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SYNTHESIS OF CARBOXYMETHYL CELLULOSE FROM RICE HUSK

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ABSTRACT

Objective: The purpose of this research was to produce carboxymethyl cellulose from rice husk (CMCRH) and used it as a raw material in food or health products.

Methods: Cellulose was extracted from husk rice and converted to CMC (CMCRH) using sodium hydroxide (NaOH) and monochloroacetic acid in isopropanol (C_3H_8O).

Results: CMCRH was characterized for chemical composition and morphology by scanning electron microscopy. Microscopy analysis showed that chemical composition changes with increasing sodium content (Na-). Likewise, morphology has changed. Physicochemical and viscosity tests showed that were similar properties compare with commercial CMC.

Conclusion: CMC is derived cellulose that is used in products for various applications. RH is an agricultural waste that is carried out to synthesize CMC (CMCRH). Finally, CMCRH has the potential to be used in raw materials in food or health products which biodegradable material.

Keywords: Cellulose, Carboxymethyl cellulose, Rice husk.

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INTRODUCTION

Rice husk or rice hull (RH) is the coating on a grain of rice. It contains silica and lignin which are very hard materials for protect the seed during the growing. RH is agricultural waste that is normally found in the first step of milling the rice with rice bran (Fig. 1) [1].

From rice mill process, that we get 0.28 kg of RH in each kilogram of paddy [2]. RH was often dumped and/or burned that because a serious environmental and human health problems. In general, RH is used as fuel. Such as RH charcoal is produced from combustion and the remaining RH ash after burning because it can be easily collected and is cheap [3].

Carboxymethyl cellulose (CMC) or sodiumcarboxylic – methylcellulose (sodium CM cellulose) is a hydrocolloid that is a hydrophilic polymer. These polymers are carbohydrates, which are cellulose derivatives modified from natural [4]. The molecular structure is as in Fig. 2.

CMC is produced by the etherification reaction of the hydroxyl groups in cellulose under alkaline conditions [5]. The process involves an equilibrium reaction between NaOH and the OH groups of cellulose, followed by the formation of CM groups using sodium monochloroacetate (SMCA) in two-step process as in (1) and (2).

$$R\text{-}OH+NaOH \rightarrow R\text{-}ONa+H_2O \quad (1)$$

$$R\text{-}OH+Cl\text{-}CH2\text{-}COONa \rightarrow R\text{-}O\text{-}CH2\text{-}COONa+NaCl \quad (2)$$

CMC is an important industrial polymer due to its high viscosity, non-toxic, non-allergenic, biodegradability as well as production at lower cost [5,6]. Furthermore, it is also a water-soluble and most important derivative that is biologically compatible. It can function as thickening, binding, emulsifying, film-forming, lubricating, dispersing, stabilizing, and gelling agents and is especially useful as additives in food, pharmaceutical, and cosmetic industries [5].

The purpose of this research was to produce CMC from RH (CMCRH) and used it's as a raw material in food or health products.

MATERIALS AND METHODS

Material

RH was collected from Klong 9, Pathumthani. RH was dried at 80°C and milled. The samples (RH) were sieved with 50 mesh sizes and stored in a desiccator. All chemicals were AR grade or equivalent.

Extraction of cellulose from RH

The milled RH approximately 150 g was boiled in solutions of H_2SO_4 (39 g in 1000 g of water) under stirring at 90°C for 2 h. Then, the solid was filtrated and purified in deionized water. Next, the solid was treated with 50 g KOH in 1000 g of water under stirring at 90°C for 2 h. The solid was filtrated and purified in deionized water again. A solution of NaClO (30g in 1000 g of water) was used in removing lignin and neutralized with glacial acetic acid to pH 4.5 [7]. The percentage of cellulose yield was calculated by the following:

% Yield of Cellulose = $(W_1/W_0) \times 100$

Where W_1 = Weight of cellulose from RH (g)

W_0 = Weight of dried RH (g).

Synthesis of CMCRH

Cellulose from RH approximately 9 g was extracted with 30% NaOH in isopropanol at room temperature for 30 min. Next, added 10.8 g of chloroacetic acid and stirred for 90 min; after that, covered with aluminum foil and keep in 55°C for 180 min. The slurry is divided into two phases. The upper phase was discarded and sedimentary phases were suspended in 70% methanol and neutralized using glacial acetic acid and then filtered and washed with 70% ethanol to remove undesirable salts. Finally, it was washed again with absolute methanol and filtered. Extracted CMC (CMCRH) was dried at 55°C in oven [6]. The percentage of CMCRH yield was calculated by the following:

% Yield of CMCRH = $(W_1/W_0) \times 100$

Where W_1 = Weight of CMC from RH (g)

W_0 = Weight of cellulose form RH (g).

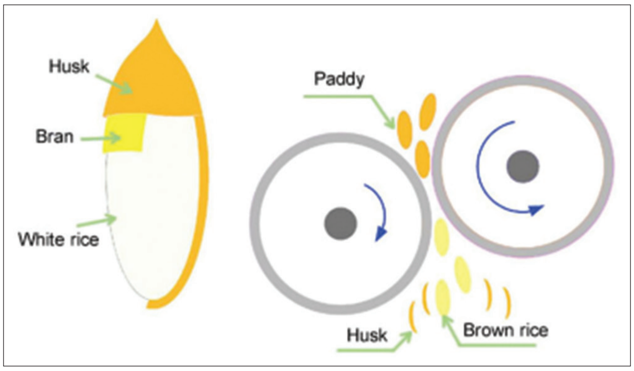

Fig. 1: The rice mill process [1]

Degree of substitution (DS)

DS value shows the average amount of hydroxyl group that was replaced by (Na-) CM group in the cellulose structure at C2, C3, and C6. The DS value of CMC from RH was measured by USP XXIII method.

Characterization of CMCRH

Scanning electron microscopy (SEM) (model JSM-5410 with the high vacuum mode) was used to observe the surface morphology of samples. The effect of the different chemical treatments was assessed using a comparison RH, extracted cellulose, and extracted CMC. All samples were then coated with gold using a vacuum sputter coater (model SC 7640). The chemical composition of samples was analyzed by energy dispersive spectroscopy (EDS) of SEM.

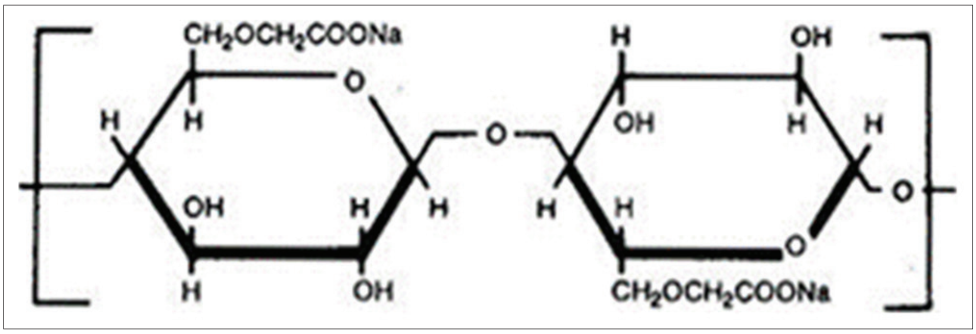

Fig. 2: The molecular structure of carboxymethyl cellulose

Fig. 3: Characteristics of rice husk (a), cellulose extracts (b) and carboxymethyl cellulose extracts (carboxymethyl cellulose from rice husk) (c)

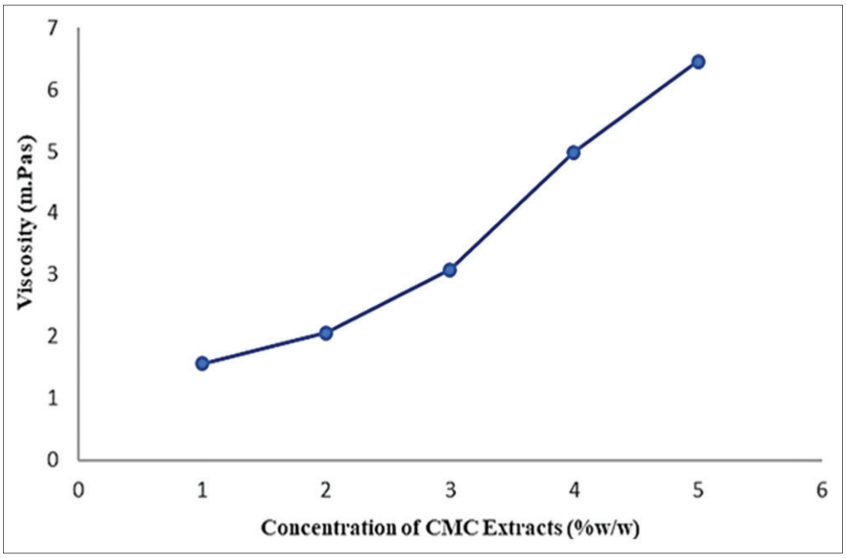

Fig. 4: Viscosity of carboxymethyl cellulose extracts (carboxymethyl cellulose from rice husk) in difference concentration

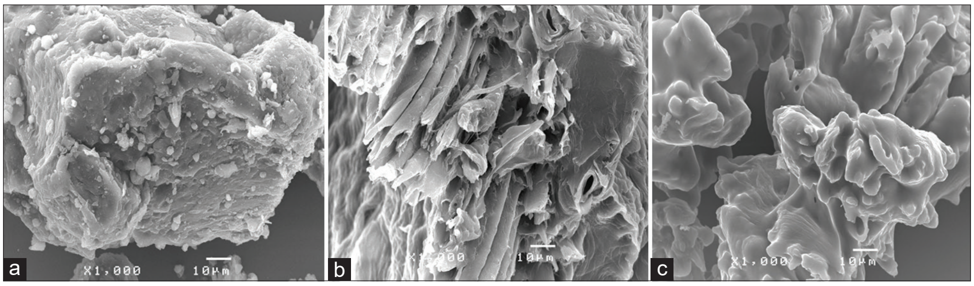

Fig. 5: Image of surface of rice husk (a), extracted cellulose (b), and extracted carboxymethyl cellulose (c) by scanning electron (magnification ×1000)

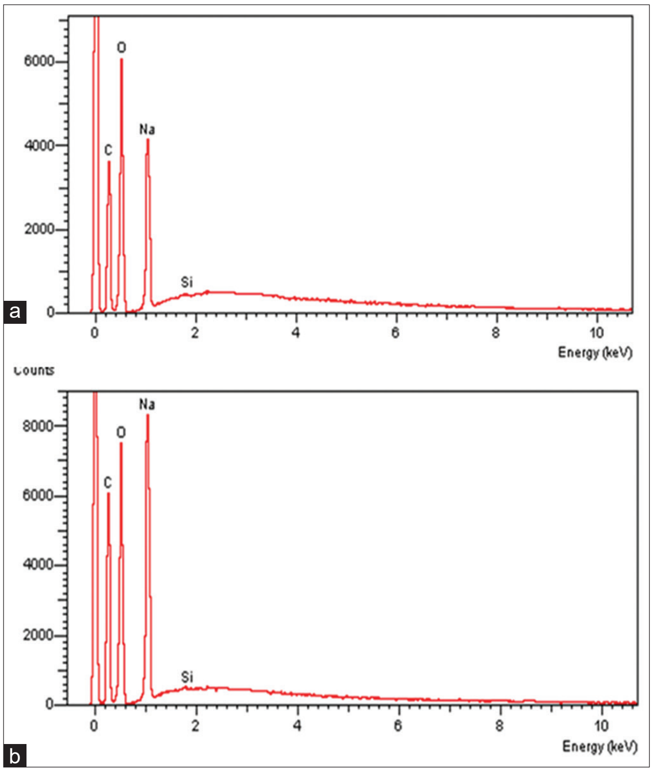

Fig. 6: Chromatogram of carboxymethyl cellulose (CMC) extracts (a) and commercial CMC (b) by energy dispersive spectroscopy

RESULTS AND DISCUSSION

CMCRH was extracted by 30% sodium hydroxide (NaOH) and monochloroacetic acid (MCA) in isopropanol (IPA). The characteristics of fibers in treatment process are shown in fig 3. Fig. 3a as the original material (RH). After treatment, we got cellulose extracts as in Fig. 3b, and CMC extracts from rice husk (CMCRH) in Fig. 3C.

CMCRH gives yellowish fibers, as shown Fig. 3c. The percentage yield of CMCRH is 143.133. The range of pH value is in 5.5 –5.8, DS value is about 0.78, as presented in Table 1.

The viscosity of a polymer solution depends mainly on the concentration, as presented in Fig. 4 and size (i.e., molecular weight) of the dissolved polymer [8]. The molecular weight of polymers is related to their molecular size, which means that the higher the molecular weight polymers provide higher viscosity.

Characterization of cellulose extracts was done by qualitative analysis of SEM. After we treated RH with 30% NaOH which indicates the presence of CM substituent, significantly increase sodium (Na). Table 2 shows the element composition in RH, cellulose extracts (CRH), and CMC extracts (CMCRH) comparing with commercial CMC (CMCMK). We found that RH and extracted cellulose are differences in silica (Si) and sodium (Na). Meanwhile, CMC extracts and commercial CMC are similar.

Table 1: Viscosity of CMC extracts from rice husk at difference concentrate

Concentration of CMC extracts (%w/w)	Viscocity (m.Pas)	pH
1	1.56	5.89
2	2.06	5.78
3	3.08	5.70
4	4.98	5.61
5	6.46	5.56

Table 2: The elements composition in RH, CRH, CMCRH, and CMCMK by qualitative analysis of SEM

Elmt	RH	CRH	CMC_{RH}	CMC_{MK}
	Wt%	Wt%	Wt%	Wt%
C	36.57	40.88	33.70	36.57
O	47.05	58.76	52.86	47.05
Si	12.64	0.06	13.33	16.35
Na	-	0.31	0.11	0.04

The surface morphological of RH (Fig. 5a) has a layer of deposits probably composed of hemicellulose, lignin, and other substances, such as pectin of cellulose fibers. In delignification reaction (Fig. 5b), most of the lignin contained in RH are removed, resulting in smooth and clean surfaces, even large fissures. In Fig. 5c, after treatment, the fibers are divided into individual microfibrils, and the surface of the microfibrils is smooth. The micrographs (Fig. 5) shown the images of extracts at different processing stages.

EDS inside the SEM is provided elemental and chemical analysis of a sample. EDS was determined the element composition in extracts cellulose (CRH) and extracts CMC (CMCRH). The extracts CMC (CMCRH) was the same element composition nearby commercial CMC (CMCMK) in Fig. 6.

CONCLUSION

The cellulose from RH was converted to CMC by sodium hydroxide (NaOH) and subsequently etherified with MCA. The DS of the carboxyl group in CMC confirmed the change of cellulose to CMC. Although, they have different morphology as compared to commercial CMC. For next, our research would be study to purity of the CMC because CMC must be purified at 99.5% if it uses for human consumption. We found the ratio of cellulose and etherifying agent (sodium hydroxide [NaOH] and MCA in isopropanol [C_3H_8O]) affects the purity of CMC [8].

All agricultural wastes are used with this concept to increase the potential of raw materials and reduce pollution. Such as CMC extraction from corn husks by etherification reaction with NaOH and MCA that can be successfully used as additives for medicines and food industries [9]. However, CMC properties were derived from lignocellulose agricultural waste, depend on three factors: Molecular weight of the polymer, DS, and the distribution of carboxyl substituents along the polymer chains [10].

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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