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REVIEW

Comprehension on the Synthesis of Carboxymethylcellulose (CMC) Utilizing Various Cellulose Rich Waste Biomass Resources

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Abstract Due to the increasing interest in the utilization of renewable feedstock's for producing the chemicals, this paper aims to present a short review compiling some efforts made to synthesize the sodium carboxymethylcellulose (NaCMC) from cellulose isolated from various waste biomass materials. NaCMC is water soluble etherified cellulose salt produced in large quantities in crude commercial grade for application in various fields due to its hydrophilic character, good film forming properties, high viscosity, and adhesive performance, etc.

Keywords Cellulose · Etherification · Carboxymethylcellulose · Biomass · Waste

Introduction

The annual biosynthetic capacity of nature to produce the cellulose is estimated to be 10^{11}–10^{12} tons/annum so cellulose has the status of most abundant natural biopolymer. It is an obvious thought of using the cellulose as the promising feedstock for the production of chemicals. The stringent environmental regulations from the federal regulatory authorities towards the use of hazardous feedstock's and depletion in natural mineral resources have also forced the industry to explore the possibility of replacing the conventional raw materials with such natural biodegradable economical renewable materials [1]. Two strategies are popular for obtaining the industrial utility chemicals. First is the degenerative process in which the biopolymer degradation is done to obtain the low molecular weight chemical entities, e.g., pyrolysis, carbonization, hydrothermal liquefaction, gasification, oxidative degradation, hydrolysis, fermentation, etc., and second one is the derivatization of high molecular weight chemical entities having the biopolymer backbone intact. The second approach is more beneficial as it is less energy intensive process so preferred. Basic monomeric unit of cellulose is D-glucose [anhydroglucose unit (AGU)], which links successively through a β-1,4 linkages between carbon 1 and carbon 4 of adjacent units (Fig. 1). Each AGU unit/cellulosic monomer unit has one primary and two secondary hydroxyl functionalities which are susceptible for chemical reactions easily but the limitations of the second process manipulation on cellulose are its rigid, highly crystalline nature and insolubility in common organic solvents. Despite it, many cellulose derivatives were synthesized which are known for their wide use in different industrial applications, e.g., cellulosenitrate, carboxymethylcellulose (CMC), methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, cellulose acetate, cellulose fatty esters, etc. [2]. Out of these derivatives, cellulose ethers are important which has tremendous industrial application, e.g., sodium CMC (NaCMC) is used in food [3] as thickener, and stabilizer in various products. It is also a constituent of many non-food products, such as varnishes and dyes [5], and textile sizing [5]. The technical grade CMC is used in detergents [6]. A further purified CMC have pharmaceutical applications [7]. An intermediate "semipurified" grade is also produced and typically used in paper applications [8]. CMC is also used in the oil-drilling industry as an ingredient of drilling mud [9]. CMC acts as a stabilizer and hydrophilic agent and is therefore used in most of the compositions of cement and building materials because it improves the dispersion of sand in the

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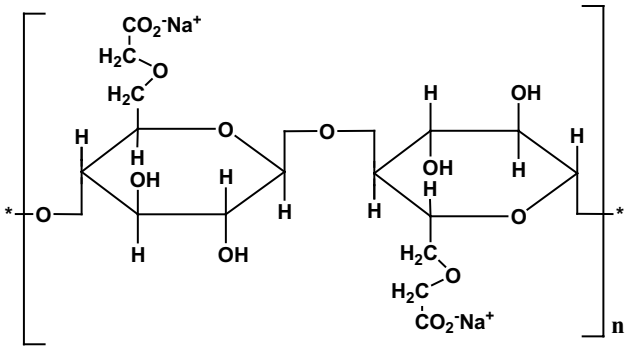

Fig. 1 Structure of sodium carboxymethylcellulose (CMC)

cement, and intensifies its adhesive action [10]. In pesticides [11] and water-based sprays, CMC acts as a suspending agent. CMC is added to various compositions of glues and adhesives [12] that are used for almost any material. The majority of water-soluble ethers are used to join pieces of porcelain hence is used in ceramic industry [13]. As CMC helps to increase the viscosity, it is used in plastics too [14]. This review presents a compiled brief account on most of efforts made in the preparation of CMC from various biomass resources.

CMC from Banana Stem

Banana stem is well known source of cellulose, though it is discarded as agricultural waste. So researchers had developed a method to utilize Cavendish banana pseudo stem for preparing NaCMC. The banana pseudo stem was obtained after harvesting the fruit. The pseudo stem was dried completely and then powdered to pass through a 20 mesh screen. The powder was obtained by using 8% sodium hydroxide (NaOH) at 100 °C for 3.5 h, and followed by bleaching using 5% NaOCl at 30 °C for 3 h. The alkalinization of cellulose was done using 5–30% NaOH at 25 °C for 1 h and then sodium monochloroacetate ($ClCH_2COONa$, NaMCA) at 3–7 g/5 g cellulose slurry was added and the temperature was maintained at 55 °C for 3 h. The CMC with highest degree of substitution (DS), viscosity, purity and crystallinity, i.e., 0.75, 4033 cps, 98.23 and 38.33%, respectively was obtained using 15% NaOH and etherification using 1.2 g (w/w) NaMCA, respectively [15].

CMC from Sago Waste

A method was also described on the isolation of sago pulp (57% w/w) from sago waste to get CMC by etherification using NaOH and NaMCA. The reaction parameters, i.e., temperature, concentration and reaction time were optimized. The product so obtained has a high DS of 0.821. The starting material sago pulp and the synthesized product CMC was characterized using Fourier transform infrared spectra (FTIR). Moreover the digital photographs of sago pulp and sago waste showed the expected rough woody structure while that of synthesized CMC from the pulp showed a smooth surface morphology [16].

CMC from Paper Sludge

The previous research work also describes the preparation of NaCMC from an industrial solid waste, paper sludge as a feasible alternative for generating value-added product. It can be considered, a good contribution in solving environmental problems resulting from paper sludge. It is basically a three step process including pretreatment, basification and etherification. The optimized conditions for pretreatment involved the addition of 6.7% hydrochloric acid to the paper sludge for 30 min at 70 °C. The optimized reactant ratios for preparing CMC was: $m_{\text{paper sludge}}$:$m_{\text{sodium hydroxide}}$:$m_{\text{sodium chloroacetate}}$ = 0.9:0.8:1.15; etherification at 60 °C, basification at 40 °C for 1 h. Moreover under these conditions, CMC with viscosity less than 20 mPa s, DS more than 0.50 and purity more than 90% was obtained. FTIR and X-ray diffraction (XRD) analysis revealed that the resulting product has high DS with low crystallinity. Furthermore the CMC prepared from paper sludge can be used as a water retention agent and can also meet the quality standards of GB/T 10335.1-2005 [17].

CMC from Cotton Stalk

A previous research paper also describes the feasible alternative, time efficient and environmentally safe synthesis of NaCMC from cotton stalk, an agricultural waste, using microwave heating. Response surface methodology (RSM) was applied to optimize the preparation of CMC. Moreover the optimization of reaction product involved pre-treatment and preparation processes. The optimum pre-treatment condition involved the addition of 12% alkali to cotton stalk for 6 min at a microwave power of 200 W keeping cotton stalk to solvent ratio of 1:9, giving 87.52% cellulose. The best conditions for preparation are: $m_{\text{cotton stalk cellulose}}$:-$m_{\text{sodium hydroxide}}$:$m_{\text{sodium chloroacetate}}$ = 1.0:1.1:1.2 with etherification at 195.5 W of microwave power for 1.97 min. Under these conditions, CMC with DS 0.77, viscosity 498.0 cps and purity 92% was produced. FTIR spectroscopy indicated the product with high DS characteristics. Scanning electron microscopy (SEM) showed the particles length ranging from about 12 to 100 μm and were nearly clava in shape. However the product met the quality standards of GB/T1904-2005 [18].

CMC from Sugarcane Bagasse

A research effort also shows the feasibility of preparing cellulose from sugarcane bagasse, involving chemical procedures including acid hydrolysis and alkaline treatment. The extracted and purified cellulose was further treated with alkali and then etherified to obtain a cost-effective additive for coal–water slurry (CWS). The DS and intrinsic viscosity of prepared sodium carboxymethylcellulose (SCMC1) was determined. FTIR and thermogravimetry analysis (TGA) was also done. Another sample SCMC2 was synthesized from microcrystalline cellulose and a commercial sample SCMC3 were used as references. The data so generated showed that SCMC1 had a DS of 0.857 which was 32.7 and 44.7% higher than SCMC2 and SCMC3, respectively. It was also shown that SCMC1 had higher intrinsic viscosity which indicated that it had a higher molecular mass. The SCMC samples so synthesized were further used as additives to prepare CWS, however their performance were evaluated on the basis of rheological behavior and static stability. The data revealed that due to the higher DS and higher molecular mass of SCMC1, CWS with SCMC1 showed lower apparent viscosity and higher static stability than others. SCMC1 could generate steric repulsive forces and stronger electrostatic repulsive forces between the coal particles via adsorption when added to CWS [19].

In another research work, the sugarcane bagasse was treated by acid and alkali separately. The acid and alkaline pulps were further submitted to a chemical bleaching using sodium chlorite. Then these bleached pulps were used to obtain CMC. CMC yield was 35% (pulp based). The mass gain of CMC was 35%, corresponding to 0.70 CH_2COONa group per unit of glucose residue (DS = 0.70) or 23.6% of substitution. The IR spectra confirmed the synthesis of CMC. Using the IR technique DS determined was 0.63, similar to the result of DS calculated by the mass gain (0.70), conductometric titration showed the DS to be 1.0 and according to potentiometric titration method the DS was 0.63 [20].

CMC from Oil Palm Fronds

It is also reported to use oil palm fronds for synthesis CMC. Oil palm fronds are obtained from the harvesting of oil palm fruit bunches which is an agricultural waste, rich in fiber and cellulosic compound. The reaction optimization conditions were studied using RSM and the optimum conditions found were, 52% NaOH and 10.7 g of MCA (monochloroacetic acid), reaction temperature 50 °C with reaction time of 3 h and highest yield of 170.1% CMC. Oil palm fronds CMC so synthesized at this condition was further characterized, which showed the DS to be 1.1, purity 97.3% and viscosity of 1% w/v CMC solution to be 685 cP and hence can be categorized as technical grade CMC [21].

CMC from Pod Husk of Cacao (*Theobroma cacao* L.)

A byproduct of the cacao industry, rich in cellulose, i.e., cacao pod husk (*T. cacao* L.) is also reported to be used to synthesize the NaCMC. It was synthesized by using 20 mL NaOH at varied concentrations (11.59, 15, 20, 25, and 28.41% w/v) at 25 °C for 1 h and with five various concentrations of sodium monochloroacetate (NMCA) samples (i.e., 3.18, 4, 5, 6 and 6.68 g, respectively) with 5 g of cellulose at various temperatures (46.59, 50, 55, 60 and 63.41 °C) for 3 h. The condition optimized using RSM are 15% NaOH with 4 g NMCA, at 55.93 °C for 3 h. Extracted NaCMC has substitution (DS) of 0.75, 2.12 g/g oil holding capacity, 3.73 g/g water holding capacity, 56.61 lightness, 206.10 cps viscosity, and 141.60% yield [22].

CMC from Palm Kernel Cake

The main raw material for cellulose extraction is wood and cotton linter. However, due to increasing environmental issues, gradually interest is increasing on agriculture products and by-products as alternative cellulose resources. Palm kernel cake (PKC) being abundant agriculture by-product consists 20–30% cellulose, hence considered as one of the alternative secondary resource of cellulose. Therefore efforts are made in which cellulose is extracted from PKC and CMC is synthesized, which is used as anti-caking agent, emulsifier, stabilizer, dispersing agent, thickener, and gelling agent. The extraction of cellulose from PKC involved NaOH and sodium chlorite using common bleaching and delignification technique. Under optimum condition, carboxymethylation of extracted cellulose leading to provide the CMC with DS, product yield and viscosity as 0.67, 1.6475 g/g and 66.6 cP, respectively [23].

CMC from Bean Hulls

Binary and ternary complexes of Ni^{2+}, Cu^{2+}, Ag^{+} and UO_2^{2+} were synthesized with sodium salt of carboxymethyl cellulose (P-NaCMC) obtained from bean hulls. Pyridine (py) was also used as secondary ligand. The structures of the synthesized binary and ternary complexes were determined by elemental analysis, spectral data (IR, mass and solid reflectance) as well as magnetic susceptibility measurements, thermal and XRD analysis. IR spectrum of P-NaCMC showed the change in selected vibrational absorption bands upon coordination with metal ions and revealed that the coordination mode of py ligand is the ring nitrogen while of P-NaCMC to be the two vicinal uncarboxylated diol groups (2- and 3-hydroxyl groups) of

the glucopyranose rings in addition to the carbonyl oxygen atom of the carboxylate group. The mass spectra also confirmed the structure of the synthesized compounds. The geometrical structures for the metal complexes were also determined by the magnetic moment measurements and solid reflectance spectral data. A mechanism for degradation of P-NaCMC and its metal complexes were also evaluated by thermal studies. Antimicrobial activities of P-NaCMC and its binary and ternary complexes were studied using agar disc diffusion method against Gram-positive bacteria (*S. aureus* and *S. pyogenes*), Gram-negative bacteria (*P. phaseolicola* and *P. fluorescens*) and the fungi; *F. oxysporum* and *A. fumigates*. The results revealed that all the synthesized metal complexes, especially Cu^{2+} ternary complex have higher antifungal and antibacterial activities than others [24].

CMC from Durian

Carboxymethylcellulose (CMC_d) was obtained from durian rind by carboxymethylation using sodium monochloroacetate (SMCA) and varied concentrations (20–60 g/100 mL) of NaOH. The chemical structure of the cellulose and the synthesized CMC was characterized using FTIR spectroscopy. Then, the properties of the CMC_d materials were determined. The highest viscosity and DS (0.87) was found to be at 30 g/100 mL NaOH concentration. Moreover the crystallinity of CMC_d was found to decline after synthesis in comparison to cellulose. The CMC_d films were prepared and tested, and found that 30 g/100 mL NaOH-synthesized CMC_d film had highest tensile strength (140.77 MPa) and water vapor transmission rate (220.85 g/day m^2). The percent elongation at break is the only property unaffected by NaOH concentration and therefore did not have a relationship with the DS values. It is believed that this new biopolymer will be a value addition to agricultural waste and is also useful for industrial utilization as a film-forming agent, binding agent, sustain release agent, gelling agent, and metal absorber [25]. The CMC was also synthesized by durian seeds having good quality to be used as filler [26].

CMC from *Ewinia chrysanthemi*

Ewinia chrysanthemi strain 3665 was reported to produce an extracellular carboxymethylcellulase aerobically in a mineral salts medium containing various carbon sources at low levels. Moreover the production of this activity was increased by varying the reaction conditions which finally reduced the growth rate. The obtained results suggested that with continuous culture the production was controlled by the means of mechanism similar to catabolite repression. Other factors might be responsible for the regulation of carboxymethylcellulase production [27].

CMC from *Eucalyptus globulus*

CMC with different DSs were reported to be obtained from *E. globulus* pulps in heterogeneous medium from miloxdelignified using media made up of 2-propanol and mixtures of NaOH:MCA:cellulose. Purity grade of CMC samples so synthesized was higher than 99.2% suitable for the applications such as paints, ceramics, textiles, adhesives, cosmetics, foods and pharmaceuticals. Rheological behavior, solubility and molar mass of the synthesized materials were also determined and examined with respect to their total DS. The dynamic and transient tests applied for this purpose showed coherent results. At higher concentrations higher shear thinning was observed with the lowest DS. Higher structuration degree resulted lower shear compliance. Lower DS showed more resistance to both flow and viscous deformation for a given concentration [28].

CMC from Pine Needles

In a previous research paper, forest waste resource, i.e., pine needles and their carboxymethyl forms were modified with 2-acrylamido-2-methylpropanesulphonic acid to prepare hydrogels in the presence of *N,N*-methylene bisacrylamide and ammonium persulfate as accelerator-initiator. The hydrogels so developed are cost effective, efficient and biodegradable supports for the removal of Cr^{6+} from waste water. A thorough study of Cr^{6+} adsorption was carried with respect to temperature, time, pH, and ionic strength. The hydrogels so synthesized were characterized by FTIR, SEM, and nitrogen analysis. Their water uptake capacities before and after sorption of the metal ion was conducted with a view to evaluate their use in the removal of toxic ions from waste water. The thermodynamic parameters such as DH0, DS0, and DG0 of adsorption have also been evaluated to understand the adsorption mechanism. The biodegradability tests for the pine needles based hydrogel and carboxymethylated needles were conducted which showed that pine needles based hydrogel are more efficient sorbent but carboxymethylation increased biodegradability of the pine needles. However even after loading of the ionic species the polymeric supports are biodegradable hence will not generate any waste even after their use [29].

CMC from *Posidonia*

The previous report is available on the value addition to the sea biomass, i.e., by using *Posidonia* which is abundantly accumulated every year on the beaches of Tunisian coasts and which must be cleaned every summer. Hence it can be used as raw material for the preparation of absorbing materials. Therefore three cellulosic qualities of varied purities are prepared from *Posidonia* wastes. From these

synthesized cellulosic materials six qualities of NaCMC are synthesized, which differ by their substitution degree. Their performance evaluation was done in terms of absorption and retention capacities. With this point of view, three types of liquids, i.e., the deionized water, the synthetic urine and the salt solution were used and their performances are evaluated and compared with those of some commercially available absorbent materials like industrial cellulosic pulp and super absorbent used in local industries. However the study shows a decrease in the retention and absorption capacities with increase in the purity of the material and for the synthesized NaCMC these capacities increase simultaneously with the DS [30].

CMC from Sugar Beet

A reported research is available on the conversion of sugar beet pulp cellulose to CMC by etherification. The films of different emulsions containing CMC from sugar beet pulp cellulose were coated on mandarin surfaces as a hydrophilic polymer while beeswax, paraffin wax and soybean oil; CMC with DS of 0.6670; Emulgin PE, oleic acid, triethanolamine and sodium oleate were taken as hydrophobic phases. Emulsifying agents along with hydrophilic polymer in mandarins coating maintain their quality as well as extend postharvest life. The mandarins were stored at 75% relative humidity and at 25 °C in a chamber, at regular intervals samples were taken for analysis. Then the coated and uncoated samples were investigated and their effects were compared in terms of changes in weight loss, pH, soluble solids, titratable acidity and ascorbic acid with storage time to determine the deterioration time of the sample by multiple regression analysis. The coatings of hydrophilic polymer decreased the soluble solids and titratable acidity loses, lowered reduction in pH, delayed ascorbic acid loss, lowered weight loss, extend the storage period until 27 days. Finally it was concluded that the emulsion prepared by the mixture of soybean oil, CMC, sodium oleate and water was suitable for the coating of mandarins [31].

In another research report the sugar beet pulp cellulose was converted to CMC by etherification. The reaction conditions were optimized and the flow behavior of CMC from sugar beet pulp cellulose was determined and found that the behavior of CMC solutions was pseudo-plastic. The rheological properties were shown to be affected by concentration, temperature and shear rate. Moreover the flow behavior of CMC solutions was found to be most adequately described by the power-law model. The experimental data so generated were fitted by mathematical models to predict, the flow behavior index, the consistency coefficient, and the apparent viscosity as a function of temperature and concentration [32].

CMC from Date Palm Rachis and *Posidonia oceanica*

The studies shows that lignocellulosic materials like an agricultural residue (date palm rachis) and a marine waste (*P. oceanica*) can be used as starting material for the preparation of different qualities of CMC and thus contribute to biomass valorization. The carboxymethylation reaction of the extracted cellulose was carried out in presence of 40% NaOH and monochloroacetic acid, in *n*-butanol as solvent. The DSs of the synthesized CMCs varied from 0.67 to 1.62 for *P. oceanica* and between 0.98 and 1.86 for date palm rachis. The spectroscopic techniques, i.e., CP-MAS ^{13}C nuclear magnetic resonance (NMR) as well as acid–base titrations were conducted for the synthesized CMCs which confirmed the purity and conversion of the original raw materials to CMC with varied DSs. The study gave clear information about the structure and the application of the synthesized cellulosic derivatives in different areas [33].

CMC from Water Hyacinth

Water hyacinth, originating from South America has become world's major free-floating aquatic weed of tropical and subtropical regions. The plant regenerates from seeds as well as fragment owing to rapid increase in plant population. It is however a fiber, rich in cellulosic compounds and hence can be derivatized into cellulosic ethers or CMC. Therefore a reported research study investigates how we could attain and characterize CMC from water hyacinth. The synthesis of CMC involves four main steps, firstly the isolation of α-cellulose from the water hyacinth, secondly alkalization of cellulose with NaOH, thirdly carboxymethylation of alkalized cellulose by chloroacetic acid and finally the purification of the synthesized CMC by removing undesirable compounds. Hence 15 samples are synthesized by varying the concentrations of NaOH and the isobutyl–ethanol mixture. The characterization is done by FTIR and DS was determined. FTIR proves that CMC is produced in the experiment as transmittance peak at 1400 and 1600 cm^{-1} indicating ether and carboxyl functional group, respectively. The highest DS, i.e., 1.76 is obtained with the highest purity of 93.24 [34].

CMC from *Agave lechuguilla* and *fourcroydes*

Agave lechuguilla (lechuguilla) and *fourcroydes* (henequen) belonging to renewable feedstock containing about 80% cellulose, 5% hemicellulose and 15% lignin are used as the raw material for attaining new products by chemical functionalization. Cellulose isolated from agave plants was converted to cellulose derivatives by chemical modification reactions like carboxymethylation, sulfation, acetylation, tritylation. Subsequent carboxymethylation of the

trityl derivative and selective oxidation of the primary hydroxyl functional groups of carboxymethylated products with TEMPO/NaBr/NaClO were also carried out successfully for cellulose which are typical reactions for it. Chemical treatment of these agave fibers with n-octanol/aqueous NaOH yields to an activated expanded gel-like material with improved accessibility soluble in DMA/LiCl (cellulose solvent) as well as in the new solvent DMSO/tetrabutylammoniumfluoride. The synthesis of the products were confirmed by of ^{13}C NMR, ^{1}H NMR, HPLC, GPC and α by solubility testing [35].

CMC from Cotton Fibers

In present paper cellulose is extracted from short cotton fibers and then CMC samples were successfully synthesized from alkaline cellulose, in the presence of 30% NaOH followed by etherification with 40% monochloroacetate (MCA) and further purified. The highest DS of 0.7 for the sample was obtained with isopropanol as solvent. The obtained CMC sample was glossy. The samples of CMC were characterized by SEM and FTIR techniques. Interestingly, the CMC powder was easily soluble in water. Hence the obtained product has the potential to be used in pharmaceutical applications and food additives [36].

CMC from Cotton Linters

Preparation of CMC from indigenous cotton linters is also reported. Special attention was given on method of purification to remove the non-cellulosic materials. Hence a two step method for purification of cotton linters was established for the synthesis of water soluble CMC with 0.89 DS and viscosity of 235 cp (0.5% solution) [37].

CMC from *Lantana camara*

Lantana camara being a weed is a threat to the ecology and therefore demands its management. Hence utilization of this cellulosic biomass as chemical feedstock to isolate α-cellulose is also reported. Further modification of this extracted cellulose to CMC by carboxymethylation reaction under varied reaction conditions with respect to maximum DS was conducted. The optimum conditions for the carboxymethylation reaction were therefore: concentration of aqueous NaOH 3.24 mol/AGU, 20% (w/v), concentration of MCA 2.05 mol/AGU, time 3.5 h and temperature 55 °C with isopropyl alcohol as the solvent to yield CMC of DS 1.22. The effect of reaction conditions on apparent viscosity of the synthesized CMC was also studied. The rheological behavior of the optimized product (1 and 2% solutions) showed their non Newtonian pseudo-plastic behavior [38].

CMC from Orange Peel

Extraction of cellulose by 10% NaOH at 35 °C for 22 h from delignified orange peel was also reported. The effects of temperature and concentration on the viscosity of cellulose solutions extracted from orange peel and were examined at temperature range 20–60 °C and a concentration range 1–10 kg/m^3. Combined effects of concentration and temperature on the viscosity were determined by 28 different models, which were fitted to the experimental data and then model parameters were determined via nonlinear regression analysis. The cellulose so extracted from orange peel was then converted to CMC and then rheological properties of the synthesized CMC were determined by using a rotational viscometer at five varied temperatures (10, 20, 30, 40 and 50 °C) and six concentrations (10, 15, 20, 25, 30, 35 kg/m^3), and found that CMC solutions exhibits pseudo-plastic behavior. The power law model fits well the shear rate and shear stress data which was among the common rheological models. With concentration the consistency index increased and decreased with temperature. At constant spindle speed, as a function of shearing time, the apparent viscosity was measured. The CMC solutions were described by the Weltman model and found to exhibit thixotrophic behavior [39].

CMC from Rice Straw, Wheat Straw and Sugarcane Straw

CMC was reported to be prepared from agricultural wastes like rice straw and wheat straw. Firstly the cellulose was extracted from these agricultural wastes and then converted via its acidic form of CMC to CoCMC by reacting it with Co(II) chloride. Hence 1.0 g of the acid form of CMC was reacted with 5.0 g of Co(II) chloride in 250 mL of water at 90 °C for 8 h. A maximum content of cobalt, i.e., 7% in the CoCMC product was recorded from both the sources [40], but the CMC obtained from sugarcane straw presented a low DS (0.4) demonstrating the carboxymethylation reaction not to be very effective due to the presence of lignin [41].

CMC from Kudzu Root

A new starch source having reasonably wide distribution which is available plentiful, particularly in the hilly region in southern of China was also studied for the synthesis and characterization of carboxymethyl derivatives of kudzu root starch. The reaction parameters were optimized to attain the DS of 0.91 with a reaction efficiency of 65.3% after 3 h. The synthesized CMC was characterized by ^{13}C NMR which showed a peak at $\delta = 177.85$ ppm assigned to carbonyl carbon. Wide angle X-ray diffractometry revealed

that carboxymethylation reduced starch crystallinity but TG and derivative TG showed improvement in thermal stability after carboxymethylation. IR spectrometry showed new bands at 1597, 1415 and 1323 cm^{-1} which was due to starch that has undergone carboxymethylation [42].

CMC from Office Waste Paper

Mixed office waste (MOW) paper pulp has been used to synthesize CMC which has varied applications. MOW was deinked prior to carboxymethylation and then yielded 80.62 ± 2.0 with $72.30 \pm 1.50\%$ deinkability factor. Then the pulp so obtained was converted to CMC by alkalization followed by etherification using NaOH and $ClCH_2COONa$, respectively, in an alcoholic medium. The optimum conditions at which maximum DS (1.07) was attained were 0.094 M of NaOH and 0.108 M of $ClCH_2COONa$, 50 °C temperature and time 3 h. Further rheological studies were conducted for the optimized CMC product which showed the non-Newtonian pseudo plastic behavior. The synthesis of the product was confirmed by NMR, FTIR and SEM [43].

CMC from Corn Husk and Cob

Corn husks and corn cob which have been used on a small scale as a fuel for direct combustion in cooking and heating, were reported to be used as chemical feedstock for large-scale production of CMC, which is a more modern concept. Cellulose was extracted from the corn biomass and etherification reaction was carried out by the treatment of cellulose with NaOH and monochloroacetic acid. The reaction conditions were optimized against the NaOH concentration, monochloroacetic acid concentration, reaction temperature and time. The DS was also determined. The produced CMC was characterized by using FTIR spectra and X-ray diffractogram. High purity food-grade CMC was successfully produced and used as an additive for pharmaceutical and food industries [44, 45].

CMC from Grapefruit Peel

The cellulose was isolated from grapefruit peel and converted to CMC .The empirical equations were developed as a function of temperature and concentration to predict the viscosity of cellulose from grapefruit peel. CMC solutions exhibited pseudoplastic rheological behaviour. It was found that the consistency index values increased with the concentration while the opposite trend was observed with temperature. The activation energy calculated with the Arrhenius model indicated that CMC solutions were most sensitive to temperature change at low shear rates. CMC solutions exhibited thixotropic flow behaviour at varied concentrations. This study provides essential data for design of processes relating CMC solutions from grapefruit peel within the temperatures (10–60 °C), the concentrations (15–35 kg/m^3) and the shear rates (1.32–13.2 s^{-1}) studied [46].

CMC from Kenyan Biomass

M. sinensis, E. crassipes and *C. papyrus* biomass can be used for the synthesis of microcrystalline cellulose and carboxylmethylcellulose with different DSs and degree of crystallinity by varying reaction parameters. The carboxymethylation conditions for cellulose from *M. sinensis* were: pure isopropyl alcohol as the solvent medium, 6.0 g of sodium monochloroacetic acid, NaOH concentration of 10 mL of 17.5%, reaction period of 120 min and reaction temperature of 50 °C. Overall, the better flow properties of the microcrystalline celluloses are dependent on source, variations in particle shape, size, and surface area of the powders which are directly related to the process of partial hydrolysis of the original cellulose [47].

CMC from Cellulosic Wastes of Textile Industry

CMC was synthesized from a textile waste of textile and garment industries (cellulosic rag) via single step to seven step carboxymethylation. Low substituted to high substituted products were obtained. In this way, it was possible to produce low cost and different grades of substituted carboxymethylated cellulose. The structure of CMC and grafted CMC were investigated by FTIR, ^{13}C NMR and SEM. The DSs of CMC from one to seven reaction steps were 0.90–2.84, respectively. Similarly, CMC content and molecular weight of CMC were 72.60–85.00% and 153,886–252,231, respectively. The prepared CMC was used as a sizing agent to develop the physico-chemical characteristics of fabric and yarn as well. Grafting of prepared CMC film with methyl methacrylate (MMA) monomer increased their strength 86.11%, although decreased rigidity and moisture content due to the incorporation of hydrophobic MMA monomer was observed [48].

Conclusions

The cellulose extracted from varied lignocellulosic waste biomass can be converted to CMC by doing alkalinization using NaOH followed by etherification by monochloroacetic acid (MCA) under heterogeneous condition. The various properties of CMC depend upon three major factors: molecular weight of the polymer, DS and also on the distribution of carboxyl substituent's along the polymer chains. DS varies by varying the reaction parameters

like NaOH %, monochloroacetic acid molar ratio, reaction temperature and time. The produced CMC have been characterized by using various spectroscopic techniques, viz., FTIR spectra, NMR, SEM, X-ray diffractogram, etc.

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Compliance with Ethical Standards

Conflict of interest The authors confirm that this article content has no conflict of interest.

References

1. Klemm, D., Heublein, B., Fink, H.P., Bohn, A.: Cellulose: fascinating biopolymer and sustainable raw material. Angew. Chem. **44**, 3358–3393 (2005)
2. Varshney, V.K., Naithani, S.: Chapter 2: chemical functionalization of cellulose derived from nonconventional sources. In: Kalia, S., Kaith, B.S., Kaur, I. (eds.) Cellulose Fibers: Bio- and Nano-polymer Composites, pp. 43–60. Springer, Berlin (2011)
3. Mohammadi, M., Sadeghnia, N., Azizi, M.-H., Neyestani, T.-R., Mortazavian, A.M.: Development of gluten-free flat bread using hydrocolloids: xanthan and CMC. J. Ind. Eng. Chem. **20**, 1812–1818 (2014)
4. Wang, M.-m., Wang, L.: Synthesis and characterization of carboxymethyl cellulose/organic montmorillonite nanocomposites and its adsorption behavior for congo red dye. Water Sci. Eng. **6**, 272–282 (2013)
5. Fakrul Alam, A.B.M., Mondal, Md.I.H.: Utilization of cellulosic wastes in textile and garment industries. I. Synthesis and grafting characterization of carboxymethyl cellulose from knitted rag. J. Appl. Polym. Sci. **128**, 1206–1212 (2013)
6. Vaughn, T.H., Smith, C.E.: The effect of sodium carboxymethyl cellulose on synthetic detergent systems. J. Am. Oil Chem. Soc. **25**, 44–51 (1948)
7. Yang, H.N., Park, J.S., Jeon, S.Y., Park, K.-H.: Carboxymethylcellulose (CMC) formed nanogels with branched poly(ethyleneimine) (bPEI) for inhibition of cytotoxicity in human MSCs as a gene delivery vehicles. Carbohydr. Polym. **122**, 265–275 (2015)
8. Shen, J., Song, Z., Qian, X., Yang, F.: Carboxymethyl cellulose/alum modified precipitated calcium carbonate fillers: preparation and their use in papermaking. Carbohydr. Polym. **81**, 545–553 (2010)
9. Zhang, L., Sun, H., Han, B., Peng, L., Ning, F., Jiang, G., Chehotkin, V.F.: Effect of shearing actions on the rheological properties and mesostructures of CMC, PVP and CMC + PVP aqueous solutions as simple water-based drilling fluids for gas hydrate drilling. J. Unconv. Oil Gas Resour. **14**, 86–98 (2016)
10. Ocampo, A., Zea, H.: Formulation and evaluation in ready mix concrete of chemical additives based on molasses, carboxymethylcellulose and polynaphthalenesulphonate. Int. J. ChemTech Res. **6**, 768–778 (2014)
11. Davidson, D.W., Verma, M.S., Gu, F.X.. Controlled root targeted delivery of fertilizer using an ionically crosslinked carboxymethyl cellulose hydrogel matrix. SpringerPlus **2**, 318–327 (2013)
12. Qiao, Z., Gu, J., Zuo, Y., Tan, H., Zhang, Y.: The effect of carboxymethyl cellulose addition on the properties of starch-based wood adhesives. BioResources **9**, 6117–6129 (2014)
13. Yu, J., Yang, J., Zeng, Q., Huang, Y.: Effect of carboxymethyl cellulose addition on the properties of Si_3N_4 ceramic foams. Ceram. Int. **39**, 2775–2779 (2013)
14. Taghizadeh, M.T., Sabouri, N., Ghanbarzadeh, B.: Mechanochemical activation of carboxy methyl cellulose and its thermoplastic polyvinyl alcohol/starch biocomposites with enhanced physicochemical properties. Int. J. Biochem. Biophys. **1**, 9–15 (2013)
15. Adinugraha, M.P., Marseno, D.W., Haryadi, P.: Synthesis and characterization of sodium carboxymethylcellulose from Cavendish banana pseudo stem (*Musa cavendishii* LAMBERT). Carbohydr. Polym. **62**, 164–169 (2005)
16. Pushpamalar, V., Langford, S.J., Ahmad, M., Lim, Y.Y.: Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. Carbohydr. Polym. **64**, 312–318 (2006)
17. He, X., Wu, S., Fu, D., Ni, J.: Preparation of sodium carboxymethyl cellulose from paper sludge. J. Chem. Technol. Biotechnol. **84**, 427–434 (2009)
18. Zhang, G., Zhang, L., Deng, H., Sun, P.: Preparation and characterization of sodium carboxymethyl cellulose from cotton stalk using microwave heating. J. Chem. Technol. Biotechnol. **86**, 584–589 (2011)
19. Ge, Y., Li, Z.: Preparation and evaluation of sodium carboxymethylcellulose from sugarcane bagasse for applications in coal–water slurry. J. Macromol. Sci. A **50**, 757–765 (2013)
20. Ruzene, D.S., Gonçalves, A.R., Teixeira, J.A., Pessoa de Amorim, M.T.: Carboxymethylcellulose obtained by ethanol/water organosolv process under acid conditions. Appl. Biochem. Biotechnol. **137**, 573–582 (2007)
21. Tasaso, P.: Optimization of reaction conditions for synthesis of carboxymethyl cellulose from oil palm fronds. Int. J. Chem. Eng. Appl. **6**, 101–104 (2015)
22. Gutawa, K., Willy, A.T., Nikita, G.R.: Synthesis and characterization of sodium carboxymethylcellulose from pod husk of Cacao (*Theobroma cacao* L.). Int. J. Food Sci. Microbiol. **3**, 99–103 (2015)
23. Bono, A., Ying, P.H., Yan, F.Y., Muei, C.L., Sarbatly, R., Krishnaiah, D.: Synthesis and characterization of carboxymethyl cellulose from palm kernel cake. Adv. Nat. Appl. Sci. **3**, 5–11 (2009)
24. Ibrahim, A.A., Adela, A.M., El-Wahab, Z.H.A., Al-Shemya, M.T.: Utilization of carboxymethyl cellulose based on bean hulls as chelating agent. Synthesis, characterization and biological activity. Carbohydr. Polym. **83**, 94–115 (2011)
25. Rachtanapun, P., Luangkamin, S., Tanprasert, K., Suriyatem, R.: Carboxymethyl cellulose film from durian rind. LWT Food Sci. Technol. **48**, 52–58 (2012)
26. Futeri, R.: Synthesis carboxyl methyl cellulose (CMC) with addition method from durian seed. Pharm. Lett. **8**, 262–268 (2016)
27. Boyer, M.H., Chambost, J.P., Magnan, M., Cattaneo, J.: Carboxymethyl-cellulase from *Ewinia chrysanthemi*. I. Production and regulation of extracellular carboxymethyl-cellulose. J. Biotechnol. **1**, 229–239 (1984)
28. Dapia, S., Tovar, C.A., Santos, V., Parajo, J.C.: Rheological behaviour of carboxymethylcellulose manufactured from TCF-bleached milox pulps. Food Hydrocoll. **19**, 313–320 (2005)
29. Chauhan, G.S., Chauhan, K., Chauhan, S., Kumar, S., Kumari, A.: Functionalization of pine needles by carboxymethylation and network formation for use as supports in the adsorption of Cr^{6+}. Carbohydr. Polym. **70**, 415–421 (2007)
30. Ramzi, K., Ikhlass, F., Farouk, M.M.: Study of liquids absorption and retention capacities of new cellulosic materials and

sodium cellulose carboxylmethylate prepared from *Posidonia*. Fiber Polym. **11**, 593–597 (2010)
31. Togrul, H., Arslan, N.: Carboxymethyl cellulose from sugar beet pulp cellulose as a hydrophilic polymer in coating of mandarin. J. Food Eng. **62**, 271–279 (2004)
32. Togrul, H., Arslan, N.: Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. Carbohydr. Polym. **54**, 73–82 (2003)
33. Khiari, R., Mhenni, M.F., Belgacem, M.N., Mauret, E.: Valorization of vegetal wastes as a source of cellulose and cellulose derivatives. J. Polym. Environ. **19**, 80–89 (2011)
34. Saputra, A.H., Qadhayna, L., Pitaloka, A.B.: Synthesis and characterization of carboxymethyl cellulose (CMC) from water hyacinth using ethanol–isobutyl alcohol mixture as the solvents. Int. J. Chem. Eng. Appl. **5**, 36–40 (2014)
35. Vieira, M.C., Heinze, T., Antonio-Cruz, R., Mendoza-Martinez, A.M.: Cellulose derivatives from cellulosic material isolated from *Agave lechuguilla* and *fourcroydes*. Cellulose **9**, 203–212 (2002)
36. Heydarzadeh, H.D., Najafpour, G.D., Nazari-Moghaddam, A.A.: Catalyst-free conversion of alkali cellulose to fine carboxymethyl cellulose at mild conditions. World Appl. Sci. J. **6**, 564–569 (2009)
37. Jahan, I.A., Sultana, F., Islam, M.N., Hossain, M.A., Abedin, J.: Studies on indigenous cotton linters for preparation of carboxymethyl cellulose. Bangladesh J. Sci. Ind. Res. **42**, 29–36 (2007)
38. Varshney, V.K., Gupta, P.K., Naithani, S., Khullar, R., Bhatt, A., Soni, P.L.: Carboxymethylation of α-cellulose isolated from *Lantana camara* with respect to degree of substitution and rheological behaviour. Carbohydr. Polym. **63**, 40–45 (2006)
39. Yasar, F., Togrul, H., Arslan, N.: Flow properties of cellulose and carboxymethyl cellulose from orange peel. J. Food Eng. **81**, 187–199 (2007)
40. Jahan, I.A., Rahman, A.H.M.M.: Studies on preparation of cobalt carboxymethyl cellulose from agricultural wastes. Bangladesh J. Sci. Ind. Res. **41**, 159–166 (2006)
41. Candido, R.G., Goncalves, A.R.: Synthesis of cellulose acetate and carboxymethylcellulose from sugarcane straw. Carbohydr. Polym. **152**, 679–686 (2016)
42. Wang, L.-F., Pan, S.-Y., Hu, H., Miao, W.-H., Xu, X.-Y.: Synthesis and properties of carboxymethyl kudzu root starch. Carbohydr. Polym. **80**, 174–179 (2010)
43. Joshi, G., Naithani, S., Varshney, V.K., Bisht, S.S., Rana, V., Gupta, P.K.: Synthesis and characterization of carboxymethyl cellulose from office waste paper: a greener approach towards waste management. Waste Manag. **38**, 33–40 (2015)
44. Mondal, M.I.H., Yeasmin, M.S., Rahman, M.S.: Preparation of food grade carboxymethyl cellulose from corn husk agrowaste. Int. J. Biol. Macromol. **79**, 144–150 (2015)
45. Singh, R.K., Singh, A.K.: Optimization of reaction conditions for preparing carboxymethyl cellulose from corn cobic agricultural waste. Waste Biomass Valoriz. **4**, 129–137 (2013)
46. Karataş, M., Arslan, N.: Flow behaviours of cellulose and carboxymethyl cellulose from grapefruit peel. Food Hydrocoll. **58**, 235–245 (2016)
47. Kimani, P.K., Kareru, P.G., Madivoli, S.E., Kairigo, P.K., Maina, E.G., Rechab, O.S.: Comparative study of carboxymethyl cellulose synthesis from selected Kenyan biomass. Chem. Sci. Int. J. **17**, 1–8 (2016)
48. Mondal, Md.I.H., Ahmed, F.: Synthesis and grafting of carboxymethyl cellulose from environmental pollutant cellulosic wastes of textile industry. Res. J. Text. Appar. **20**, 126–135 (2016)