

## PERIODATE OXIDATION OF CARBOXYMETHYLCELLULOSE

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### Abstract.

This paper presents the results of studies of the oxidation reaction of carboxymethylcellulose (Na-CMC) with sodium periodate using microwave irradiation. The influence of reaction time, oxidant concentration, solution pH and reaction temperature to the content of aldehyde groups in the product and the reaction yield were studied. The physicochemical properties of the obtained samples were studied by chemical, IR-spectroscopic and thermogravimetric analysis methods. As a result of periodate oxidation of Na-CMC in a microwave irradiation high degree of oxidation samples were obtained.

**Key words:** *sodium carboxymethylcellulose, dialdehyde carboxymethylcellulose, periodate oxidation, microwave irradiation.*

### Introduction.

Carboxymethyl cellulose (Na-CMC) is a linear structure, and its structure includes mutual crosslinking of several 1-4  $\beta$ -glucopyranose rings [1]. Nowadays, there are technical and high-purity Na-CMC samples available worldwide, and they are used in different industries [2]. High-purity samples of Na-CMC have been used in food industries, pharmaceuticals, and the medical field because Na-CMC is biocompatible and has non-toxic properties [3]. Currently, many researchers are working with Na-CMC [4] because it is obtained from local raw materials, it is easy and cheap to synthesize, and it is not biologically toxic [5]. In particular, great attention is being paid to increasing the reactivity of Na-CMC samples, along with their physicochemical and biological properties, by changing the structure and creating new functional groups [6]. Therefore, many researchers use a selective oxidant for Na-CMC oxidation; for example, sodium periodate ( $\text{NaJO}_4$ ) oxidizes Na-CMC samples, breaking  $\text{C}_2\text{-C}_3$  covalent bonds and opening Na-CMC rings [7]. Na-CMC oxidation with a selective oxidant result in the formation of dialdehyde carboxymethyl cellulose (DCMC), which is used in various fields such as medicine, food, and perfumery industries [8]. Nowadays, DCMC and its derivatives are finding increasing applications [9], especially in the textile field, adsorption of heavy metals [10], as a crosslinking agent [11], in obtaining various hydrogels [12], and in biomaterials based on DCMC/protein for tissue engineering [13].

### Experimental.

#### Materials.

In this work, the following chemical reagents were used:

Carboxymethyl cellulose (Na-CMC) under standard conditions 19515439-01:2017 (in Uzbekistan);

Sodium periodate ( $\text{NaJO}_4$ ) under standard conditions 3305—52 (in Russia);

Sodium hydroxide ( $\text{NaOH}$ ) under standard conditions 4328-77 (in Uzbekistan);

Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) under standard conditions 10749—64 (in Uzbekistan).

#### Periodate oxidation of carboxymethyl cellulose.

About 1.0 g of CMC was dissolved in 30 mL of distilled water. Then, 10 mL of periodate solution (0.25 g/mL) was added to the CMC solution under stirring. The pH was adjusted to 3.5 with a 1 M hydrochloric acid solution. After the mixture was stirred under

ultrasonic irradiation at 30°C for 10 minutes, the oxidized product, referred to as DCMC, was precipitated by pouring the solution into a large amount of ethanol. It was then recovered and rinsed with distilled water and ethanol until all iodic compounds were removed. The product was dried in a lyophilic dryer to a constant weight for subsequent use.

### Determination of aldehyde group content

0.5 g of DCMC is dissolved in 25 mL of distilled water. The pH is adjusted to 5 with NaOH (1.0 M). Then, 20 mL of an aqueous solution of hydroxylamine hydrochloride (1 M) adjusted with NaOH (1.0 M) to pH=5 is added to the previous solution of DCMC. The stirring is left for 4 hours at a temperature of 40°C. The hydrochloric acid titration is monitored with NaOH (1.0 M) until pH=5 is reached. The consumption of the NaOH solution is recorded as  $V_a$ . The same procedure is repeated on the CMC as a control, and the consumption of the alkaline solution is recorded as  $V_b$ . The amount of aldehyde in the oxidized CMC is calculated using the following equation:

$$AC = \frac{C_{NaOH} (V_a - V_b)}{\frac{m}{240}} \times 100 \%$$

Where:

$V_a$  is the volume (in mL) of NaOH (1.0 M) consumed during the titration of DCMC;

$V_b$  is the volume (in mL) of NaOH (1.0 M) consumed during the titration of CMC;

$C_{NaOH}$  is concentration of sodium hydroxide solution;

$m$  is the mass of DCMC used;

240 is the molar mass of the repeating unit of DCMC.

### IR-spectroscopy

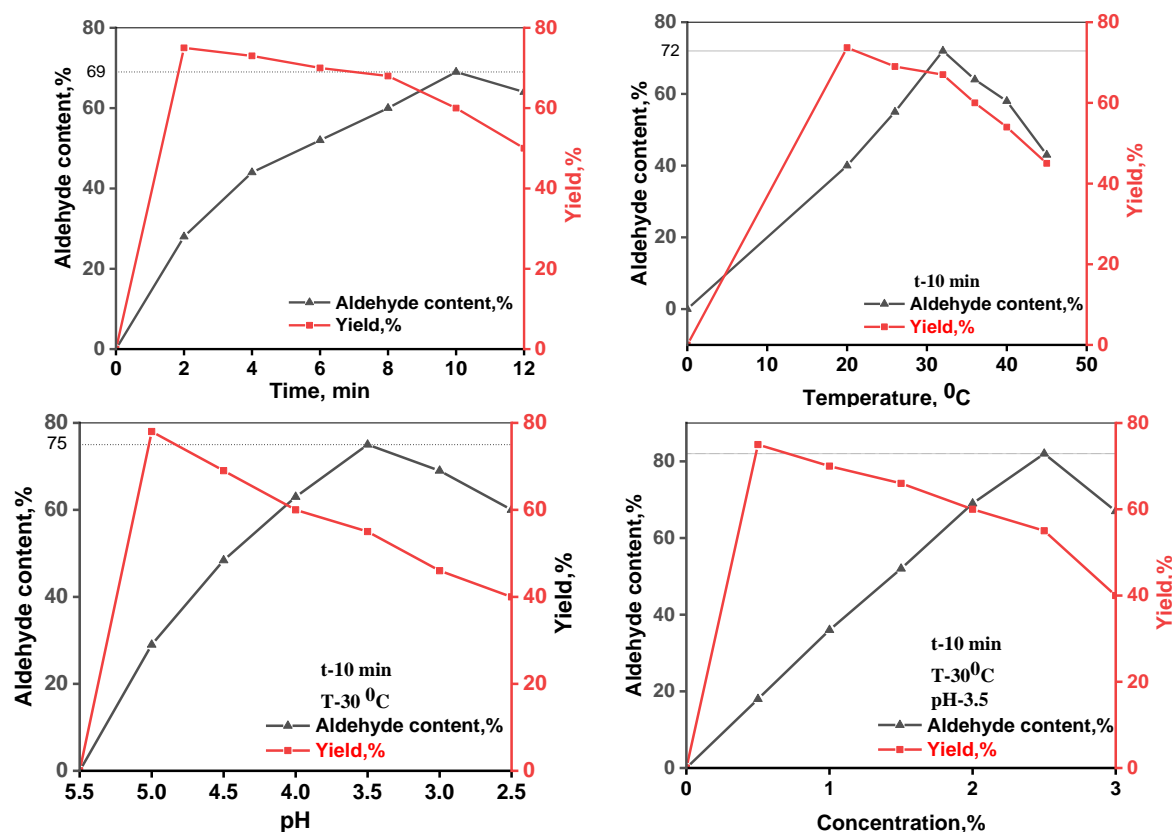
IR spectroscopy was performed using an Inventio-S IR Fourier spectrometer (Bruker, Germany). The spectra were analyzed, specifically focusing on changes in the 0.085  $\mu\text{m}$  and 500-4000  $\text{cm}^{-1}$  regions.

### Thermogravimetric analysis

The thermal properties of the samples were analyzed using a TG-DSC/DTA synchronous thermal analyzer, specifically the STA PT1600 model from Linseis (Germany). Approximately 20 mg of samples were heated from 25°C to 900°C at a rate of 10°C/min under atmospheric conditions.

### Results and discussion.

The effect of time, temperature, and solution treatment on the oxidation process of Na-CMC samples was studied. As the duration of the oxidation reaction increased, the formation of aldehyde groups also increased. However, after 10 minutes, both the amount of aldehyde groups in the samples and the yield of the reaction decreased significantly. The results are presented in Figure 1.



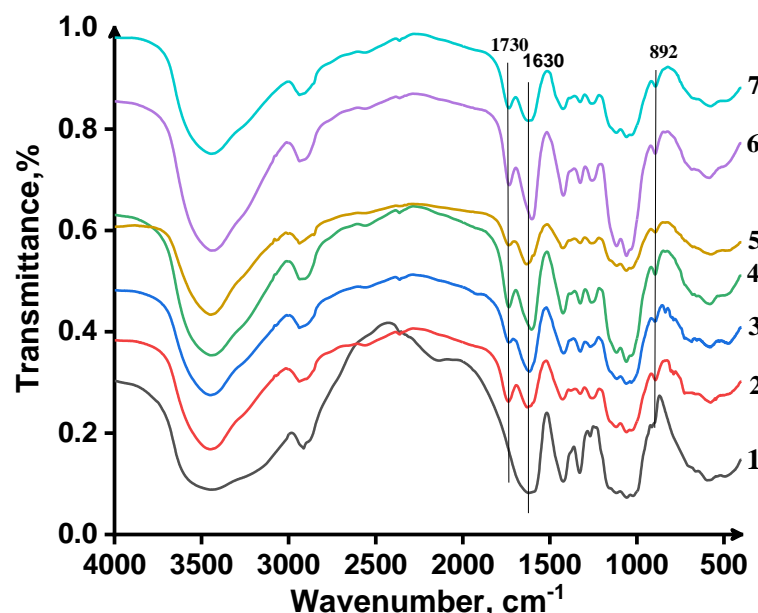
**Figure 1.** Influence of oxidation time, oxidant concentration, solution pH, temperature amount of aldehyde content and reaction yield.

The influence of oxidation reaction time on the amount of aldehyde content indicates that when Na-CMC samples were oxidized for 10 minutes, DCMC samples were obtained with 69% aldehyde content and a 60% product yield. At a solution temperature of 30°C, DCMC samples were obtained with an aldehyde content of 72% and a reaction yield of 65%. However, as the temperature increased, both the amount of aldehyde content and the product yield decreased.

The influence of solution pH on the amount of aldehyde content in DCMC samples and the reaction yield was studied. As the pH of the solution decreased, the amount of aldehyde content increased. DCMC samples were obtained with an aldehyde content of 75% and a product yield of 55% at pH 3.5.

Different concentrations of oxidant were studied during the oxidation reaction to determine their effect on the amount of aldehyde content and the reaction yield. Although the amount of aldehyde content increased with higher oxidant concentrations, the reaction yield decreased significantly. DCMC samples were obtained with 82% aldehyde content and a 58% product yield when the oxidant concentration was 2.5%, which was determined to be the optimal condition for the oxidation reaction of Na-CMC.

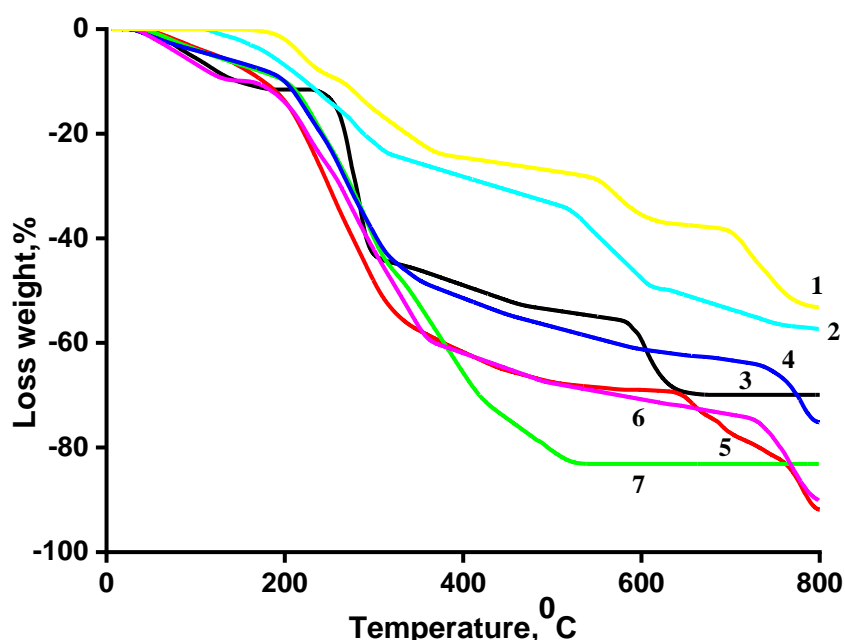
The functional groups and thermal stability properties of the obtained DCMC samples were studied using FTIR spectroscopic and thermogravimetric methods. The results are presented in Figure 2.



**Figure 2.** FTIR spectra of Na-CMC and DCMC samples.

1-Na-CMC, oxidized CMC samples with aldehyde content of 2-34%, 3-58%, 4-67%, 5-74%, 6-82%, 7-82%

The results presented in Figure 2 indicate that the spectrum of DCMC exhibited a new characteristic peak at  $1730\text{ cm}^{-1}$ , while the band around  $892\text{ cm}^{-1}$  was assigned to the formation of hemiacetal bonds between the aldehyde groups and neighboring hydroxyl groups. These findings suggest that the aldehyde group has been successfully introduced into the structure through the selective periodate oxidation of CMC.



**Figure 3.** Thermogravimetric analysis of Na-CMC and different aldehyde content DCMC samples.

1-Na-CMC, oxidized CMC samples with aldehyde content of 2-34%, 3-58%, 4-67%, 5-74%, 6-82%, 7-82%.

Figure 3 presents the results of the thermogravimetric analysis of CMC and DCMC at different aldehyde contents (34%, 58%, 67%, 63%, and 82%). As depicted in the figure, CMC exhibited rapid mass loss between  $275\text{--}325^\circ\text{C}$ , while DCMC showed rapid mass loss in the range of  $150\text{--}500^\circ\text{C}$ . Upon heating above  $325^\circ\text{C}$ , the mass of CMC gradually stabilized,

whereas for DCMC, the mass loss slowed down as the temperature increased above 400°C. Additionally, the decomposition temperature of DCMC decreased with increasing aldehyde content. This observation suggests that the thermal stability of DCMC is weaker than that of CMC and tends to decrease with increasing aldehyde contents, consistent with findings in the literature [14]. It is known that chemical modification of cellulose significantly alters its thermal decomposition behavior compared to unmodified cellulose. This phenomenon is attributed to the destruction of the crystal structure in CMC after oxidation to DCMC, facilitating thermal scission of covalent bonds and leading to the generation of volatile substances [15].

### Conclusion

In conclusion, the oxidation of Na-CMC to DCMC was investigated under various conditions, including reaction time, temperature, solution pH, and oxidant concentration. It was observed that the amount of aldehyde content increased with longer reaction times but decreased after 10 minutes, indicating an optimal reaction duration. Similarly, the temperature and pH of the solution played crucial roles in determining the aldehyde content and reaction yield of DCMC. Higher temperatures led to decreased aldehyde content and reaction yield, while lower pH values resulted in increased aldehyde content. Furthermore, the concentration of the oxidant influenced the aldehyde content and reaction yield, with higher concentrations leading to increased aldehyde content but decreased reaction yield.

The characterization of DCMC through FTIR spectroscopy and thermogravimetric analysis revealed the successful introduction of aldehyde groups into the structure. FTIR analysis showed a characteristic peak at 1730 cm<sup>-1</sup>, indicating the presence of aldehyde groups, while thermogravimetric analysis demonstrated changes in thermal stability with increasing aldehyde content. DCMC exhibited lower thermal stability compared to CMC, attributed to the destruction of the crystal structure and thermal scission of covalent bonds.

Overall, this study provides valuable insights into the oxidation process of Na-CMC to DCMC and its implications for the modification of cellulose-based materials for various applications. Further research could focus on optimizing reaction conditions to enhance the yield and properties of DCMC for specific industrial applications.

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