

The optimal reaction time of HAC-H₂O₂ in synergistic oxidative degradation Chitosan

Chen-xi Li ^{1,a}, Li-na Zheng ^{1,2,b*}, Yue-ting Lang ^{1,c}, Qiu-shi Wang ^{1,d} and He-nan Chen ^{1,e}

¹ College of Marine Technology and Environmental, Dalian Ocean University, Dalian 116023,

² Key Laboratory of Nearshore Marine Environmental Research, Dalian 116023, China

^a1010989942@qq.com, ^{b*}zln@dlou.edu.cn,

^clangyueting814@163.com, ^d945529598@qq.com, ^e416955893@qq.com

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Abstract: In this paper, taking industrial grade chitosan as raw materials, CO oxidation degradation method for degradation of raw materials by using HAC-H₂O₂, carried out in cooperation with oxidation degradation of raw material system of the reaction process is studied in different degree, viscosity, and reaction time on the yield and the effect of the results showed that chitosan was 3h is the best reaction time.

Introduction

Using industrial grade chitosan as raw material degradation, removal of ash in the process, improve the purity of chitosan, the final product yield determines the method of the process is efficient production process of HAC-H₂O₂ CO oxidation degradation of chitosan has the advantages of low cost, easy processing, no residue and other advantages, these features are easy to achieve environmental protection industrialization. Through collaborative experiment to find the oxidative degradation, high yield, low viscosity, high degree of deacetylation reaction time.

The experimental materials and methods

Experimental apparatus and equipment.

Tab.1 Experimental apparatus and equipment

Instrument	Model	Manufacturer
Electronic balance	AL204	Mettler Toledo Instruments Co. Ltd.
Heat collection type constant temperature magnetic stirrer with heating	DF-101S	Gongyi Yuhua Instrument Co., Ltd.
Vacuum drying oven	Type DZF-6050	Shanghai Heng Heng Technology Co., Ltd.
Acid estimation apparatus	ZD-2	Shanghai Hongyi instrument and Meter Co.,
Rotary viscosimeter	NDJ-1 type	Shanghai Hengping Scientific Instrument Co. Ltd.
Ultrasonic cleaner	SB-5200D	Ningbo Xinzhi biological Polytron Technologies Inc

Experimental drugs.

Tab.2 Experimental drugs

Drug Name	Specifications	Manufacturer
Chitosan	The degree of deacetylation is about 80%	A Dalian company of Chitosan
30% H ₂ O ₂	AR	Tianjin Kermel Chemical Reagent Co., Ltd.
Glacial acetic acid	AR	Tianjin Hengxing Chemical Reagent Factory
Hydrochloric [chlorhydric] acid	AR	Tianjin Damao Chemical Reagent Factory
Caustic soda	AR	Tianjin city Dongli District Tianda Chemical Reagent Factory
Absolute ethyl alcohol	AR	Tianjin Damao Chemical Reagent Factory
Sodium acetate	AR	Tianjin Damao Chemical Reagent Factory

Experiment methods

- (1) Electronic balance accurately weigh a certain chitosan, slowly adding a certain concentration of acetic acid solution in the beaker, the chitosan acetic acid solution and stirring, adding once needed in the experiment and H₂O₂ in ultrasonic Concussion instrument in ultrasonic vibration 2-3min;
- (2) The magnetic vibrator in a beaker, wrap up the mouth of the beaker, and set up the beaker in the water bath heating constant temperature magnetic stirrer with heating temperature specified in the rotor speed is adjusted to 120r/min, constant temperature reaction time;
- (3) After the reaction was finished, the beaker was removed and the pH value of the reaction liquid was adjusted to 7.2-7.4 by 2mol/L NaOH solution;
- (4) For cooling the reaction liquid to less than 50 DEG C, to filter to remove impurities in the reaction solution, and then get the clear liquid is about 3-5 times the volume ratio of ethanol to precipitate material;
- (5) Again filtering, obtained precipitate;
- (6) The precipitate was repeatedly rinsed with deionized water to neutral, and finally dried at 60 DEG C in the drying chamber for 12h, ground to obtain water-soluble oligo chitosan.

Results and discussion

Different reaction time setting

Based on the literature review and preliminary experiments, a set of initial conditions, the reaction temperature is 80 DEG C, the amount of chitosan was 8%, the concentration of acetic acid was 1%, the concentration of hydrogen peroxide is 8%, the only change the reaction time under the condition that the effects of HAC-H₂O₂ CO oxidation of Chitosan degradation reaction time on the yield, viscosity and effect of degree of deacetylation.

The effect of reaction time on Yield

The influence of different reaction time on the yield of figure 1.

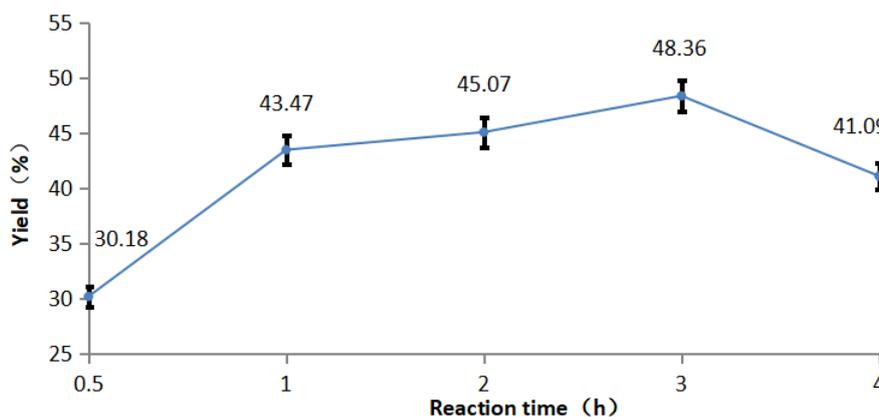


Fig.1 Effect of reaction time on the yield

We can see from Figure 1, the only change the time conditions, the yield increased with the increase of time, reach the maximum at 3h, then began to decline. The reaction time is too short, chitosan can not be obtained, with the increase of reaction time, the reaction more fully; but time is too long will lead to the degradation of chitosan a chitosan molecular weight is too small, can not be precipitated in alcohol precipitation, leading to yield a small decline.

Influence of reaction time on the viscosity

The effect of different reaction time on viscosity is shown in figure 2.

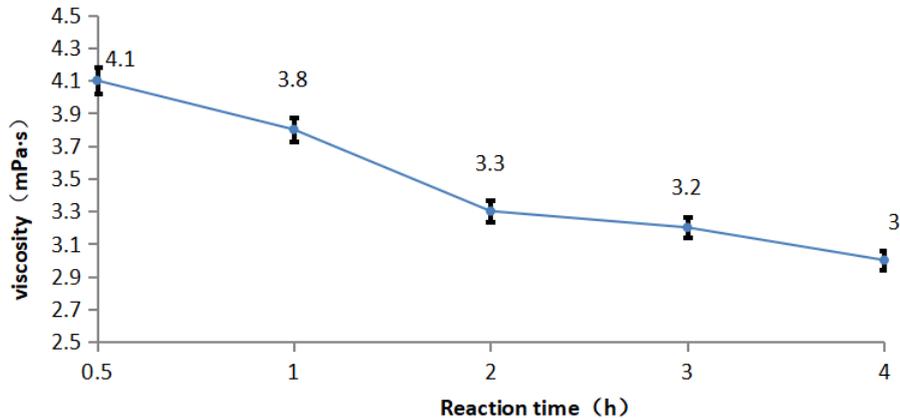


Fig.2 Effect of reaction time on viscosity

We can see from Figure 2, the only change the time conditions, the viscosity decreases with the increase of time, 2h changes slowly. Chitosan in full reaction before, the viscosity will increase with time and quickly reduce the mean molecular weight in this period is rapidly decreased, but the full reaction of poly sugar in shell after the viscosity decline slowed significantly, mean molecular weight decreased more slowly. The experimental results show that chitosan in the degradation process, is divided into two stages, the first stage with the increase of reaction time, molecular weight decreased rapidly, after a turning point after entering the second stage, the relative molecular. The decline in the quality of speed stabilized the cause of this phenomenon. There is a weak bond to some of the degradation of chitosan molecular link in the reaction at the beginning, the first weak bond fracture, the molecular weight during this period of time is falling rapidly, the strong bonds remaining in the reaction fracture need some reaction time, molecular weight in this section time decreased more slowly.

The effect of reaction time on the degree of deacetylation

The effect of different reaction time on the degree of deacetylation is shown in figure 3.

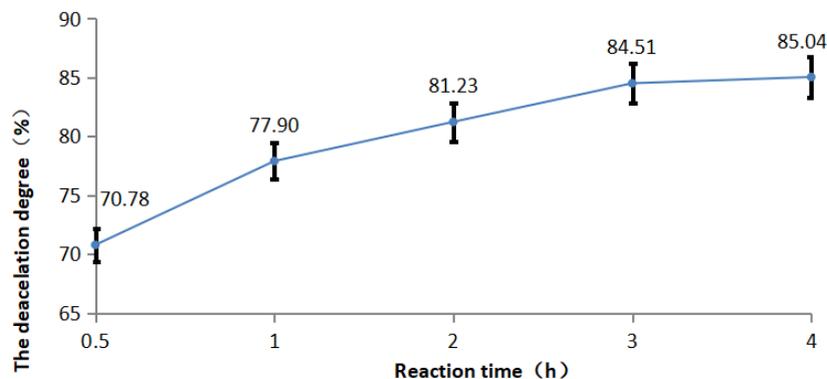


Fig.3 Effect of reaction time on degree of deacetylation

We can see from Figure 3, the only change the time conditions, the degree of deacetylation as time increases, 3h changes slowly. Chitosan in full reaction before the deacetylation degree will increase with time and rapid increase, but the full reaction of chitosan, deacetylation degree rising speed becomes slow.

Conclusion

The experimental results show that the highest yield in 3h, the viscosity of 4H was lowest in the highest degree of deacetylation of 4h, taking into account the 4H yield than 3H 7.27% lower, but the viscosity is lower than that of 3H 0.2mPa 4H s 4h, deacetylation degree is lower than that of 3H 0.53%, the best choice reaction time 3H for the degradation of Chitosan.

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References

- [1] Chen Hao, Chitosan modification and its adsorption of heavy metals Cu,Cd in water.Zhejiang University,2014,6-12.
- [2] Cui Lingzhi,Preparation technology and application of water-soluble chitosan. Shandong Light Industries College,2012,7-12.
- [3] Chu-Kuang Chou,Shih-Ming Chen,Yi-Chieh Li,Tzu-Chuan Huang,Jen-Ai Le,Low-molecular-weight chitosan scavenges methylglyoxal and N ε -(carboxyethyl) lysine, the major factors contributing to the pathogenesis of nephropathy. Chou et al,SpringerPlus,2015,4:132.
- [4] Zhang Yong, Zhang Xiaowei,Li Yaming. Study on the preparation of chitosan oligomers by hydrogen peroxide degradation of chitosan [J]. Anhui Agricultural Sciences,2011,39 (21): 13060-13062.
- [5] Liu Jun, Preparation and Study of Chitosan for Flocculated Properties in Water Treatment .Wuhan University Of Technology, 2013,23-28.