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Study of the influence of processing parameters on the production of carboxymethylchitin

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Abstract

Carboxymethylchitin was prepared at different reaction temperatures and from alkali chitin with different concentrations of alkali. Properties of the product were studied. Alkali chitin were prepared using freshly prepared sodium hydroxide of 45, 50, 55, 60 and 65% (w/w) concentration and carboxymethylated using monochloroacetic acid at controlled (35–40 °C) and uncontrolled (30–80 °C) temperature conditions. Molecular weight, viscosity, degree of deacetylation, etc. of the resultant product, i.e. carboxymethylchitin were determined. It was found that the reaction temperature has a profound influence on the property of the product than alkali concentration. A hygroscopic and completely water-soluble product was formed. Optimum conditions for the production of carboxymethylchitin were found to be 60% NaOH concentration and at 35–40 °C reaction temperature. At these conditions, it was obtained with a molecular weight of 4.11×10^6 Da, viscosity 1926 cP and degree of deacetylation 45.02%.

Keywords: Chitin; Carboxymethylchitin; *Parapenaeopsis stylifera*

1. Introduction

Aquatic organisms like shrimp, crab, etc. contribute a very good participation in our foods. Processing of these organisms gives head, shell, etc as waste materials. They will be easily spoiled and arises threats to the public health. Conversion of waste materials into useful products is one of the solutions of environmental pollution, nowadays. Shrimp shell contains 8–10% chitin [7], which is the most abundant biopolymer after cellulose [6]. So, shrimp shell can be converted to chitin, a nitrogen containing polysaccharide.

Polysaccharides and their derivatives hold a major part in our lives as medicines, cosmetics, textiles, paper, food and other branches of industry because of their unique nature in properties such as low toxicity, biocompatibility, hydrophobicity, etc. [12]. In the midst of these polysaccharides, people show growing interest in chitin, since, it is widely distributed in nature [8,9]. The most commonly prepared derivative of chitin is chitosan by partial deacetylation of chitin [8]. The importance of chitin and chitosan has grown partly because they are renewable and biodegradable source of materials and partly because of the recent increased applications in biology, biotechnology and medicine. Carboxymethylchitin is another value shot derivative of chitin. The conversion of chitin into carboxymethylchitin came into practice by carboxymethylation reaction [2,9,13].

Carboxymethylchitin has successfully proven its use in the field of cosmetics as moisturizer, smoothener, cell activator and a cleaner for face skin conditioning. Carboxymethylchitin is widely used in food products also. Another innovative use of Carboxymethylchitin is in wound dressing, due to its hydrophobicity.

When, molecular characteristics of carboxymethylchitin are concerned the information available is very poor [3,5]. Here, comes the importance of the present work. This effort puts light on the preparation of carboxymethylchitin at different alkali concentrations and temperatures and the study of its properties.

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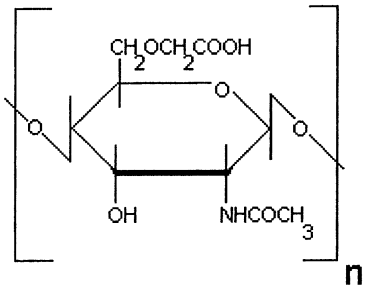


Fig. 1. Structure of carboxymethylated monomer.

2. Experimental

Raw material—*Parapenaeopsis stylifera* procured from processing plant near Cochin, Kerala, India.

All chemicals were of analytical grade and were obtained from BDH (India).

Dialysis membrane obtained from Sigma chemicals (UK), which can retain material of molecular weight 12,000 or greater. Capacity—640 ml/feet.

Freeze drier-Heto drywinner(Denmark).

2.1. Preparation of chitin [10]

The fresh shell waste was washed in water and heated to boiling with 0.5% aqueous NaOH in the ratio of 2:3 for 30 min. Alkali was drained off and the shell was washed free of alkali. The residue was demineralised by immersing in 1.25 N HCl. at room temperature for 1 h with intermittent stirring. The residue was filtered, washed repeatedly with water to make it acid free. Then the product, chitin obtained was dried and pulverized.

2.2. Preparation of carboxymethylchitin

Carboxymethylchitin was obtained by the treatment of alkali chitin with monochloroacetic acid.

Fresh alkali chitin was prepared with different concentrations of alkali viz. 45, 50, 55, 60 and 65% (w/w) NaOH.

2.2.1. Alkali chitin

About 10 g of chitin was mixed well with 40 ml respective alkali prepared and kept in ice for 1 h. Then, it was kept overnight at −20 °C.

Table 1
Yield of carboxymethylchitin prepared at different alkali concentrations and temperature

Percentage of NaOH for the preparation of alkali chitin	Yield in percentage	
	Uncontrolled temperature	Controlled temperature
45	36.7±1.5	37.4±1.4
50	49.8±2.12	44.7±1.2
55	56.5±1.7	52.0±1.6
60	69.6±2.2	65.8±1.85

2.2.2. Carboxymethylchitin

To the alkali chitin prepared, poured 200 ml isopropanol and monochloroacetic acid added, at intervals, with continuous stirring. Addition of monochloracetic acid was stopped, when the whole mixture became neutral. When monochloroacetic acid was added to the mixture, reaction temperature went on increasing. For each concentration of alkali used, one set of carboxymethylation was allowed to take place at room temperature and in another set of experiment, reaction temperature maintained at 35–40 °C by using ice bath.

Resulting viscous solution was dissolved in 1 l of distilled water and then precipitated using 5 l of acetone. The precipitated mass was carboxymethylchitin and it was redissolved in distilled water. The solution was then dialysed for 24 h in running water, using a dialysis membrane, for the removal of salts and then freeze dried and stored.

Important quality parameters of carboxymethylchitin like molecular weight, degree of deacetylation, viscosity, yield, etc. were estimated. Molecular weight was determined by using Schott Gerate AVS 410 equipment [14]. By applying Schrodinger equation, degree of deacetylation was measured [11] using Spectronic Genysis spectrophotometer. Fungilab viscometer was used for viscosity determination.

3. Results and discussion

The carboxymethylchitin (Fig. 1) was prepared with alkali chitin using different concentrations of NaOH viz. 45, 50, 55, 60 and 65% (w/w). When 45, 50, 55 and 60% NaOH were used for alkali chitin preparation and when it was subjected to carboxymethylation, temperature was raised from 30 to 80 °C as more and more monochloroacetic acid was added to it and finally a neutral viscous milky solution was obtained, which was water soluble. This water-soluble product was carboxymethylchitin. Carboxymethylation was a highly exothermic reaction and so only the temperature was raised. It was found that when alkali chitin prepared with NaOH, having concentration above 60%, was used for carboxymethylation, the whole mass turned to a colloidal elastic material as the reaction proceeded, which did not show characteristic reactions of carboxymethylchitin. It implied that at higher alkali concentration of alkali chitin, carboxymethylation may not be possible.

In another set of experiment, with the same as above concentrations of alkali chitin (45, 50, 55 and 60%), reaction temperature was maintained at 35–40 °C and the reaction was slow compared to the other set, where, temperature remained uncontrolled. It was also found that carboxymethylation reaction was not possible at low temperatures below 35 °C.

Yields of carboxymethylchitin obtained at different experimental conditions were given in Table 1. Maximum

Table 2
Viscosity of 1% solution of carboxymethylchitin in water

Percentage of NaOH for the preparation of alkali chitin	Viscosity of 1% solution (cP)	
	Uncontrolled temperature	Controlled temperature
45	36±2	2114±15
50	30±1	2010±10
55	28±1	1928±7
60	22±2	1926±12

yield was obtained when 60% NaOH was used for the preparation of alkali chitin, which was used for carboxymethylation. Under controlled temperature, carboxymethylation was very slow and the reaction would not occur completely. As a result, we got comparatively less yield at controlled temperature than uncontrolled temperature condition.

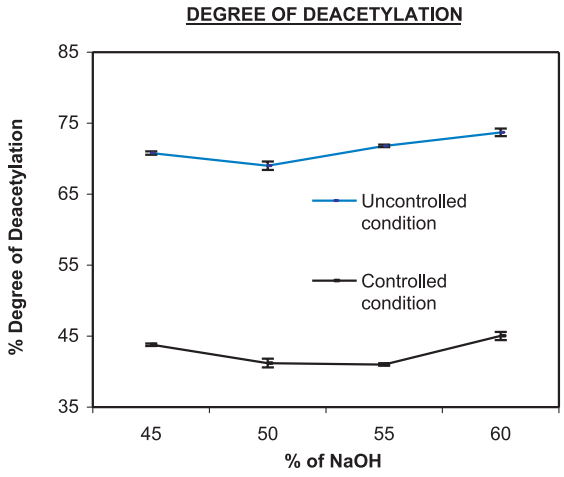
Viscosity of the samples prepared at controlled and uncontrolled temperatures using different concentrations of alkali were given in Table 2. It is well clear from the table that there was remarkable difference in viscosity of the samples prepared at controlled and uncontrolled temperatures. Thus, it was found that the temperature of the reaction had a great influence on the viscosity of the product as was in the case of the production of chitosan [8]. There was a reduction in the viscosity of the final product with increasing alkali concentration for the preparation of alkali chitin. Carboxymethylchitin with good viscosity was obtained at controlled temperature, since, the operating temperature was around 35 °C. But, at uncontrolled temperature condition, temperature was increased to a large extent and as a result thermal degradation occurred [1,4] and viscosity decreased.

Molecular weight of the samples prepared was given in Table 3. Considerable difference was noticed in the case of molecular weight when the samples were prepared under controlled and uncontrolled conditions. It was found that degradation of the compound had taken place at high temperatures. Due to degradation of the product, depolymerisation of chains occurred and as a result molecular weight was decreased. The effect of alkali concentration on the molecular weight of the product under the same temperature conditions was negligible.

The degree of deacetylation of the product prepared under different conditions were shown in Graph-I. Degree of deacetylation up to 75% was reported in products obtained by carboxymethylation at uncontrolled temperature condition. But in the controlled condition, degree of deacetylation was in the range of 40–45% depending on the alkali concentration.

Table 3
Molecular weight of carboxymethylchitin prepared from alkali chitin of different alkali concentrations

Percentage of NaOH for the preparation of alkali chitin	Molecular weight ($\times 10^6$ Da)	
	Controlled temperature	Uncontrolled temperature
45	4.86±0.55	1.33±0.21
50	4.92±0.23	1.01±0.10
55	4.21±0.33	1.21±0.18
60	4.11±0.42	1.29±0.32



Graph-I. Degree of deacetylation of carboxymethylchitin.

Thus, a 65.8% yield of good quality carboxymethylchitin with high viscosity and high molecular weight was obtained when alkali chitin prepared at 60% NaOH was used for carboxymethylation and the reaction temperature was controlled at 35–40 °C. It is a hygroscopic product, which contains 10–12% moisture. From the experiment, it is well understood that the reaction temperature and alkali concentration had a great influence on its properties like viscosity, molecular weight and degree of deacetylation. Product prepared at controlled temperature condition had better properties than that obtained at uncontrolled conditions.

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