

Evaluating the Impact of Cellulose Extraction via Traditional and Ionosolv Pretreatments from Domestic Matchstick Waste on the Properties of Carboxymethyl Cellulose

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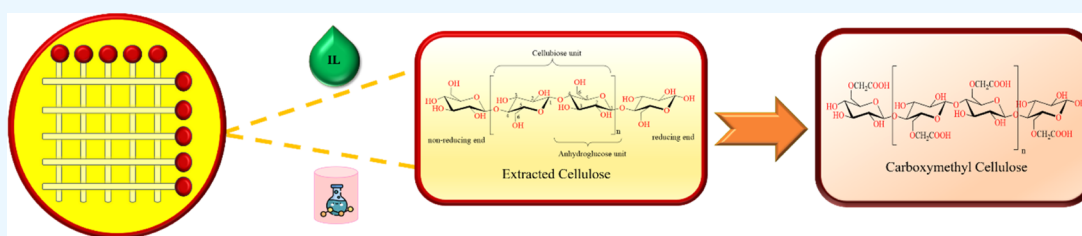


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ABSTRACT: Carboxymethyl cellulose (CMC) is a hydrophilic derivative of cellulose whose large volumes have been used in textile processing, protective coatings, detergents, papers, and drilling fluids, while cellulose gum, which is the purified form of CMC, has extensive applications in food, cosmetic, and pharmaceutical industries. Therefore, this work reflects the production of CMC by extracting cellulose with traditional and ionosolv methods from domestic matchstick waste, providing an in-depth view of the overall process where two different kinds of cellulose were obtained from two different pretreatments, and the influence of cellulose on the profile of CMC was checked. All of the procedures have been performed under optimized conditions to reduce the cost and maximize the productiveness. The results depict that cellulose extracted by the ionosolv method using a protic ionic liquid, tetramethylguanidinium hydrogen sulfate (TMG-HSO₄), is more degraded than that extracted by the traditional sulfide method using sodium sulfide (Na₂S) and sodium hydroxide (NaOH). Thus, the produced CMC-2 via ionic liquid-extracted cellulose has more yield, DS (2.3), purity (98.5%), and solubility with less salt and moisture contents than CMC-1 produced by the conventional method due to an effective substitution of the hydroxyl group by the carboxymethyl group. Further, instrumental analyses like FTIR, XRD, ¹H NMR, ¹³C NMR, and SEM emphasize the results that CMC-2 has more reduction of the hydroxyl peak in FTIR, a more amorphous structure in XRD, intense peaks in NMR, and the roughness of the surface in SEM.

1. INTRODUCTION

Over the past few years, surging environmental concerns have motivated the researchers to explore the potential of plant biomass as a renewable resource for the production of industrially useful materials. The plant biomass is mainly composed of cellulose, lignin, hemicellulose, gums, pectin, proteins, starch, and mucilage. Among all of them, the major component of the rigid cell wall is cellulose; a higher percentage (33%) makes cellulose the most common organic compound on earth. The amount of cellulose varies in different raw materials, starting from the highest in cotton (>90%)¹ to wood (40–50%)² and grasses (20–30%).³ The industries mostly rely on cotton and wood pulp for their cellulose. Thus, cellulose with a β acetal linkage is composed of glucose monosaccharide units with a high-molecular-weight linear chain. The dense hydrogen bonding in the cellulose structure limits its use in industries because it neither dissolves nor melts in any organic solvents. But the hydroxyl functional groups on the surface of cellulose make it susceptible to chemical derivation for conversion into useful chemical feedstock.⁴ The

versatile transformation of cellulose via carboxymethylation gives hydrophilic, water-swallowable intermediates and polymers with value-added features.^{5,6} One of them is carboxymethyl cellulose (CMC), which is an anionic, linear, water-soluble, and long-chain man-made polysaccharide.^{7,8}

CMC is produced from cellulose, which can either be commercially available or extracted from some biosources.⁹ Cellulose extraction from various kinds of lignocellulosic biomass has already been reported, likewise Costa et al. obtained cellulose from corn stover,¹⁰ Mondal et al. and Kampeerappun et al. from corn husk,¹¹ Singh et al. from corn cobic,¹² Reddy et al. and Liu et al. from wheat straw,^{13,14}

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Figure 1. Schematic representation of the overall extraction of cellulose from matchstick waste and conversion into CMC.

Boonterm et al. and Chen et al. from rice straw,^{15,16} Feng et al. and Sun et al. from sugarcane bagasse,^{17,18} and others. They have performed cellulose extraction by various biological,¹⁹ chemical,^{20,21} physical,²² and multiple combinatorial pretreatments.²³ These pretreatment methods affect the morphology of cellulose, which in turn decides the fate of its derivative. Broadly, there are two chemical pretreatment methods: the conventional method,²⁴ which includes treatment with acids, bases, and organic solvents, and the ionosolv method, which entails organic salts like ionic liquids (ILs).²⁵ ILs are low in cost and thermally stable, which are effective for extraction of lignin and hemicellulose, leaving behind the cellulose pulp in pure form.²⁶ Recently, a protic ionic liquid based on a super basic cation (tetramethylguanidine (TMG)) has been reported for dissolution of cellulose fibers with reduction in the crystallinity of recovered fibers,²⁷ likewise King et al. synthesized an ionic liquid having TMG cations and acetate, propionate, and formate anions for cellulose dissolution,²⁸ Pezoa-Conte et al. used TMG propionate for the release of carbohydrate from green algae for the production of platform chemicals and biofuels,²⁹ and Kumar and Wahlström et al. used TMG-based ionic liquids for cellulose hydrolysis.^{30,31}

Thus, the treatment of biomass via any of these above-mentioned methods involves the delinking of cellulose from a recalcitrant intervening network of other polymers (hemicellulose and lignin). The effective separation of cellulose from its source would definitely make the hydroxyl group ($-OH$) more available for carboxymethylation. As there are three hydroxyl groups on one pyranose ring of cellulose at C_2 , C_3 , and C_6 that are susceptible to be replaced by the precedence order $C_2 > C_6 > C_3$.^{32,33} The production of CMC involves the alkali treatment, which makes the $-OH$ groups of cellulose highly active³⁴ with increased accessibility of chemicals.³⁵ Thus, the derivatization of cellulose is directly linked to its pretreatment methods.

Moreover, a survey of literature has disclosed that CMC has been produced by extracting cellulose from ample biosources like sago waste,³⁶ wheat straw,³⁷ rice straw,³⁸ corn husk,³⁹ rice husk,⁴⁰ cotton linters,⁴¹ banana leaves,⁴² bagasse,⁴³ and

others.⁴⁴ But the most common waste on the domestic level that is overlooked is matchstick (MS) waste made of bamboo.

Matchstick (MS) waste is an essential consumer commodity in many Asian countries and is dumped after usage to exacerbate environmental pollution. This waste could be productive, as it mainly consists of cellulose, a long-chain biopolymer, whose derivatization could make desirable and beneficial chemicals. Thus, there is a dire need to screen the cellulose renewable resources for its cheap extraction with efficient derivatization into valuable chemicals. The present study has made an effort to highlight the dumping of matchstick waste along with its usage for cellulose extraction and conversion into CMC.

The main aim of this study is to prudently utilize the common domestic matchstick (MS) waste for cellulose extraction via two different approaches, conventional and ionosolv, to dig deeper for the understanding of the cellulose structure and morphology and derivatization of cellulose into CMC. The complete analyses of CMC from two different cellulose meticulously provide the influence of cellulose on the profile of CMC, and characteristic tests further accentuate the importance of work (Figure 1). Our previous work also provided a comparative study of different conventional methods for cellulose extraction, which further endorsed this finding.⁴² To the best of our knowledge, there is no published work related to our study. So, this work could be considered as one of its own kind.

2. MATERIALS AND METHODS

2.1. Materials. The used matchsticks (MSs) were collected from a kitchen in Lahore, Pakistan. The waste biomass was cut to remove the oxidized part. The remaining portion was washed, dried, and sieved with a size of $250\ \mu\text{m}$. The undesired waxes and ashes were removed by dewaxing with toluene and ethanol (2:1). The chemicals and solvents employed in research work were obtained from Sigma-Aldrich except for sodium sulfide (Scharlau), 2,7-dihydroxynaphthalene (Alfa Aesar), microcrystalline cellulose (J.T. Baker), glycolic acid (Fluka), monochloroacetic acid (Dae Jung), and sodium chlorite (Uni-Chem).

2.2. Sulfide Pretreatment (Traditional Method). The dewaxed matchsticks were pretreated with alkaline sodium sulfide. In a round bottom flask of 250 mL, 1 g of biomass, a 6% w/v sodium sulfide (Na_2S) solution, and an 8% w/v NaOH solution were added.⁴⁵ The mixture was allowed to stir and heated at 95 °C for 180 min. The extracted cellulose was in the solid form, labeled cellulose-1. It was filtered and neutralized with distilled water to obtain pure cellulose.

2.3. IL Pretreatment (Ionosolv Method). The method used for IL preparation and its pretreatment of biomass was reported in the paper of our research group.⁴⁶ After the synthesis of TMG- HSO_4 , in a round bottom flask, IL and water were added in a ratio of 80:20⁴⁷ with 15% loading of MS waste.^{48,49} The mixture was allowed to reflux at 140 °C for 4 h with continuous stirring. After completion, the antisolvent ethanol was added, and the reaction mixture was allowed to stir for half an hour to regenerate the pulp. After filtration, the residue was washed with ethanol and distilled water. The obtained cellulose was oven-dried at 70 °C and labeled cellulose-2.

2.4. Bleaching of Extracted Cellulose. Both the cellulose extracted from sulfide and IL pretreatments were bleached with a 3% solution of sodium chlorite (NaClO_2) and few drops of acetic acid to maintain 3–4 pH at 90 °C for 1 h. The bleached mixtures were filtered and neutralized with distilled water till the smell of chlorine vanished.⁵⁰

2.5. Synthesis of Carboxymethyl Cellulose. The obtained cellulose from sulfide and IL pretreatments were converted into CMC, separately. The method followed was as follows: In a round bottom flask, a 4 M solution of NaOH was added with 1 g of cellulose. The mixture was allowed to stir overnight to obtain alkali cellulose; the very next day, 1 equiv of monochloroacetic acid (MCA) was added for etherification. The reaction mixture was allowed to stir for 3 h at 55 °C. After that, 15 mL of methanol was added for the suspension of the solid. The alkaline mixture was neutralized with few drops of glacial acetic acid and washed twice with methanol and ethanol. After that, the product was oven-dried at 60 °C.⁵¹ CMC samples obtained were labeled CMC-1 and CMC-2.

2.6. Characteristics of CMC. **2.6.1. Calculation of CMC Yield.** The yield of CMC on cellulose was calculated by the following equation

$$\text{yield of CMC(\%)} = \frac{W^1}{W^2} \times 100$$

where W^1 is the dry mass of CMC, and W^2 is the dry mass of cellulose.⁵²

2.6.2. Solubility of CMC. A sample of 0.1 g of CMC was taken in an Erlenmeyer flask. Then, 10 mL of distilled water was added, and the flask was shaken on a shaker at 150 rpm for 24 h. After that, the solution in the flask was centrifuged for 15 min. The precipitates obtained were filtered and dried in an oven at 100 °C to constant weight. The solubility (%) of the sample was calculated by the following equation

$$\text{solubility(\%)} = \frac{W^3 - W^4}{W^3} \times 100$$

where W^3 is the weight of the sample taken initially, and W^4 is the dry weight of precipitates.⁵³

2.6.3. Moisture Content of CMC. The moisture content of CMC was determined by taking accurately weighed CMC and dried in an oven for 2 h at 105 °C. After being placed in a

desiccator for 30 min, it was weighed again, and moisture (%) was calculated by the following equation

$$\text{moisture(\%)} = \frac{W^5 - W^6}{W^5}$$

where W^5 is the weight of air-dried CMC, and W^6 is the weight of oven-dried CMC.⁵⁴

2.6.4. Ash Content in Biomass. An accurately weighed sample was preashed in a fume hood till the smoke ceased. The ashed sample was placed in a muffle furnace for 3 h at 560 °C. The ash content in the biomass sample was calculated by the following equation

$$\text{ash content(\%)} = \frac{W^7}{W^8} \times 100$$

where W^7 is the weight of ash, and W^8 is the weight of the sample.¹¹

2.6.5. Degree of Substitution (DS). The degree of substitution was calculated by the method reported by Wongvitvichot et al.⁵⁵ One gram of CMC with 18.75 mL of ethanol was stirred for 5–6 min. Then, 1.25 mL of nitric acid (65%) was added to change CMC into acid CMC. The obtained acid CMC was washed with ethanol and methanol two times and dried in an oven for 3 h at 105 °C. After that, 0.5 g of acid CMC was mixed with deionized water (50 mL) and 12.5 mL of NaOH (0.3 M). The mixture was boiled for 10 min. The mixture was titrated against HCl (0.3 M) using phenolphthalein as an indicator. The formula used to calculate DS was as follows

$$Y = \frac{AB - CD}{E}$$

$$DS = \frac{0.162 \times Y}{1 - (0.058 \times Y)}$$

where Y = milliequivalents of HCl consumed per gram of sample, A = volume of NaOH (mL), B = molarity of NaOH used, C = HCl used for titration of NaOH (mL), D = molarity of HCl used, E = weight of acid CMC (g), 162 is the molecular weight of the glucose unit (anhydrous), and 58 is the increase due to addition of the carboxymethyl group.

2.6.6. Salt Content in CMC. **2.6.6.1. Sodium Chloride (NaCl) Content.** An accurately weighed sample of 0.5 g was taken in 100 mL of distilled water. The solution was titrated with N/10 silver nitrate (AgNO_3) using potassium chromate as an indicator. The NaCl content was calculated by the following equation

$$\text{NaCl(\%)} = \frac{0.5846 (A) (\text{volume of (N/10) AgNO}_3 \text{ required})}{\text{weight of dry sample (g)}}$$

where A = the factor N/10 AgNO_3 .

2.6.6.2. Sodium Glycolate Content. The CMC sample (0.1 g) was taken with 1 mL of water and 1 mL of glacial acetic acid in a flask. After that, 0.2 g of sodium chloride and 10 mL of acetone were added with continuous stirring for several minutes to ensure the precipitation of CMC. The obtained mixture was filtered, and the supernatant was subjected to prepare test solutions. A blank solution similar to the test solution was prepared using only reagents. Acetone was removed from both solutions by heating on a water bath for 20

Table 1. Protic Ionic Liquids for Lignocellulosic Biomass and Cellulose Processing

feedstocks	cation	anion	cellulose dissolution/ conversion	conditions	refs
<i>Acacia nilotica</i>	tetramethylguanidinium	hydrogen sulfate	delignification of lignocellulosic biomass	140 °C for 4 h	46
commercial cellulose	tetramethylguanidinium	hydrogen sulfate	hydrolysis of cellulose	160 °C for 3 h	59
microcrystalline cellulose (MCC)	tetramethylguanidinium	acetate propionate formate	dissolution of cellulose	5% of cellulose at 100 °C for 18 h	28
eucalyptus	tetramethylguanidinium	acetate propionate	cellulose hydrolysis		31
green alga (<i>Ulva rigida</i>)	tetramethylguanidinium	propionate	removal of carbohydrate from green algae	140–160 °C for 6 h	29
rice straw	2-hydroxyethyl ammonium	acetate	cellulose extraction and conversion	2 h with 15% loading	60
ash tree (<i>Fraxinus excelsior</i>)	pyridinium	formate	cellulose conversion	75 °C for 2 h	61
creosote-treated timber	<i>N,N,N</i> -dimethylbutylammonium	hydrogen sulfate	delignification	175 °C for 45 min	62
woody biomass (pine, almond, walnut, and fir)	ethanol amine	acetate	cellulose extraction	160 °C for 3 h	63
corn stover	diazabicyclo [4.3.0]-5-nonene	levulinic acid	cellulose conversion	140 °C for 6 h	64
<i>Pinus radiata</i>	triethylammonium	hydrogen sulfate	cellulose extraction	170 °C for 3 h	65
poplar wood	monoethanolammonium	hydrogen sulfate	cellulose extraction	150 °C for 3 h	66
coconut waste	<i>N,N,N</i> -dimethylbutylammonium	hydrogen sulfate	cellulose extraction and conversion	170 °C for 45 min	67
paper mill sludge	tetraethylammonium	hydrogen sulfate	cellulose extraction	150 °C	68
matchsticks	tetramethylguanidinium	hydrogen sulfate	cellulose extraction	140 °C for 4 h	our study

min. After cooling, 2,7-dihydroxynaphthalene (4 mL) was added to each prepared solution. Absorbance of solutions was measured at 540 nm using a UV–vis spectrophotometer. The calibration curve of standard glycolic acid was plotted and used to determine the sodium glycolate concentration in the unknown solutions by the following formula⁵⁶

$$\text{sodium glycolate(\%)} = \frac{a \times 1.29}{b}$$

where a = mg of glycolic acid from the calibration curve, b = dry weight of the sample in g, and 1.29 is the integer that converts standard glycolic acid into sodium glycolate.

2.7. Characterization of CMC. **2.7.1. Fourier Transform Infrared Spectroscopy (FTIR).** An Agilent Cary 630 was used to record various spectra of cellulose and CMC with a transmission range of 4000–400 cm^{-1} . The oven-dried samples (2 mg) were prepared to avoid any moisture content.

2.7.2. X-ray Diffraction (XRD). A Rigaku MiniFlex 600-C with a Cu ($K\alpha$)-based X-ray tube operating at 600 W, a silicon strip detector, and a graphite monochromator was used to record the XRD diffractograms of both CMC samples. The oven-dried samples (2 mg) were prepared for analysis.

2.7.3. Proton Nuclear Magnetic Resonance (^1H NMR). The ^1H NMR spectra of both CMC samples were recorded at 600 MHz in Bruker's Avance Neo Technology in solvent D_2O . The oven-dried samples (2 mg) were prepared for analysis.

2.7.4. Carbon Nuclear Magnetic Resonance (^{13}C NMR). The ^{13}C NMR spectra of both CMC samples were recorded at 600 MHz in Bruker's Avance Neo Technology in solvent D_2O . The oven-dried samples (2 mg) were prepared for analysis.

2.7.5. Scanning Electron Microscopy (SEM). SEM images of both CMC-1 and CMC-2 were recorded by SEM (VEGA TESCON) with varying pressures.

3. RESULTS AND DISCUSSION

Matchsticks (MSs), which are a common domestic commodity, have been made from different kinds of woods, mainly poplar and bamboo, with 60–70% of cellulose.^{57,58} These MSs

comprised two portions: match heads and wooden sticks; the head has oxidizing agents to light the flame, and the stick part is rich in cellulose due to the wooden framework. After initial use, the sticks are considered waste and dumped immediately after the first usage. In this work, these waste sticks have been utilized to obtain cellulose from them in purified form by two different methods based on conditions. In this study, the waste MSs have 0.6% ash and 70% cellulose contents. A thorough protocol was designed to extract cellulose via two different methods and then conversion into CMC under optimized conditions.

3.1. Pretreatment Process Optimization. The optimization of cellulose extracted via ionosolv pretreatment using an ionic liquid, TMG- HSO_4 , has already been reported in our paper.⁴⁶ Different protic ionic liquids have been used recently for dissolution, extraction, and hydrolysis of cellulose. Table 1 gives a clear insight into newly used protic ionic liquids for lignocellulosic biomass and cellulose processing.

The other traditional method, sulfide pretreatment's optimizations, was performed by MS (Table 2). Different parameters like time, temperature, and reagent concentrations were varied to ensure the maximum yield with the pure and pristine product.

The obtained optimized conditions for cellulose extraction from the sulfide method were adopted to carry out the further reaction, and the same suit was followed with ionosolv pretreatment. The obtained cellulose pulps from the traditional method, cellulose-1, and from the ionosolv method, cellulose-2, were bleached to get rid of undesired color and lignin that might hinder the properties of the end product. The bleaching agent used was NaClO_2 with glacial acetic acid to maintain the pH, which bleached the pulps by sustaining the fiber strength and preventing any damage. The decrease in cellulose yield after bleaching might be due to the reduction in impurity content.^{69,70} The yield of cellulose-1 was 91%, and that of cellulose-2 was 99%, which illustrated that the ionic liquid used in the process had higher efficiency to extract cellulose without any loss compared to the sulfide process.

Table 2. Extraction of Cellulose via Sulfide Method Optimization

conditions of pretreatment	NaOH (%)	Na ₂ S (%)	time (h)	temperature (°C)	yield (%)
Na ₂ S conc.	8	6	3	90	91.4
	8	8	3	90	77.1
	8	10	3	90	85.7
	8	12	3	90	57.1
NaOH conc.	2	6	3	90	51.4
	4	6	3	90	59.2
	6	6	3	90	57.7
	8	6	3	90	60.3
time	8	6	1	90	77.2
	8	6	2	90	79.5
	8	6	3	90	83.1
	8	6	4	90	70.0
temperature	8	6	3	80	80.1
	8	6	3	90	80.3
	8	6	3	95	82.4
	8	6	3	100	82.0

3.2. Etherification Process Optimization. After obtaining cellulose from both methods, the optimized conditions for CMC production were quintessential to obtain highly substituted CMC and study the complete profile of two different kinds of CMC. The conditions were optimized by taking commercial microcrystalline cellulose (MCC), and a number of runs were applied to it (Table 3).

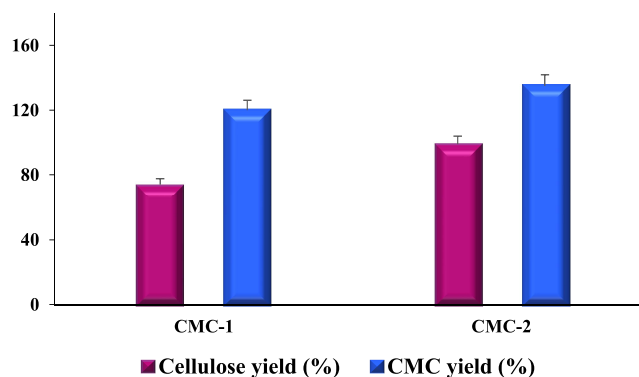
Table 3. Optimization of CMC Production from Cellulose

run no.	NaOH (M)	stirring time (h)	temperature (°C)	monochloroacetic acid (MCA) equivalents (g)	yield (%)
1	4	24	60	1	122 ^a
2	6	24	60	1	182
3	8	24	60	1	222
4	10	24	60	1	209
5	4	24	60	1	140 ^a
6	4	1	60	1	140
7	4	2	60	1	126
8	4	3	60	1	154
9	4	24	55	1	96 ^a
10	4	24	60	1	82
11	4	24	70	1	140
12	4	24	reflux (85)	1	100
13	4	24	55	1	104 ^a
14	4	24	55	2	184 ^a
15	4	24	55	3	164

^aHighly substituted CMC samples that are ensuring the highest DS.

After optimizing the conditions with MCC, the same process was applied to cellulose-1 and cellulose-2. Both CMC samples obtained after cellulose's etherification were different. CMC-2 is leading over CMC-1 because the purity, degree of substitution, moisture content, and solubility of this CMC is better than those of CMC-1. Different analyses further accentuated the results.

3.3. Physicochemical Properties of CMC. The yield of both synthesized CMC samples has been calculated on the dry weight basis of cellulose (Figure 2). The yield of CMC is mostly greater than that of cellulose because bulky carboxymethyl groups replace the hydroxyl groups (–OH) on the pyranose ring, which results in an increase in the weight

**Figure 2.** Yields of extracted cellulose from MS and CMC samples.

of cellulose. The factor that influences is the size of cellulose powder; the smaller the size, the higher the surface area, which in turn exposes more hydroxyl groups on the surface to be replaced by carboxymethyl groups. Here, the yields of both CMC samples are greater than that of cellulose, which indicates efficient etherification.⁷¹

The solubility of synthesized CMC is directly related to its DS and yield.⁷² As a matter of fact, cellulose is not soluble in water because of its strong inter- and intramolecular hydrogen bonding. When cellulose is alkalinized in the first step of CMC, hydrogens are replaced with sodium, making oxygen on the ring a better nucleophile to attack the methylene group of MCA and delinks the hydrogen bonding of cellulose. After that, etherification of the polar carbonyl group occurs on the surface, which makes the solubility of CMC molecules in water facile due to bulkiness and good bonding with the water molecules. Now the direct relation between DS and yield can be described as follows: if more substitutions occur on the cellulose surface, then higher yield is obtained, as more polar groups would attach and make the solubility of CMC possible, causing bulkiness in the structure.⁷³ Here, both synthesized CMC samples are soluble in water, but the solubility of CMC-2 is greater than that of CMC-1 due to better replacement on the cellulose molecule, which is more porous after pretreatment with super basic, less toxic TMG-HSO₄.⁴⁶

The prior literature has shown evidence that CMC is a hygroscopic molecule;⁷⁴ the moisture content of both synthesized CMC samples has been checked by placing them in an oven and drying them in a desiccator. This treatment showed that the yield, which was quite high, decreased, indicating the water-absorbing ability of CMC and the release of entrapped moisture that results in the reduction of yield.

DS is the most important factor in the study of CMC as more substitution takes place (Figure 3); a better grade CMC will be obtained due to greater viscosity. CMC-2 has greater viscosity than CMC-1 because the ionosolv pretreatment has reduced the crystallinity of cellulose-2, which has provided a greater surface area for replacement of –OH groups with hydrophilic carboxymethyl groups. These hydrophilic groups could directly interact with water molecules, showing greater solubility and viscosity.⁷⁵ The DS of CMC-2 was 2.3, and that of CMC-1 was 2.1, showing that CMC-2 is also dominating in further properties that are associated with the DS factor. In addition to that, both prepared CMC samples have greater DS than commercial CMC purchased.

The purity of both CMC samples has been checked by the method already reported in the literature. There are two possible byproducts in the production of CMC, sodium

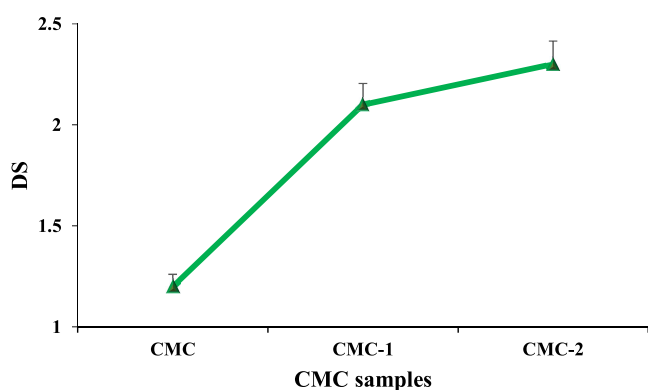


Figure 3. Degree of substitution of prepared CMC samples compared with commercial CMC.

chloride and sodium glycolate;⁷⁶⁷⁶ checking the contents of both and subtracting them from 100 would yield the percentage purity of the samples (Table 4). First, NaCl

Table 4. Purity (%) of CMC Samples from MS Waste

CMC samples	NaCl (%)	sodium glycolate (%)	purity (%)
CMC-1	1.16	0.77	98.1
CMC-2	0.7012	0.74	98.5

content was determined by Mohr's method by titrating with AgNO_3 solution; both samples showed minute amounts of NaCl, which could further be removed by excessive washing with solvents ethanol and methanol. Second, sodium glycolate content was calculated by preparing test and blank solutions of both CMC samples and glycolic acid as the standard. A single beam UV–visible spectrophotometer was used to check the absorbance. Glycolate content was minor in both CMC products. The overall purity was determined by subtracting both content values from 100. Both samples were >98% pure, and CMC-2 was 98.5, again leading over CMC-1. The purity of the CMC sample determines the different grades of CMC.⁵⁶

3.4. Structural Analysis. **3.4.1. FTIR Spectra of Cellulose and CMC.** The matchstick (MS) waste, extraction of cellulose via two pretreatments, and production of CMC have been

confirmed by recorded FTIR spectra (Figure 4). Both methods efficiently extracted the cellulose and showed CMC production (Table 5). Matchstick waste and cellulose peaks are almost

Table 5. Assignment of Peaks in FTIR of both CMC Samples

MS (cm^{-1})	cellulose (cm^{-1})	CMC (cm^{-1})	assignment
3322	3322	3322	–OH stretching
2900	2900	2900	–CH stretching
		1588	–CO stretching
1030	1030	1030	C–O–C vibration

similar in both spectra, showing –OH stretching and bending peaks at 3322 and 1314 cm^{-1} , respectively, while the methine (–CH) stretching peak was at 2900 cm^{-1} and the rocking peak of the β -glycosidic linkage of –CH was at 895 cm^{-1} . The antisymmetric vibration of the C–O–C bond and the stretching vibration of pyranose ring peaks appeared at 1020–1170 cm^{-1} . However, cellulose peaks are more prominent than MS peaks because of delignification and removal of residual waxes. Both CMC samples have all of the peaks of cellulose and the characteristic peak of carbonyl (–CO) at 1588 cm^{-1} .^{42,77} The –OH peak in CMC-2 has very much reduced, indicating the substitution of the hydroxyl group by the carboxymethyl group, which emphasized the physiochemical properties of CMC-2 over CMC-1.

3.4.2. XRD Analysis. The XRD diffractograms of both CMC-1 and CMC-2 are shown in Figure 5. Cellulose has a characteristic peak at 22.3°, indicating crystallinity; both synthesized CMC samples have shown a reduction of this peak. But CMC-2 has shown slightly more reduction than CMC-1 because the prepared CMC is more amorphous than CMC-1. This reduction in crystallinity directly affects the other properties of CMC, as given in the literature. It has been reported that with an increase in amorphous character, there is 1.1 DS of CMC. This statement of the literature perfectly justifies the more DS of CMC-2 than that of CMC-1.⁷⁸ Moreover, during CMC production, the destruction of crystallinity has occurred in the first step because of the swelling of cellulose, which causes rupturing of hydrogen

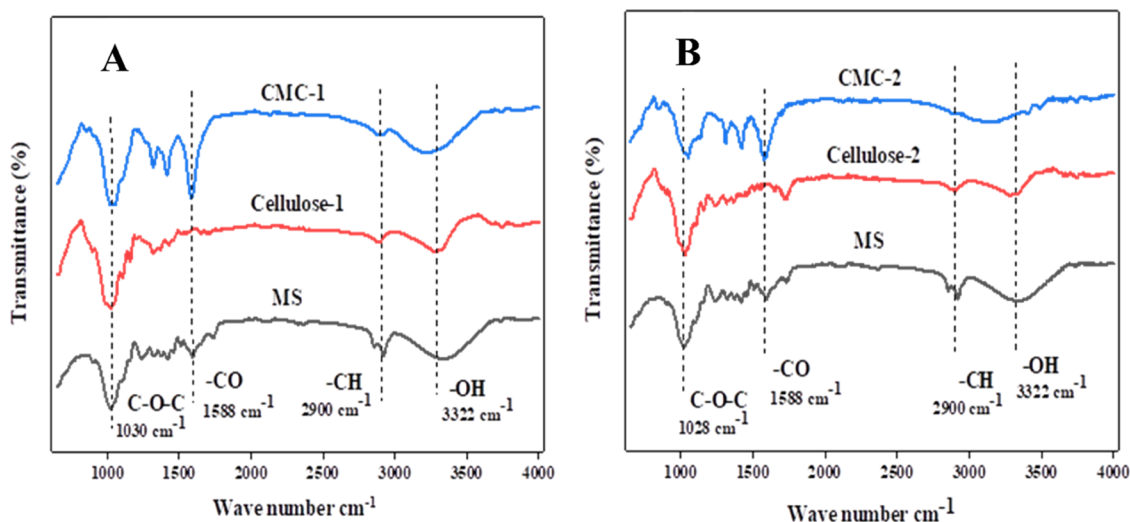


Figure 4. Recorded FTIR spectra of matchstick waste, extracted cellulose via two methods, and CMC production: (A) MS, extraction of cellulose-1 by the traditional method, and CMC-1 production and (B) MS, extraction of cellulose-2 by the ionosolv method, and CMC-2 production.

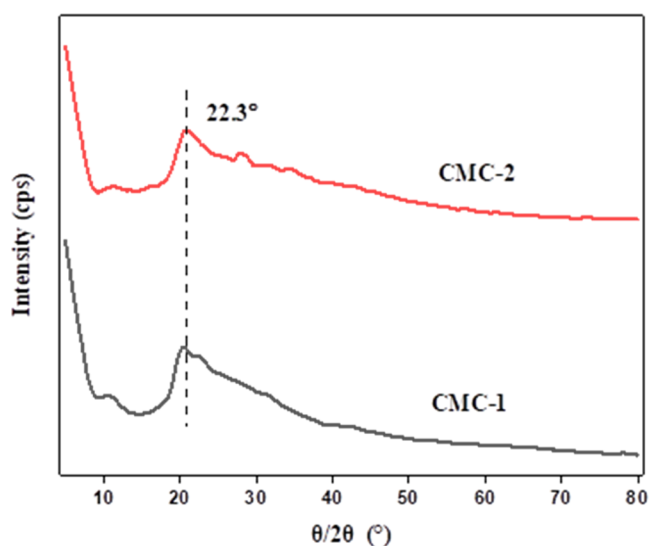


Figure 5. XRD diffractograms of prepared CMC-1 and CMC-2.

bonds in cellulose and increases the solubility of prepared CMC due to its amorphous structure. Again, this step is more pronounced in CMC-2 than that in CMC-1.^{44,79}

3.5. NMR Analysis of CMC. **3.5.1. ¹H NMR.** The ¹H NMRs of both CMC samples comprise very complicated spectral lines in between the region of 3–5 ppm. A set of doublets at lower and higher fields in the region of 4.5–5 ppm can be assigned to α and β anomers of C₁ carbon, respectively. The signals in the region of 3–4 ppm are attributed to the protons of the glucose unit. The sharp signal at 4–4.5 ppm is due to the protons of the carboxymethyl (–CH₂COOH) group.³² However, the appearance of a plethora of signals makes it difficult to properly differentiate between the prepared samples of CMC (Figure 6).

3.5.2. ¹³C NMR. The ¹³C NMRs of both synthesized CMC samples are shown in Figure 7. The downfield signals in both spectra at 180 and 182 ppm explicitly illustrate the attachment

of carboxymethyl groups at the two positions on the side chain and ring hydroxyl groups. The replacement of the ring hydroxyl group by the carboxymethyl group has shown the downfield shift of carbonyl carbon, while replacement at pendant carbon appears quite upfield. The upfield signals at 63 and 72 ppm enunciate the methylene carbon of the side chain. Kono et al. related the DS with the fluctuation of the signals.⁸⁰ The intensity of the signal decreases at 63 ppm and increases at 72 ppm, which might be due to the increase of DS. The intensity of this fluctuation was greater in CMC-2 than that in CMC-1, which further accentuates the experimental results.⁸¹

3.6. Morphology Analysis. **3.6.1. SEM Analysis.** The SEM images of both CMC samples are shown in Figure 8; the CMC-1 images with different magnifications are ribbon- and rodlike, indicating some crystallinity in the structure. The CMC-2 structure has holes and groves over the surface, in contrast to CMC-1. The roughness of the CMC-2 structure gives it leverage because of less crystallinity and more amorphousness. This leads us to believe that the ionsolv pretreatment efficiently yields cellulose with a large surface area, and during the first step of CMC production, the porous structure of cellulose shows more swelling.^{82,11} The increase in swelling might be due to the less crystallinity of cellulose, and the more alkali solution has got the chance to penetrate deep into the cellulose structure. Therefore, the efficiency of cellulose to convert into CMC has been enhanced. Thus CMC-2 leads over CMC-1 with respect to the large surface area, less crystallinity, and more amorphousness.⁸³

4. CONCLUSIONS

Biomass pretreatment affects the interaction and contents of its components, which are taken together in characterization analyses. In the current investigation, a complex framework of lignocellulosic biomass that is waste matchsticks has been degraded by conventional and ionsolv pretreatments to obtain cellulose pulps. Ionic liquid, TMG-HSO₄, treated pulp was more degraded and yielded porous cellulose, which was

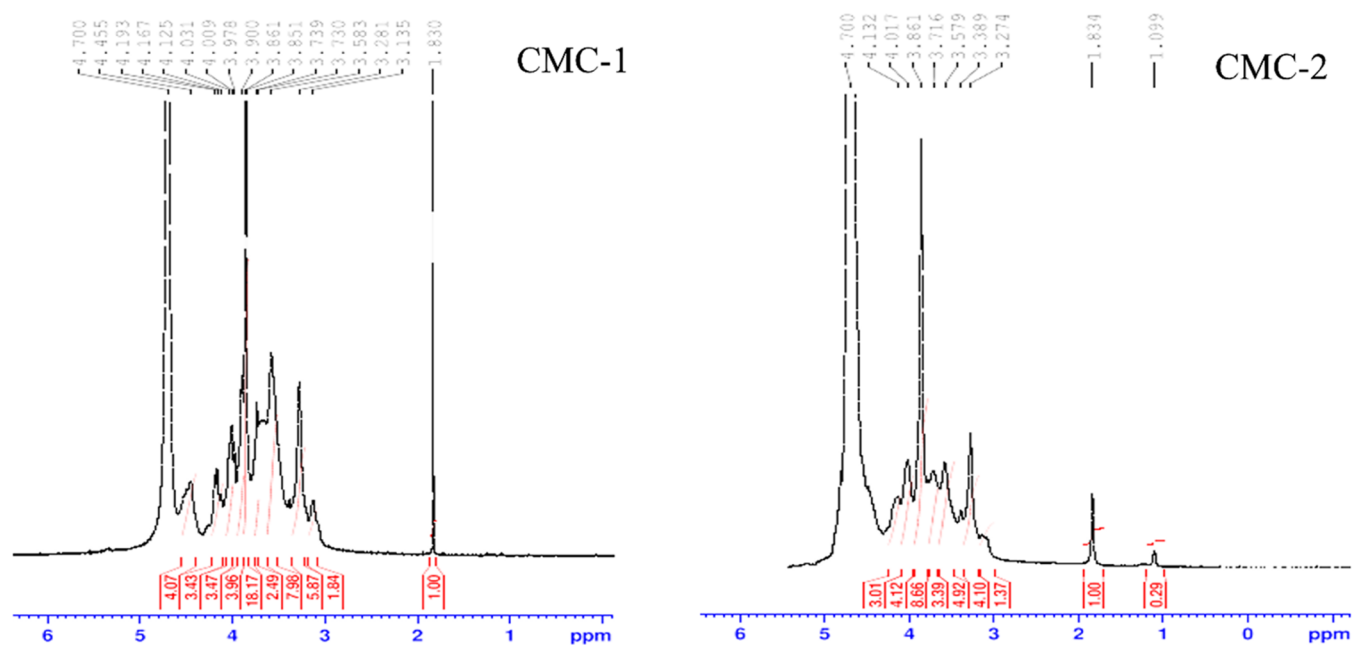


Figure 6. ¹H NMR of synthesized CMC-1 and CMC-2.

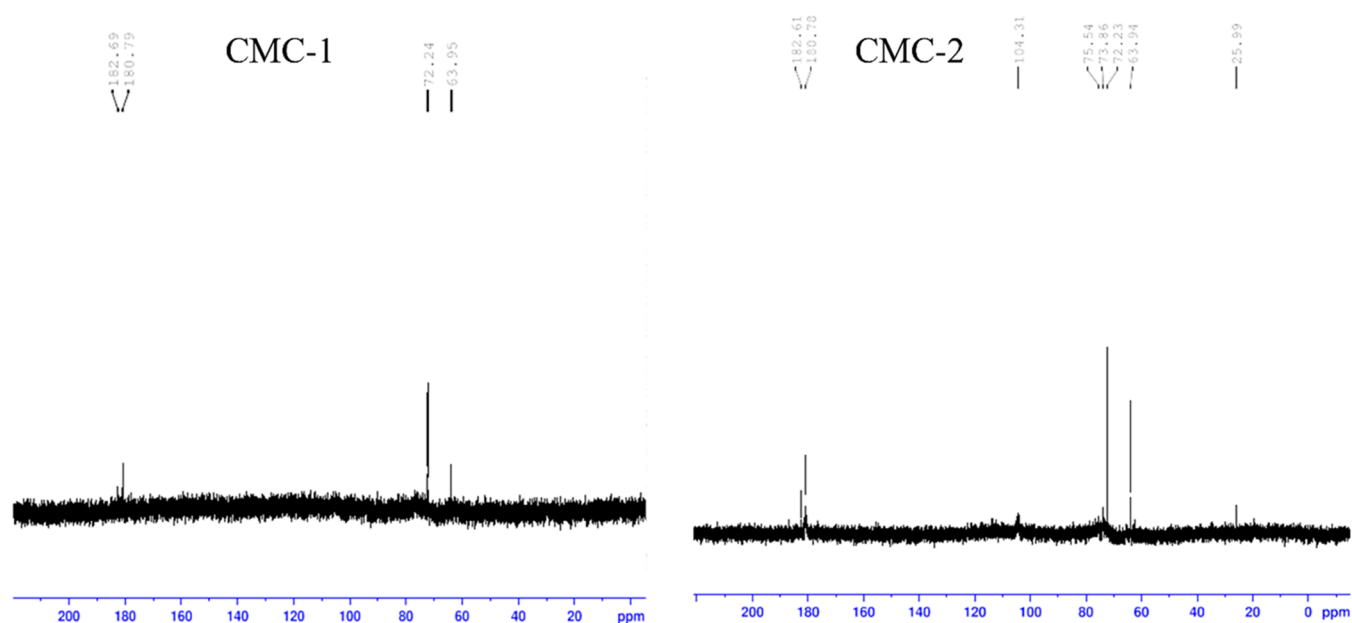


Figure 7. ^{13}C NMR of synthesized CMC-1 and CMC-2.

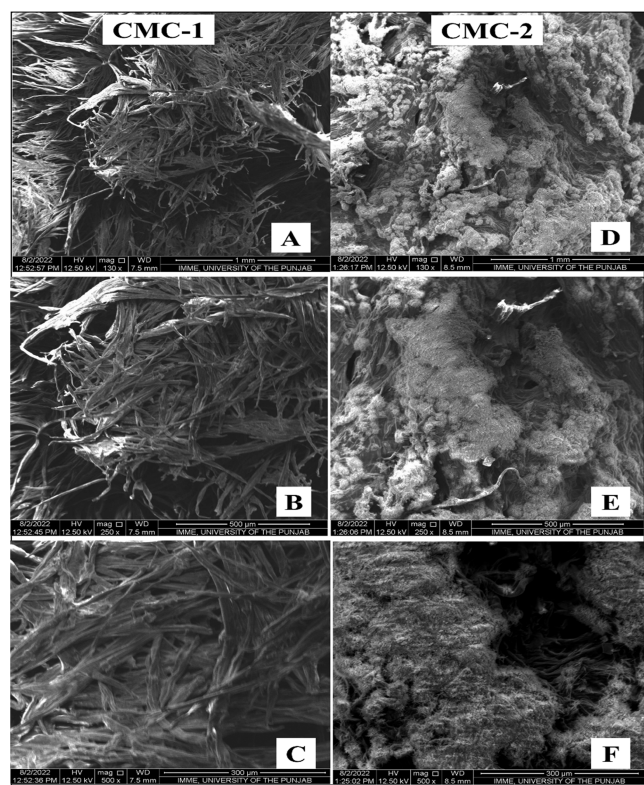


Figure 8. SEM images of CMC-1 ((A) 130 \times , (B) 250 \times , and (C) 500 \times) and CMC-2 ((D) 130 \times , (E) 250 \times , and (F) 500 \times).

later converted into CMC-2. CMC-1 produced by cellulose extracted from the sulfide method lagged behind in physiochemical properties than CMC-2 in terms of DS, yield, purity, moisture content, and salt content. CMC-2 had an excellent yield of 135%, DS of 2.3, and less moisture and salt contents. In addition, FTIR showed that the peak of the $-\text{OH}$ group became almost flat at 3322 cm^{-1} in CMC-2, which indicated substitution. XRD depicted more loss of the crystalline peak at 22.3° , and NMR data showed intense peaks

in both ^1H NMR in the region of 4.5–5 ppm and ^{13}C NMR in carbonyl group signals at 180–182 ppm and the methylene group at 63 and 72 ppm. SEM analysis again showed more holes and groves on the CMC-2 surface than those on CMC-1, supporting the experimental and physiochemical results. Altogether, we can conclude that ionsolv pretreatment degrades lignocellulose more efficiently than the conventional method, and obtained cellulose could be further converted into its water-soluble derivative, CMC, with improved properties, which has a wide range of applications in different arenas.

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Notes

The authors declare no competing financial interest.

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