Effect of Crosslinker Concentration and Drying Method in Cellulose Nanofiber Hydrogel Formulation for Controlled-release Application

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ABSTRACT

Kenaf-derived cellulose nanofiber (KCNF)–CMC hydrogels were formulated using citric acid as a natural crosslinker to evaluate the effects of formulation and drying conditions on their swelling behaviour. Two formulations were prepared: one with a higher citric acid concentration (3.75%) and dual stage curing at 30 °C and 80 °C, and another with a lower concentration (1.75%) cured at 50 °C, followed by oven or freeze drying. The oven-dried hydrogels were dense and sturdy, while the freeze-dried hydrogel was porous and cotton-like. Swelling tests showed that the oven-dried hydrogel with higher crosslinking exhibited the greatest stability, maintaining over 4000% swelling after 24 hours, whereas the others disintegrated after prolonged immersion. These findings indicate that citric acid crosslinking combined with controlled thermal curing produces a robust and stable CNF–CMC hydrogel suitable for further development as a sustainable matrix for controlled-release applications.

1. INTRODUCTION

Hydrogels are three-dimensional polymeric networks capable of retaining large amounts of water while maintaining structural integrity, making them attractive for biomedical, agricultural, and environmental applications. Natural polymer-based hydrogels have gained attention due to their biodegradability, biocompatibility, and sustainability, overcoming the toxicity and persistence issues of synthetic hydrogels (Lu et al., 2021; Wypij et al., 2023). Among natural polymers, cellulose nanofibers (CNF) are promising materials owing to their high surface area, tuneable porosity, and reactive surface chemistry (Munhoz-Garcia et al., 2025).

Hydrogel formulation methods using CNF greatly influence the physicochemical properties of the final product, including porosity, swelling behaviour, and structural stability (Piazzoni et al., 2022). A crosslinker is required in the hydrogel formulation to bridge the cellulose polymer chain, forming a suitable hydrogel matrix (Nasution et al., 2022). Citric acid is one of the crosslinking agents which offers an eco-friendly approach to forming stable hydrogels through esterification between carboxyl and hydroxyl groups (Pengiran et al., 2024). Therefore, this study focuses on the formulation and characterization of kenaf- derived cellulose nanofiber (KCNF)–CMC hydrogels crosslinked with citric acid, emphasizing the effects of crosslinking concentration, and drying methods on hydrogel morphology and swelling performance.

2. EXPERIMENTAL PROCEDURE

2.1 Hydrogel Formulation

Hydrogels were synthesized using kenaf cellulose nanofiber (KCNF) and carboxymethyl cellulose (CMC-Na), crosslinked with citric acid as a natural crosslinking agent. Two formulations were conducted to evaluate the effect of citric acid concentration, curing temperature, and drying methods on hydrogel formation and swelling performance.

In the first formulation, referred to as the oven-dried hydrogel (Sample A), a total of 3.0 g of dried KCNF was dispersed in 150 mL of deionized water under continuous stirring. Subsequently, 9.0 g of CMC-Na was gradually added into the KCNF suspension and homogenized using an overhead stirrer until a uniform viscous mixture was obtained. A 3.75% (w/w) citric acid solution was prepared by dissolving 0.45 g of citric acid in 1 mL of deionized water, which was then added dropwise into the KCNF–CMC mixture while stirring for 1 hour. The resulting mixture was subjected to a two-step curing process in a water bath at 30 °C for 12 hours, followed by 80 °C for another 12 hours to promote crosslinking between the citric acid and the hydroxyl groups of KCNF and CMC-Na. The hydrogel was then poured into aluminium moulds and oven-dried at 30 °C for 12 hours to obtain the dried sample, which was labelled as Sample A.

The second formulation investigated the effect of drying methods and was carried out using the same KCNF and CMC-Na ratio but with a lower citric acid concentration. A KCNF suspension equivalent to 3.0 g of dried KCNF was prepared and mixed with 9.0 g of CMC-Na under continuous stirring until a homogeneous mixture was obtained. A 1.75% (w/w) citric acid solution was prepared by dissolving 0.21 g of citric acid in 1 mL of deionized water and added dropwise into the KCNF–CMC mixture with continuous stirring for 1 hour. The mixture was then placed in a 50 °C water bath for 24 hours to complete the crosslinking reaction. After curing, the mixture was divided into two portions to compare the effects of different drying techniques: one portion was oven-dried at 40 °C overnight (labelled Sample B), while the other was frozen at −80 °C for 24 hours and subsequently freeze-dried using a lyophilizer (labelled Sample C).

2.2 Swelling Test

Each dried hydrogel sample was weighed to obtain its initial dry weight (W_d). The samples were then immersed in 200 mL of distilled water at room temperature (25–30 °C). At predetermined time intervals of 1, 3, 6, 9, 12, and 24 hours, the hydrogels were removed from the water, gently blotted with Kim tech wipes to remove excess surface moisture, and immediately weighed to determine the wet weight (W_w). The swelling degree (%) of each sample was calculated using Equation 1:

$$\text{Swelling Degree (\%)} = [(W_w - W_d)/W_d] \times 100\% \quad (1)$$

The swelling behaviour was evaluated for Sample A, Sample B, and Sample C, corresponding to the different formulation and drying conditions described earlier.

3. RESULTS AND DISCUSSION

3.1 Physical Observation of KCNF–CMC Hydrogels

Distinct differences in texture and structure were observed among the three hydrogel samples after drying. The oven-dried hydrogels (Samples A and B) appeared hard and sturdy, indicating a dense and compact network structure. In contrast, the freeze-dried hydrogel (Sample C) exhibited a cotton-like texture but remained mechanically stable. The softer and more fibrous appearance of Sample C suggested the presence of a more porous and interconnected microstructure, which likely resulted from sublimation of frozen water during the freeze-drying process. This observation aligns with previous findings that freeze-dried cellulose-based hydrogels tend to exhibit enhanced porosity compared to oven- dried (Borsoi et al., 2016; de Lima et al., 2020).

3.2 Swelling Behaviour of KCNF–CMC Hydrogels

The swelling performance of the KCNF hydrogels is presented in Figure 1. Overall, all samples demonstrated rapid water uptake within the first six hours of immersion, followed by either stabilization or disintegration depending on their formulation and drying method.

Sample A exhibited the highest and most stable swelling behaviour, reaching a maximum swelling degree of approximately 4800% at 6 hours, before maintaining equilibrium between 4200–4400% up to 24 hours. This stable swelling profile indicates that the higher citric acid concentration (3.75%) and dual stage curing process (30 °C and 80 °C) produced a well-crosslinked polymeric network with good water retention and mechanical integrity.

Sample B reached a moderate swelling degree of around 3800% at 6–9 hours but collapsed completely after 12 hours, resulting in zero swelling thereafter. The early disintegration of Sample B may be attributed to its lower crosslinker concentration (1.75%), which led to weaker intermolecular bonding and reduced structural stability upon prolonged water exposure.

Sample C initially absorbed water rapidly, reaching a maximum swelling degree of about 3000% at 3 hours, but then decreased sharply and lost its structural integrity after 9 hours. Although freeze-drying produced a more porous structure, the weaker crosslinking density and fragile pore walls made it more susceptible to breakdown during extended immersion.

These results indicate that crosslinking concentration and drying method play critical roles in determining the swelling capacity and stability of KCNF–CMC hydrogels. The higher citric acid concentration and dual thermal curing in Sample A created a denser yet flexible network capable of sustaining water absorption without degradation. Conversely, the lower crosslinking level in Samples B and C caused network loosening and eventual disintegration.

4. CONCLUSION

Kenaf-derived CNF–CMC hydrogels were successfully formulated usig citric acid as a natural crosslinker. The study showed that both crosslinking concentration and drying method strongly influenced the hydrogel's texture and swelling performance. The oven-dried sample with higher citric acid content (Sample A) exhibited the highest swelling stability and structural integrity, maintaining over 4000% swelling after 24 hours. In contrast, the lower crosslinked and freeze-dried samples (Samples B and C) showed rapid swelling followed by disintegration. Overall, citric acid crosslinking with dual-stage thermal curing produced a stable and eco-friendly hydrogel suitable for future controlled-release applications.

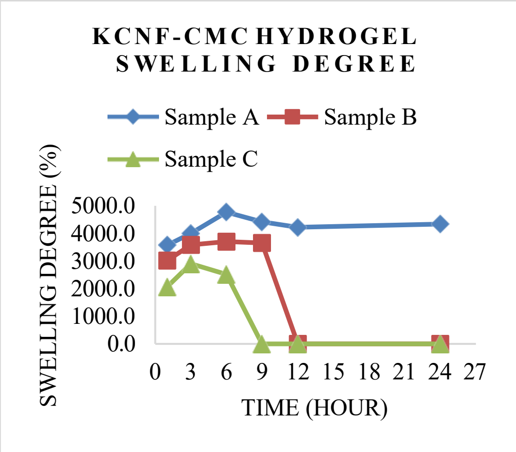

Figure 1. Swelling behaviour of KCNF–CMC hydrogels (Sample A–C) over 24 hours immersion in distilled water.

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