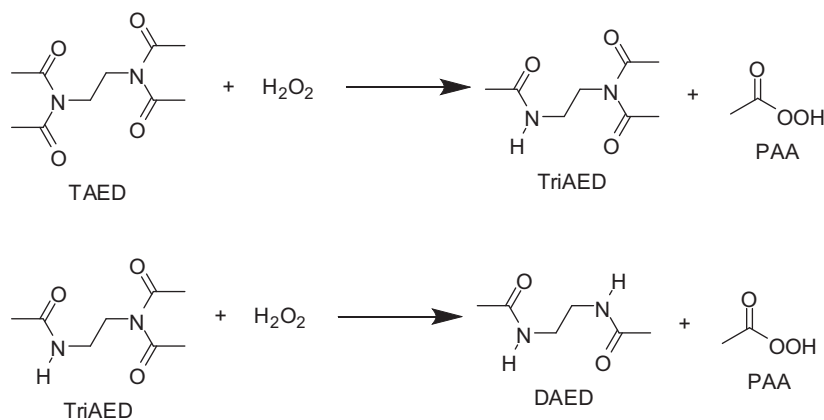
Cotton contains natural yellowish impurities which significantly impair the inherent whiteness of cellulose (Wakelyn et al., 2007). These yellowish impurities must be removed in bleaching for the preparation of cotton-based textiles unless cotton is dyed with dark shades. Bleaching of cotton with hydrogen peroxide (H₂O₂) is the most widely used method in the textile industry and is conventionally carried out under alkaline conditions (pH 11–12) at temperatures close to the boil (>95 °C) or room temperature for a long dwell time (e.g. 24 h) (Zeronian & Inglesby, 1995). In recent years, great efforts have been made to lower temperature and (or) shorten time period for industrial textile bleaching by incorporating bleach activators and catalysts into aqueous H₂O₂ solution (Abdel-Halim & Al-Deyab, 2013; Cai & Evans, 2007; Cai, Evans & Smith, 2001; Gursoy, Lim, Hinks & Hauser, 2004; Hashem, El-Bisi, Sharaf & Refaie, 2010; Ibrahim, Sharaf & Hashem, 2010; Lim, Lee, Hinks & Hauser, 2005; Qin et al., 2012; Scarborough & Mathews, 2000; Shao, Huang, Wang & Liu, 2010; Topalovic et al., 2007; Wang & Washington, 2002; Xu, Hinks & Shamey, 2010, 2011; Xu, Shamey, et al., 2010). These low-temperature bleaching systems have been shown to have advantages over conventional H₂O₂ bleaching methods in reducing energy consumption and protecting cotton from chemical damage.

Tetraacetylenediamine (TAED) is a bleach activator for use in industrial bleaching of cellulosic fibers (Cai, Evans, & Smith, 2001; El-Shafie, Fouda, & Hashem, 2009; Hebeish et al., 2009; Scarborough & Mathews, 2000; Shao, Huang, Wang, & Liu, 2010). As shown in Scheme 1, TAED can react with H₂O₂ to consecutively form triacetylenediamine (TriAED) and diacetylenediamine (DAED) with the release of two molecules of peracetic acid (PAA) (Davies & Deary, 1991). This reaction is also called perhydrolysis. PAA is a more kinetically active species than H₂O₂ and allows bleaching to be conducted at low temperatures (Hofmann, Just, Pritzkow, & Schmidt, 1992). In most previous investigations of TAED for low-temperature bleaching of cellulose-based textiles, TAED was deliberately used with a large excess of H₂O₂ under alkaline conditions in that the excess amount of H₂O₂ was expected to produce an additive effect on bleaching performance. As a matter of fact, it has been demonstrated in a recent study that TAED enables low-temperature bleaching to be more effective under near-neutral pH conditions instead of alkaline conditions and the use of an excess amount of H₂O₂ has no additive effect on bleaching performance under near-neutral pH conditions but significantly reduces bleaching performance under alkaline conditions (Xu, Long, Du, & Fu, 2013).

Sodium bicarbonate (NaHCO₃) has been shown to be a desired alkaline agent for maintaining near-neutral pH for low-temperature bleaching with the TAED-activated peroxide system (Xu et al., 2013). This provides the impetus to conceive a low-temperature and near-neutral pH bleaching system for cotton by incorporating TAED, H₂O₂ and NaHCO₃. In this study, the

* Corresponding authors. Tel.: +86 510 85912007; fax: +86 510 85912009.

E-mail addresses: changhai.xu@jiangnan.edu.cn, xuchanghai@hotmail.com (C. Xu), shaohaiFu@hotmail.com (S. Fu).



Scheme 1. Perhydrolysis of TAED.

Table 1
Coded and actual levels of design variables.

Variable	Symbol	Coded and actual levels				
		−2	−1	0	+1	+2
[TAED], g L ^{−1}	X_1	0.50	2.25	4.00	5.75	7.50
[NaHCO ₃], g L ^{−1}	X_2	7.00	9.00	11.00	13.00	15.00
T , °C	X_3	30.0	45.0	60.0	75.0	90.0
t , min	X_4	10.0	25.0	40.0	55.0	70.0

TAED/H₂O₂/NaHCO₃ system is investigated and optimized using central composite design (CCD) combined with response surface methodology (RSM). The performance of the TAED-activated peroxide system on bleaching of cotton is evaluated in terms of the degree of whiteness (WI), water absorbency (WA), dyeability and degree of polymerization (DP) of bleached cotton fabrics.

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 and purchased from Dynamic Chemicals Ltd., China. Disodium ethylenediaminetetraacetate (EDTA) was used as a chelating agent and purchased from Sinopharm Group Co., Ltd., China. Cupriethylene diamine (1.0M) was used for preparing dispersions of cellulose from bleached cotton and purchased Fisher Scientific Company, USA. All other chemicals were of analytical grade unless otherwise stated. Tap water was used throughout the bleaching experiments.

2.2. Design of experiment

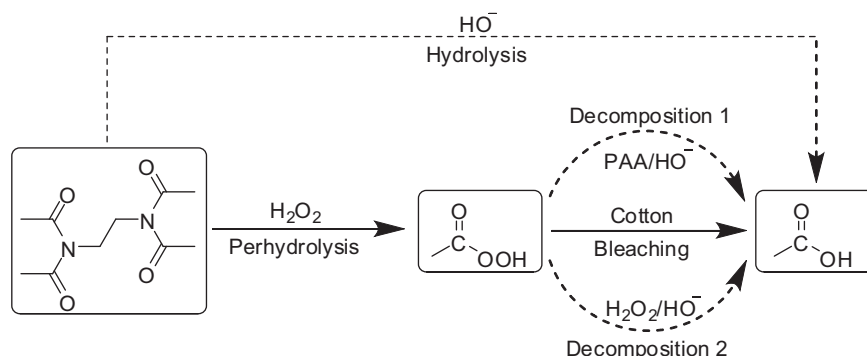
The CCD included four design variables, namely concentration of TAED ([TAED]), concentration of NaHCO₃ ([NaHCO₃]), temperature (T) and time period (t). The design of experiment was carried out using the Design Expert software 7.0 (Stat-Ease Inc., USA). The coded and actual levels of each variable are shown in Table 1, and the design matrix is shown in Table 2. The total number of bleaching experiments was 30 including sixteen factorial points (coded as −1 or +1), eight axial points (coded as −2 or +2) and six replications of the center point (coded as 0). The six replications of the center point were used to estimate the pure error. The response variable was monitored by measuring WI of bleached cotton fabric.

2.3. Bleaching method

Bleaching was carried out in a reciprocating shaker bath using a liquor-to-goods ratio of 20:1. Each bleaching solution contained 1 g L^{−1} wetting agent and 1 g L^{−1} chelating agent. A sample of cotton fabric (around 5 g) was immersed in a bleaching solution, followed by adding TAED and NaHCO₃ (according to the levels shown in Tables 1 and 2) as well as H₂O₂ at a 2.4:1 molar ratio with respect to

Table 2
CCD design matrix with coded levels of design variables.

Standard	Run	X_1	X_2	X_3	X_4
1	18	−1	−1	−1	−1
2	22	+1	−1	−1	−1
3	3	−1	+1	−1	−1
4	19	+1	+1	−1	−1
5	15	−1	−1	+1	−1
6	12	+1	−1	+1	−1
7	20	−1	+1	+1	−1
8	9	+1	+1	+1	−1
9	4	−1	−1	−1	+1
10	14	+1	−1	−1	+1
11	13	−1	+1	−1	+1
12	1	+1	+1	−1	+1
13	8	−1	−1	+1	+1
14	25	+1	−1	+1	+1
15	5	−1	+1	+1	+1
16	17	+1	+1	+1	+1
17	11	−2	0	0	0
18	24	+2	0	0	0
19	10	0	−2	0	0
20	7	0	+2	0	0
21	27	0	0	−2	0
22	6	0	0	+2	0
23	26	0	0	0	−2
24	2	0	0	0	+2
25	30	0	0	0	0
26	23	0	0	0	0
27	28	0	0	0	0
28	29	0	0	0	0
29	21	0	0	0	0
30	16	0	0	0	0



Scheme 2. Possible reactions related to TAED in aqueous H_2O_2 solution.

TAED. H_2O_2 was slightly in excess of TAED for driving the reactions to completion. The bleaching solution with the sample was maintained at a desired temperature for a time period. The bleached cotton fabric was rinsed thoroughly in copious amounts of tap water and dried under ambient conditions. Each bleaching was performed randomly according to the run number shown in Table 2 to minimize the effect of various sources of error on treatment results.

For the purpose of comparison, a commercial method was used for bleaching of cotton. The bleaching solution contained 5 g L^{-1} H_2O_2 (30%, w/w), 2.5 g L^{-1} NaOH, 1 g L^{-1} wetting agent and 1 g L^{-1} chelating agent. A sample of cotton fabric was bleached at 95°C for 40 min using a liquor-to-goods ratio of 20:1. The bleached cotton fabric was rinsed thoroughly in copious amounts of tap water and dried under ambient conditions.

2.4. Testing

2.4.1. WI

The bleached cotton fabric was measured on an X-Rite 8400 spectrophotometer with the settings of illuminant D_{65} and CIE 1964 standard observer. WI was represented in the CIE whiteness index according to the AATCC Test Method 110-2005, and is given by Eq. (1):

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

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

2.4.2. WA

WA was evaluated by measuring the elapsed time of a water drop on cotton fabric according to the AATCC Test Method 79-2007. A shorter elapsed time of water drop on cotton fabric indicates a better water absorbency.

2.4.3. Dyeability

The dyeability of bleached cotton fabric was tested using three Remazol RGB dyes (Red, Yellow and Navy), respectively, following commercial recipes. The cotton fabrics bleached with the TAED/ H_2O_2 /NaHCO₃ system and the commercial method were immersed in a same dyeing bath for competing dyeing. Dyeing was performed on a rotary infrared laboratory dyeing machine.

The dyed cotton fabrics were measured on the X-Rite 8400 spectrophotometer according to the AATCC Evaluation Procedure 6-2008. The color attributes were specified in CIELAB color space. The color difference between the dyed cotton fabrics was calculated by the CMC (2:1) formula (i.e. ΔE_{cmc}) according to the AATCC Test Method 173-2009.

2.4.4. DP

A dispersion of cotton fabric in cupriethylenediamine solvent was prepared for measurement of the fluidity (F) according to the AATCC Test Method 82-2007. DP of cotton fabric was calculated by Eq. (2):

$$\text{DP} = 2032 \log_{10} \left(\frac{74.35 + F}{F} \right) - 573 \quad (2)$$

3. Results and discussion

3.1. Theoretical base of the TAED/ H_2O_2 /NaHCO₃ system

As shown in Scheme 2, TAED may undergo perhydrolysis and alkaline hydrolysis in aqueous H_2O_2 solution (Davies & Deary, 1991). As a matter of fact, the hydrolysis can be ignored compared to the perhydrolysis because the nucleophilicity of perhydroxyl anions is far higher than the nucleophilicity of hydroxyl anions in aqueous solution (Heller & Weiler, 1987; Jencks & Carriuolo, 1960; McIsaac, Subbaraman, Subbaraman, Mulhausen, & Behrman, 1972; Pearson & Edgington, 1962; Pearson, Edgington, & Basolo, 1962; Wiberg, 1955). Hence, TAED is preferably converted into PAA which is the desired compound to contribute to bleaching of cotton. However, PAA may undergo bimolecular decomposition (Decomposition 1 in Scheme 2) and nucleophilic attack by H_2O_2 (Decomposition 2 in Scheme 2) under alkaline conditions (Ball, Edwards, Haggett, & Jones, 1967; Goodman, Robson, & Wilson, 1962; Koubek et al., 1963), and is converted into acetic acid (AA) to lose its performance on bleaching of cotton. It is thus essential to inhibit the PAA decomposition for maximizing the bleaching performance. Assuming that the PAA decomposition is avoided in the system, TAED would be converted into AA after bleaching of cotton. The release of AA will result in a drastic drop in pH. Consequently, the perhydrolysis of TAED as well as bleaching of cotton is decelerated or eventually terminated. Hence, an alkaline agent must be added to neutralize AA so as to drive these reactions to completion. It was shown in a previous study that NaHCO₃ was capable of maintaining pH in a near-neutral pH range at which TAED exhibited the best performance for bleaching of cotton (Xu et al., 2013). Hence, an effective strategy for maximizing the performance of TAED on bleaching of cotton is to incorporate NaHCO₃ into the TAED-activated peroxide system. It is propose to use a 1:2.4 molar ratio of TAED to H_2O_2 in the TAED/ H_2O_2 /NaHCO₃ system. The excess amount of H_2O_2 should have no effect on WI of cotton fabric but drive the reactions to completion (Xu et al., 2013).

3.2. Response surface quadratic model (RSQM) based on CCD

RSM is a powerful tool for quantifying the relationship between multiple design variables and one or more response variables, and

Table 3
ANOVA for RSQM excluding insignificant model terms.

Source	Sum of squares	Degree of freedom	Mean square	F value	p-Value
Model	1803.45	8	225.43	89.74	<0.0001
X_1	674.69	1	674.69	268.57	<0.0001
X_2	0.26	1	0.26	0.10	0.7516
X_3	701.89	1	701.89	279.40	<0.0001
X_4	88.97	1	88.97	35.42	<0.0001
X_3X_4	35.25	1	35.25	14.03	0.0012
X_1^2	228.07	1	228.07	90.79	<0.0001
X_2^2	8.93	1	8.93	3.55	0.0733
X_3^2	69.37	1	69.37	27.61	<0.0001
Residual	52.76	21	2.51		
Lack of fit	48.61	16	3.04	3.66	0.0788
Pure error	4.15	5	0.83		
Cor. total	1856.20	29			

thus can be used to evaluate the main and interactive effects of design variables on process performance (Montgomery, 2005). CCD is the most commonly used type of RSMs, in which each design variable has five levels permitting the design to generate sufficient data to fit a RSQM. CCD has been successfully used in considerable research on developing low-temperature bleaching systems for cotton-based textiles (Gursoy et al., 2004; Lavrič, Kovač, Tavčer, Hauser, & Hinks, 2007; Lim, Gursoy, Hauser, & Hinks, 2004; Lim, Lee, Hinks, & Hauser, 2005; Xu, Shamey, et al., 2010; Xu, Shamey, Hinks, & El-Shafei, 2012).

The CCD experimental data (in this case, WI of bleached cotton fabrics) were fitted to create a RSQM using the backward regression method by which the model terms with p-values greater than 0.05 were eliminated from the RSQM since they were statistically insignificant at a 95% confidence level. The analysis of variance (ANOVA) for the RSQM is shown in Table 3. The model term X_2 having a p-value greater than 0.05 is included in the ANOVA table to support hierarchy of the RSQM.

The RSQM was found to have a p-value less than 0.0001, indicating that the model is significant. The lack of fit test compares the residual error from excess design points to the pure error from replicated design points and is used to evaluate whether the model adequately describes the actual response. The lack-of-fit p-value for the RSQM was found to be 0.0788 which exceeds the 0.05 threshold value, indicating that the lack of fit is insignificant. The RSQM was also diagnosed by plotting the predicted WI values against the actual WI values. As shown in Fig. 1, the points are randomly distributed near the straight line, suggesting that the WI

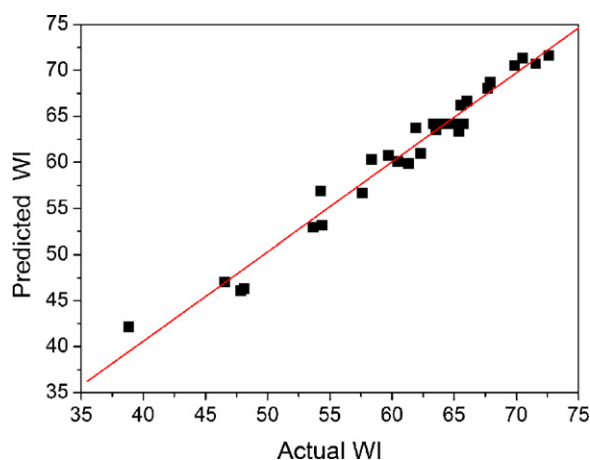


Fig. 1. Plot of the WI values predicted from the RSQM against the WI values observed in experiments (the diagonal line represents an exact agreement).

values predicted from the RSQM highly agree with the WI values observed from the bleaching experiments. Hence, the RSQM would not present a significant lack of fit.

In Table 3, the significance of design variables can be evaluated in terms of F values. As can be seen from the table, temperature (X_3) is the most significant variable affecting WI of cotton, followed by [TAED] (X_1) and time period (X_4), while [NaHCO₃] is not a significant variable. The model terms X_1^2 and X_3^2 indicate that there is a quadratic relationship between WI of cotton fabric and [TAED] as well as temperature. Additionally, the model term X_3X_4 indicates an interaction between temperature and time which significantly affects WI of cotton fabric.

The RSQM is represented in Eq. (3) which is based on the actual levels of design variables. Eq. (3) can be used to describe WI of cotton fabric bleached with the TAED/H₂O₂/NaHCO₃ system at a high level of confidence ($R^2 = 0.9716$) within the investigated range of variables.

$$\begin{aligned} \text{WI} = & 64.17 + 5.3X_1 - 0.1X_2 + 5.41X_3 + 1.93X_4 - 1.48X_3X_4 \\ & - 2.85X_1^2 + 0.56X_2^2 - 1.57X_3^2 \end{aligned} \quad (3)$$

The 3D response surfaces of WI predicted from Eq. (3) is shown in Fig. 2, from which the effect of design variables on the performance of the TAED/H₂O₂/NaHCO₃ system for bleaching of cotton can be evaluated for optimization.

3.3. Effect of variables on bleaching performance

3.3.1. Effect of [TAED]

TAED is a precursor of PAA which is the essential species contributing to bleaching of cotton. In the presence of an adequate amount of H₂O₂ (in this case, a 2.4:1 molar ratio with respect to TAED), the amount of PAA generated in the system depends on [TAED]. The slightly excess amount of H₂O₂ was deliberately used to drive the perhydrolysis of TAED to completion, but has no effect on WI of cotton fabric at a near-neutral pH which was maintained by using NaHCO₃ (Xu et al., 2013). Hence, [TAED] is a most important variable to affect WI of cotton fabric. As shown in Fig. 2 a–c, [TAED] exhibits positive effects on WI of cotton fabric. However, the effects of [TAED] on WI tends to be flat as [TAED] increases to a higher level range because of the quadratic relationship between [TAED] and WI. This indicates that increasing [TAED] in a lower level range is more beneficial to improving the performance of the TAED/H₂O₂/NaHCO₃ system on bleaching of cotton.

3.3.2. Effect of [NaHCO₃]

In the CCD of bleaching experiments, [NaHCO₃] was used in excess of the stoichiometric amount (equimolar with respect to AA assuming reactions related to TAED are complete). As an alkaline agent, NaHCO₃ plays two roles in bleaching: neutralizing AA and maintaining pH in a near-neutral range, which ensures that the perhydrolysis of TAED as well as bleaching of cotton would not be decelerated or eventually terminated due to the formation of AA but also the decomposition of PAA could be effectively inhibited due to its weak alkaline in nature. Fig. 2 a, d and e shows that [NaHCO₃] has no apparent effect on WI of cotton fabric. This indicates that an excess amount of NaHCO₃ presenting in the TAED/H₂O₂/NaHCO₃ system would not result in a loss of bleaching performance. Hence, it is advisable in a practical bleaching process to use a slightly excess amount of NaHCO₃ with respect to the generated AA.

3.3.3. Effect of temperature

As suggested in Table 3, temperature is the most significant variable for the TAED/H₂O₂/NaHCO₃ system to improve WI of

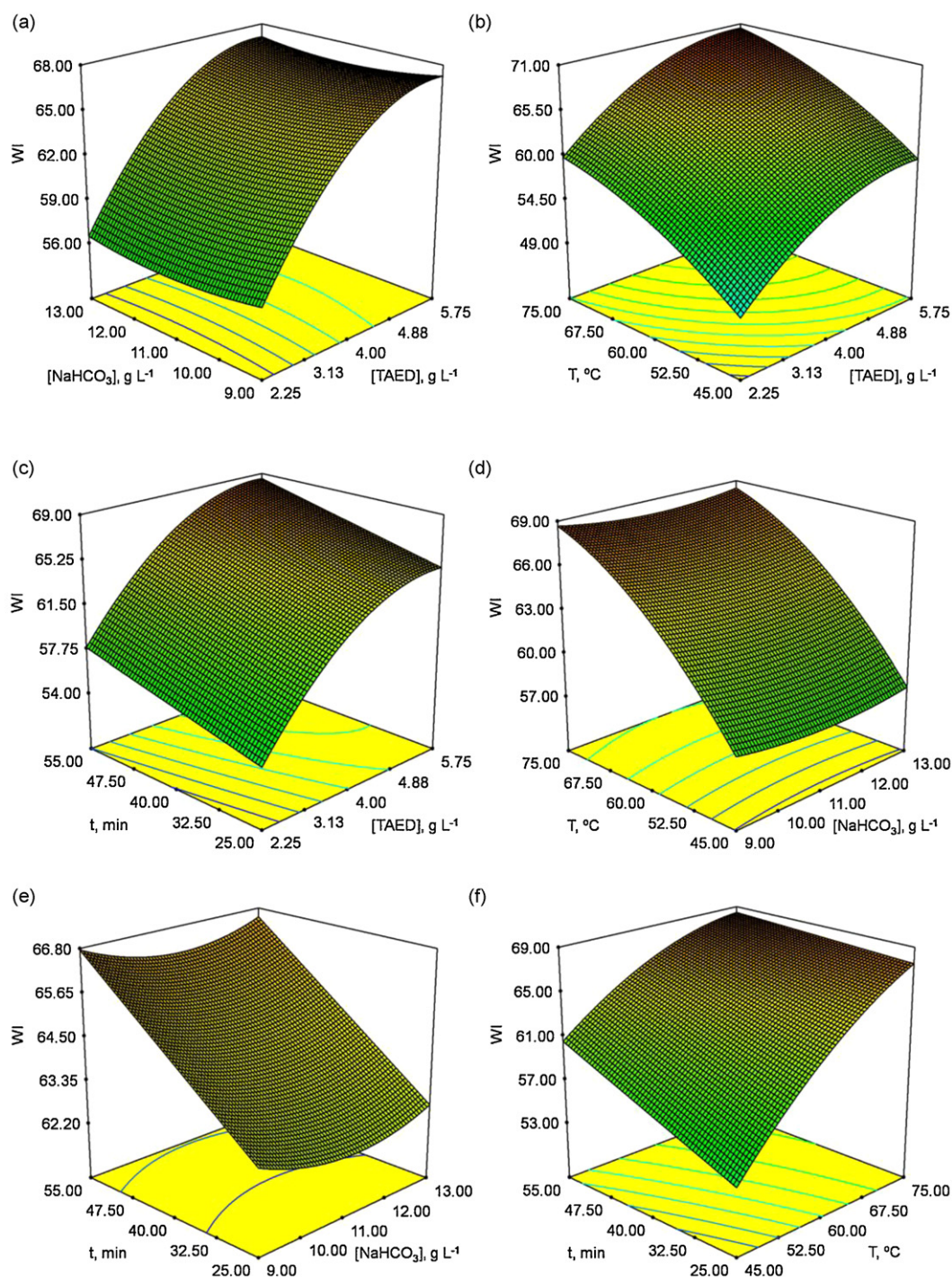


Fig. 2. Response surface of WI predicted from the RSQM with respect to the variables (a) [TAED] and [NaHCO₃], (b) [TAED] and T, (c) [TAED] and t, (d) [NaHCO₃] and T, (e) [NaHCO₃] and t, and (f) T and t.

cotton fabric. Fig. 2b, d and f shows that an increase in temperature results in a higher WI. This is most likely due to the fact that a fast bleaching system was conducted with the increase in temperature by increasing the rates of reactions represented by solid arrows in Scheme 2. Though temperature affects WI by a quadratic relationship, there is no apparent tendency for WI to be flat in the investigated temperature range. It is thus thought that a temperature of 70 °C is appropriate for maximizing the performance of the TAED/H₂O₂/NaHCO₃ system on bleaching of cotton.

Table 4
Comparison of the TAED/H₂O₂/NaHCO₃ system and a commercial method in terms of WI, WA and DP of bleached cotton fabric.

Bleaching method	WI	WA	DP
Control	10.54	>60 s	4072 ± 85
TAED/H ₂ O ₂ /NaHCO ₃	69.34 ± 1.23	4–6 s	3794 ± 70
Commercial	70.99 ± 1.31	1–2 s	1247 ± 30

Table 5
Results of color measurement of dyed cotton fabrics using CIELab system.

Remazol RGB	Dosage ^a	Bleaching method	<i>L</i> [*]	<i>a</i> [*]	<i>b</i> [*]	<i>C</i> [*]	<i>h</i>	ΔE_{cmc}
Red	0.5	Commercial	73.32	30.15	−6.50	30.84	347.83	0.80
		TAED/H ₂ O ₂ /NaHCO ₃	72.29	30.94	−5.86	31.46	350.37	
	1.0	Commercial	67.75	36.80	−6.45	37.36	350.05	0.69
		TAED/H ₂ O ₂ /NaHCO ₃	67.44	37.56	−5.56	37.97	352.27	
	2.0	Commercial	62.36	41.60	−6.15	42.05	351.59	0.54
		TAED/H ₂ O ₂ /NaHCO ₃	62.53	42.19	−5.38	42.54	353.34	
Yellow	0.5	Commercial	79.28	15.03	57.08	59.02	75.25	0.74
		TAED/H ₂ O ₂ /NaHCO ₃	78.24	15.02	58.66	60.56	75.73	
	1.0	Commercial	76.35	21.46	66.75	70.12	72.17	0.75
		TAED/H ₂ O ₂ /NaHCO ₃	75.78	22.03	68.79	72.23	72.24	
	2.0	Commercial	72.74	27.05	73.47	78.29	69.79	0.40
		TAED/H ₂ O ₂ /NaHCO ₃	72.40	27.62	74.43	79.39	69.99	
Navy	0.5	Commercial	45.28	−10.73	−17.09	20.18	237.88	0.85
		TAED/H ₂ O ₂ /NaHCO ₃	43.62	−11.10	−17.14	20.42	237.24	
	1.0	Commercial	37.39	−10.26	−17.61	20.38	239.78	0.94
		TAED/H ₂ O ₂ /NaHCO ₃	35.65	−10.16	−17.64	20.36	239.23	
	2.0	Commercial	29.40	−8.63	−16.78	18.87	242.77	1.03
		TAED/H ₂ O ₂ /NaHCO ₃	27.81	−8.44	−16.46	18.50	242.18	

^a On weight of fabric (owf, %).

3.3.4. Effect of time period

The process for the TAED/H₂O₂/NaHCO₃ system working on bleaching of cotton comprises the perhydrolysis of TAED and subsequent bleaching of cotton. However, it is not quite clear how long the perhydrolysis of TAED and the bleaching of cotton take to be completed, respectively. Hence, a total time period of the process is often considered for practical application. As shown in Fig. 2 c, e and f, the time period exhibits an positive effect on WI of cotton fabric. However, the effect of time period is much less significant than those of temperature and [TAED]. This indicates that extending the time period can improve the performance of the TAED/H₂O₂/NaHCO₃ system on bleaching of cotton to some extent. From the point of view of time effectiveness, the time period of the bleaching process needs be shortened as much as possible but temperature and, or, [TAED] should be increased for improving the bleaching performance.

3.3.5. Effect of interaction between temperature and time

As shown in Fig. 2f, there exists an interaction between temperature and time significantly affecting WI of cotton fabric. It can be seen from the figure that time exhibits a significant positive effect on WI at a low level of temperature but tends to lose the effect with an increase in temperature. Such an interaction is helpful for optimizing the performance of the TAED/H₂O₂/NaHCO₃ system on bleaching of cotton. For example, extending the time is an effective way to improve the degree of whiteness of cotton fabric when a low-temperature bleaching process is desired, but it is necessary to turn to [TAED] when a fast bleaching process is desired.

3.4. Comparison of the TAED/H₂O₂/NaHCO₃ system with a commercial method

Based on the response surface analysis, the TAED/H₂O₂/NaHCO₃ system was conducted by adding 5.75 g L^{−1} TAED together with H₂O₂ and NaHCO₃ at a molar ratio of 1:2.4:2.8, and applied to bleaching of cotton fabric at 70 °C for 40 min. The TAED/H₂O₂/NaHCO₃ system was compared to a commercial method in terms of WI, WA and DP of bleached cotton fabrics as shown in Table 4. The TAED/H₂O₂/NaHCO₃ system is comparable to the commercial method for improving WI but is slightly inferior to the commercial method for improving WA. It is likely that the process conditions for the TAED/H₂O₂/NaHCO₃ system are much milder than the commercial method (70 °C versus 95 °C and NaHCO₃ versus NaOH), resulting in inadequate scouring of cotton.

Since WA is very important for subsequent processing such as dyeing, the cotton fabrics bleached with the TAED/H₂O₂/NaHCO₃ system and the commercial method were dyed with Remazol RGB dyes in same dyeing baths to test whether the slight difference WA could cause a difference in dyeability between them. Table 5 shows the results of color measurements using the CIELab system. It can be seen that the cotton fabric bleached with the TAED/H₂O₂/NaHCO₃ system has similar color attributes to the cotton fabric bleached with the commercial method, and the color differences (ΔE_{cmc}) are close to or less than a tolerance of 1.0. This indicates that the TAED/H₂O₂/NaHCO₃ system can match the commercial method in providing cotton fabric with satisfactory WA for subsequent dyeing.

DP is a repeatable quantitative measurement of damage to cotton fiber resulting from bleaching, and is known to correlate with the strength loss of cotton fabric. In general, a lower DP indicates more severe damage of cotton fiber. As shown in Table 4, the DP value of cotton fabric bleached with the TAED/H₂O₂/NaHCO₃ system is far higher than that of cotton fabric bleached with the commercial method. Therefore, the TAED/H₂O₂/NaHCO₃ system is superior to the commercial method in protecting cotton fiber from chemical damage.

4. Conclusions

The TAED/H₂O₂/NaHCO₃ system was conducted for bleaching of cotton under low-temperature and near-neutral pH conditions. CCD combined with RSM was used for investigating and optimizing the TAED/H₂O₂/NaHCO₃ system for bleaching of cotton. CCD experimental data were fitted to create a RSQM describing WI of bleached cotton fabric. ANOVA for the RSQM revealed that temperature was the most significant variable affecting WI, followed by [TAED] and time, while [NaHCO₃] was an insignificant variable. The TAED/H₂O₂/NaHCO₃ system could be optimized for improving WI of cotton fabric by raising temperature, increasing [TAED] and extending time. The response surface analysis suggested that it was advisable to conduct the TAED/H₂O₂/NaHCO₃ system by adding 5.75 g L^{−1} TAED together with H₂O₂ and NaHCO₃ at a molar ratio of 1:2.4:2.8, and apply it for bleaching of cotton at 70 °C for 40 min.

The TAED/H₂O₂/NaHCO₃ system was compared to a commercial bleaching method by measuring WI, WA, DP and dyeability of bleached cotton fabrics. It was found that the TAED/H₂O₂/NaHCO₃ system was comparable to the commercial method for improving WI but slightly inferior to the commercial method for improving WA. Color measurement indicated that the

TAED/H₂O₂/NaHCO₃ system matched the commercial method in improving dyeability of cotton. Working under low-temperature and near-neutral pH conditions, the TAED/H₂O₂/NaHCO₃ system had competitive advantage over the commercial method in protecting cotton from severe chemical damage in bleaching.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (Grant No. 21276106), the Open Project Program of Key Laboratory of Eco-textiles, Ministry of Education, Jiangnan University (Grant No. KLET1118), and the Self-determined Research Program of Jiangnan University (Grant No. JUSRP11203).

References

- Abdel-Halim, E. S., & Al-Deyab, S. S. (2013). One-step bleaching process for cotton fabrics using activated hydrogen peroxide. *Carbohydrate Polymers*, 92(2), 1844–1849.
- Ball, R. E., Edwards, J. O., Haggett, M. L., & Jones, P. (1967). A kinetic and isotopic study of the decomposition of monoperoxyphthalic acid. *Journal of the American Chemical Society*, 89(10), 2331–2333.
- Cai, J. Y., & Evans, D. J. (2007). Guanidine derivatives used as peroxide activators for bleaching cellulosic textiles. *Coloration Technology*, 123(2), 115–118.
- Cai, J. Y., Evans, D. J., & Smith, S. M. (2001). Bleaching of natural fibers with TAED and NOBS activated peroxide systems. *AATCC Review*, 1(12), 31–34.
- Davies, D. M., & Deary, M. E. (1991). Kinetics of the hydrolysis and perhydrolysis of tetraacetylenediamine, a peroxide bleach activator. *Journal of the Chemical Society, Perkin Transactions*, 2, 1549–1552.
- El-Shafie, A., Fouda, M. M. G., & Hashem, M. (2009). One-step process for bio-scouring and peracetic acid bleaching of cotton fabric. *Carbohydrate Polymers*, 78(2), 302–308.
- Goodman, J. F., Robson, P., & Wilson, E. R. (1962). Decomposition of aromatic peroxacids in aqueous alkali. *Transactions of the Faraday Society*, 58, 1846–1851.
- Gursoy, N. C., Lim, S.-H., Hinks, D., & Hauser, P. (2004). Evaluating hydrogen peroxide bleaching with cationic bleach activators in a cold pad-batch process. *Textile Research Journal*, 74(11), 970–976.
- Hashem, M., El-Bisi, M., Sharaf, S., & Refaie, R. (2010). Pre-cationization of cotton fabrics: An effective alternative tool for activation of hydrogen peroxide bleaching process. *Carbohydrate Polymers*, 79(3), 533–540.
- Hebeish, A., Hashem, M., Shaker, N., Ramadan, M., El-Sadek, B., & Hady, M. A. (2009). New development for combined bioscouring and bleaching of cotton-based fabrics. *Carbohydrate Polymers*, 78(4), 961–972.
- Heller, R. A., & Weiler, R. (1987). Kinetics of the reaction of p-dinitrobenzene with basic hydrogen peroxide. *Canadian Journal of Chemistry*, 65(2), 251–255.
- Hofmann, J., Just, G., Pritzkow, W., & Schmidt, H. (1992). Bleaching activators and the mechanism of bleaching activation. *Journal für Praktische Chemie/Chemiker-Zeitung*, 334(4), 293–297.
- Ibrahim, N. A., Sharaf, S. S., & Hashem, M. M. (2010). A novel approach for low temperature bleaching and carbamoylethylolation of cotton cellulose. *Carbohydrate Polymers*, 82(4), 1248–1255.
- Jencks, W. P., & Carriuolo, J. (1960). Reactivity of nucleophilic reagents toward esters. *Journal of the American Chemical Society*, 82(7), 1778–1786.
- Koubek, E., Haggett, M. L., Battaglia, C. J., Ibne-Rasa, K. M., Pyun, H. Y., & Edwards, J. O. (1963). Kinetics and mechanism of the spontaneous decompositions of some peroxyacids, hydrogen peroxide and *t*-butyl hydroperoxide. *Journal of the American Chemical Society*, 85(15), 2263–2268.
- Lavrič, P. K., Kovač, F., Tavčer, P. F., Hauser, P. J., & Hinks, D. (2007). Enhanced PAA bleaching of cotton by incorporating a cationic bleach activator. *Coloration Technology*, 123(4), 230–236.
- Lim, S. H., Gursoy, N. C., Hauser, P., & Hinks, D. (2004). Performance of a new cationic bleach activator on a hydrogen peroxide bleaching system. *Coloration Technology*, 120(3), 114–118.
- Lim, S. H., Lee, J. J., Hinks, D., & Hauser, P. (2005). Bleaching of cotton with activated peroxide systems. *Coloration Technology*, 121(2), 89–95.
- McIsaac, J. E., Subbaraman, L. R., Subbaraman, J., Mulhausen, H. A., & Behrman, E. J. (1972). Nucleophilic reactivity of peroxy anions. *Journal of Organic Chemistry*, 37(7), 1037–1041.
- Montgomery, D. C. (2005). *Design and Analysis of Experiments*. New York: Wiley.
- Pearson, R. G., & Edgington, D. N. (1962). Nucleophilic reactivity of the hydrogen peroxide anion: Distinction between SN₂ and SN₁ CB mechanisms. *Journal of the American Chemical Society*, 84(23), 4607–4608.
- Pearson, R. G., Edgington, D. N., & Basolo, F. (1962). Nucleophilic substitution reactions in octahedral complexes. *Journal of the American Chemical Society*, 84(17), 3233–3237.
- Qin, X., Song, M., Ma, H., Yin, C., Zhong, Y., Zhang, L., et al. (2012). Low-temperature bleaching of cotton fabric with a binuclear manganese complex of 1,4,7-trimethyl-1,4,7-triazacyclononane as catalyst for hydrogen peroxide. *Coloration Technology*, 128(5), 410–415.
- Scarborough, S. J., & Mathews, A. J. (2000). Using TAED in bleaching fiber blends to improve fiber quality. *Textile Chemist and Colorist & American Dyestuff Reporter*, 32(3), 33–37.
- Shao, J., Huang, Y., Wang, Z., & Liu, J. (2010). Cold pad-batch bleaching of cotton fabrics with a TAED/H₂O₂ activating system. *Coloration Technology*, 126(2), 103–108.
- Topalovic, T., Nierstrasz, V., Bautista, L., Jocić, D., Navarro, A., & Warmoeskerken, M. (2007). Analysis of the effects of catalytic bleaching on cotton. *Cellulose*, 14(4), 385–400.
- Wakelyn, P. J., Bertoniere, N. R., French, A. D., Thibodeaux, D. P., Triplett, B. A., Rouselle, M.-A., Jr., et al. (2007). Chemical composition of cotton. In *Cotton Fiber Chemistry and Technology*. Boca Raton: CRC Press., p. 15.
- Wang, J., & Washington, N. M. (2002). Hydrophobic bleach systems and textile preparation: a discontinuity in fabric care. *AATCC Review*, 2(6), 21–24.
- Wiberg, K. B. (1955). The mechanisms of hydrogen peroxide reactions. II. A comparison of the reactivity of hydroxyl ion and hydroperoxide ion toward benzonitrile. *Journal of the American Chemical Society*, 77(9), 2519–2522.
- Xu, C., Hinks, D., & Shamey, R. (2010). Bleaching cellulosic fibers via pre-sorption of N-[4-(triethylammoniomethyl)-benzoyl]-butyrolactam chloride. *Cellulose*, 17(4), 849–857.
- Xu, C., Hinks, D., & Shamey, R. (2011). Development of a novel bleaching process for cotton. *AATCC Review*, 11(6), 73–77.
- Xu, C., Long, X., Du, J., & Fu, S. (2013). A critical reinvestigation of the TAED-activated peroxide system for low-temperature bleaching of cotton. *Carbohydrate Polymers*, 92(1), 249–253.
- Xu, C., Shamey, R., & Hinks, D. (2010). Activated peroxide bleaching of regenerated bamboo fiber using a butyrolactam-based cationic bleach activator. *Cellulose*, 17(2), 339–347.
- Xu, C., Shamey, R., Hinks, D., & El-Shafie, A. (2012). Cotton bleaching optimization using a butyrolactam-based cationic bleach activator. *AATCC Review*, 12(1), 66–70.
- Zeronian, S. H., & Inglesby, M. K. (1995). Bleaching of cellulose by hydrogen peroxide. *Cellulose*, 2(4), 265–272.