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Synthesis of highly substituted carboxymethyl cellulose depending on cellulose particle size

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ABSTRACT

Corn husk is an abundant agricultural waste. It has great potential for use as a cellulose source for the production of carboxymethyl cellulose (CMC). The chemical composition of corn husk, such as cellulose, hemicelluloses, lignin, fatty and waxy matter, pectic matter and aqueous extract was determined. The cellulose extracted from corn husk was carboxymethylated using sodium hydroxide (NaOH) and monochloroacetic acid (MCA), in aqueous ethanolic medium, under heterogeneous conditions. The carboxymethylation reaction was optimized as to the NaOH concentration, MCA concentration, reaction temperature, reaction time and cellulose particle size. The degree of substitution (DS) was determined with respect to the reaction conditions using chemical methods. The produced CMC was identified by FTIR and the crystallinity of the CMC was determined by XRD. The CMC product had an optimized DS of 2.41 and the optimal conditions for carboxymethylation were NaOH concentration, 7.5 mol/L; MCA concentration, 12 mol/L; reaction temperature, 55 °C; reaction time, 3.5 h and cellulose particle size, 74 μm. These optimization factors allowed to prepare highly substituted CMC with higher yield, 2.40 g/g, providing plenty of opportunities for its many applications.

1. Introduction

Many unwanted agricultural waste products or by-products from agricultural activities and agro-based processing litter the environment and constitute pollution [1]. Most of these agricultural wastes are composed of cellulose from plant cell walls. Cellulose is a linear and high molecular weight polymer which neither melts nor dissolves readily in water. It also does not melt or dissolve in most common organic solvents, making it unsuitable for most industrial uses. Cellulose is suitable for chemical derivatization reactions, so it can be converted to useful chemical feedstock [2].

Sodium carboxymethyl cellulose (CMC) is a man modified water-soluble cellulose derivative that is produced by the reaction of cellulose with alkali and monochloroacetic acid, using organic solvents, under heterogeneous conditions [3]. Recently CMC has got ample scientific attention, especially due to its polyelectrolyte character. It is the most widely used cellulose ether today with applications in various industries [4]. Large quantities are produced in crude commercial grades, without any refining, for use as a constituent in detergents, adhesives, pesticide, lubricants, cloth, cement, ceramics, oil drilling mud, and in the paper and coating industry [5]. High-purity grades are also employed as food additives.

The properties of cellulose derivatives are mainly compared by the degree of substitution (DS). The maximum DS can be achieved is 3 [6]. The selection of carboxymethylation condition is essential in order to prepare high substituted CMC [7]. In commercial CMC, the most common DS obtained is usually lower which is from 0.4 to 1.4 [8]. Researchers are trying to develop alternative ways of increasing the degree of substitution for CMC in order to produce better commercial products.

Many researchers have synthesized CMC, by different methods from different agro-cellulosic sources, such as rice straw [9], water hyacinth [10], sugar cane bagasse [11], beet pulp [12], banana stem [13], sago waste [14], orange peel [15], etc. To date, there has been no published work on the synthesis of highly substituted or high DS CMC based on cellulose particle size from corn husk.

The aim of this study is to investigate the optimization factors to prepare highly substituted CMC in terms of particle size from corn husk cellulose. The husk is a waste part of the maize/corn plant. Corn (*Zea mays* L.) is one of the most important cereal crops grown in Bangladesh, with annual production of about 1,850,656 MT [16]. However, this production creates an enormous amount of agro-waste. In an attempt to utilize this waste for useful material production, this article seeks to determine the optimum conditions for producing highly substituted or high DS CMC from corn husk. So far, this has never been achieved.

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2. Experimental

2.1. Materials

Corn husks were collected from the Regional Wheat Research Institute, Rajshahi, Bangladesh. Chemicals used during the study were sodium hydroxide (BDH, England), monochloroacetic acid (BDH, England), hydrochloric acid (BDH, England), ethanol (Merck, Germany), methanol (Merck, Germany), glacial acetic acid (BDH, England), silver nitrate (BDH, England), ammonium oxalate (Merck, Germany), *n*-hexane (Merck, Germany), sodium chlorite (Merck, Germany), sulfuric acid (Merck, Germany), etc. All chemicals were of reagent grade and used without further purification.

2.2. Methods

2.2.1. Preparation of sample

Locally collected corn husk sample was cut manually into small pieces and dried in the sun to remove moisture. The dried sample was ground into powder using a grinding disk mill (model: FFC-15, China). The powdered sample was then sieved (Sieve type: OHIO 44060, USA) and separated into different particle sizes by passing the sample through sieves of different mesh sizes such as 10, 44, 100, 150 and 200. The samples were stored in a desiccator for compositional and chemical analysis.

2.2.2. Isolation and estimation of constituents of sample

The compositional data of corn husk was investigated. The husk consists of α-cellulose, hemicellulose (β- and γ-cellulose), Klason lignin, pectic matter, fatty and waxy matter, etc. (as the average of four replicate analyses) were determined. The results were expressed as weight percent and calculated according to the TAPPI standard [17,18]. The other components, including uronic acids, soluble lignin, acetyl groups, etc. were not noted, owing to their minor importance for the purposes of this work.

2.2.3. Estimation of aqueous extracts

The powdered corn husk sample was treated with distilled water at 100 °C for 2 h, filtered and dried at 105 °C until a constant weight was obtained. The amount of aqueous extracts was calculated as follows:

$$\text{Aqueous extracts,} \quad \% = \frac{W_1 \times 100}{W_0}$$

where W_1 is the loss in weight and W_0 is the initial weight of the sample (before treatment).

2.2.4. Estimation of fatty and waxy matter

The sample was immersed in an *n*-hexane–alcohol mixture (2:1, v/v), in the solid to liquor ratio of 1:100, and then allowed to stand for 10 h with occasional stirring. The sample was then washed with fresh *n*-hexane–alcohol mixture and finally with alcohol. Then the sample was dried at 105 °C until a constant weight was obtained. The amount of fatty and waxy matter was estimated as follows:

$$\text{Fatty and waxy matters,} \quad \% = \frac{W_1 \times 100}{W_0}$$

where W_1 is the loss in weight and W_0 is the initial weight of the sample (before treatment).

2.2.5. Determination of pectic matter

The defatted and dewaxed sample was heated in an 0.5% ammonium oxalate solution, in the solid to liquor ratio of 1:100, at 70–80 °C for 3 days in a heating mantle. The sample was filtered, washed thoroughly with hot distilled water and then dried at 105 °C until a constant weight was obtained. The percentage of pectic matters was then calculated as:

$$\text{Pectic matters,} \quad \% = \frac{W_1 \times 100}{W_0}$$

where W_1 is the loss in weight and W_0 is the initial weight of the sample (before treatment).

Table 1
Composition of corn husk.

Composition	Weight % on oven dry basis
α-Cellulose	45.13 ± 0.87
Hemicellulose (β- and γ-cellulose)	31.15 ± 0.55 (16.86 and 14.29 respectively)
Klason lignin	14.32 ± 0.23
Fatty and waxy matters	2.20 ± 0.11
Pectic matters	3.65 ± 0.17
Hot water extract	2.50 ± 0.07
Others	1.05 ± 0.05

Results are expressed as mean ± standard deviation; $n = 4$.

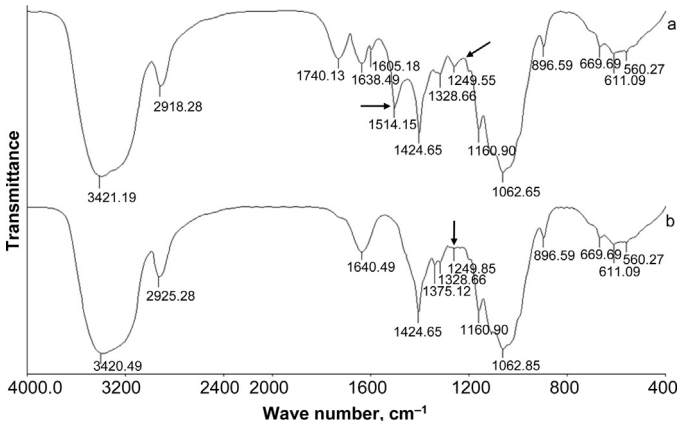

Fig. 1. FTIR spectra of (A) raw corn husk powder and (B) purified extracted cellulose.

2.2.6. Determination of Klason lignin

The dewaxed and depectinized sample was dried at 105 °C and treated with 72% sulfuric acid, in the solid–liquid ratio of 1:15, with frequent stirring at room temperature. The mixture was allowed to stand for 2 h and then diluted to 3% acid concentration. After refluxing the mixture for 4 h it was allowed to stand overnight. Then the mixture was filtered through a sintered glass funnel and washed thoroughly with hot distilled water. The constant weight of the residue in the sintered funnel, dried at 105 °C, was taken as the amount of the lignin content.

2.2.7. Estimation of α-cellulose and hemicellulose

In this step, all noncellulosic matters were removed from samples by treatment with bleaching agents, such as $NaClO_2$, and chlorite holocellulose. A combination of α-cellulose and hemicelluloses was obtained.

2.2.8. Preparation of chlorite holocellulose

A suitable amount of dewaxed and depectinized sample was dried at 105 °C and heated with 0.7% $NaClO_2$ solution. This solution was buffered at pH 4, in the solid to liquor ratio of 1:80, and the heating was carried out at 90–95 °C for 90 min. After filtering and washing the sample, it was then treated with 0.2% sodium meta bisulphite solution for 15 min. It was again filtered and washed thoroughly with distilled water. Finally the solution was dried at 105 °C until achieving a constant weight.