The Oxidative Pretreatments of Cellulose for Cellulosic Superabsorbents

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Received date: 01.11.2019  Accepted date: 10.12.2019


Abstract: Cellulosic superabsorbents (SAP) are produced by using cellulose and cellulose derivative blends with different binding methods, generally. But cellulose in SAP leads decrease in water absorption and water bonding ability because of nonreactive character of cellulose based on its chemical structure. The oxidative pretreatments of cellulose were attempted for the resolve of disadvantage of cellulose in SAP, in this study. Hydrogen peroxide and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) were used for oxidative pretreatments of cellulose. Oxidized cellulose and carboxymethylcellulose (CMC) blended and cross-linked by epichlorohydrin for cellulosic SAP production. Water absorption capacity of cellulosic SAP were determined in pH:2, 7 and 10. The results show that the oxidative pretreatments of cellulose had affirmative effect of water absorption capacity of cellulosic SAP according to control samples.

Keywords: Cellulose, carboxymethylcellulose, crosslinking, epichlorohydrin, superabsorbents.

SELÜLOZİK SÜPERABSORBENT ÜRETİMİNDE OKSIDATİF ÖN İŞLEMLER

Öz: Selülozik superabsorbent (SAP) üretiminde genelde selüloz ve selüloz türevi farklı oranlarda karıştırılarak kullanılmaktadır. Ancak kullanılan selüloz oranı arttıkça selülozu kimiyasal yapısına bağlı olarak superabsorbentlerin su alma ve absorplama kapasitesi azalmaktadır. Bu çalışmada selüloza uygulanan oksidatif ön işlemlerle bu olumsuz etkini azaltılması amaçlanmıştır. Selülozu oksidasyon reaksiyonları için hidrojen peroxide ve TEMPO (2,2,6,6- tetramethylpiperidine-1-oxyl) kullanılmıştır. Okside selüloz ile karboksimetil selüloz epiklorohidrinin çapraz bağlıma yöntemi ile işleme tabi tutularak superabsorbentler üretimiştir. Üretilen selülozik SAP'ların su alma ve absorplama kapasiteleri pH:2,7 ve 10 koşullarında test edilmiştir. Kontrol örnekleriyle yapılan karşılaştırmalarda selüloza uygulanan oksidatif ön işlemlerin SAP’ların su alma kapasitelerinde olumlu etki gösterdiği tespit edilmiştir.

Anahtar sözcükler: Çapraz bağlıma, epiklorohidrin, karboksimetil selüloz, selüloz, süperabsorbent.
INTRODUCTION

Superabsorbent hydrogels (SAP) are three-dimensional cross-linked hydrophilic polymers with the ability to absorb large quantities of water, saline or physiological saline solutions compared to ordinary absorbing materials (Chang et al., 2010). They are able to absorb water and other liquids tens to thousands times their own weight in a relatively short time. They can also retain a swollen state even under some pressure. They have superabsorbent properties conferred by their hydrophilic groups or domains. Given all these advantages, superabsorbent polymers are widely applied in various fields, such as in hygiene, medicine, nutrition, petrochemistry, agriculture, and horticulture (Sannino, 2009; Wu et al., 2012).

Most of the current SAPs available commercially are synthetic polymers based on acrylic acid or acrylamide, which are expensive, poorly degradable and harmful to the environment (Khoo et al., 2014). Some natural resources such as polysaccharides and inorganic clay minerals have also been used to produce superabsorbent polymers (Li et al., 2012). Cellulose and its derivatives is often used in the biomedical field, and cellulose-based superabsorbents (cel-SAP) have been prepared using radiation-induced and chemical crosslinking. (Rémond et al., 2010). In previous studies, it was determined that the main drawback of cel-SAPs is the decrease in swelling rate depend on cellulose content increases in cel-SAP (Bao et al., 2011; Chang et al., 2010; Hubbe, 2013).

In this study, it was aimed to be minimize the negative effect of high cellulose content in cel-SAP on swelling rate by using hydrogen peroxide and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) oxidative pretreatments of cellulose.

MATERIAL and METHODS

Materials: Spruce dissolving pulp was used as cellulose resource. Alpha cellulose content, Kappa no and DP of spruce dissolving pulp were determined 95.2%, ≤1 and 1406, respectively. Carboxymethylcellulose (CMC) was used as Mw: 700000. Epichlorohydrin (ECH), NaOH, urea, hydrogen peroxide and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) were obtained as analytical-grade.

Methods

Oxidative Pretreatments of Cellulose: Hydrogen peroxide and TEMPO were used for oxidative pretreatments of cellulose (spruce dissolving pulp). Hydrogen peroxide, NaOH (o.d. dry pulp) and pulp consistency were selected as 10%, 3% and 10%, respectively. Temperature and pretreatment time were applied with 80 °C and 180 min, respectively.

Cellulose sample (5 g) was dispersed in water (375 mL), containing TEMPO (0.0625 g) and sodium bromide (0.625 g). TEMPO mediated oxidation was applied by adding NaClO solution containing 5 mmol NaClO to the cellulose suspension at room temperature. The cellulose suspension was stirred at pH 10 by continuous addition of 0.5 M NaOH. The TEMPO-oxidized cellulose thus obtained was washed thoroughly with ethanol by filtration (Puangsin et al., 2013).

Preparation of cel-SAP: Untreated cellulose (UC) and oxidative pretreated cellulose (OPC) solutions were prepared as follows: 5 g spruce dissolving pulp cellulose samples (UC and OPC) were suspended into 195 g of 6 wt% NaOH/4 wt% urea/90 wt% water mixture with stirring and then was stored under refrigeration (-20 °C) for 12 h. The frozen solid was thawed and stirred with IKA Ultraturrax at 10000 rpm at room temperature to obtain a transparent cellulose solution. CMC was dissolved in the same solvent to obtain a polymer concentration. ECH and NH₂OH (25 ml) was added to the mixture as cross-linker, stirred at 40 °C for 4 h to obtain a homogeneous solution, and to prepare hydrogels. Cellulosic hydrogels were washed with ethanol and water to obtain hydrogels (Chang, 2010). The conditions of cel-SAP preparation are presented in Table 1.

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<th>Table 1. Cel-SAP preparation conditions.</th>
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<td>Cellulose (%)</td>
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Determination of Water Absorption Capacity: The synthesized cel-SAPs were immersed in water at constant room temperature (25 °C) for 12 h. Water absorption capacity and swelling in acidic, alkaline and neutral conditions of cel-SAPs was determined by adjusting the water to pH 2, 7 and 10. Cel-SAPs were filtrated to remove excess distilled water. Water absorption capacity was calculated by the following equation:

\[ \text{WAC} = \frac{(M_2 - M_1)}{M_1} \]  

Where, M₁ and M₂ are the mass of the dried and swollen sample, respectively. The WAC value was calculated as grams of water per gram of sample.

SEM Analysis: Surface properties of superabsorbents were investigated by scanning electron microscopy images (Jeol JSM-6060- Zeiss Evo LS-10). Cel-SAP sample were coated with Au before SEM observation.

RESULTS and DISCUSSION

Water Absorption Capacity of Cel-SAPs: Cel-SAPs were prepared cellulose and CMC at different ratios (10/90, 30/70 and 50/50) by using ECH crosslinking method, as can
be seen in Table 1. HCl (pH:2) and NaOH (pH:10) were used for acidic and basic adjustment, before water absorption capacity determination. The results of water absorption capacity in distilled water at 25 °C for cel-SAPs which were prepared with untreated cellulose (UC) and CMC mixture are presented in Figure 1.

The results of water absorption capacity in distilled water at 25 °C for cel-SAPs which were prepared UC and CMC mixture are presented in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Water Absorption Capacity of Cel-SAPs which were prepared UC and CMC mixture.

It was determined that water absorption capacity of cel-SAPs increased evidently with an increase CMC content in cel-SAPs. CMC has highly hydrophilic carboxyl group. These groups could absorb to enhance WAC of cel-SAPs (Wüstenberg, 2015). As can be seen in Fig 1, high UC content in cel-SAPs had negative effect on WAC of hydrogels. Chang et al., (2010) studied on water absorption capacity of cellulose/CMC hydrogel. They found that the highest WAC for cellulose /CMC (90/10) hydrogel was 1000% after immersing in distilled water for a week at 25 °C. CMC is a polyelectrolyte, which shows sensitivity to pH and ionic strength variations. Indeed the presence of CMC in a cellulose-based hydrogel provides the hydrogel itself with electrostatic charges anchored to the network, which have a double effect on the swelling capability. On one side, the electrostatic repulsion established between charges of the same sign forces the polymer chains to a more elongated state than that found in a neutral network, thus increasing the swelling. On the other, the counterions that are present in the gel to ensure macroscopic electrical neutrality induce more water to enter the network (Sannino, 2009).

WAC ratios of cel-SAPs which were prepared with hydrogen peroxide treated cellulose (HP-PC) and CMC mixture are presented in Fig 2. The results showed WAC in distilled water at 25 °C of cel-SAPs increased for pH:2 and pH:7, when it decreased for pH:10. Wu et al., (2012) investigated the absorption capacity of cellulose superabsorbent composites in various solutions between pH:1 and pH:13. They found that absorption capacity of SAP composite was lower at pH:1 and pH:13 than neutral pH. They explained this finding that the screening effect of the Na+ counterions in the swelling medium led to decreased water absorption in highly alkaline solutions. WAC ratio found higher at 30% HP-PC content in cel-SAP than other HP-PC contents for pH:2 and pH:10, in this study.

TEMPO oxidative pretreatment applied to spruce pulp samples (T-PC), after blended with CMC at different ratios. Cel-SAPs formed T-PC and CMC mixture produced with epicholohydrin crosslinking method. WAC of cel-SAPs which formed T-PC and CMC mixture are presented in Fig 3.

![Figure 2](image2.png)

**Figure 2.** Water Absorption Capacity of Cel-SAPs which were prepared HP-PC and CMC mixture.

![Figure 3](image3.png)

**Figure 3.** Water Absorption Capacity of Cel-SAPs which were prepared T-PC and CMC mixture.

As can be seen in Fig 3, It was determined TEMPO oxidation pretreatment had more effective on WAC of cel-SAPs than hydrogen peroxide pretreatment. Saito & Isogai, (2004) found that crystallinities and crystal sizes of cellulose I were nearly unchanged during the oxidation, and thus, carboxylate and aldehyde groups were introduced selectively on crystal surfaces and in disordered regions of the water-insoluble fractions. Water retention values of cotton linter could be increased from 60% to about 280% through the introduction of hydrophilic carboxylate groups and morphological changes from fibrous forms to short fragments by the TEMPO-mediated oxidation.

**SEM Analysis:** SEM photos of cel-SAPs which were formed UC, HP-PC and T-PC, and CMC are presented in Fig 4. SEM photos showed that its surface were uneven and wide surface area. It was determined that surface SEM
photos of cel-SAPs were changed with oxidative pretreatments (hydrogen peroxide and TEMPO) of cellulose. It can be said that the ECH crosslinking mechanism between cellulose and CMC changes according to oxidative pretreatments.

Figure 4. SEM photos of cel-SAPs (A) which were prepared UC and CMC mixture, (B) which prepared HP-PC and CMC mixture, (C) which were prepared T-PC and CMC mixture.
CONCLUSION

It was determined that spruce dissolving pulp had affirmative effect on cel-SAPs compared to previous studies. TEMPO pretreatment had more effective on WAC at pH:7 of cel-SAPs than hydrogen peroxide pretreatment, but not at acidic medium (pH:2). It was found that WAC at basic medium (pH:10) of cel-SAP decreased with TEMPO and hydrogen peroxide pretreatments of cellulose.

ACKNOWLEDGEMENTS

The Authors wish to thank The Scientific and Technological Research Council of Turkey for financial support (Project No: TUBITAK TOVAG 215O313).

REFERENCES


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