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# The Evaluation of Performance Properties of CMC-Based Copolymer Hydrogels Reinforced with Cellulosic Fibers Subjected to Stepwise Chemical and Mechanical Pretreatments: Moderate Alkaline Oxidation Treatment*

# Kademeli Kimyasal ve Mekanik Ön İşlemlerden Geçirilmiş Selülozik Liflerle Güçlendirilen CMC Bazlı Kopolimer Hidrojellerin Performans Özelliklerinin Değerlendirilmesi: Ilımlı Alkali Oksidasyon Uygulaması

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## Abstract

In this study, mechanical refining and alkaline oxidation pretreatments were applied to cellulose reducing the side effect of it on hydrogel performance. In addition to moderate oxidation with hydrogen peroxide at 80°C, mechanical treatment was performed using PFI or supermasscolloider. The effectiveness of epichlorohydrin and citric acid as crosslinkers for hydrogel formation was investigated separately. The liquid absorption capacity, water uptake and swelling ratios of the produced hydrogels were measured and evaluated. The structural, morphological and thermal properties of the hydrogels were analyzed using FTIR, SEM and DSC. IR spectrum revealed that the interactions with both crosslinkers were effective. Although hydrogels with 10% cellulose ratio and cross-linked with citric acid can absorb liquid up to 50 times the initial mass, the overall performance of the samples produced with epichlorohydrin was found to be superior. SEM images showed that the porosity of the hydrogel decreased and the surface closedness increased in the samples with citric acid. These phenomena were considered as a reduction in diffusion of liquids and absorption capacity.

**Keywords:** Hydrogel, CMC, alkaline oxidation, supermasscolloider refining, PFI refining

## Özet

Bu çalışmada, selülozun hidrojelin performans özelliklerinde yan etkilerini azaltmak için selüloza mekanik rafinasyon ve alkalin oksidasyon ön işlemleri uygulanmıştır. $H_2O_2$ ile 80°C'de ılımlı oksidasyonun yanında, mekanik işlemler PFI veya supermasscolloider ile gerçekleştirilmiştir. Hidrojel üretiminde çapraz bağlayıcı olarak epiklorohidrin ve sitrik asidin etkinliği ayrı ayrı incelenmiştir. Üretilen hidrojellerin sıvı emme kapasitesi, su alma ve şişme oranları üzerinden değerlendirilmiştir. Hidrojellerin yapısal, morfolojik ve termal özellikleri FTIR, SEM ve DSC ile belirlenmiştir. IR spektraları, çapraz bağlayıcılar ile hidrojel sentezinin başarılı olduğunu göstermiştir. %10 selüloz içeren ve sitrik asit ile çapraz bağlanmış hidrojeller başlangıç kütlesinin 50 katına kadar sıvı absorbe etmesine rağmen, epiklorohidrin ile üretilen örneklerin performansının daha üstün olduğu görülmüştür. SEM görüntüleri, sitrik asit ile sentezlenen örneklerde gözenekliliğin azaldığını ve yüzey kapalılığının arttığını bu durumunda difüzyon ve absorpsiyon kapasitesinde azalmayla sonuçlandığı değerlendirilmiştir.

**Anahtar Kelimeler:** Hidrojel, CMC, alkali oksidasyon, süpermaskolloider rafinasyonu, PFI rafinasyonu

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# 1. Introduction

Hydrogels, which are three-dimensional cross-linked polymer, are an important industrial intermediate product attracting attention with their behavior in water or other liquids. They are used in the fields of food, hygiene, cosmetics, pharmaceutical, agricultural, and biomedical products. Compared to their own mass, they have the capacity to hold several hundred times more liquid (Chen et al., 2010). The number of hydrophilic functional groups carried by the polymer backbone is important in this regard (Esposito et al., 1996). An ideal hydrogel is expected to have high gelation resistance and liquid absorption capacity, high biocompatibility, and low environmental impact.

Petroleum-derived (synthetic) polymers are more preferred for hydrogel production. They have significant advantages, such as superior swelling performance in water or various liquids compared to natural polymers, price advantage, product range diversity, and easy availability. However, in today's world of sustainability and environmental impact, researchers are looking for alternatives to synthetic polymers. In general, synthetic polymers also have significant disadvantages in terms of biocompatibility. Nanocellulose (NCC) (Kelly et al., 2013), nanofibrillated cellulose (NFC) (O-chongpian et al., 2021), carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC), methylcellulose (MC), microcrystalline cellulose (MCC), or their derivatives are used for hydrogel production (Fekete et al., 2014).

Due to its superior hydrophilicity, CMC is one of the best natural polymers with properties such as biocompatibility and the ability to hold large amount of liquids. However, CMC does not show sufficient gel resistance due to behaviors such as dispersion and dissolution in liquids (Eldin et al., 2013). In order to overcome the problem of insufficient binding organization, stronger crosslinkers such as glutaraldehyde, epichlorohydrin (ECH) or citric acid (CA) are preferred, or various additives are used to hold the hydrogel together (Nasution et al., 2022). However, it is inevitable that the crosslinking agents used have a negative effect on biodegradability and increase the resistance of the gel. Therefore, studies are being carried out on the synthesis of copolymer hydrogels using additives that reduce the amount of crosslinker. It is known that polymers such as chitosan, alginate, poly-N-isopropylacrylamide, polyacrylamide, poly(vinyl alcohol), polyaniline and cellulose (in the form of fibers or micro/nanoscaled) are used for this purpose (Ren et al., 2016; Wang & Wang, 2016; Li et al., 2017; Godiya et al., 2019; Su et al., 2020; Feng et al., 2021; Uyanga & Daoud, 2021).

Cellulose, which is the raw material of different industries such as the paper industry, textiles, biofuels, food, cosmetics, and pharmaceutical industries, stands out as a suitable starting material for hydrogels thanks to its abundant availability in nature, renewable and biodegradable. However, when natural cellulose (cellulose I) is used directly to make hydrogels, it results in a product with very limited absorption of liquids due to some structural defects such as crystalline domains and complex intracellular and intercellular hydrogen bonding structure. So, it needs to be modified to cellulose-based polymers with different properties before hydrogel production. Nevertheless, there is another issue that should be noted at this point, the studies show that as the amount of cellulose in copolymer hydrogels increases, the liquid absorption capacity of the hydrogel decreases (Esposito et al., 1996).

Using different types of modification, like mechanical, chemical, biological, or thermal, on native cellulose can make it better for making hydrogels (Laine et al., 2004; Cabiac et al., 2011). These methods modify the physical and chemical structure of cellulose, thereby increasing its reactivity with water and other chemicals (Liebert, 2010; Li et al., 2012). Mechanical processes such as beating and refining change internal delamination of the cell wall structure. Also they increase the specific surface area of cellulosic fibers, shorten the fiber size, peel off the S1 layers of the primary wall and secondary wall with limited reactivity, and increase the number of functional groups. However, if its liquid absorbency is to be increased, the studies have shown that the degree of refining should be kept low (Hubbe et al., 2013). On the other hand, alkaline treatments applied under moderate conditions affect the network structure consisting of hydrogen bonds; swelling of the fiber is achieved, the surface morphology of the fiber changes (a more permeable structure is obtained), polymorphic transformations take place (cellulose I to cellulose II transformation), and the degree of polymerization decreases. Furthermore, carboxyl (COOH) groups can be increased in the cellulose chain by oxidation of cellulose in alkaline environment (Knill and Kennedy, 2003). In oxidation of cellulose, hydrogen peroxide is preferred because of the easy use and limited environmental effects. Thanks to the synergistic effects of all these treatments, it is inevitable to increase the reactivity and accessibility of cellulose.

In this study, which focuses on the synthesis of CMC-based copolymer hydrogels, one- and two-step pretreatments were applied to cellulose as an additive in the copolymer hydrogel and the effects of pretreatments to the performance properties of hydrogels were investigated. For this purpose, cellulose was subjected to oxidation with hydrogen peroxide

($H_2O_2$) under mild alkaline conditions and mechanical pretreatment with PFI mill and supermasscolloider (SMC). The pretreated cellulose was mixed with CMC and hydrogel synthesis was carried out in a reaction medium using ECH or CA as crosslinker. The physical, chemical, thermal and morphological properties of the obtained hydrogels were investigated.

## 2. Material and Method

### 2.1. Material

The characteristics of 100% bleached spruce sulfite wood pulp utilized in this research, supplied by Borregard (Norway), were 924 $ml.g^{-1}$ of Intrinsic Viscosity (ISO 5351:2004); ≤ 1 of Kappa Number (TAPPI T 236 om-13); 93.1 of Brightness (ISO 2470:2009); 95.2% of Alpha Cellulose (TAPPI T203 cm-99); 5.8% of Alkali Solubility S10 (TAPPI T 235 cm-00); 3.3% of Alkali Solubility S18 (TAPPI T 235 cm-00) which are detailed in previous studies (Büyüküstün et al., 2025). The COOH content of the pulp was determined according to the research conducted by Milanovic et al. (2012) as 0.1269 mmol/g. The freeness of the pulps, as measured by SCAN C-15:62 standard, is 12 °SR. The water retention value (WRV) of the pulp was established at 88.4% according to the research by Chen et al. (2010). Sodium carboxymethyl cellulose (CMC-Na) (Mw ~ 700,000), utilized in this investigation, was acquired from Sigma Aldrich (DS: 0.80-0.95). All additional compounds were procured from Merck KGaA or Sigma Aldrich and utilized without any modification.

### 2.2. Method

#### 2.2.1. Pretreatments for Modification of Cellulosic Fibers

Chemical pretreatments were applied alone or sequentially with mechanical pretreatments in order to increase the reactivity and accessibility of cellulose.

a. Chemical pretreatments

For this purpose, $H_2O_2$ oxidation in moderately alkaline medium was performed without any mechanical processes before or after the oxidation. In this step, a mini optimization was performed using NaOH (3.0% w) and $H_2O_2$ (5.0, 10.0 or 15.0% w) for a 10% suspension of cellulose (75.0 g, oven-dry). The prepared suspension was oxidized in a water bath at 80°C for 180 minutes. After oxidation, the mixture was washed on a 150-mesh screen with distilled water until neutralized. The samples on the screen were collected, squeezed well, placed in a sealed bag, and stored in a refrigerator operating at +4°C.

WRV and -COOH content values of the pulps that were oxidized in alkaline medium were determined based on the previously described methods. The WRV values of the pulps oxidized with 5.0% and 15.0% $H_2O_2$ were the same (112.5%). On the other hand, the pulp oxidized with 10.0% $H_2O_2$ resulted in a higher WRV compared to these two pulps (113.7%). While the highest results were obtained in terms of -COOH content by applying 10.0% $H_2O_2$ (0.1344 mmol/g), it was determined that a 0.1120 mmol/g value was reached when the peroxide amount was applied at 5.0% and a 0.1216 mmol/g value was reached when the peroxide amount was increased to 15.0%. According to these results, it is seen that 10.0% $H_2O_2$ gives the best results; therefore, in the following stages of the study, only these conditions were used for alkaline oxidation.

b. Mechanical Methods

For mechanical refining, the PFI mill and the Masuko supermassocolloider (Model: MKCA6-2J, SMC) were used to refine the fibers to the micro-/nano-scale.

PFI Refining: In many recent studies, the term of beating has been replaced by refining. For this reason, the application carried out within the scope of this study is called refining. It was carried out in a two-roller laboratory-type PFI mill at 4000 rpm at 10.0% pulp concentration in accordance with TAPPI T248 sp-15 standard.

SMC Refining: Cellulose was refined using a SMC with one fixed and one rotating $Al_2O_3$ stones (80.0 grit coarseness). For refining, the gap between the stones was set to 20 µ and passed between the stones 5 times to obtain the desired dimensions. The rotation speed of the stones was set at 1500 rpm, and the working concentration was kept at 2.0%.

### 2.2.2. Synthesis of Hydrogels

The first sample group is the control group. No pretreatment was applied to the pulps in this group and hydrogel synthesis was carried out using raw cellulose and CMC. The second sample group is the sample group in which only chemical pretreatments were applied to the cellulose. For these samples, hydrogel synthesis was started after oxidation was completed. No mechanical treatment was applied to this sample group. In the third and last sample group, chemical and mechanical pretreatments were applied to cellulose. Here, the chemical and mechanical pretreatments were switched and their effects on the fibers were also studied. The process variables for hydrogel synthesis are summarized in Table 1.

**Table 1.** The variables of process for the preparation of Cellulose/CMC copolymer hydrogels

| **Type of Variable** | **Process Variables** | | | | | |
|---|---|---|---|---|---|---|
| Crosslinking agent | ECH | | | CA | | |
| Cellulose Content in Hydrogel | %10 | | %30 | | %50 | |
| CMC Ratio in Hydrogel | %90 | | %70 | | %50 | |
| Pretreatment of Cellulose | Never pretreated | Just alkaline oxidation | PFI after alkaline oxidation | Alkaline oxidation after PFI | SMC after alkaline oxidation | Alkaline oxidation after SMC |

The coding of the samples is based on the abbreviation of the crosslinking agent type (ECH or CA), of the pre-treatment type (**Control** for raw cellulose, **Soda** for only alkaline oxidation, **Soda PFI** for treatments in the first stage: alkaline oxidation, in the second one: PFI refining, **PFI Soda** for treatments in the first stage: PFI refining, in the second one: alkaline oxidation, **Soda SMC** for treatments in the first stage: alkaline oxidation in the second one: SMC refining and **SMC Soda** for treatments in the first stage: SMC refining in the second one: alkaline oxidation), and of the cellulose content in hydrogel (for examples: **ECH Control 30**, **CA PFI Soda 10**).

### 2.2.2.1. Hydrogel synthesis with ECH

Hydrogel synthesis with ECH was carried out in two steps. Initially, 195.0 ml of a solution comprising 6.0%wt NaOH, 4.0%wt urea, and 90.0 %wt filtered water was prepared. A homogeneous blend of cellulose (raw or pretreated) and CMC was included into this solution. The concentration of cellulose in the suspension was adjusted as 10.0-90.0%, 30.0-70.0% and 50.0-50.0% by weight ensuring the total mass of the hydrogel remained below 5.0 grams. A mechanical mixer operating at 200 rpm was run for 10 minutes to homogenize the prepared suspension, then it was left to freeze at -20°C for 12 hours. The frozen substance was allowed to thaw and homogenized using IKA Ultraturrax at 10000 rpm for 15 minutes. At the end of this homogenization process, cellulose-CMC solution was obtained.

In the subsequent step, 25.0 ml of ECH and 25.0 ml of ammonium hydroxide ($NH_4OH$) were added to the solution for the crosslinking reaction. The reaction was carried out at 40°C for 4 hours. After the time, the hydrogel was immersed in ethyl alcohol to conclude the crosslinking procedure. The hydrogel was subsequently rinsed with deionized water using a 150-mesh screen.

#### 2.2.2.2. Hydrogel synthesis using citric acid

Unlike the ECH hydrogel synthesis, this was carried out in a single step. Cellulose (raw or pre-treated) was dispersed in some deionized water with a mechanical mixer running at 200 rpm for 10 min. CMC was added to the pulp suspension and vigorously mixed using an IKA Ultraturrax at 15000 rpm for 15 min. The concentration of cellulose in the suspension was adjusted as 10.0-90.0%, 30.0-70.0% and 50.0-50.0% by weight ensuring the total mass of the hydrogel remained below 5.0 grams. The suspension of cellulose and CMC was diluted with deionized water to a concentration of 2.0%wt, followed by the addition of 5.0%wt citric acid to the total mass. The resulting high viscosity mixture was poured into a beaker and kept at 30°C for 24 hours until the water was removed. To complete the cross-linking reaction, it was kept in a water bath at 80°C for 24 hours. After the time, the hydrogel was immersed in ethyl alcohol to conclude the crosslinking procedure. The hydrogel was subsequently rinsed with deionized water using a 150-mesh screen.

### 2.2.3. Characterization of Hydrogels

#### 2.2.3.1. Determination of Swelling Properties

Hydrogels are often favored in fields such as biomedicine, hygiene products and diapers because of their superior liquid absorption ability. This ability is often determined by measuring the change in weight after immersion in liquids with different properties. In this study, pH 2, 7 and 10 solutions and the different salt solutions including NaCl, KCl, $MgCl_2$ and $NH_4Cl$ were used to swelling tests. Each salt solution was formulated at a concentration of 0.9%. Each salt (0.9 g) was diluted with water to a final volume of 100 ml. A hydrogel sample with an exact dry weight was fully immersed in a container containing the appropriate solution. The sample was kept in the liquid for 12 hours at room temperature. At the end of the time, excess liquid was removed from the sample. The rates of liquid absorption and swelling of the hydrogels were determined using the following formula:

$$\text{Liquid uptake (\%)} = m_1 - m_0 \qquad (1)$$

$$\text{Swelling rate (\%)} = (m_1 - m_0) * 100 / m_0 \qquad (2)$$

Here, it presents the mass of the hydrogel after immersion ($m_1$), while the mass of the sample before immersion is expressed by ($m_0$).

#### 2.2.3.2. Chemical Characterization

Based on the study by Erişir and Gümüşkaya (2024a), samples were prepared prior to FTIR spectroscopy analysis. For this purpose, the hydrogel samples were carefully ground in a Wiley mill. KBr-disks of the milled hydrogels were prepared before measurement. IR measurements of the samples were performed with a Schimadzu IRPrestige-21 instrument supported by a PIKE MIRacle ATR instrument. An operating range ranging from 4000 to 400 cm$^{-1}$ was used in the spectral examination and the spectral resolution was set to 4 cm$^{-1}$. The measurements were obtained from the hydrogel samples that gave the highest swelling rate in each experimental group.

#### 2.2.3.3. Morphological Characterization

The evaluations were performed on the hydrogel samples that exhibited the maximum swelling rate in each experimental group. The samples were studied using Jeol JSM-6060 and Zeiss Evo LS-10 electron microscopes at magnifications of 250X and 1000X. The operating voltage used for imaging was 5 - 15 kV. To assess the surface characteristics of the hydrogels, the samples were gold coated prior to imaging.

#### 2.2.3.4. Thermal Characterization

The thermal characteristics of hydrogels were established according to the research conducted by Erişir and Gümüşkaya (2024b). Before measurement, the air-dried materials were ground up in a Wiley mill and subsequently fractionated with 40 and 60-mesh sieves. The fraction of the samples retained on the 40-mesh sieve was utilized for thermal analysis. For each measurement, about 5-7 mg of the sample was placed in disposable aluminum crucibles. The thermal transformations of each hydrogel at different temperatures were monitored using a Netzsch DSC 200F3-Maia instrument. Measurements were conducted within a temperature range of 20-500°C, employing a heating rate of 10°C/min and a nitrogen flow rate of 30 ml/min. Each measurement was conducted three times, and the NETZCH Proteus Thermal Analysis software was employed to compute the average of the values obtained. Measurements were taken from the hydrogel samples exhibiting the maximum swelling rate in each experimental group.

## 3. Results and Discussion

CMC-based hydrogels exhibit problems related to dissolution and dispersion in various liquids. This study examined the impact of cellulose reinforcement on hydrogel performance to reduce the problems arising from low gelation resistance, particularly under pressure. Prior studies indicate that the liquid absorption capacity of the hydrogel increases with the concentration of CMC, which is attributed to the ionic groups of the sodium salt (Esposito et al., 1996). In other words, increasing the cellulose content in the hydrogel decreases its liquid absorption capacity. On the other hand, Lindström and Carlsson (1982) observed that the water absorption capacity of Kraft fibers increased as the pH level shifted from acidic to alkaline. Comparable results were observed for cellulose-reinforced copolymer hydrogels utilizing both ECH and CA as crosslinking agents (Figures 1 and 2). These findings suggest that pH level plays a significant role in the water absorption properties of materials incorporating cellulose fibers.

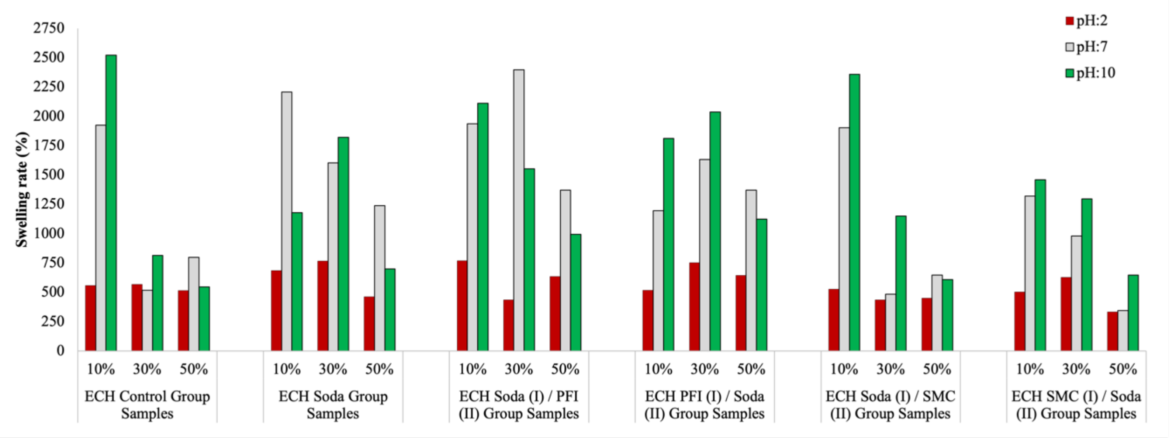

**Figure 1.** The changes in swelling ratios of CMC copolymer hydrogels reinforced with cellulose using ECH as crosslinker in liquids with different pH values.

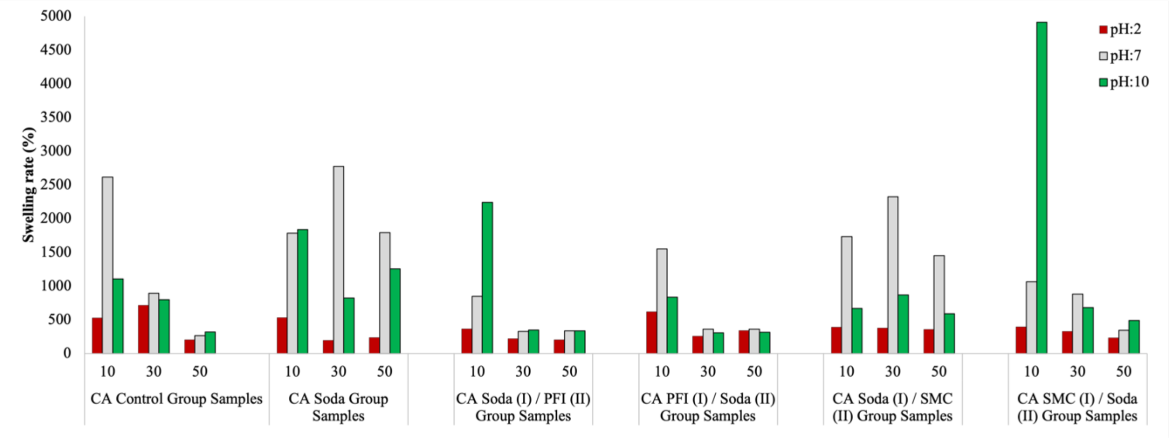

**Figure 2.** The changes in swelling ratios of CMC copolymer hydrogels reinforced with cellulose using CA as crosslinker in liquids with different pH values.

In certain groups of samples (e.g., ECH Soda 30%, ECH PFI(I)/Soda(II) 30%, CA Soda(I)/SMC(II) 30%), pretreatments positively influenced swelling results. It also indicates that the hydrogel's swelling performance in liquids is less influenced by cellulose reinforcement than in the control group. The incorporation of nanocellulose in the hydrogel adversely affects absorbency performance (Hubbe et al., 2013), while enhancing the mechanical strength of the gel (Spagnol et al., 2012). This phenomenon is attributed to the influence of nanoscale cellulosic particles acting like a binding agent (Karaaslan et al., 2011).

The comparison of copolymer hydrogels crosslinked with ECH in liquids of varying pH values revealed that they typically outperformed those crosslinked with CA. Notably, the most significant finding across all sample groups was identified in the CMC copolymer hydrogel (Citric acid SMC (I)/Soda(II) 10% cellulose reinforced) that was crosslinked with citric acid and reinforced with cellulose, which underwent moderate soda oxidation following mechanical treatment with a supercolloider at pH 10. This sample group demonstrated the capability to absorb up to approximately 50 times its initial mass. A study conducted by Esposito et al. (1996) established that this value may reach up to 400 times per gram of hydrogel.

The diluted solutions containing chloride salts of sodium, potassium, magnesium, and ammonium play a crucial role in the effective management of liquid waste categorized as medical and hazardous in healthcare settings. The effectiveness of the hydrogel employed to inhibit the spread of contamination becomes a critical consideration for public health when such liquids are accidentally released to any surface. The performance analysis of copolymer hydrogels in dilute saline solutions (Figures 3 and 4) indicates that the choice of crosslinker is crucial. The capacity of hydrogels to absorb liquids when using ECH as a crosslinker is notably greater than that of those synthesized with CA.

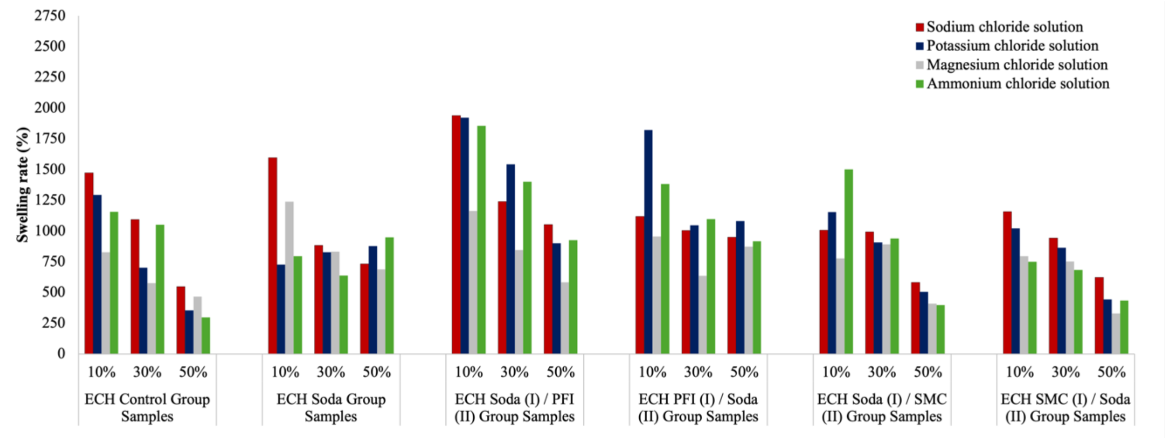

**Figure 3.** The changes in swelling ratios of CMC copolymer hydrogels reinforced with cellulose using ECH as crosslinker in various saline liquids.

In this study, it is projected that using the technique of mechanical and alkaline oxidation pretreatments to cellulose will result in modifications in the cellulose chain and potentially affect functional groups. This may lead to the formation of carboxylic acids, aldehydes, and ketones, which are expected to enhance the reactivity of the cellulose chain. FT-IR spectroscopy is crucial for identifying these functional groups. The spectrometry results for unreinforced and reinforced copolymer hydrogels are displayed individually in Figures 5 and 6, categorized by the type of crosslinker utilized.

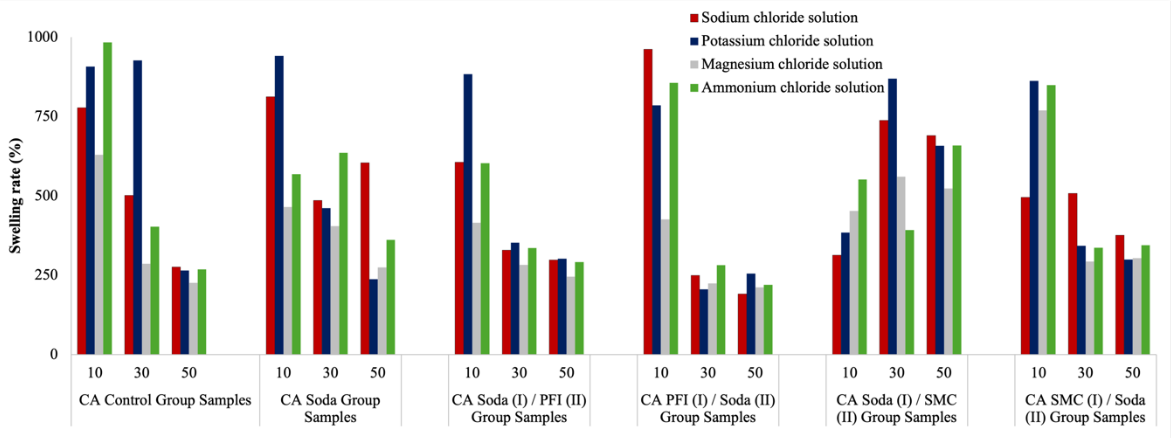

**Figure 4.** The changes in swelling ratios of CMC copolymer hydrogels reinforced with cellulose using CA as crosslinker in various saline liquids.

During the FTIR spectroscopic analysis, only the samples with the most significant swelling values were chosen from each group, instead of assessing all samples. The FTIR analysis of the copolymer hydrogels provided insights into the crosslinking reaction, hydrogen bonding interactions, and the performance variations among the hydrogels. The peak observed at 1041 $cm^{-1}$ corresponds to the -C-O- functional group and indicates a correlation between the degree of crosslinking and the structural framework of the hydrogel

(Cui et al., 2019; Kundu et al., 2022). The reduction in signal intensity suggests that the polymers within the hydrogel framework have been effectively crosslinked through chemical means (Zhao et al., 2016). The bands noted in the 1020 to 1160 cm$^{-1}$ range are linked to C-OH stretching vibrations on CMC (Wang et al., 2017). The peak with a shoulder around 1320 cm$^{-1}$ is associated with OH groups present in CMC (Qiu and Yu, 2008).

Another observation is the intensity noted in the 3000-3600 cm$^{-1}$ band of the samples, which is attributed to -OH groups (Buhus et al., 2009; Kurtuluş et al., 2024). For both crosslinkers, it is evident that the band intensity in this range, indicative of OH groups, diminished with copolymerization of cellulose and CMC. With the mechanical and chemical treatments applied to cellulose, the intensity of the bands was clearly reduced. Overall, it is observed that the intensity diminishes more consistently across the entire band range as a result of the refining process with SMC.

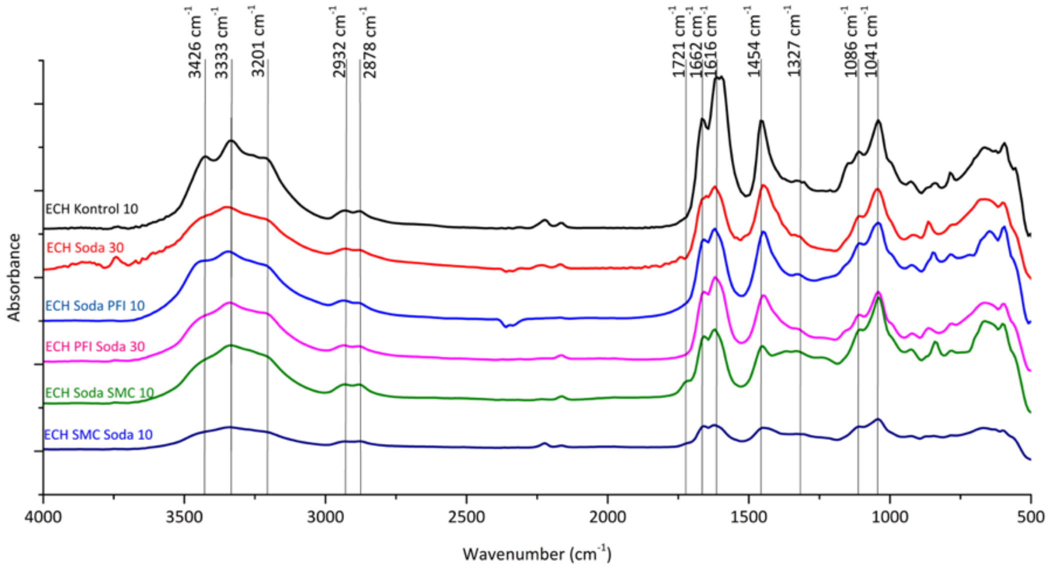

**Figure 5.** FTIR spectra of hydrogels synthesized through copolymerization with ECH.

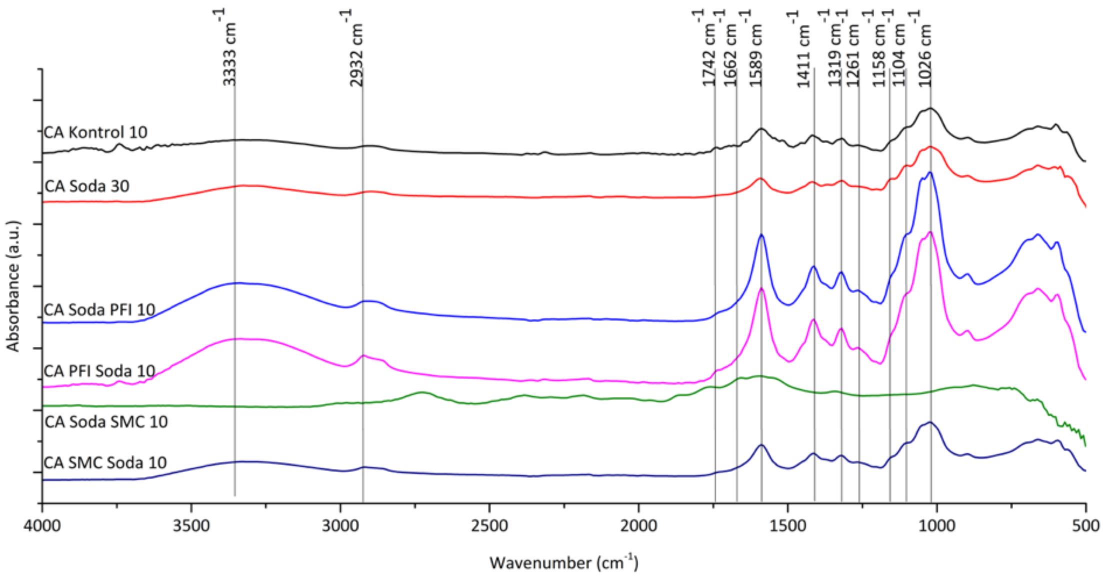

**Figure 6.** FTIR spectra of hydrogels synthesized through copolymerization with CA.

This phenomenon can be attributed to the physical cutting of the fibers, which are reduced to smaller sizes during the refining process with SMC (Motaung and Mokhotu 2016). Thus, the surface area of the fibers expands, leading to greater exposure of $OH^-$ groups, which enhances bonding and consequently results in a decrease in the intensity of the obtained bands. The characteristic vibrations at approximately 1614, 1596, and 1450 cm$^{-1}$ are ascribed to the COO- groups of CMC (Ma et al., 2007; Seki et al., 2014; Uyanga and Daoud 2021), indicating a correlation between the intensity of these peaks and the increased water absorption of the hydrogel (Barbucci et al., 2000). In the FTIR spectra of hydrogels synthesized via ECH, the band at 1660 cm$^{-1}$ overlaps with the bands near 1614 cm$^{-1}$. The band observed in the region of 1700-1750 cm$^{-1}$ is ascribed to ester groups (-C=O) (Kumar et al., 2019; Büyüküstün et al., 2025) and is not present in the spectra of cellulose and CMC (Seki et al., 2014).

Figure 7 displays the surface images of the copolymer hydrogels exhibiting the most significant swelling behavior. Upon evaluating the type of crosslinker utilized, it becomes evident that the surface regions of the hydrogels synthesized with CA exhibit a more closed structure. This clarifies how the swelling behavior in liquids differs, depending on the specific type of crosslinker used. Cracks and pores are clearly visible on the surface of the hydrogels produced with ECH. Previous studies have indicated that the capacity of hydrogels to absorb liquids rises as the surface area expands, attributed to the increase in pore quantity (Nasution et al., 2022). This suggests that the duration needed for the same volume of absorbed liquid will be reduced. A film that fully covers the surface is observed on the hydrogels synthesized using the crosslinking properties of CA. As the surface area and diffusion rate diminishes the liquid can slowly infiltrate from the exterior to the core. It is believed that the absorption of the liquid diminishes once the swelled hydrogel layer is established and fully envelops the surface (Hubbe et al., 2013).

In the images of hydrogel samples with CA examined at 1kx magnification, cellulosic fibers were clearly observable, but in the samples synthesized with ECH, they remained undetectable even at 10kx magnification. Moreover, as a result of the mechanical treatments applied to the samples, the compressed fibers can be observed in the images.

Similarly, SEM images of the CA Soda SMC 10 sample, which attracts attention with its superior liquid absorption capacity, show that the fibers are dispersed with a decrease in length compared to other samples. The effect of SMC, utilized in the production of microfibril cellulose and nanofibril cellulose, is anticipated. The PFI refining process demonstrated a notable decrease in the number of selectable fibers in comparison to the SEM images of the control group and the hydrogels including cellulose that underwent only alkali oxidation pretreatment.

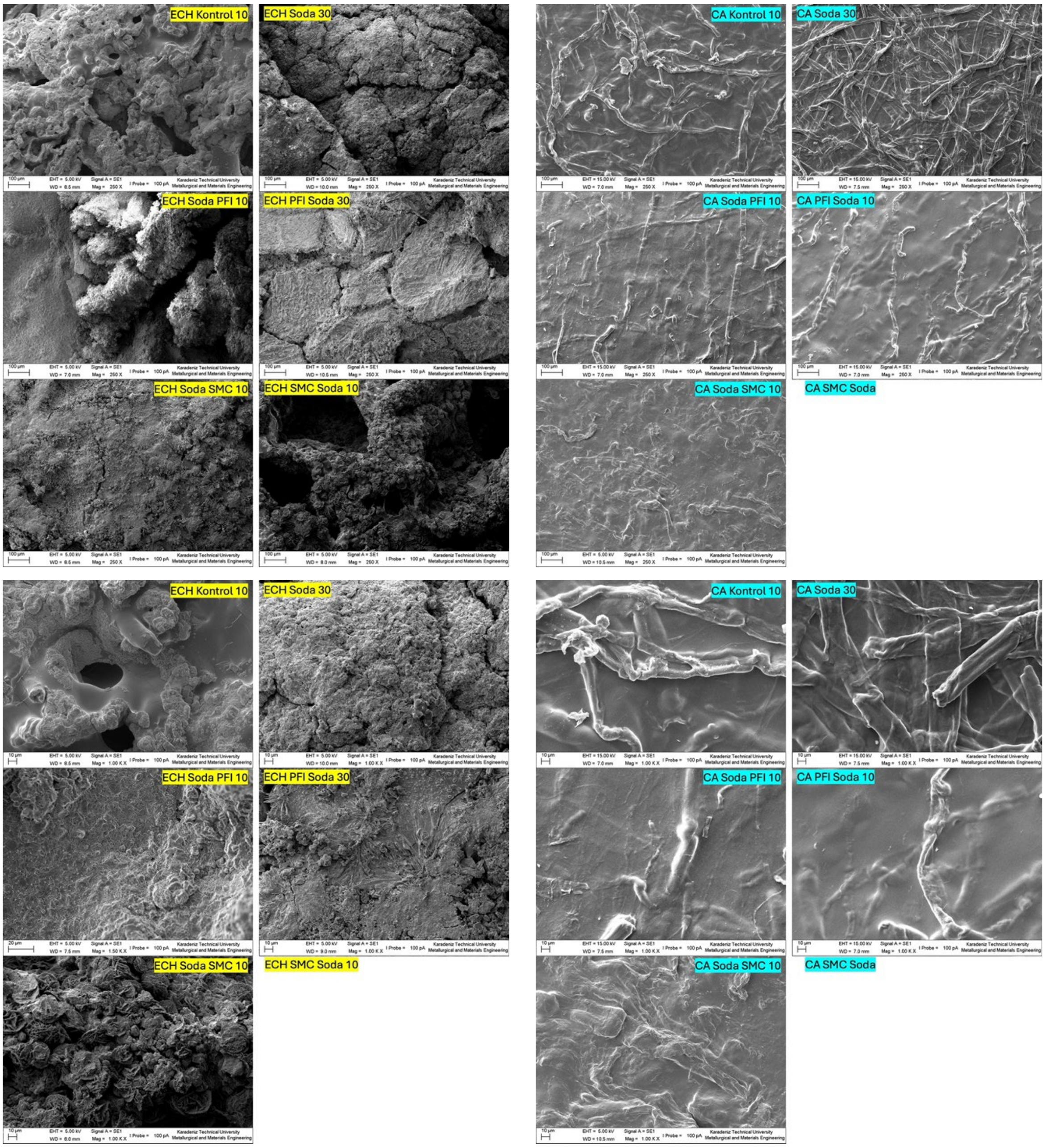

**Figure 7.** SEM images of hydrogels (250X magnification in the top row, 1000X magnification in the bottom row).

The thermal characteristics of the synthesized hydrogels were analyzed through DSC, and the resulting thermograms are presented in Figure 8. Thermal analysis was performed on the samples demonstrating the highest swelling rate. The energy absorption of the ECH PFI Soda 30 sample was determined to be superior to the other samples. The crystallinity of cellulose exceeds that of CMC crystallinity (He et al., 2009). Earlier studies indicate that crystalline regions function as obstacles in the process of heat transfer (Das et al., 2021). Based on these facts, it is reasonable to conclude that the energy absorption of the ECH PFI Soda 30 sample outperforms the other samples. Conversely, as illustrated in Figure

8, a different scenario was noted in the CA Soda 30 sample, which is one of the hydrogels created through crosslinking with CA.

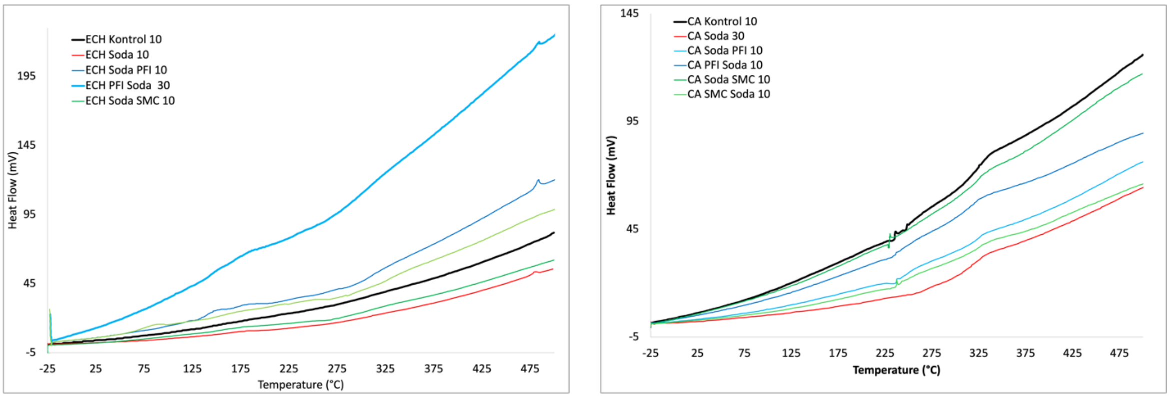

**Figure 8.** Thermograms from differential scanning calorimetry of hydrogels produced using ECH (left) or CA (right).

CA exhibits a notably lower performance as a crosslinking agent compared to ECH (Nasution et al., 2022). It was known that the crosslinking ratio influences thermal stability and various other properties (Bigi et al., 2001). Furthermore, CA has an adverse impact on the primary chains of cellulose polymers because of its acidic characteristics (Golor et al., 2020). Figure 8 distinctly illustrates that hydrogels begin to deteriorate around 225°C, accompanied by a reduction in energy absorption resulting from these adverse effects. No degradation changes were observed in the samples created under the influence of ECHin crosslinking.

## 4. Results

This study investigated the effect of cellulose reinforcement on the performance of CMC-based hydrogels to eliminate or reduce the problems caused by low gelation resistance, especially under pressure. Previous research shows that the liquid uptake capacity of the hydrogel increases with CMC concentration and decreases with cellulose concentration.

It was observed that there was a clear relationship between the cellulose content in the hydrogel content and the liquid absorption performance in accordance with previous studies. On the other hand, it was observed that the performance of cellulose as an additive can be slightly increased by the processes applied to cellulose. In summary, the effects of oxidation in alkaline environment without mechanical pretreatment were limited.

The overall performance properties of ECH crosslinked copolymer hydrogels were higher than those of hydrogels crosslinked by CA. In SEM images, hydrogels crosslinked with CA exhibited fewer pores and cracks, which explains the lower performance of the samples synthesized with this agent, especially the liquid uptake and swelling rate. However, the most remarkable finding among all sample groups was obtained with CMC copolymer hydrogel (CA SMC (I)/Soda (II) 10% cellulose reinforced) crosslinked with CA. In pH 10 liquid, this sample was able to absorb up to 50 times its mass of liquid. This value is comparable to that of superabsorbent (Hubble et al., 2013).

IR spectroscopic investigations provided insight into the cross-linking reaction, hydrogen bonding interactions and performance differences between the hydrogels. The characteristic vibrations in the region around 1614, 1596 and 1450 $cm^{-1}$ are attributed to the $COO^{-}$ groups of CMC and the decrease in the intensity of these bands is associated with crosslinking. In the SEM images, the changes occurring in the fibers were more clearly observed in the film-like structure of the hydrogels crosslinked by CA. In addition, the number of fibers that can be observed in the SEM images of these samples was significantly reduced in the mechanically treated samples. Also, it was observed from the SEM images that the effect of refining with PFI was less than that of refining with SMC. In the SEM images of ECH cross-linked hydrogels, it was observed that the samples had a sponge-like structure and there was a relationship between this structure, which facilitated the liquid penetration of the hydrogel, and the liquid uptake and swelling performance. The thermal stability of the hydrogels was investigated using DSC and it was observed that there was a relationship between the energy absorption of crosslinking agent samples and cellulose concentration. On the other hand, the effects of citric acid on cellulosic polymers due to its nature were found to have an impact on thermal stability.

Although the effects of chemical and mechanical treatments on cellulose have already been studied in the literature, it is recommended that future studies include crystallographic analyses to better understand the effects of hydrogels on performance parameters.

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