Carboxymethyl cellulose a derivative of commercial importance: A concise review

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***Abstract*: In the last few decades increased environmental pollution, population, and demand for biodegradable materials considerably shifted attention of researchers toward natural products. Although, numerous bio-polymers are explored for industrial applications but substituting the synthetic material's abundant availability on a sustainable basis is strongly required. Among the various natural polymers, cellulose is one of the most abundant biopolymers on Earth and is therefore explored for large-scale applications. It is produced by a large variety of living organisms, such as oomycetes, algae, acetobacter, rhizobium, etc. Numerous derivatized form of cellulose is reported among which the anionic derivative, carboxymethyl attracted of attention of academics as well as industries. As a result, numerous patents and research papers are published on this subject but there is a lack of a detailed review comprising the effect of solvent, applications, and statistical approach towards derivatization, etc.**

1. Introduction

Polysaccharides are an attractive class of eco-friendly and biodegradable polymers due to their abundant availability from renewable natural sources, cheap, non-toxic, and availability on a sustainable basis. In the last few decades increased environmental pollution, population, and demand for biodegradable materials considerably shifted attention of researchers toward natural products. Therefore, biopolymers attracted considerable attention as a substitute for synthetic polymeric counterparts to overcome the drawbacks of synthetic materials such as non-biodegradability, toxicity, non-renewability, etc. One of the most important achievements in this direction is the successful utilization of biopolymers in various commercial utilities; an example includes hyaluronic acid[1], chitin and chitosan [2], xanthan gum [3], soy protein [4] Poly-γ-glutamic acid [5], poly (glutamic acid) [6], lignin [7], guar gum [8-9], cellulose [10], starch [11-12], etc. Although, numerous bio-polymers are explored for industrial applications but substituting the synthetic material's abundant availability on a sustainable basis is strongly required.

Among the various natural polymers, cellulose is one of the most abundant biopolymers on Earth and is therefore explored for large-scale applications. It is produced by a large variety of living organisms, such as oomycetes, algae, acetobacter, rhizobium, etc. Chemically cellulose is composed of a linear chain of β-(1-4)-linked glucose repeating units (Figure-1).

But in native form biopolymers are reported to exhibit numerous disadvantages such as uncontrolled ate of hydration, solution clarity, insoluble impurities, etc. Chemical modification is reported as one of the most effective methods to overcome the undesired traits and impart the desired characteristic to the native polysaccharide for end applications. Based on the charge of the substituted group derivatization is broadly classified into three categories; (a) cationic, (b) anionic, and (c) non-ionic, etc. Among these methods of derivatization, cationization and substitution of the anionic group onto the polymeric backbone is of special importance due to the introduction of charged groups onto the polymeric substrate.

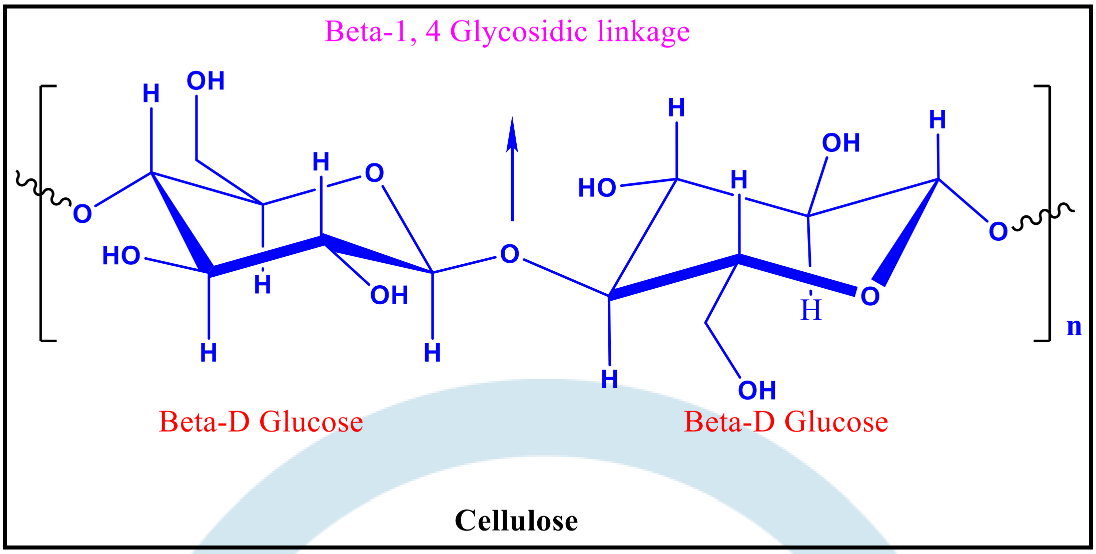

Figure 1. Structural representation of β-(1,4)-glycosidic linkage in Cellulose moiety.

Numerous derivatized form of cellulose is reported among which the anionic derivative, carboxymethyl attracted of attention of academics as well as industries. As a result, numerous patents and research papers are published on this subject but there is a lack of a detailed review comprising the effect of solvent, applications, and statistical approach towards derivatization, etc. The present review provides a detailed introduction to the source of cellulose followed by the basic notions and systematic approaches to carrying out the carboxymethylation of cellulose and the effects of various conditions on the derivatization process and outputs.

2. Carboxymethyl cellulose from different sources

Since cellulose is one of the most widely distributed biopolymers in nature. Therefore numerous studies are reported on the carboxymethylation of cellulose extracted from diverse sources such as; flax shaves [13], sugarcane straw [14], bagasse [15], palm kernel cake [16], date palm rachis, and Posidonia oceanic [17], peel of pineapple [18], papaya [19], and banana [20], bleached bagasse [21], maize waste such as stalks, husks, cobs, and leaves [22], corn husk [23], rice husk [24], orange mesocarp [25], cotton ginning industry [26], crop straw [27], cubic agricultural waste [28], and Egyptian rice straw [29], textile waste [30], cotton (*Gossypium*) linters [31], *Lantana camara* [32], sugar beet pulp [33], *Terminalia superba* [34], *Eucalyptus globulus* wood [35], terry towel [36], etc. are reported. In another study carboxymethylation of bacterial cellulose was reported by Schlufter & Heinze, (2010) [37].

3. Mechanism and scheme of carboxymethylation of cellulose

Carboxymethylation of cellulose is a base-catalyzed nucleophilic substitution reaction. The hydroxyl groups present in the cellulose structure is converted to alkoxide ion by the alkali. The produced alkoxide reacts with the etherifying reagent monochloroacetic acid or sodium salt of monochloroacetic acid to produce carboxymethyl cellulose. The scheme of the carboxymethylation of cellulose under the catalytic action of NaOH is displayed in Figure-2.

Generally, carboxymethyl cellulose is characterized by the degree of substitution (DS). DS is defined as the (average) number of substituent groups attached per base unit. The most frequently used method for calculating the DS of carboxymethyl cellulose is acid-base titration. In this method, the acid form of carboxymethyl cellulose is titrated against alkali. The DS of the carboxymethylated cellulose is governed by several reaction factors. Therefore, it is of critical importance to select the appropriate reaction conditions for synthesizing CMC of desired characteristics.

4. Effect of various reaction parameters on DS of CMC

Various studies are dedicated to the optimization of reaction conditions towards DS. Zhao, Li, & Mi. (2013) prepared carboxymethyl cellulose with DS of 0.43, under the reaction conditions optimized against the concentration of reactant, reaction temperature, and time[38]. The carboxymethylation process was optimized against the concentration of alkali, concentration of sodium chloroacetate, reaction temperature, and time for cellulose obtained from sugar beet pulp [33]. Borsa, Kálmán & Rusznák (1999) reported the effect of reaction time on the DS of carboxymethylated cellulose fabrics [39].

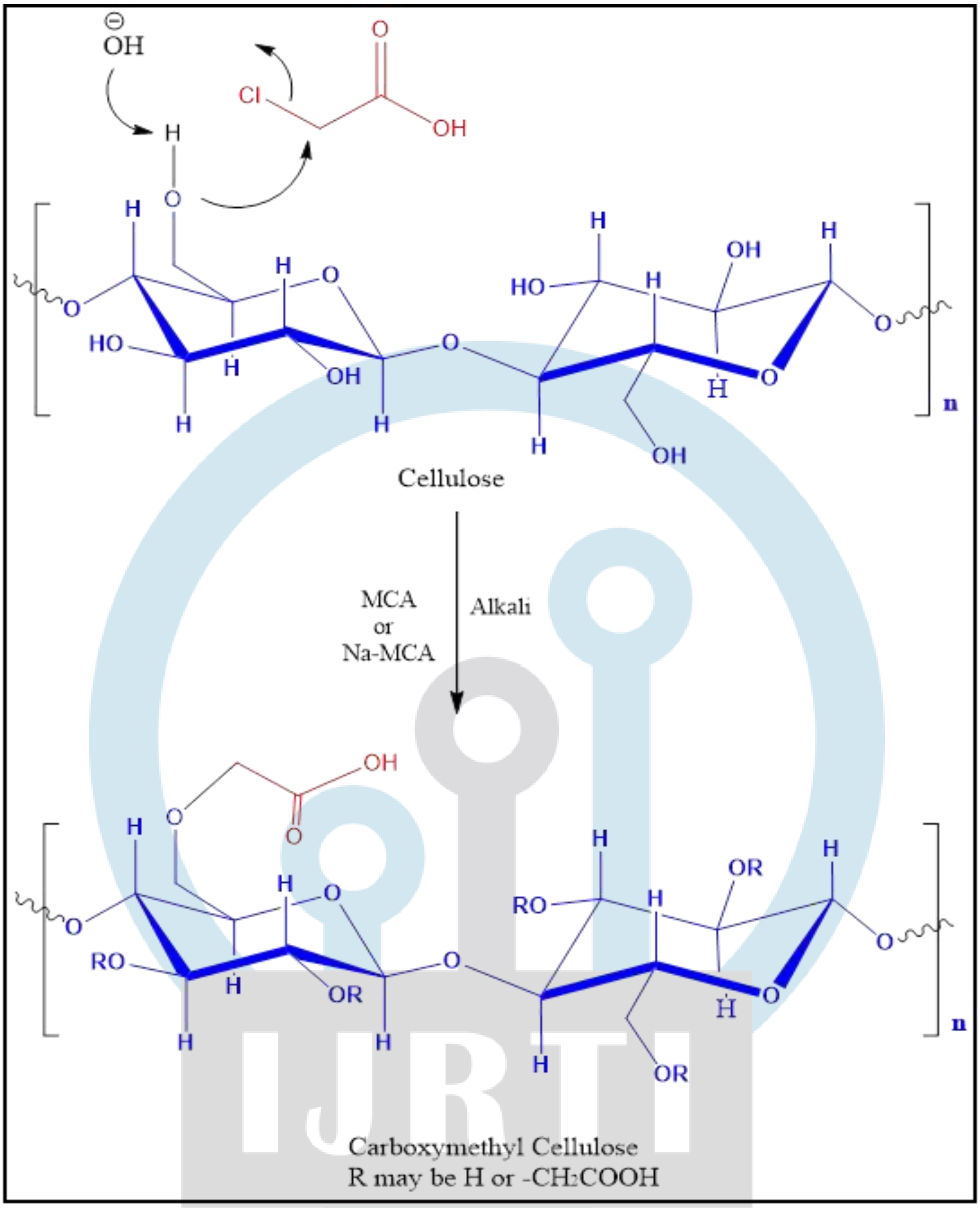

Figure 2. Schematic representation of carboxymethylation of cellulose.

Effect of reaction time, temperature, and reactant concentration on DS of cellulose obtained from cotton (*Gossypium*) linters were studied Khullar et al. (2005) [31]. Cellulose extracted from various sources such as cotton gin waste [40] and *Lantana camara* [32], etc. is subjected to optimization of various reaction conditions to obtain higher DS.

5. Effect of reaction solvent and medium on DS of CMC

Further, the derivatization process of polysaccharides is not only sensitive to the concentration of reactant, reaction time, and temperature but the reaction medium is also reported to show a marked influence on the DS of CMC. For carboxymethylation of cellulose mixture of ethanol and acetone was reported to be a better solvent in comparison to acetone [41]. The carboxymethylation process of cellulose extracted from *Terminalia Superba* wood showed marked influence by the solvent composition of the reaction medium, the highest DS (0.438) was reported in benzene/isopropanol (1:1) [42].

Volkert & Wagenknecht (2008) reported a difference in the substitution pattern of carboxyl groups in carboxymethyl cellulose in the reaction carried out in homogenous and heterogeneous solvent medium which further affects solubility as well as the rheological behavior of carboxymethyl cellulose [43]. Fischer, Thümmler, Pfeiffer, Liebert & Heinze (2002) employed inorganic salt hydrates as a reaction solvent for the carboxymethylation process of cellulose and a DS of 3 was achieved [44]. In a study dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride (TBAF) was used as a solvent for carboxymethylation of mercerized cellulose extracted from sisal and cotton linters [45]. Heinze, Liebert, Klüfers & Meister (1999) carried out carboxymethylation of cellulose in a different solvent medium, namely Ni(tren)$(OH)_2$, melts of $LiClO_4 \cdot 3H2O$ or N-methyl-morpholine-N-oxide (NMMNO), solvent medium showed a marked influence on substitution pattern [46]. Isopropyl alcohol-water was used as a solvent medium in the slurry state and showed better results in terms of DS (1.24) for the carboxymethylation process of cellulose [47]. Ammonium-based solvents with tri-ethylmethylammonium and tri-butylmethylammonium cations were reported to be better for the carboxymethylation of cellulose by Köhler, Liebert & Heinze (2009) [48]. In ionic liquid 1-N-butyl-3-methylimidazolium acetate, Liebert & Heinze (1998) reported the preparation of carboxymethyl cellulose in LiCl/N, N-dimethylacetamide, and further, the substitution pattern was determined with HPLC. The distribution pattern of the carboxymethyl group on cellulose was found to be dependent on the state of the reaction medium i.e, slurry, heterogeneous, or homogenous [49].

Carboxymethyl derivative of cellulose was prepared by Olaru & Olaru (2001) in different organic solvents such as acetone, isopropanol, a mixture of methanol-acetone, and methanol-isopropanol, etc, and best DS (0.69) was reported in the methanol-acetone mixture [41]. The heterogeneous condition was employed for carboxymethylation of cellulose obtained from *Eucalyptus globulus* wood [35].

Cellulose extracted from water hyacinth was carboxymethylated in isopropyl alcohol [50], isopropyl-isobutyl alcohol [51], and in a mixture of varied ratios of isopropyl alcohol and 2-butanol [52]. Musfiroh, I. et al (2018) reported carboxymethylated cross-linked derivative of water hytchin by employing various solvents such as isobutyl alcohol, isopropyl alcohol, and isobutyl alcohol-isopropyl alcohol in a ratio of 1:4 [53]. The solvent system was also reported to affect the viscosity of the carboxymethylated products [54].

6. Effect of DS on various characteristics of CMC

DS significantly affects various properties of CMC such as viscosity [55], Chen, Wan, Dong, Ma (2016) reported a direct correlation between fiber property (fiber swelling ability [56], the crystal structure of cellulose, fiber surface morphology, etc.) and carboxyl content for eucalyptus kraft pulp.

SEM images reflected smoothness in the surface after carboxymethylation [40]. Carboxymethylated and cyanoethylated cotton were reported to increase abrasion resistance, crease recovery and moisture regain of fiber [57]. Polyelectrolyte gel behavior of hollow spheres based on carboxymethyl cellulose was found dependent on the charge of anionic cellulose [58]. Dominguez, Engler, & Soltes, (1985) found that carboxymethylated cellulose with lower carboxyl content was more pronto to enzymatic degradation in comparison to higher carboxyl group-containing derivative [59]. Electrical conductivity and tensile strength of carboxymethylated cellulose-based sheet were found dependent on charge density. The metal ion absorption capacity of fibers based on carboxymethyl cellulose showed dependency on the charge of anionic cellulose [60]. Wang, Liu, Duan, Sun & Xu (2007) reported that carboxymethylated cellulose showed higher water and saline absorbencies than the untreated fibers [61]; additionally better uptake of wound exudates was also reported by Qin, Y., (2005) [62]. Naderi, Lindström & Sundström (2004) reported high elasticity and shear thinning behavior in carboxymethylated nanofibrils [63]. Pulp with high carboxyl content resulted in more stable suspension due to increased electrostatic repulsion [64]. Tame et al. (2011) reported increased graft copolymerization of acrylamide after carboxymethyl for cellulose [65].

The derivatization process was also reported to cause a change in the surface morphology of biopolymer. Singh, R. K. et al (2013) carried out an XRD analysis of carboxymethylated cellulose [66]. X-ray analysis showed that the crystalline structure of cellulose decreased with an increase in DS and the structure was amorphous in high DS material [67]. Bhandari, Jones & Hanna (2012) studied the impact of the content of the reaction solvent on the crystallinity of carboxymethyl cellulose by X-ray diffraction [68]. Carboxymethyl cotton cellulose was analyzed by employing SEM and X-ray techniques, former revealed the carboxymethylation throughout the cotton fiber cross-section, however, the latter concluded the difference was due to morphological variations [69]. Casaburi, A. et al. (2018) prepared CMC with various DS and characterized by X-ray diffraction, ^{1}H-NMR, size exclusion chromatography (SEC), thermogravimetry (TG), and differential scanning calorimetry (DSC) [70]. Carboxymethyl derivative of cellulose extracted from bleached pulps was characterized by TGA and DSC, further suitability of using TGA data for estimating the carboxymethylation extent was also proposed [71]. Electronic scanning electron microscope studies revealed more fibrillation on the carboxymethylated fiber surface [72]. TGA of CMC revealed a decrease in thermal stability due to carboxymethylation [73]. The crystallinity of the carboxymethyl cellulose derivative of corn husk cellulose was characterized by XRD [74]. The structure of the carboxymethyl derivative of Sugarcane bagasse cellulose was characterized by Chen, Y. et al. (2015) with X-ray diffraction (XRD) [56]. SEM images showed a change in the morphology of cellulose after carboxymethylation [40].

7. Application of CMC

Carboxymethyl cellulose (CMC) is one of the most important water-soluble derivatives of cellulose having applications in diverse fields such as preparation of metal ions [75] and saline water [76] absorbent [77]. In the formulation of water-permeable [78] film [79] or sheet [75], polyester printing [29]. In papermaking, CMC is being used for various purposes such as wet [80] strengthening agent [81], for paper coating [82]. In oil drilling practices as mud drilling agents [25], etc.

Further, this biodegradable derivative of cellulose due to owing biocompatibility and non-toxicity not only finds its way to the industrial applications but is also being used for various pharmaceutical practices; carboxymethylated and reduced (with silver nitrate) cotton gauze was tested for antimicrobial activity against Escherichia coli and Staphylococcus aureus [83]. Balasubramanian, Balasubramanian, Babu, Devika & Rajendran, (2013) reported that the antibacterial activity of carboxymethylated cotton gauze can be used for the fabrication of wound dressing material [84]. Chen, J., et al (2016) compared the whole blood clotting time (WBCT) and water absorption behavior of carboxymethylated cotton gauze with untreated cotton gauze and found it suitable for the preparation of surgical cotton [85]. Similar results were also reported by Qin, Y. (2005) for the absorption of water and wound excaudate [62]. Miraftab, Qiao, Kennedy, Knill & Groocock (2004) reported that the inclusion of 10% w/w sodium carboxymethyl cellulose improved the fiber wet strength as well as structural integrity and maybe potential wound dressing material [86]. Ohta, S. et. al. (2005) developed a hemostatic agent from carboxymethyl cellulose-based nonwoven sheet and shortens the bleeding time [87]. El-Hag Ali, Abd El-Rehim, Kamal & Hegazy (2008) prepared drug carrier hydrogels based on carboxymethyl cellulose[88].

Nano-materials based on CMC are also reported to be applied in various pharmaceutical activities. Rakhshaei & Namazi (2017) prepared carboxymethyl cellulose-based flexible nanocomposite hydrogel impregnated with mesoporous silica and used it as a drug carrier[89]. Periodate oxidized carboxymethylated nano cellulose was found applicable in wound dressing practices [90]. The drug release profile of interpenetrating network microbeads based on sodium carboxymethyl locust bean gum and sodium salt of CMCS was tested for the release of Diclofenac sodium [91].

8. Miscellaneous

Various kinds of studies are also reported on the carboxymethylation of cellulose; the effect of heat pre-treatment on DS of carboxymethyl cellulose was studied by Youssef, Nada & Ibrahem (1989) [92]. Musfiroh, I. et al. (2018) reported crosslinking of carboxymethylated hytchin cellulose[53] the kinetics of carboxymethylation of hytchin cellulose, was also studied by Xiquan, et al. [54]. In another study Bulloc, Guthrie & Mack (1964) used vapors of hydrochloric acid and paraformaldehyde as cross-linking agents for partially carboxymethylated and printed cotton [93]. Yu, S. et al (2013) prepared a hollow fibers membrane from hydrolyzed Cellulose triacetate semi-permeable membrane [94]. Cellulose was converted into cellulose triacetate (CTA) intermediate which was further converted to CMC by deportation, followed by etherification Benke, N., Takács, E., Wojnárovits, L., & Borsa, J. (2007). Pre-irradiation grafting [95] and graft copolymer of acrylamide holocellulose containing carboxymethyl moieties was reported by Tame, A. et al (2011) [96]. Hebeish, et al. (1992) reported that cellulose showed a better response toward carboxymethylation after hydrolysis[13]. Gorodnov, Timokhin, Teslenko, Rusaev (1975) added Silica during the carboxymethylation of cellulose to improve its applicability to stabilizing highly mineralized oil drilling solutions [97].
The effect of heat pre-treatment on the DS of carboxymethyl cellulose was studied by Youssef, Nada & Ibrahem (1989) [27]. The solid-phase mechanochemical method was employed for the carboxymethylation of cellulose [98]. Steam explosion treatment was applied for the carboxymethylation of cellulose by Yang et al. (2009) [27]. Volkert & Wagenknecht (2008) studied the substitution pattern of carboxyl groups of carboxymethyl cellulose [43]. The influence of organic diluent on the carboxymethylation process of cellulose was also reported [28].

CMC is an industrially important derivatized biopolymer and industries constantly strive for the processes which are efficient in terms of consumption of energy and reactant. Statistical-based design of the experiment reduces the no of the experiment without compromising the number of factors to be studied, hence the design of the experiment is becoming one of the popular methods for process optimization. Only a few reports were available on the studies on carboxymethylation by employing the design of the experiment. Bhandari, Jones & Hanna, (2012) carried out carboxymethylation of cellulose by extrusion methodology by adopting a 5×3 blocked factorial design to study the effect of amounts of NaOH, water: ethanol ratio, and their interactions on the physical, chemical, and morphological properties of the carboxymethylated product [99]. A full-factorial 23 central composite design was applied to study the impact of various reaction factors including reaction time, amount of monochloroacetic acid, and reaction temperature on average DS of the cellulose derivative [100].

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