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Extraction of Carboxymethyl Cellulose from Barley

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Abstract

Carboxymethyl Cellulose (CMC) or sodium carboxymethyl cellulose (NaCMC) is a cellulose derivative with carboxymethyl groups (-CH_2-COONa) bonded to some of hydroxyl groups on cellulose backbone. The application of CMC is becoming attractive and promising in the fields of superabsorbent due to polar, chemically reactive and strongly hydrophilic carboxyl group. Superabsorbent polymers (SAPs) can absorb and retain extraordinary large amounts of water or aqueous solution relative to their own mass. SAPs materials are widely used for the products that require high hygienic, such as baby diapers and sanitary napkins. Cellulose which is the raw material of generating modified cellulose is a common natural polymer found vastly in plants and one among them is Barley (Hordoleum vulgare). It is a crop/grain cultivated in the various parts of Nepal ranging from East to west. This research has investigated, isolated, and characterized CMC in Barley collected from Siraha District of Nepal with the aim of improving socio-economic condition of farmers.

Key words: *carboxymethyl cellulose, superabsorbent, disposable diapers, Barley.*

Introduction

Carboxymethyl cellulose (CMC) or sodium carboxymethyl cellulose (NaCMC) is a cellulose derivative with carboxymethyl groups (-CH -COONa) bonded to some of hydroxyl groups on cellulose backbone. The polar carboxyl groups provide the cellulose soluble, chemically reactive and strongly hydrophilic and so the application of CMC in superabsorbent fields becomes attractive and promising[1]. Superabsorbent polymers, otherwise known as SAPs, are super soakers, or water holding crystals which are materials that swell in water to form a clear gel and unlike a sponge, in which water can be wrung out easily, the hydrated gel particles retain the absorbed water even under pressure. This unique ability to hold absorbed water, even against pressure is the primary benefit of using superabsorbent polymers. Superabsorbent materials are widely used for products that require high hygienic, such as baby diapers and sanitary napkins.

The versatility of cellulose has been re-evaluated as a useful structural and functional material. The environmental benefits of cellulosics have become even more apparent[2]. In the global arena of superabsorbent polymers (SAPs) related research works some of the names and their works are notable. Most of the superabsorbent material found in present markets uses a synthetic material such as acrylic compounds. However, the use of such superabsorbent material in large quantities as a disposable material is causing environmental problems[3]. Therefore, the use of environmental-friendly materials needs to be developed more. Polysaccharide that can be used as raw material superabsorbent material is the cheapest,

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most abundant, available and renewable organic material[4]. Among the various types of polysaccharides, cellulose is the most potential one, since it is the most abundant natural polymer with excellent biodegradability and biocompatibility. Chemical functionality of cellulose include reactions of hydroxyl groups such as esterification, etherification, intermolecular cross-linking reactions, and macrocellulosic free radical reactions, particularly in the formation of graft cellulose copolymers to increase the usefulness of cellulose by altering its properties. These cellulose derivatives are grouped according to the processes and substituents, for instance, esters- cellulose acetate through esterification and ethersmethyl cellulose/cyanoethyl cellulose/carboxymethyl cellulose (CMC) via etherification[5].

Optimization of reaction conditions for preparing carboxymethyl cellulose is necessary to obtain carboxymethyl cellulose (CMC) by etherification using sodium monochloroacetate and sodium hydroxide[6]. There are two reactions occurring simultaneously during the carboxymethylation; that are the primary reaction which produces pure CMC and the side reaction that produces undesired sodium glycolate[7]. Chemical pre-treatments of the agro wastes are done followed by enzymic saccharification. Emphasis has been given toward investigating the appropriate conditions leading to good delignification with the least loss of cellulose and hemicellulose contents[8]. Cellulose isolation is performed by extraction followed by acetylation resulting cellulose diacetate[9]. Chemical functionalization of cellulose derived from non-conventional sources has been reported which continue to play a dominant role in improving the overall utilization of cellulosic polymers[10].

CMC can be obtained from various plants resources and their extraction from agro wastes of rice, wheat and barley has multi dimensional importance. The following table shows the chemical composition of some fibres[11]. The table 1 shows the chemical composition of the fibres from several types of non-timber plant. Some of cultivated plants such as cotton, flax, hemp, ramie, jute, kenaf and sisal have a high cellulose content up to 99%-w. Bagasse, rice straw, wheat stalks, bamboo, oil palm empty bunches, barley etc are some examples of the cultivation/non-cultivation sources of cellulose.

Carboxymethyl cellulose obtained from these plants wastes has a higher degree of substitution (DS) and is expected to be more valuable. The use of non-wood cellulose sources has been explored and developed since the wood price is relatively expensive and associated with forest conservation issues. Among the plants that are not cultivated, oat and rice contains relatively high cellulose at 44-50 %-w, so these have the potentiality to be used as a source of cellulose for various applications. In addition, with relatively low lignin content (*i.e.*, 0-11%-w) from these plants will be more easily removed to obtain high-purity cellulose[11].

Table 1: Chemical composition of several types of fibers (%-w)[11]

Fibre	**Cellulose**	**Hemicellulose**	**Ligin**	**Pectin**	**Fat/Wax**
Cotton	90-99	-	-	-	-
Flax	64-84	16-18	0.6-5.0	18-20	15
Hemp	67-78	16-18	35-55	0.8	0.7
Jute	51-78	12-13	10.0-15.0	2-44	05
Barley	48	-	-	-	-
Oat	44-53	-	-	-	-
Rice straw	38.3	38.3	31.6	11.8	
Wheat straw	39	38.7	17	-	19
Sugarcane Bagasse	43.6	33.5	18.1	-	0.8

Currently, several useful applications for these plants have been found[12,13]. This project will utilize the CMC of Barley/rice to synthesize SAPs for the preparation of cost effective disposable diaper /napkins for babies as well as adults' health care.

Experimental Methods

Collection of Barley

Barley husks were collected from Dhangadhimai municipality, Siraha district of Nepal. The whole plant except grain was dried and milled. An ideal pre-treatment was done to reduce the lignin content in the barley and further processing was carried out in the P.N. Campus Chemistry laboratory.

Pretreatment with Alkali

Pretreatment was carried out in Erlenmeyer flasks (250 ml) by treating with 2%, 4%, 6%, 8% and 10% NaOH solution varying time duration at 100 ^oC as shown in the table below

Sample set-A	NaOH Concentration	Time (Minutes)	Temperature (^oC)
A1	2 %	20	100
A2	4 %	60	
A3	6 %	100	
A4	8 %	140	
A5	10 %	180	

Carboxymethylation

The cellulose obtained after pre-treatment phase is converted to carboxy-methyl cellulose (CMC) by etherification process using sodium monocloroacetate and sodium hydroxide[14]. There are two reactions occur simultaneously during carboxymethylation. These are (i) the primary reaction which produces pure CMC and (ii) side reaction that produces undesired sodium glycolate[14].

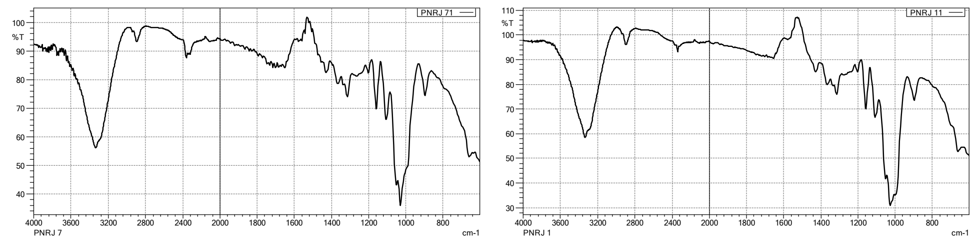
$$\text{Cell-OH} + ClCH_2COOH + NaOH \longrightarrow \text{Cell-OCH}_2\text{COONa} + NaCl + H_2O$$

(Cellulose) (Monochloroacetic acid) (Sodium carboxymethyl cellulose)

$$ClCH_2COOH + NaOH \longrightarrow HOCH_2COONa + NaCl$$

Characterization

CMC pellets being ground with KBr were subjected to Fourier Transforms IR (FTIR) measurement at the wave number range of 4000-400 cm^{-1}. The FTIR of the samples were taken from the laboratory of the department of tax & revenue, Tripureshwor, Kathmandu and Nepal Academy of Science and Technology (NAST), Khumaltar.



(A_1) (A_5)

Figure 1: *FTIR of the samples A1 and A5*

As evident from the FTIR plots (above), frequency range between 3200-3600 cm^{-1} is found to be the hydrogen bonded alcohols, phenols whose intensity lies to be variable. From the graph, the frequency 3446.79 cm^{-1} lies in between the range 3250-3500, which confirms the presence of hydrogen bonded alcohols, phenols. Also the frequency 1639.49 cm^{-1} shows that the presence of alkenes whose intensity is variable and lies within the range (1610-1680) cm^{-1}.

Conclusions

CMC extracted from Barley showed the presence of alcohol and phenol groups proving its potentiality to be used as SAP. Although the majority of the superabsorbents are nowadays manufactured from synthetic polymers (essentially acrylics) due to their superior price-to efficiency balance the world's firm decision for environmental protection potentially support the ideas of partially/totally replacing the synthetics by "greener" alternatives like barley.

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