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Study on the heterogeneous degradation of chitosan with hydrogen peroxide under the catalysis of phosphotungstic acid

Qun Zeng Huang [a,*], Shi Ming Wang [b], Jin Feng Huang [b], Li Hong Zhuo [a], Ying Chen Guo [a]

[a] *College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang, China*
[b] *College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, China*

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Abstract

The oxidative degradation of chitosan with H_2O_2 aqueous solution was carried out under the catalysis of phosphotungstic acid in heterogeneous phase. The optimal conditions of degradation were determined by orthogonal tests. The structure of the degraded product was characterized by Fourier-transform infrared spectra (FTIR), diffuse reflectance spectra (DRS) and X-ray diffraction (XRD) analysis. The mechanism of the degradation was correlated with cleavage of the glycosidic bond. The experimental results showed that chitosan can be effectively degraded with H_2O_2 under the catalysis of phosphotungstic acid.

Keywords: Chitosan; Phosphotungstic acid; H_2O_2; Catalysis; Degradation

1. Introduction

Chitosan, (1 → 4)-2-amino-2-deoxy-β-D-glucan, is a natural polymer generally obtained by full or partial deacetylation of chitin. Due to many unique properties such as biocompatibility, biodegradability, bioactivity and nontoxicity (Carmen & Roland, 1997; Cheng et al., 2003), chitosan has broad range of actual and potential applications. Much attention is focused on the use of chitosan in many areas such as biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science and textiles, etc. (Li, Dunn, Grandmaison, & Goosen, 1997).

However, chitosan has a high molecular weight resulting in its low solubility in most solvents, which limits its wide applications especially in medicine and the food industry. To improve its solubility and biological, chemical and physical properties, several methods have been tried to prepare a water-soluble low molecular weight chitosan (LWCS) without altering its chemical structure, some of which show advantages, but also disadvantages (Rege & Block, 1999; Tanioka et al., 1996; Terbojevich, Cosani, & Muzzarelli, 1996; Vårum, Ottøy, & Smidsrød, 2001; Wang, Huang, & Wang, 2005; Zhang & Neau, 2002).

H_2O_2 has long been used in the treatment of chitosan because it is easy to handle, easily available and environmentally friendly (Chang, Tai, & Cheng, 2001; Qin, Du, & Xiao, 2002; Shao, Yang, & Zhong, 2003). This technique is based on the formation of free radicals, which can attack the β-D-(1 → 4) glucosidic linkages of chitosan. However, the formation of radical groups is inefficient when H_2O_2 is used alone. Recently, to improve the efficiency, other degradation patterns of chitosan with H_2O_2 have been reported (Shao et al., 2003; Wang et al., 2005). But to date there have been few reports about the degradation with H_2O_2 under the catalysis of heteropoly acids in heterogeneous phase.

Heteropoly acids with Keggin anion structures have received considerable attention due to many advantages (Okuhara, 2002; Okuhara, Mizuno, & Misono, 2001), such as simple preparation, high reactivity, non-corrosive, nonpollutive and excellent stability. Specifically, phosphotungstic acid is among the most extensively studied (Dias, Caliman, Dias, Paulo, & de Souza, 2003; Hu & Xu, 2004;

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[*] Corresponding author. Tel./fax: +86 377 63513540.
E-mail address: qz_huangny@126.com (Q.Z. Huang).

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Kozhevnikova & Kozhevnikov, 2004) since it possesses high acidic strength and relatively high thermal stability (Devassy et al., 2005), which can be used as acid, oxidative and bifunctional catalysts in homogeneous or heterogeneous phase.

Usually the oxidative degradation of chitosan with H_2O_2 occurs in homogeneous phase, such as in acetic acid solution. However, in this paper, the degradation in heterogeneous phase was studied, which avoided using acetic acid, furthermore, made the precipitation process of LWCS convenient. The effect of volume of H_2O_2, dosage of phosphotungstic acid, reaction temperature and time on the degradation was discussed by orthogonal tests. The degradation mechanism was also discussed by FTIR, DRS and XRD analysis.

2. Experimental details

2.1. Materials

Original chitosan, obtained from Yuhuan Biology Engineering (Zhejiang, China), whose degrees of acetylation is 95.54%, its viscosity-average molecular weight (*M*v) is about 700,000, determined based on viscosity measurements (Wang et al., 2005). Phosphotungstic acid, phosphomolybdic acid, tungstosilicic acid, hydrogen peroxide and other reagents used, supplied by Fuzhou Chemical Agent Corporation (Fujian, China), were utilized without further purification.

2.2. Heterogeneous degradation of chitosan

Chitosan 1.5000 grams was put into 50 mL conical flask, then phosphotungstic acid, H_2O, 30% (wt%) H_2O_2 aqueous solutions were also added. The volume of mixing solution was 20 mL. The solution was stirred and reacted at the desired temperature for different duration. After the reaction, the solution was filtrated, the collected solid was washed with distilled water until reaching pH 7, and then dried at 50 °C in vacuum. LWCS was precipitated by adding ethanol to the filtrate and collected after drying in vacuum.

2.3. Characterization techniques

The degradation ratio of chitosan was calculated according to the following equation:

$$R(\%) = \frac{M_0 - M_x}{M_0} \times 100 \qquad (1)$$

where R refers to degradation ratio, M_0 refers to the quantity of original chitosan, M_x refers to the quantity of collected solid chitosan without degraded at different condition, respectively.

The IR spectra of original chitosan and LWCS were obtained using a Nicolet Nexus 670 FTIR spectrometer using KBr pellets, respectively.

The DRS of original chitosan and LWCS were recorded on a Cary-500 Scan UV–vis-NIR spectrophotometer equipped with a HARRICK diffuse reflectance accessory.

X-ray diffraction patterns of original chitosan and LWCS were carried out on a XPERT PRO diffractometer and used a CuKα target at 40 kV and 50 mA.

3. Results and discussion

3.1. Oxidative degradation of chitosan under the catalysis of different heteropoly acids

In order to reveal the contrast of catalysis between phosphotungstic acid and other heteropoly acids, four experiments on the degradation of chitosan were designed. In these experiments, catalyst was tungstosilicic acid, phosphotungstic acid and phosphomolybdic acid in experiment 1, 2 and 3, respectively, the quantity of each catalyst was 0.02 g. In experiment 4, catalyst was not used. The other reaction conditions were determined as follows: chitosan 1.5000 g, 30% (wt%) H_2O_2 3 mL, H_2O 17 mL, reaction temperature 70 °C, reaction time 30 min. The degradation ratio of chitosan was confirmed according to Eq. (1). The contrast of degradation ratio under different condition is depicted in Fig. 1.

As can be seen from Fig. 1, the degradation ratio is only 43% without catalyst, which indicated that the degradation is inefficient when H_2O_2 was used alone. But in the presence of tungstosilicic acid, phosphotungstic acid and phosphomolybdic acid, the degradation ratio increased, which added up to 64,100 and 79%, respectively. Therefore, it can be predicated that phosphotungstic acid is the best catalyst for oxidative degradation of chitosan with H_2O_2 in heterogeneous phase.

3.2. Orthogonal test

The optimal condition for degrading chitosan was studied by an orthogonal test. Four controllable variables, the

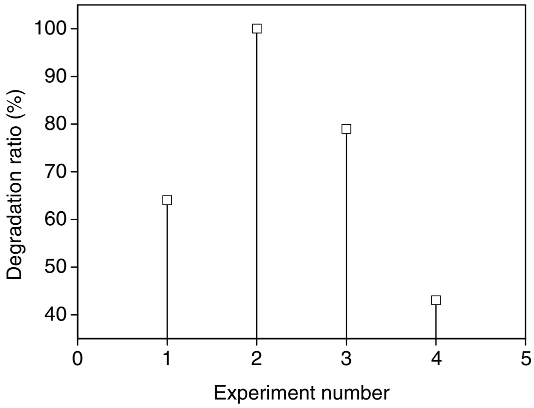

Fig. 1. The contrast of degradation ratio under different conditions.