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PII: S0144-8617(96)00166-X

Carbohydrate Polymers 32 (1997) 229–231

0144-8617/97/$17.00 + .00

Optimization of a process for preparing carboxymethyl cellulose from water hyacinth (*Eichornia crassipes*)

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(Received 28 May 1996; revised version received 29 October 1996; accepted 22 November 1996)

α-Cellulose was isolated from water hyacinth (*Eichornia crassipes*), a free floating weed growing on shallow water. It was etherified with chloroacetic acid in a solvent medium. The process of carboxymethylation was optimized with respect to the solvent medium, alkali concentration, acid concentration, time and temperature of the reaction. © 1997 Elsevier Science Ltd

INTRODUCTION

Water hyacinth (*Eichornia crassipes*) is an obnoxious weed growing on shallow water, ponds, lakes, etc. Due to various socio-economic problems that it causes, several attempts have been made to seek outlets for this waste material into useful products. Several reviews on the utilization of water hyacinth are available in the literature (Ramachandran *et al.*, 1971; Anon., 1976).

The possibility of preparing microcrystalline cellulose (MCC) from this weed has been successfully attempted in our laboratories (Gaonkar & Kulkarni, 1986). This work reports on the possibility of using this weed for the manufacture of carboxymethyl cellulose (CMC), a versatile ingredient, useful in the food and chemical industries.

MATERIALS AND METHODS

Water hyacinth (*Eichornia crassipes*) was procured from local ponds in the Bombay suburbs. The plants were washed, cut into small pieces and dried in a Sapphire fluidized bed drier at 65°C for 6 h. The dried product was then ground into powder and passed through an 80 mesh sieve. α-Cellulose was isolated from this powder by the method of Gaonkar and Kulkarni (1987).

Conversion of α-cellulose to carboxymethyl cellulose was carried out as outlined in Fig. 1. The effect of solvent system, alkali concentration for steeping, concentration of chloroacetic acid, time and temperature of the reaction on the degree of substitution (DS) was studied. The reaction was optimized with respect to DS by varying each of these parameters. Initially constant weights of sodium hydroxide, cellulose, and monochloro acetic acid were added to 110 ml of solvent. Carboxymethylation was then carried out as per Fig. 1.

The DS of the prepared CMC and its purity were determined by the standard method (ASTM, 1961).

$$DS = \frac{0.162A}{1 - 0.058A}$$

where A is the equivalent weight of alkali required per gram of sample.

RESULTS AND DISCUSSION

Initially, the effect of solvents on the DS was studied. The solvents used were isobutyl alcohol, isopropyl alcohol, ethanol and water. A maximum DS of 0.68 was obtained with isopropyl alcohol as the solvent medium (Fig. 2), whereas both ethyl alcohol and water resulted in a lower DS. The role of the solvent in the carboxymethylation reaction is to provide accessibility of the etherifying reagent to the reaction centres of the cellulose chain (Savage *et al.*, 1954). The differences in the extent of carboxymethylation as reflected by the DS using these solvents can probably be explained by taking into consideration their polarities and stereochemistry. The polarity index of isobutyl alcohol, isopropyl alcohol, ethyl alcohol and water are 3.9, 4.3, 5.2 and 9.0. This implies that as the polarity of the solvent decreases the reaction efficiency increases. Isobutyl alcohol has three bulky methyl groups surrounding the primary carbon atom which may

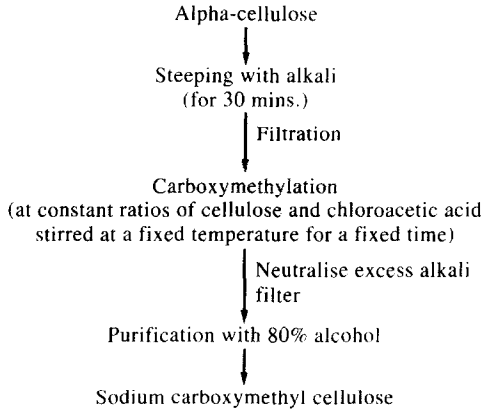

Fig. 1. Carboxymethylation of α-cellulose obtained from water hyacinth.

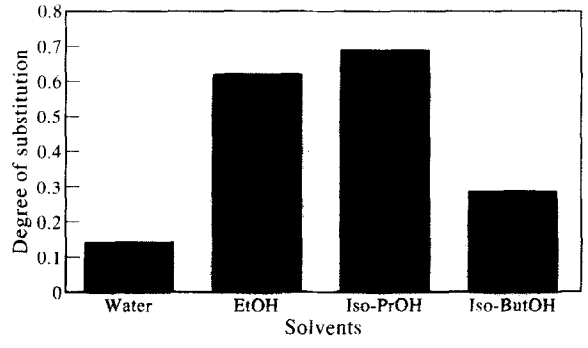

Fig. 2. Solvents effect on carboxymethylation.

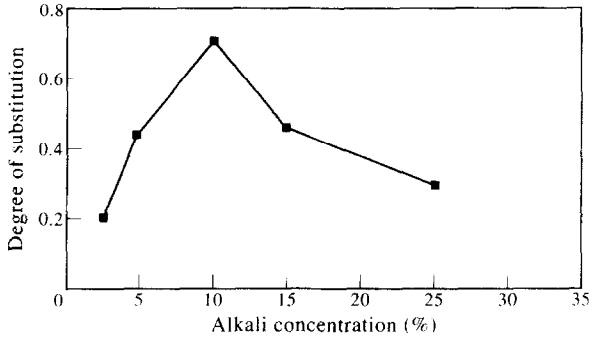

Fig. 3. Alkali concentration for steeping. Effect on carboxymethylation.

provide steric hindrance to the reacting groups. This probably accounts for the lower DS obtained with isobutyl alcohol as the solvent during the carboxymethylation process.

Using isopropyl alcohol as the solvent medium, the effect of alkali concentration used for steeping α-cellulose on the DS was studied. As shown in Fig. 3, it was observed that the degree of substitution increased with increasing sodium hydroxide concentration and reached a maximum at an alkali concentration of 10% (2.5 M), and thereafter a sharp decline in the DS was observed. The carboxymethylation process involves two competitive reactions which take place simultaneously (Mark *et al.*, 1965). The first involves a reaction between cellulose and monochloroacetic acid in the presence of alkali to yield CMC as suggested by the following equation:

$$\underset{\text{Cellulose}}{\text{Cell}-\text{OH}} + \underset{\text{Chloroaceticacid}}{\text{ClCH}_2\text{COOH}} + \text{NaOH} \rightarrow \underset{\text{Sodiumcarboxymethylcellulose}}{\text{Cell}-\text{OCH}_2\text{COONa}} + \text{NaCl} + \text{H}_2\text{O} \quad (1)$$

The second reaction involves the reaction of sodium hydroxide with monochloro acetic acid to form sodium glycollate:

$$\underset{\text{Sodiumcarboxymethylcellulose}}{\text{Cell}-\text{OCH}_2\text{COONa}} + \text{NaOH} \rightarrow \underset{\text{Sodiumglycollate}}{\text{HOCH}_2\text{COONa}} + \text{NaCl} \quad (2)$$

Hence the first reaction seems to prevail above the second up to a sodium hydroxide concentration of 2.5 M. Above this concentration, the second reaction predominates with the formation of larger amounts of glycolate, thereby lowering the DS. Similar findings have been reported in case of carboxymethylation of maize starch (Khalil *et al.*, 1990).

With isopropyl alcohol as the solvent medium and an alkali concentration of 2.5 M the degree of substitution of sodium CMC was found to increase with an increase in the concentration of monochloroacetic acid. As shown in Fig. 4, from a DS of 0.453 for a cellulose: chloroacetic acid ratio (w/w) of 1:0.46, the DS increases to 0.721 for a cellulose:acid ratio of 1:0.92. This may be due to the greater availability of the acid molecules at higher concentrations in the proximity of the cellulose molecules.

There was a significant and gradual increase in the degree of substitution with temperature, within the range (30–75°C) as seen in Table 1. A similar effect was observed with an increase in the duration of carboxymethylation (0.5–6 h). However, there was hardly any difference observed between the DS reached at 3 h and that reached at 6 h.

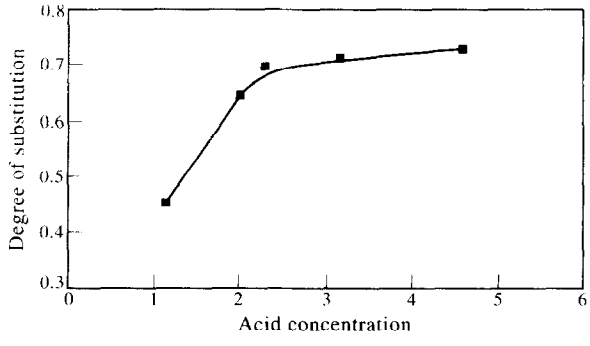

Fig. 4. Chloroacetic acid concentration effect on carboxymethylation.

Table 1. Effect of temperature and time of reaction on degree of substitution (DS) of CMC

Temperature (°C)	DS
30	0.24
50	0.52
60	0.62
75	0.71
Time (mins)	
60	0.42
90	0.56
180	0.72
360	0.73

The enhancement of DS with temperature and duration of reaction may be due to the fact that there is a better reaction environment created and a prolonged time available for carboxymethylation. This may lead to better reaction efficiency and higher DS of the final product. The favourable effect of temperature on carboxymethylation was reported previously (Naterova & Polein, 1974).

The optimized product had a DS of 0.73 and purity 99.0% which complies with ISI standards (IS: 5306, 1968) for food grade Na-CMC. The yield of the prepared product was found to be 110% on a dry weight basis.

CONCLUSIONS

The best set of conditions for carboxymethylation of α-cellulose obtained from water hyacinth was found to be a cellulose:chloroacetic acid concentration of 1:0.92 (w/w), an alkali concentration of 10% with a steeping time of 30 min, reaction temperature and time of 75°C and 6 h with isopropyl alcohol as the solvent medium. Within the above optimized procedure, a low viscosity food grade Na-CMC having a DS of 0.72 could be prepared.

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