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Study on H_2O_2/TAED and H_2O_2/TBCC bleaching mechanism related to hydroxyl radical with a fluorescent probe

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ABSTRACT

The generation of hydroxyl radical (HO•) in H_2O_2/TAED and H_2O_2/TBCC systems for cotton fabric bleaching was proved and detected with a novel fluorescent probe benzenepentacarboxylic acid (BA). Effect of HO• generation on the cotton fabric bleaching performances was further discussed. The results show that HO• yield in H_2O_2/TAED and H_2O_2/TBCC systems was respectively about 11 and 15 times higher than that in H_2O_2 system without activators under the same alkali condition. Meanwhile, TAED and TBCC apparently promoted fabric whiteness and H_2O_2 decomposition rate. As the addition of HO• scavenger dimethylsulfoxide (DMSO), fabric whiteness decreased while tensile strength increased. It proves that HO• played a significant role in H_2O_2/TAED and H_2O_2/TBCC bleaching. Two main bleaching routes were suggested. The present work brought new insight into H_2O_2/TAED and H_2O_2/TBCC bleaching mechanism. It is quite instructive to develop efficient and ecological bleaching processes.

1. Introduction

Pretreatment of cotton fabric is required to remove size and impurities including pigments, pectin, waxiness and also cotton shell, etc., to facilitate subsequent dyeing and finishing process. Conventional pretreatment contains three separate courses of desizing, scouring and bleaching. The long duration process has been gradually substituted by one bath pretreatment of desizing, scouring and bleaching, which is commonly called H_2O_2-alkali one bath treatment. Although shorten pretreatment duration greatly, H_2O_2 bleaching consumes large amounts of energy for near boiling temperatures to obtain excellent fabric performances. In order to save energy, great efforts have been made to explore low temperature bleaching with activators. Tetra-acetylethylenediamine (TAED) and N-[4-(triethylammoniomethyl)-benzoyl]-caprolactam chloride (TBCC) are promising activators to improve fabric bleaching performances at lower temperature (Cai, Evans, & Smith, 2001; Hou, Zhang, & Zhou, 2010; Lim, Hinks, & Hauser, 2004; Lim, Lee, Hinks, & Hauser, 2005; Shao, Huang, Wang, & Liu, 2010; Willey et al., 1997; Xu, Shamey, & Hinks, 2010; Xu, Long, Du, & Fu, 2013). Further research of H_2O_2/TAED and H_2O_2/TBCC bleaching mechanism will be instructive for industrially application of TAED and TBCC to H_2O_2 activated bleaching in large-scale.

The generally considered H_2O_2/TAED and H_2O_2/TBCC bleaching mechanism is a perhydrolysis process (James, & MacKirdy, 1990; Kott, Willey, & Miracle, 1996; Lim et al., 2004; Sain, Daneault, & Parenteau, 1997). TAED and TBCC react with HOO^- ionized in alkali H_2O_2 solution to form organic peroxide acid (RCOOOH) with higher redox potential and stronger oxidizing properties than HOO^- (Castiglione, Baggioli, Citterio, Mele, & Raos, 2012; Proska, 1952). Thus, RCOOOH would directly interact with natural pigments to improve fabric whiteness at lower temperatures. However, RCOOOH is probably unstable, especially peroxyacetic acid (PAA) formed by reaction between TAED and H_2O_2 is quite unstable under dilute solution (Coucharriere, Mortha, Lachenal, Briois, & Larnicol, 2002; Ebrahimi, Kolehmainen, Oinas, Hietapelto, & Turunen, 2011). H_2O_2/TAED and H_2O_2/TBCC bleaching mechanism involved in free radicals still remains ambiguous. Detailed research about whether relevant free radicals are further generated after the formation of RCOOOH has not been conducted.

Free radicals have been frequently studied in physiological and pathological processes of biological molecules, such as DNA, protein and fat (Lagouge & Larsson, 2013; Miral & Pawel, 2012). In textile industry, various processes especially H_2O_2 bleaching also involve in free radicals, though the bleaching mechanism is still under debate (Dannacher & Schlenker, 1996). Among the free radicals

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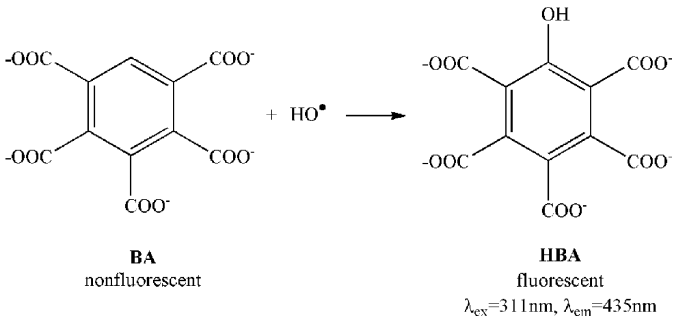

Scheme 1. The process of HO• addition to BA.

probably generated in H_2O_2 bleaching, HO• possesses the strongest oxidizing ability owing to its high standard redox potential in aqueous solution (Klaning, Sehested, & Holcman, 1985; Koppenol & Liebman, 1984). HO• can induce chain reaction and interact with various organic compounds primarily by means of electronic transfer, electrophilic addition, dehydrogenation reaction (Ek, Gierer, & Jansbo, 1989). Hence, the presence and generation of HO• are prior to investigate H_2O_2/TAED and H_2O_2/TBCC bleaching mechanism in the paper.

In the present study, benzenepentacarboxylic acid (BA), as a specific and reproducible fluorescent probe of HO• developed by our lab (Zhang, Si, &Yan, 2013), was utilized to prove and detect the generation of HO• in H_2O_2/TAED and H_2O_2/TBCC alkali systems with and without HO• scavenger dimethylsulfoxide (DMSO). The present probe has only one reaction site for HO• addition that results in the formation of a single fluorescent product, hydroxybenzenepentacarboxylic acid (HBA) (Scheme 1), which has been demonstrated by ESI-MS analysis system in our previous work. The generation of the single pure fluorescent product by BA made the present probe sensitive, accurate and reproducible in detection of HO•. Effect of HO• generation on the whiteness and tensile strength of the cotton fabrics was further studied, to discuss the role of HO• plays in H_2O_2/TAED and H_2O_2/TBCC bleaching.

2. Experimental

2.1. Apparatus and materials

2.1.1. Apparatus

The fluorescence intensity was measured on Hitachi F-7000 spectrophotofluorometer with a xenon lamp and a quartz cuvette (1.0 cm optical path) as the container. The spectrometer slit was set for 5.0 nm band-pass, with the PMT voltage 400 V.

All bleaching processes were carried out by RY-25012 room temperature oscillation dyeing machine (Shanghai Long Ling Electronic Technology Co., Ltd.).

2.1.2. Materials

Benzenepentacarboxylic acid (BA) was provided by TCI (purity > 98%, Japan). Sodium benzenepentacarboxylate stock solution was prepared from benzenepentacarboxylic acid through neutralization with NaOH, and diluted to prepare relative working solutions.

Gray fabric used was 100% woven twill cotton. TBCC was synthesized and purified according to the patent reported previously by Willey et al. (1997). TAED (purity 99%), DMSO and H_2O_2 (30 wt% in H_2O) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were of analytical grade. Distilled water was used throughout except the washing process of fabrics.

2.2. Experimental procedure

2.2.1. Detection of HO•

Molarity of fluorescent substances near or lower than 10^{-3} mol/L is acceptable to detect fluorescence intensity by the spectrophotofluorometer, or the fluorescent substances need to be diluted before determination. Reagents used in detection of HO• contained BA (400 μmol/L), NaOH (4 mmol/L), TAED (400 μmol/L), TBCC (400 μmol/L), H_2O_2 (220 μmol/L), and reacted for 60 min at a certain temperature. Then the reactions were promptly cooled and quenched. A certain amount of working solution was placed in the four-pass optical quartz cuvette, and the fluorescence intensity was measured at maximum excitation wavelength (311 nm) to characterize the concentration of HO•.

2.2.2. Scavenging of HO•

DMSO was used as HO• scavenger to decrease HO• concentration and clarify its effect on fabric performances during bleaching processes. Before that, HO• scavenging efficiency of DMSO (2.4 mmol/L) was tested at 70 °C, other reaction regents and test conditions are the same as that used in detection of HO•.

2.2.3. Fabric bleaching

Gray cotton fabric samples were impregnated with distilled water for a while to avoid the influence of transitional metal ions which were probably carried on the surface of fabric during previous processes, then air dried under ambient temperature. The process did little to fabric performances. Impregnation bleaching method was used and performed at a certain temperature for 60 min with a liquor ratio of 1:20. Each bleaching solution contained NaOH (1.5 g/L), 30% H_2O_2 (5 g/L), TAED 2 g/L or TBCC 4 g/L. After reactions, the bleached fabric was rinsed thoroughly in copious amounts of tap water, then air dried under ambient temperature.

Corresponding to scavenging of HO• in Section 2.2.2, varying amounts of DMSO (1–4 g/L) was added into each fabric bleaching bath to evaluate effects of HO• generation on fabric bleaching performances. Other reaction conditions are the same as that used in fabric bleaching without DMSO.

2.3. Measurement

CIE Whiteness Index (WI) of cotton fabric samples was measured by Datacolor 65° color matching instrument (USA) according to ISO 105-J02: 1997 standard. Each sample was measured for five times in different positions to give an average value.

Tensile strength of cotton fabric samples was determined by H10KS fabric strength tester and the test method referred to ISO 13934.1, 1994 standard.

H_2O_2 decomposition rate (DR) was measured by a certain concentration of potassium permanganate solution and calculated by the following equation.

$$\mathrm{DR} = \frac{V_0 - V_1}{V_0} \times 100\% \quad (1)$$

where V_0 is the volume of potassium permanganate solution consumed by titration of 10 mL bleaching liquid before reaction and V_1 is the volume of potassium permanganate solution consumed by titration of 10 mL bleaching liquid after reaction.

3. Results and discussion

3.1. Detection of HO•

HO• is the strongest single electron oxidant existed in aqueous solution, leading to its poor selectivity in rapid reaction with