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Short communication

Removing polysaccharides-and saccharides-related coloring impurities in alkyl polyglycosides by bleaching with the H_2O_2/TAED/$NaHCO_3$ system

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ABSTRACT

The effect of H_2O_2/TAED/$NaHCO_3$ system, namely $NaHCO_3$ as alkaline agent with the (tetra acetyl ethylene diamine (TAED)) TAED-activated peroxide system, bleaching of alkyl polyglycosides solution was studied by spectrophotometry. The results showed that the optimal bleaching conditions about H_2O_2/TAED/$NaHCO_3$ system bleaching of alkyl polyglycosides solution were as follows: molar ratio of TAED to H_2O_2 was 0.06, addition of H_2O_2 was 8.6%, addition of $NaHCO_3$ was 3.2%, bleaching temperature of 50–65 °C, addition of MgO was 0.13%, and bleaching time was 8 h. If too much amount of $NaHCO_3$ was added to the system and maintained alkaline pH, the bleaching effect would be greatly reduced. Fixing molar ratio of TAED to H_2O_2 and increasing the amount of H_2O_2 were beneficial to improve the whiteness of alkyl polyglycosides, but adding too much amount of H_2O_2 would reduce the transparency. In the TAED-activated peroxide system, $NaHCO_3$ as alkaline agent and buffer agent, could overcome the disadvantage of producing black precipitates when NaOH as alkaline agent.

1. Introduction

Alkyl polyglycosides are products which are obtained under the catalysis of acid by losing a molecule of water from hemiacetal hydroxyl of glucose and fatty alcohol hydroxyl. The products are not a pure compound, but alkyl glycoside with different degree of glucose polymerization, commonly known as alkyl polyglycosides (abbreviation APGs) (Czichocki, Fiedler, Haage, Much, & Weidner, 2002; Wang, 2001). Alkyl polyglycosides are the fourth generation of world-class green surfactant developing in the 1990s which do not use petroleum-derived products. APGs have many advantages of both nonionic and anionic surfactants. In addition to their good dermatological compatibility, biodegradability and excellent behavior at interfaces, APGs show interesting application properties, specifically for applications such as detergents, cleaning agents, cosmetic products and pesticide formulations (Hill, von Rybinski, & Stoll, 1997; Kahl, Quitzsch, & Stenby, 1997; Ruegsegger, Zhang, & Marchant, 1997; von Rybinski, 1996).

Generally pure alkyl polyglycosides are white powder (Wang, 2001). However, in practical industrial synthesis, recombination reaction and decomposition reaction are liable to occur at high temperature and acid environment, generating polysaccharides and other colored substances. The color bodies were presumed as polymerized dehydration and degradation products of saccharides, such as levulinic acid, furfural, or hydroxymethyl furfural. These polymers, known as humins, show conjugated unsaturated moieties that absorb light and may be responsible for the dark-hued

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discoloration of the alkyl polyglucosides (Balzer & Lüders, 2000). Alkyl polyglycosides are generally brown after dealcoholization reaction, which seriously affects its application scope and commercial value. Therefore, bleaching of alkyl polyglycosides solution becomes extremely important.

The well-known environmentally safe bleaching method is hydrogen peroxide bleaching (Hou, Zhang, & Zhou, 2010). While only using hydrogen peroxide, the bleaching effect is not satisfactory, so bleach activators need to be added. The most commonly used bleach activator is tetra acetyl ethylene diamine (TAED). It has been considered to be a non-toxic, non-sensitive and non-mutagenic product which can be degraded by microorganism to form carbon dioxide, water, ammonia and nitrate (Chen, 2008; Hsieh, Agrawal, Maurer, & Mathews, 2006). The main advantage of TAED-activated peroxide bleaching is that the reaction can be conducted at low temperature and near-neutral pH conditions (Xu, Long, Du, & Fu, 2013). In this paper the method of H_2O_2/TAED/$NaHCO_3$ system bleaching of alkyl polyglycosides was studied, and the effect of TAED, H_2O_2, $NaHCO_3$, MgO bleaching temperature and bleaching time on extinction coefficient was investigated.

2. Experimental

2.1. Materials

Alkyl polyglycosides (unbleached) was kindly provided by Shijiazhuang Jin Mo Er Chemicals Co., Ltd., China. TAED (purity 92%) was purchased from Zhejiang Jinke Chemicals Co. Ltd., China. Sodium bicarbonate was used as alkaline agent & buffer agent and purchased from Tianjin Yingda Rare Chemical Reagents Factory, China. Magnesium oxide was used as stabilizer and purchased from Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd., China. Hydrogen peroxide (30%) & sodium hydroxide were purchased from Tianjin Hedong Hongyan Chemical Reagent Factory, China. All other chemicals were of analytical grade unless otherwise stated. Distilled water was used to experiment test.

2.2. Bleaching method

Unbleached alkyl polyglycosides were used as the experimental material in the bleaching process. The solid content of unbleached alkyl polyglycosides was 62.1%. In each bleaching experiment the dosage of alkyl polyglycosides was 50 g, and stirrer speed was 150 r/min. Firstly, the water bath was set at a certain temperature (45–70 °C), then MgO (0–0.12 g that was 0–0.39% of APGs, in this paper all the data were based on the solid content of APGs), $NaHCO_3$ (0.5–1.4 g that was 1.6–4.5% of APGs), TAED and H_2O_2 (5–10 ml, and the molar ratio of TAED to H_2O_2 was 0.05–0.07) were added in turn, in which H_2O_2 was added in batches to prevent the materials from overflowing. Additionally adding H_2O_2 in batches could make H_2O_2 and peracetic acid participate in bleaching reaction timely so as to reduce their ineffective decomposition. The concrete operations were adding 1–2 ml H_2O_2 each time, and adding once every hour. Under stirring, the whole bleaching reaction was maintained for 8 h (including H_2O_2 addition time and subsequent bleaching time). After that, the pH value (10% APGs solution) was adjusted to 11.5–12.5 with NaOH.

2.3. Analysis

The absorbance of alkyl polyglycosides solution after bleaching was measured at wave length of 470 nm with spectrophotometer (721G, Shanghai Precision and Scientific Instrument Co., Ltd., China). The color of solution was characterized by extinction coefficient. The calculation formula is shown by Eq. (1) (Roth, Edwards, & Patrick McCurry, 2001):

$$E_{470} = \frac{A}{(C \times L)} \tag{1}$$

where E_{470} is extinction coefficient at 470 nm, A is measured absorbance of APGs solution at 470 nm, C is concentration in grams per cm^3, and L is path length in centimeters.

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

Scheme 1. H_2O_2 dissociation.

3. Results and discussion

3.1. Theoretical base of the TAED/H_2O_2/$NaHCO_3$ system

TAED-activated peroxide system under alkaline condition reacts as follows:

HOO^- is believed to be the effective bleaching species. Under alkaline condition, H^+ will be reduced, thus promoting the dissociation of H_2O_2 (as shown in Scheme 1). Perhydrolysis and hydrolysis of TAED will take place in alkaline solutions, as shown in Scheme 2 (Davies & Deary, 1991; Suchy & Argyropoulos, 2001) and Scheme 3 (Cai, Evans, & Smith, 2001; Davies & Deary, 1991; Scarborough & Mathews, 2000; Shao, Huang, Wang, & Liu, 2010). Because the nucleophilicity of perhydroxyl anions is far higher than the nucleophilicity of hydroxyl anions in aqueous solution, TAED reacts preferentially with perhydroxyl ion to release a stable peracid. It has been postulated that TAED forms hydrogen bonds with hydrogen peroxide during perhydrolysis, thus stabilizing the transition state and favoring perhydrolysis. Moreover, TAED does not form diacyl peroxides (Milne, 1998). Thus, perhydrolysis of TAED is the main reaction under alkaline condition. The oxidation potential of peracetic acid (1.81 eV) is higher than oxidation potential of hydrogen peroxide (1.33 eV) (Xu & Cha, 2012). So generally peracids are considered to be better and more active bleaching agents than peroxide (Leduc, Montillet, & Daneault, 1998).

However, under alkaline environment, generated peracids would be decomposed in the following ways:

$$R{-}CO{-}OOH + OH^- \rightarrow R{-}COO^- + H_2O_2 \tag{1}$$

$$2R{-}CO{-}OO^- \rightarrow 2R{-}COO^- + O_2 \tag{2}$$

R is alkyl. In most cases, formula (2) is the main reaction (Deng & Feng, 2005; Reichert, McNeight, Elston, & Niagara Falls, 1944).

NaOH was usually used as alkaline agent in hydrogen peroxide bleaching of alkyl polyglycosides. While TAED-activated peroxide system bleaching of alkyl polyglycosides has higher requirements for the solution pH. Using NaOH as alkaline agent, the black precipitate could be formed easily in the APGs solution after bleaching, which affected the product quality. For the TAED-activated peroxide system, the active ingredient peracetic acid released acetic acid, and pH value decreased gradually with the process of bleaching reaction, which would lead to the perhydrolysis of TAED decelerated or eventually terminated. Hence a buffer agent was required to sustain the acid and alkali environment. In this study $NaHCO_3$ was to be thought of the appropriate alkaline agent. As strong base-weak acid salt, $NaHCO_3$ has strong ability to cushion and stabilize solution, meeting the requirements of system pH. More importantly, it basically avoided the disadvantage of producing black precipitate when NaOH as the alkaline agent.