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Studies on Indigenous Cotton linters for Preparation of Carboxymethyl Cellulose

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Abstract

Studies were carried out to find out a suitable method for preparation of carboxymethyl cellulose (CMC) from indigenous cotton linters. Special emphasis was given on purification method to remove most of the non-cellulosic materials. A two-step purification method of cotton linters for preparation of water soluble carboxymethyl cellulose (CMC) with degree of substitution (DS) 0.89 and viscosity 235 cp (0.5 % solution) have been described.

Introduction

It is well known that sodium carboxymethyl cellulose is one of the most important cellulose derivatives. It has a vast importance in the industry and in everyday life. In Bangladesh, carboxymethyl cellulose is being imported at the cost of considerable amount of foreign exchange. It has been prepared from different cellulosic sources by different researchers following many different methods (Rahman, *et. al.*, 1985; Majid, *et. al.*, 1990; Hasan and Nurhan, 2003; Egbuchunam and Okicimen, 2003; Bray, 2002; Sato, *et. al.* 2001; Nagieb, *et. al.* 2001). The importance of sodium carboxymethyl cellulose are increasing day by day (Parith, *et. al.*, 2003) and still now no local industry is producing CMC of any grade. Cotton linters are one of the widely used raw materials for preparation of CMC. According to Hahn and Bradshaw (Doree, 1950) these cotton linters, when purified, sometimes have viscosity even higher than that from long staple cotton fibre, This obviously depends on its purification methods. Different types of purification methods are reported on cotton and cotton linters (Ward, 1955). We now report a new method of purification of indigenous cotton linters for preparation of its water-soluble cellulose derivative (CMC) with good solubility and, fair degree of substitutions (DS) and appreciably high viscosity.

Materials and Methods

i) Raw Materials

Cotton linters (2.0 kg) of CB-4 (Delta pine-50) variety were collected from Sreepur Cotton Cultivation Center, Gazipur, Dhaka, Bangladesh. The linters were freed from hulls and other foreign matters and used as raw material for the present research.

ii) Chemicals

Chemicals used during the present study were monochloro acetic acid, sodium hydroxide, hydrogen peroxide, acetic acid, sulfuric acid, ammonia solution, sodium thio-sulphate, potassium dichromate, potassium iodide, copper sulfate; they were of analar grade, E Mark, Germany. Absolute alcohol used was prepared by double distillation of rectified spirit over anhydrous lime.

vi) Purification of Cotton Linters

The following two-step purification method was taken up for the removal of most of the noncellulosic constituents.

a) Scouring with caustic

1.0 Kg of cotton linters was boiled with distilled water for 15 minutes. It was then filtered and submerged into four liters (w/v) of 1 % sodium hydroxide solution and boiled for 2 hours. The fibers were filtered and the fibres were again boiled for half an hour with four liters of distilled water and washed with two liters of normal water. It was then washed with one litre of 0.5 % acetic acid solution and washed finally with water until neutral. The whole mass was then dried in air and then under vacuum. It was then analyzed for its cellulose contents, methyline blue absorption and copper number.

b) Bleaching with hydrogen peroxide

To 10.0 g of the pretreated linters contained in a 1 litre flask fitted with a stirrer and a condenser in reflux position, 300 ml of 0.1 % H_2O_2 solution containing 1 % by weight of each of Na_2CO_3 and Na_2SiO_3 (based on weight of linters) was added and the mixture was heated at 70^O C for four hours with occasional stirring. After the reaction, the mixture was allowed to cool down to room temperature and filtered. The fibre on filter was thoroughly washed with water and dried in air.

The above reaction was repeated changing only one of the reaction conditions at a time within the desired range keeping other conditions unchanged. The following changes of the reaction conditions were studied

a) Concentration of H_2O_2 from 0.1 % to 1.0 %.

b) w/v ratio of the linters to H_2O_2 solution from 1:30 to 1:100

c) Time of reaction from 1 to 24 hours

d) Temperature of reaction from 40^O to 100^O C

The effect of the change of the bleaching conditions on subsequent carboxymethylation is shown in Tables I to IV.

viii) Preparation of carboxymethyl cellulose

Carboxymethyl cellulose was prepared from all the cellulose samples purified above. Carboxymethylation reactions were carried out at an identical condition following the method of Khundkar and co-workers (Khundkar and Bhattacharjee, 1964) with a slight modification. The preparation method consists of the following three steps:

a) Steeping in aq alcoholic NaOH sol. 18 %, (1:4, H_2O: alc.)

b) Carboxymethylation by 80 % monochloroacetic acid (alc. soln.)

c) Purification of crude carboxymethyl cellulose.

a) Steeping of purified cotton linters

Purified cotton linters (5.0 g) were placed in a 100 ml reaction flask and then 40 ml of aqueous, ethanolic (1:4) NaOH solution was added with continuous stirring. The reaction was continued for 2 hours at 30^{O} C with occasional stirring.

b) Carboxymethylation by 80 % monochloroacetic Acid (alc. soln.)

The flask containing the cellulose alkali mixture was placed in a thermostatic water bath, set at 50^{O} C, 10 ml of 80 % aqueous solution of monochloroacetic acid was added, drop by drop, through a dropping funnel and the mixture was occasionally stirred. The flask was left into the water bath with condensers in reflux position for 6 hours.

c) Purification of Carboxymethyl Cellulose

The reaction was carried out for 6 hours and the flask was removed from the bath, cooled to room temperature and the content was filtered under suction. The mass on the filter was washed thoroughly with 80 % alcohol and finally washed with 80 % alcohol containing a drop or two of acetic acid. The product was first dried in air and then over phosphorus pentaoxide and stored in a desiccator. The same method was followed for preparation of CMC from all of the purified samples. Degree of substitution was determined by the modified copper precipitation method (Rahman, *et. al.*, 1985) and the viscosity of 0.5 % aqueous solution was determined by Canon Finask-Ubelhod viscometer.

Results and Discussion

The short fibres left on the seeds of cotton lints after the first ginning constitutes linters. In the present study a two-step method was carried out for purification of cotton linters. This consists of a caustic treatment followed by an oxidative treatment. The process of caustic treatment is described in the experimental section. The caustic treatment mainly destroys or destructs the primary wall of the cellulosic materials, which contains a large

portion of the wax, proteins and pectic substances. After scouring treatments of the cotton linters with 1 % of caustic soda for 2 hours in an open kier at 100^{O} C, cotton linters were treated with hydrogen peroxide. An alkaline solution of H_2O_2 decomposes more easily than acid solutions and at pH values above 7 hydrogen peroxide gradually loses its inherent stability, and the stability is greatly decreased in the pH range 11.5-13 where gradually most of the peroxide molecules yield ions (Ward, 1955). So in the present study reactions were carried out in presence of alkali and sodium silicate at pH values between 11-12. Bleaching was carried out at different conditions of hydrogen peroxide concentrations (0.1-1.0 %), temperatures (40-100^{O} C), time (1-5h) and at different volume of hydrogen peroxide solutions (w/v, linters: H_2O_2) to find out a suitable bleaching condition for preparation of CMC.

The mechanism of oxidation with hydrogen peroxide is said to proceed with the formation of OOH^- ions which infact causes the bleaching of the linters (Ward, 1955). In course of bleaching some degradation of cellulose is also caused by elemental oxygen liberated by decomposition of neutral hydrogen peroxide.

The sodium silicate was used to fix the alkaline pH at the required range for efficient bleaching.

All the bleached cotton linters samples were converted into their water-soluble cellulose derivatives of carboxymethyl celluloses with identical reaction conditions (experimental section). Degree of substitution and the solution viscosity of 0.5 % aqueous solution of all the CMC samples prepared were determined. The effect of bleaching conditions during H_2O_2 treatments of cotton linters on the solution viscosity and the degree of substitution of the corresponding CMC samples prepared is quite note worthy. The results are expressed in Table (I-IV) & Graph (1-8).

Table I. Effect of H_2O_2 concentrations on degree of substitution and viscosity of Carboxymethyl cellulose

% conc. H_2O_2	D.S	Viscosity in cp*	Physical characteristics
0.1	0.65	300	Soluble in water with some fibre
0.2	0.73	286	Soluble in water
0.3	0.86	265	Soluble in water
0.4	0.89	235	Highly soluble in water
0.5	0.87	217	Highly Soluble in water
0.6	0.83	203	Soluble in water
0.8	0.81	190	Soluble in water
1.0	0.77	145	Soluble in water

* 0.5 % aqueous solution

Table II. Effect of volume of H_2O_2 solution on degree of substitution and viscosity of Carboxymethyl cellulose

linters : H_2O_2 (w/v)	D.S	Viscosity in cp*	Physical characteristics
1:30	0.65	300	Soluble in water with some fibre
1:40	0.78	270	Soluble in water
1:50	0.89	235	Highly soluble in water
1:60	0.81	210	Highly soluble in water
1:70	0.73	185	Soluble in water
1:80	0.64	160	Soluble in water
1:100	0.58	148	Soluble in water

* 0.5 % aqueous solution

Table III. Effect of time of H_2O_2 treatment on degree of substitution and viscosity of Carboxymethyl cellulose

Time of H_2O_2 treatment 'hour'	D.S	Viscosity in cp*	Physical characteristics
1	0.51	300	Soluble in water with some fibre
2	0.61	270	Soluble in water
3	0.78	256	Soluble in water
4	0.89	235	Highly soluble in water
5	0.89	192	Highly soluble in water
24$^{\otimes}$	0.78	165	Soluble in water

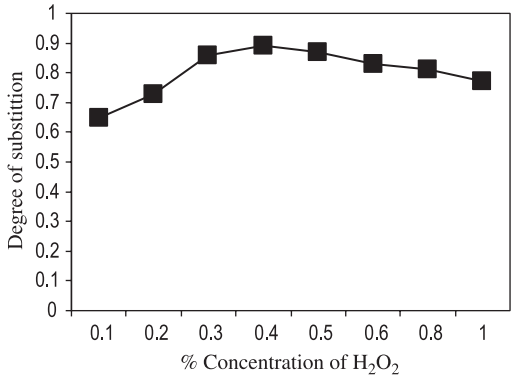
* 0.5 % aqueous solution.

⊗ Reaction carried out at room temperature.

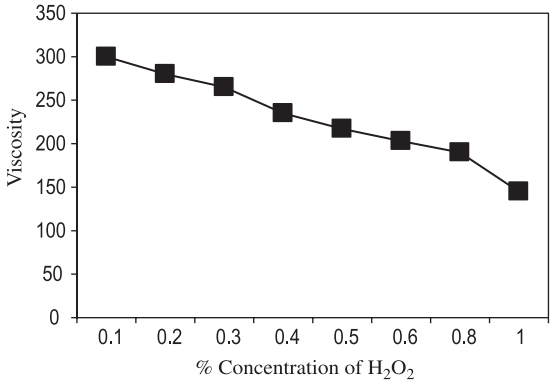
Table IV. Effect of temperature of H_2O_2 treatment on degree of substitution and viscosity of Carboxymethyl cellulose

Time of H_2O_2 treatment ^{O} C	D.S	Viscosity in cp*	Physical characteristics
40	0.48	310	Soluble in water with some fibre
50	0.61	285	Soluble in water
60	0.77	260	Soluble in water
70	0.89	235	Highly soluble in water
80	0.73	203	Soluble in water
100	0.62	175	Soluble in water

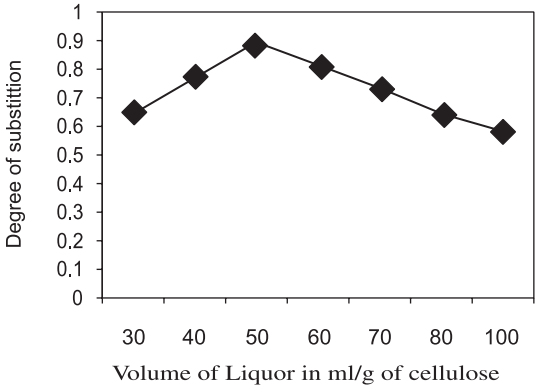
* 0.5 % aqueous solution.



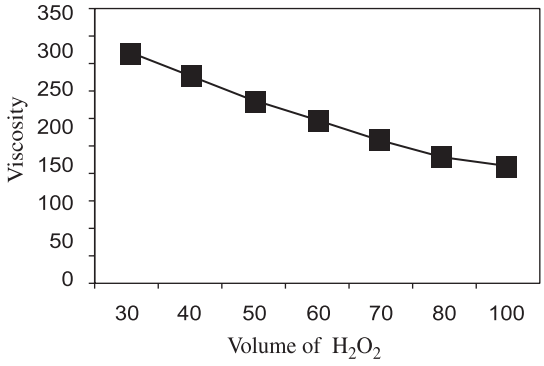
Graph 1. Degree of substitution of CMC Vs Percentage of H_2O_2 concentration



Graph 2. Viscosity of CMC in cp Vs Concentration of H_2O_2 of bleaching treatment



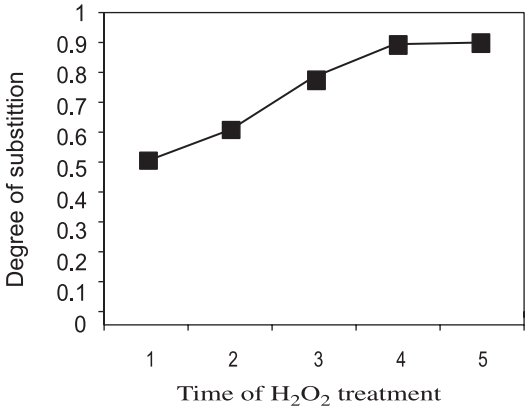
Graph 3. Degree of substitution of CMC Vs volume of hydrogen peroxide solution



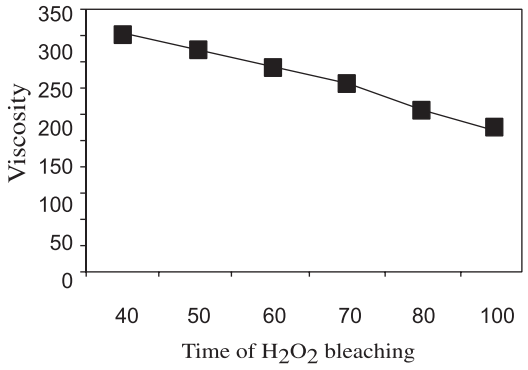
Graph 4. Viscosity of CMC in cp Vs volume of H_2O_2 liquor

From the results of Tables I to IV it transpires that a highly water soluble CMC with a maximum D. S. of 0.89 having a viscosity of 235 cp (0.5 % solution) can be obtained from cotton linters when the latter, prior to carboxymethylation is subjected to scouring with 1% NaOH and then bleached with 0.4 % H_2O_2 at 1: 50 linters-liquor ratio at 70^{O} C for 4 hours. Purification of the linters resulted a weight loss of about 6.7 %. The analysis of the linters after bleaching was as follows:

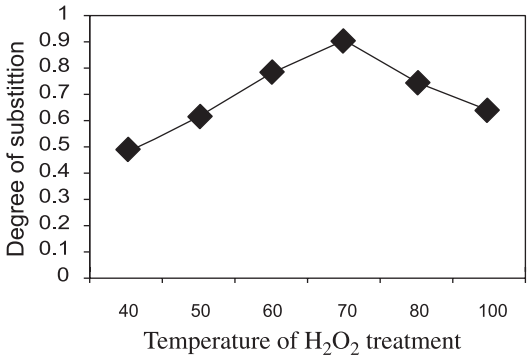
Residual wax, 0.3 %; Methylene blue absorption, 1.32 Copper number, 0.02 and α-cellulose, 99.7 %.



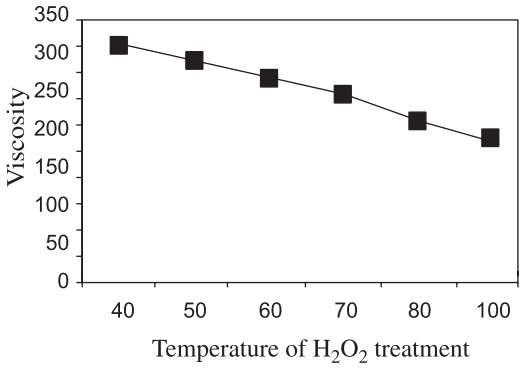
Graph 5. Degree of substitution of CMC Vs time of H_2O_2 treatment in hour



Graph 6. Viscosity of CMC in cp Vs Time of H_2O_2 treatment



Graph 7. Degree of substitution of CMC Vs time of hydrogen peroxide treatment in hour



Graph 8. Viscosity of CMC in cp Vs Temperature of H_2O_2 treatment

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