



Synthesis and Characterization of Carrageenan-Chitosan Milkfish Scales-Based Hydrogel for Slow-Release Fertilizer

Asri Azizah^a, Diana Triyanti^a, Putri Sahira^a, Anisa Putri^a, Retno Sulisty Dhamar Lestari^a,
Jayanudin Jayanudin^b

^aDepartment of Chemical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University
Jalan Jend. Soedirman KM 3, Kec. Purwakarta, Kota Cilegon, Banten, 42435, Indonesia

^bMaster of Chemical Engineering, Sultan Ageng Tirtayasa University
Jalan Raya Jakarta KM.04 Serang, Indonesia

*Corresponding author: rsdlestari@untirta.ac.id

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ABSTRACT. This study aims to develop a superabsorbent hydrogel as a slow-release fertilizer based on a combination of carrageenan-glucomannan and carrageenan-chitosan derived from milkfish (*Chanos chanos*) scale waste. The hydrogel was synthesized by chemical crosslinking with glutaraldehyde concentrations of 2%, 4%, 6%, and 8%. Hydrogel characterization included swelling ratio tests, gel fraction analysis, Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), urea absorption (X_o), and urea release kinetics in both aqueous and soil media. The results indicate that a 8% glutaraldehyde concentration yielded optimal performance in both hydrogel systems, achieving the highest gel fractions (>90%) and maximum urea absorption capacities of 8.05 g/g for carrageenan-glucomannan and 13.31 g/g for carrageenan-chitosan. The carrageenan-glucomannan hydrogel exhibited a higher swelling ratio of 630% at 2% glutaraldehyde concentration and slower urea release in soil, ranging from 0.192% to 4.113% over 7 days. In contrast, the carrageenan-chitosan hydrogel demonstrated stronger chemical affinity for urea but released it more rapidly, ranging from 1.037% to 7.092% over the same period. SEM and FTIR analyses confirmed the formation of a three-dimensional network structure and chemical interactions among the components.

INTRODUCTION

Indonesia's complex environmental and agricultural problems require innovative technology-based solutions. Meanwhile, milkfish production in Banten Province reaches 12,585 tons per year (BPS, 2020), resulting in scale waste with the potential to pollute the environment. On the other hand, the agricultural sector, which employs 38.77 million workers (BPS, 2021), faces a water crisis due to climate change, which reduces groundwater recharge and leads to nutrient loss. These two problems create an urgency to develop technology that can improve water efficiency while utilizing waste in a value-added manner.

As a solution, natural-made superabsorbent hydrogels were chosen for their ability to absorb water up to 1,000 times their dry weight and release the liquid in a controlled manner even under certain pressure conditions (Chang *et al.*, 2010). The hydrogel's responsiveness to environmental factors such as pH, temperature, and ion concentration makes it a dynamic, adaptive material. In agricultural applications, superabsorbent hydrogels offer several benefits, including reduced irrigation water requirements, reduced plant mortality, increased soil moisture retention, improved soil structure (reduced compaction and erosion), increased fertilizer use efficiency, and the ability to immobilize heavy metals (Azeem *et al.*, 2014). The selection of glucomannan and carrageenan materials is based on their synergistic properties: carrageenan provides good gelation ability and stability to absorb and retain water (Yegappan *et al.*, 2018), while glucomannan is biodegradable and is able to increase water retention and nutrient release in a controlled manner (Wu *et al.*, 2022). In addition, chitosan can be extracted from milkfish scale waste; therefore, it serves not only as a waste utilization solution but also as a material with hydrophilic, biodegradable properties and a reactive amine functional group, making it suitable for chemical modification.

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The chemical crosslinking method using glutaraldehyde solution allows the formation of covalent crosslinks that can improve the mechanical stability of the material and control the swelling rate and hydrogel form in aqueous environments (Hoffman, 2012). In contrast to gamma irradiation methods (Erizal *et al.*, 2017) or hydrothermal (Adi and Heryani, 2020), chemical crosslinking with glutaraldehyde offers precise control of cross-bond density through concentration variations, thus allowing for the optimization of hydrogel structure for slow-release fertilizer applications, such as those that have been studied in carrageenan-CMC-based bead synthesis (Distantina *et al.*, 2018)

In this study, hydrogels derived from milkfish scale waste and a combination of carrageenan-glucomannan and carrageenan-chitosan were developed using the crosslinking method. The novelty of this research is that it can develop slow-release fertilizer materials that effectively control nutrient release, increase groundwater retention, and provide value-added solutions to the problems of fishery waste and water resource efficiency in the agricultural sector. This study focuses on the characterization of the functional performance of hydrogels as slow-release fertilizers under environmental conditions commonly found in Indonesian agricultural land. The main analyses include hydrophilic properties (swelling ratio), mechanical stability (gel fraction), morphology by scanning electron microscopy (SEM), infrared Fourier transform (FTIR) spectroscopy, and urea absorption and release kinetics. Thermal studies (TGA/DSC) were specifically not conducted, given that the temperature range of agricultural environments in Indonesia is relatively stable (25 – 35 °C), where natural polysaccharide hydrogels such as carrageenan, glucomannan, and chitosan have been reported to exhibit adequate thermal stability.

RESEARCH METHODS

The ingredients used in this study are glucomannan, carrageenan from Sigma-Aldrich, milkfish scales from the Cilegon Kranggot Market, 25% glutaraldehyde solution from Merck, acetic acid solution, acetone, 70% technical ethanol, and urea from PT. SmartLab. The research equipment used is a magnetic stirrer and a Memmert UNB400 oven.

Chitosan Isolation Process from Milkfish Scales

The milkfish scales used in this study are adult milkfish scales, scales taken from all parts of the fish's body. The method for isolating chitosan from milkfish scales was adapted from Triyanti *et al.* (2022) with modifications. The milkfish scales were washed, dried at 100 °C for 25 minutes, and ground into a powder. The chitin isolation stage began with a deproteinization step using 0.1 N NaOH (1:10 w/v) at 65 °C for 2 hours, followed by filtration, neutral pH washing, and drying. The results obtained (75.6 g) were then subjected to a demineralization process with 1 N HCl (1:10 w/v) for 30 minutes at room temperature, washed to neutrality, and dried, yielding 35.4 g of chitin. This chitin was then deacetylated with 20% NaOH (1:10 w/v) at 121 °C for 1 hour, washed, and dried, yielding 17.3 g of chitosan. The degree of deacetylation (DD) was determined by the acid-base titration method, resulting in a DD value of 86.92%.

Hydrogel Synthesis

The synthesis of hydrogels was carried out by adapting the method developed by Distantina *et al.* (2020). For carrageenan-glucomannan hydrogels, a flour mixture with a 1:1 mass ratio is dissolved in 100 mL of water, then homogenized using a magnetic stirrer at 85 °C. An equal proportion of carrageenan-chitosan mixture (5 g total) was dissolved in 100 mL of 5% acetic acid. The two solutions are then molded separately and frozen until solid.

The initial gel formation was carried out by dripping the homogeneous mixture into a solution containing 0.2 M CaCl₂·H₂O, 0.2 M KCl (1:1 ratio), and 5 mL of palm oil, in an ice bath. Then, the initial hydrogel is rinsed with acupine for 1 minute, followed by soaking in 70% ethanol (100 mL) for 4 hours. For carrageenan-chitosan hydrogels, after freezing, they were washed with 2 M NaOH, followed by aqueducts, and then immersed in acetone for 1 hour.

The crosslinking stage was performed by soaking the hydrogel in glutaraldehyde solutions at concentrations of 2%, 4%, 6%, and 8% for 1 hour. The carrageenan-glucomannan hydrogel was then dried in an oven at 110 °C for 25 minutes, washed again with distilled water, and soaked in ethanol. Meanwhile, the carrageenan-chitosan hydrogel was dried at 50 °C for 1 hour, rinsed with aqueducts, and soaked in acetone. After the treatment, both types of hydrogels were dried at room temperature before characterization.

Gel Fraction

The gel fraction test involved soaking the hydrogel for 24 hours with 1 g (W_0) in 100 mL of distilled water. Next, the sample was dried in a vacuum oven at 50 °C for 24 hours, and its weight was reweighed (W_1). The percentage of gel fractions is calculated using Equation 1. The purpose of reweighing is to measure the cross-degree of the hydrogel to indicate the number of cross-bonds between polymers

$$\% \text{ gel fraction} = \frac{W_1}{W_0} \times 100\% \quad (1)$$

Swelling Ratio

This test was carried out by weighing the entire hydrogel (W_d). The hydrogel was then soaked in distilled water at a 1:100 ratio and weighed at regular intervals (W_s) of 5 minutes, 60 minutes, and 1 day. After that, the swelling ratio is calculated using Equation 2.

$$\text{Swelling ratio} = \frac{W_s - W_d}{W_d} \times 100\% \quad (2)$$

Urea Loading

Urea was loaded into the hydrogel by soaking 1 g of hydrogel in 100 mL of a 0.74 g/mL urea solution. The wet weight of the hydrogel after 1 hour was weighed (Lestary *et al.*, 2018).

Urea Release Test

Urea fertilizer release tests in water and soil media were conducted to quantify the amount of urea that diffused from the hydrogel matrix. In water media, 0.2 g of hydrogel was immersed in 50 mL of water in a glass beaker and then observed over days 1, 2, 3, 4, and 7. The urea release test on soil media used 50 g of yard soil, placed in a plastic bottle with a diameter of ± 7.5 cm. Next, 100 mL of water was added to the tube, and 1 g of hydrogel was added to the container and observed in the time range of days 1, 2, 3, 4, to day 7. Analysis of the amount of urea fertilizer released from the hydrogel in both media using a UV-Vis spectrophotometer (Thermo Scientific Genesys 10UV) at a wavelength of 420 nm. The measured absorbance value was used to determine the concentration of urea fertilizer in water and soil media. Five release kinetics models were applied, referring to research conducted by Dozie-Nwachukwu *et al.* (2017) and Jayanydun and Lestari (2020), namely the zero-order (Equation 3), the first-order (Equation 4), the Higuchi model (Equation 5), the Hixson-Crowell model (Equation 6), and the Korsmeyer-Peppas model (Equation 7).

$$\frac{M_t}{M_\infty} = k_0 t \quad (3)$$

$$\frac{M_t}{M_\infty} = 1 - \exp(-k_1 t) \quad (4)$$

$$\frac{M_t}{M_\infty} = k_H t^{1/2} \quad (5)$$

$$W_0^{1/2} - W_t^{1/2} = k_{HC} t \quad (6)$$

$$\frac{M_t}{M_\infty} = k_{KP} t^n \quad (7)$$

Where M_t is the cumulative amount of urea released at time t , M_∞ is the equilibrium release amount (total urea loaded in the hydrogel), M_t/M_∞ represents the fractional urea release at time t , k_0 is the zero-order release rate constant (Equation 3), k_1 is the first-order release rate constant (Equation 4), k_H is the Higuchi release rate constant (Equation 5), t is the release time, W_0 is the initial mass of the hydrogel or matrix before release, W_t is the remaining mass of the matrix at time t , k_{HC} is the Hixson-Crowell release rate constant (Equation 6), k_{KP} is the Korsmeyer-Peppas release rate constant (Equation 7), and n is the release exponent that indicates the urea release mechanism (Fickian diffusion, anomalous transport, or Case-II transport).

RESULTS AND DISCUSSION

Hydrogel Appearance

Visual analysis using the Dino Lite Microscope in Figure 1 revealed the difference in morphological characteristics between the carrageenan-glucomannan hydrogel (Figure 1(a)) and carrageenan-chitosan (Figure 1(b)). Carrageenan-glucomannan hydrogels exhibit a darker color, due to the natural color of the constituent

materials: light brown glucomannan (Dipahayu and Kusumo, 2020) and yellowish-white carrageenan (Ferdiansyah *et al.*, 2017). In contrast, carrageenan-chitosan hydrogels have a lighter color because the two constituent materials (carrageenan and chitosan extracted from milkfish scales) are naturally white to yellowish in color. Both types of hydrogels have a hard, clay-like texture, indicating the formation of a dense, compact matrix. This property results from the synergistic interaction of carrageenan, glucomannan, and chitosan, which together form a strong polysaccharide network (Kaya *et al.*, 2014).

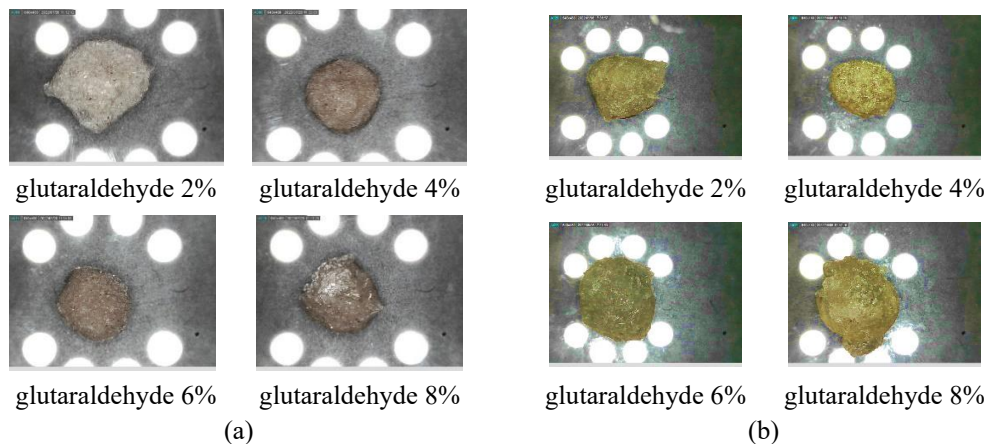


Figure. Surface appearance of hydrogels: (a) carrageenan-glucomannan hydrogel and (b) carrageenan-chitosan hydrogels.

Swelling Ratio

The water-absorption capacity of carrageenan-glucomannan and carrageenan-chitosan hydrogels was assessed using swelling ratios. The test results presented in Figure 2 show that the swelling ratio in both types of hydrogels decreased significantly as the glutaraldehyde concentration increased from 2% to 8%. The highest swelling ratios were obtained in carrageenan-glucomannan and carrageenan-chitosan hydrogels with 2% glutaraldehyde variations, 630% and 530%, respectively. The test data showed that the swelling ratio was in the range of 100 – 1000 times its dry weight, consistent with the characteristics of hydrogels, which are able to absorb and retain water tens to thousands of percent of their dry weight (Hekmat *et al.*, 2009). This expandability and high permeability make the hydrogel suitable as a controlled release matrix.

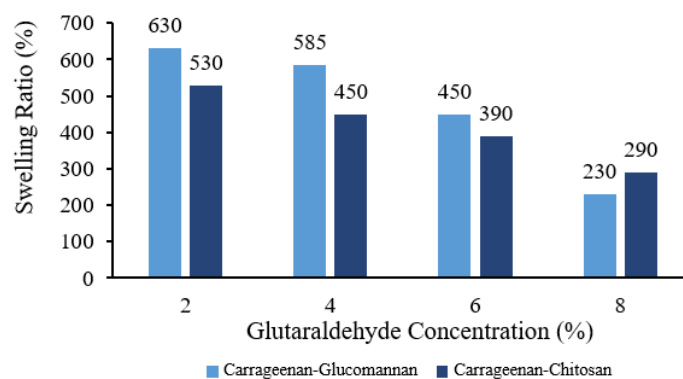


Figure 2. Swelling ratio.

Three main factors can explain the difference in swelling ratio between the two hydrogels. First, glucomannan is more hydrophilic due to its higher density of free hydroxyl groups ($-OH$). In contrast, chitosan with a deacetylation degree (DD) of 86.92% has a high content of free amine group ($-NH_2$). Although this amine group is hydrophilic, its affinity to water is generally lower than that of the $-OH$ group in glucomannan. This high degree of deacetylation also contributes to the formation of stronger crosslinks with glutaraldehyde, which can ultimately decrease the water-absorption capacity of chitosan hydrogels (Chen *et al.*, 2018; Zhang *et al.*, 2014). Second, structurally, glucomannans have a branched architecture that creates greater free volume for water absorption than chitosan's linear structure (Yu *et al.*, 2011). Third, in the process of cross-binding with glutaraldehyde, the amine

group in chitosan forms a more rigid Schiff base bond (C=N), while the hydroxyl group in glucomannan forms a relatively more flexible acetal (C–O–C) bond. The stiffer bonds to these chitosan limit the mobility of the polymer chain and the hydrogel's development capacity (Jayanudin *et al.*, 2019b; Patel and Patel, 2014).

The phenomenon of decreasing swelling ratio at higher glutaraldehyde concentrations can be explained by an increasingly intensive crosslinking mechanism. High concentrations of glutaraldehyde result in a denser, more compact tissue structure, thereby reducing the free volume available to hold water (Wu *et al.*, 2008). In chitosan with a DD of 86.92%, the greater number of available amine groups will react more readily with glutaraldehyde, thereby accelerating the formation of dense tissues and limiting swelling. The research of Guo *et al.* (2005) and Nasution *et al.* (2019) supports the idea that an increase in the number of cross-ties increases cross-bond density, limits the stretching of polymer chains, and can result in excessive crosslinking that inhibits water penetration.

These differences in characteristics have direct implications for applications as a slow-release fertilizer. Hydrogels with a high swelling ratio (glutaraldehyde variation 2 – 4%) are suitable for dry areas due to their ability to store large volumes of water, but looser structures can lead to faster urea fertilizer release. In contrast, hydrogels with a low swelling ratio (glutaraldehyde variation 6 – 8%) are more suitable for moist soils or applications that require slower fertilizer release. A denser matrix structure due to high cross-linkage, reinforced by chitosan reactivity with a high degree of deacetylation, can slow down urea diffusion, so that nutrients are available longer and minimize losses due to leaching (Chen *et al.* 2018; Savana, 2018).

Gel Fraction

The gel fraction test aims to determine the presence and effectiveness of crosslinking in a hydrogel polymer matrix. Glutaraldehyde, as a crosslinking agent, has been shown to form hydrogel structures suitable for slow-release fertilizer applications. According to Distantina *et al.* (2020), increasing glutaraldehyde concentration results in a denser hydrogel structure with shrinking pore size, thereby increasing the material's mechanical properties. This is consistent with the observation that the gel fraction in both types of hydrogels increased with increasing glutaraldehyde concentration from 2% to 8%. The increase indicates that, at higher concentrations of the cross-binding agent, more crosslinks form between the polysaccharide chains. As a result, the fraction of polymers permanently bound within the three-dimensional network of hydrogels is also increasing (Distantina *et al.*, 2020).

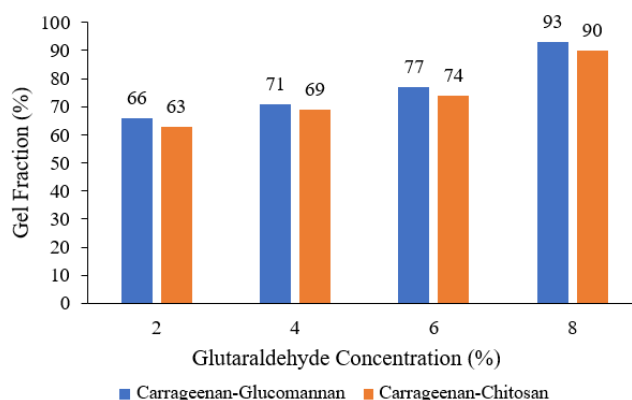


Figure 3. Gel fraction.

Consistently, carrageenan-glucomannan hydrogels showed higher gel fractions than carrageenan-chitosan across all glutaraldehyde concentrations (Figure 3). Several factors can explain this difference. First, glucomannan has more hydroxyl groups (–OH) and is more reactive with glutaraldehyde than the amine group (–NH₂) in chitosan (Zhang *et al.*, 2014). Especially for chitosan with a deacetylation degree (DD) of 86.92%, although the content of free amine groups is high and highly reactive with glutaraldehyde, this can lead to rapid, intensive crosslinks in the early stages. This condition can lead to less homogeneous, denser tissue in certain areas, potentially limiting overall crosslinking efficiency and affecting the mechanical integrity of the gel. Second, the interaction between carrageenan and glucomannan shows better polymer compatibility, thus facilitating the formation of more homogeneous crosslinking tissues. Third, glucomannan has a branched structure that supports a higher cross-bond density, whereas chitosan is more linear (Yu *et al.*, 2011). Chitosan linear structures with high

DD, combined with the reactivity of their amine groups, tend to form tissues with high *crosslink density*, but may be more fragile, which may contribute to lower gel fractions compared to more flexible glucomannan systems.

Consistent with previous literature, [Distantina *et al.* \(2020\)](#) reported that increasing glutaraldehyde concentration from 2% to 8% increased the fraction of carrageenan-pectin-based hydrogel from 65% to 89%. Similarly, [Savana \(2018\)](#) states that chitosan-silica hydrogels with gel fractions above 85% exhibit 50% slower urea release than 70% gel fractions, confirming that a high degree of cross-binding is the key to optimal slow-release performance. In this context, chitosan with a DD of 86.92% has the potential to achieve a high degree of crosslinking due to its reactivity. However, optimizing glutaraldehyde concentration is critical to avoid over-crosslinking, which can reduce tissue elasticity and swelling capacity, although the gel fraction (the amount of bound polymers) may still increase. Thus, the performance of chitosan hydrogels results from a balance between the high gel fraction (from intensive crosslinking) and the water-absorption capacity (which can decrease due to overcrowding).

Scanning Electron Microscopy (SEM)

The surface morphology of carrageenan-glucomannan and carrageenan-chitosan hydrogels was analyzed using SEM at 300 \times , 500 \times , and 2000 \times magnifications, with samples containing 8% glutaraldehyde, as shown in [Figure 4](#).

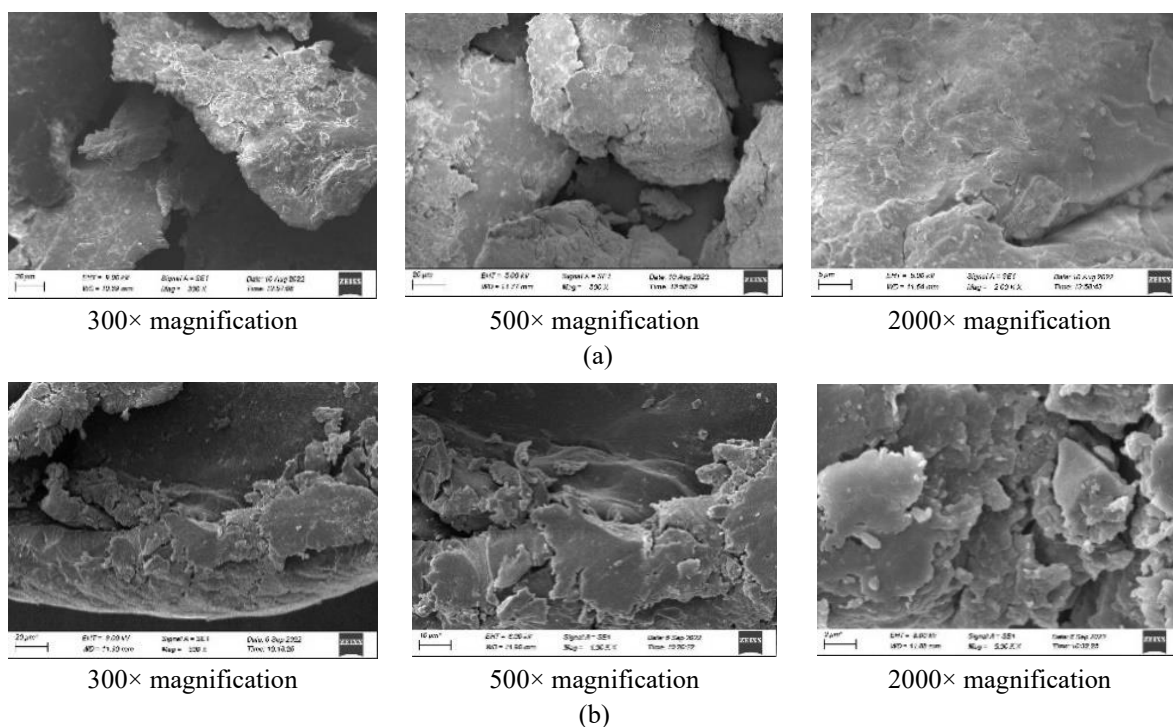


Figure 4. SEM image for hydrogel (a) carrageenan-glucomannan and (b) carrageenan-chitosan.

The results showed that both hydrogels had uneven, textured, and porous surfaces with non-uniform cavity distribution—a characteristic of natural polysaccharide hydrogels that have undergone chemical crosslinking. However, there are clear morphological differences between the two types of hydrogels. Carrageenan-glucomannan hydrogels exhibit a smoother, more compact surface, especially at high magnification (2000 \times), indicating the formation of dense, homogeneous polymer tissues. In contrast, carrageenan-chitosan hydrogels exhibit a coarser structure with relatively larger, open pores, which are clearly visible at 500 \times and 2000 \times magnification.

These differences in surface morphology can be attributed to the different crosslinking mechanisms between the two polymer systems. In carrageenan-glucomannan hydrogels, cross-bonds are mainly formed through the reaction between hydroxyl groups ($-\text{OH}$) of glucomannan with glutaraldehyde, and are strengthened by ionic interactions between carrageenan and K^+ and Ca^{2+} ions from the printer solution. This combination tends to yield a more homogeneous, smoother structure ([Distantina *et al.*, 2018](#)). Meanwhile, in carrageenan-chitosan hydrogels, in addition to the chemical bond with glutaraldehyde, there is also an electrostatic interaction between the sulfate

group ($-\text{OSO}_3^-$) in the carrageenan and the amine group ($-\text{NH}_3^+$) in chitosan. This dual interaction can create local variations in cross-bond density, which morphologically manifests as a rougher surface with larger pores (Jayanudin *et al.*, 2019b). Thus, although limited to the surface, SEM analysis still provides valuable insights into the influence of composition and crosslinking mechanisms on the hydrogel's final texture.

FTIR

FTIR testing is performed to identify functional groups present in a hydrogel sample, especially when there is a complexation or separation between two or more substances. The FTIR spectra of the carrageenan-glucomannan hydrogel are shown in Figure 5. The results of the FTIR analysis in Figure 5 show that κ -carrageenan exhibits a characteristic absorption of sulfate groups at 1261 cm^{-1} and an elongated $-\text{OH}$ vibration at 3324 cm^{-1} . Meanwhile, glucomannan showed β -glycosidic peaks at 3714 cm^{-1} (vibration $-\text{OH}$) and 1022 cm^{-1} ($\text{C}-\text{O}-\text{C}$ bond) as reported by Kusuma *et al.* (2022). In carrageenan-glucomannan hydrogels, peaks appear that indicate the interaction of the two polymers, namely the vibration $-\text{OH}$ at 3337 cm^{-1} , the strain $\text{C}-\text{O}-\text{C}$ at 1018 cm^{-1} , and the peak $\text{C}=\text{O}$ at 1720 cm^{-1} , which is not very strong and significant. The peak of the κ -carrageenan sulfate group shifted to 1265 cm^{-1} , while the glucomannan β -glycosidic group was observed at 3734 cm^{-1} .

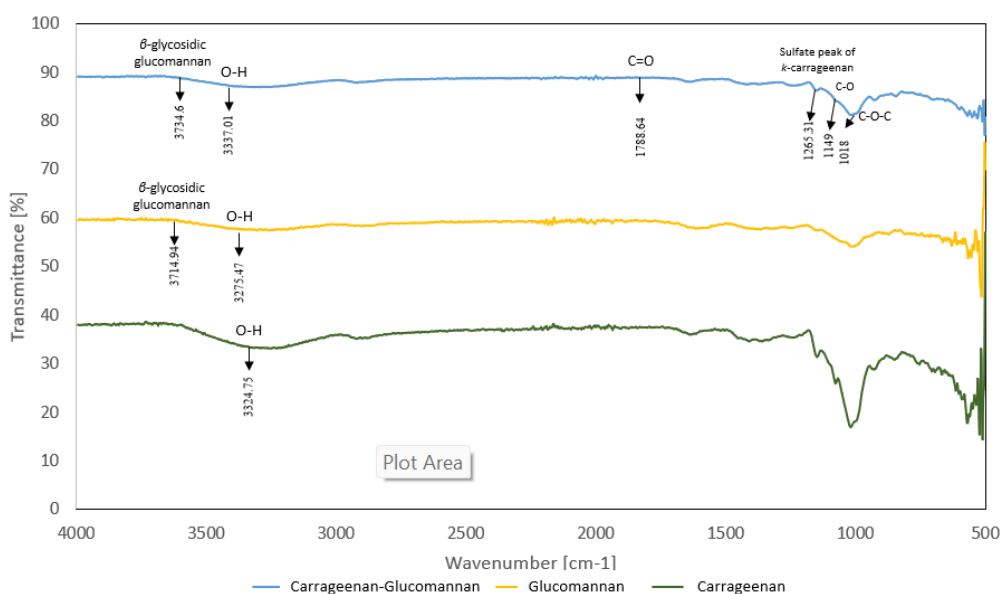


Figure 5. FTIR spectra of carrageenan-glucomannan hydrogel.

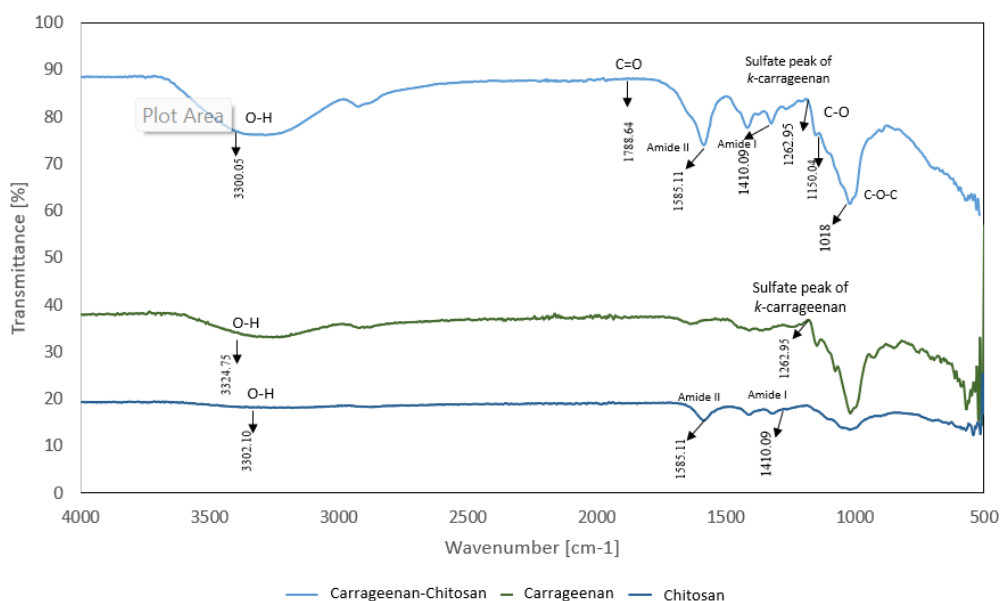


Figure 6. FTIR spectra of carrageenan-chitosan hydrogel Milkfish scales.

The FTIR spectra of carrageenan, chitosan, and carrageenan-chitosan hydrogels are shown in Figure 6. A peak at 1261 cm^{-1} indicates the sulfate group in κ -carrageenan. The amide I band of chitosan appears at 1410 cm^{-1} , and the amide II band is observed at 1585 cm^{-1} (Li *et al.*, 2013). In chitosan-carrageenan hydrogels, an absorption peak of 3300 cm^{-1} was observable, indicating $-\text{OH}$ vibration, as well as a peak at 1018 cm^{-1} derived from $\text{C}-\text{O}-\text{C}$ strain. The emergence of new absorption bands in the range of $1525 - 1540\text{ cm}^{-1}$, which is characteristic of the vibration of the $-\text{NH}_3^+$ group, proves that there has been an electrostatic interaction between the positively charged amine group of chitosan and the negatively charged sulfate group of carrageenan.

Urea Absorption

Urea adsorption tests were performed to determine the adsorption capacities of carrageenan-glucomannan and carrageenan-chitosan hydrogels, which are critical parameters in the development of superabsorbent hydrogels as slow-release fertilizer matrices. The results of urea absorption with the variation in glutaraldehyde concentration in Figure 7 show that the optimal absorption capacity is achieved at a glutaraldehyde concentration of 8%. Under these conditions, carrageenan-glucomannan and carrageenan-chitosan hydrogels achieved the highest X_o (grams of urea/gram of solids), at 8.05 and 13.31, respectively. The X_o value represents the amount of urea adsorbed into the hydrogel matrix during immersion in a 10% urea solution. It was observed that the final mass of the hydrogel after urea absorption increased proportionally with increasing glutaraldehyde concentration. This phenomenon is caused by glutaraldehyde's role as a chemical crosslinking agent, which reacts with hydroxyl groups ($-\text{OH}$) on polymers, forming a denser, more compact network of crosslinks. Increased glutaraldehyde concentrations lead to more cross-binding molecules that bind to the $-\text{OH}$ functional group, thereby strengthening the matrix structure and increasing its capacity to bind to urea (Distantina *et al.*, 2018).

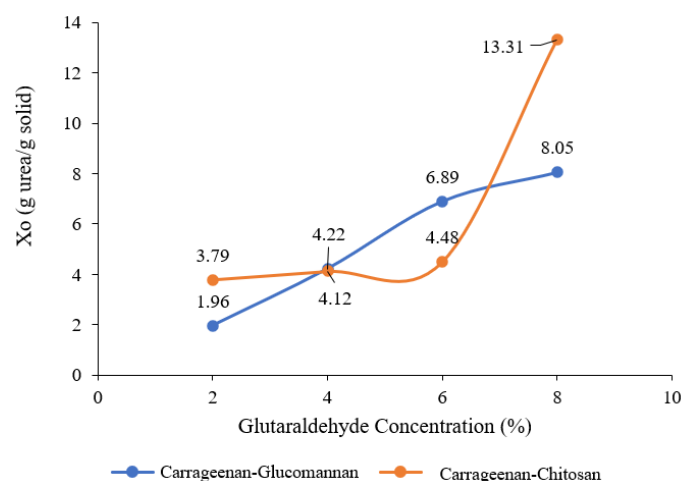


Figure 7. Urea adsorption test results.

Urea Release Test

The urea release graphs in Figures 8 and 9 show a significant difference in urea release between the water and soil media for the two types of hydrogels. In the aqueous medium (Figure 8), both hydrogels showed a rapid initial release rate on the first to third days, followed by a slowed release phase. Carrageenan-chitosan hydrogels released urea at a higher rate and cumulative amount than carrageenan-glucomannan over 7 days of observation. This pattern corresponds to the Fickian diffusion mechanism, which is dominated by a concentration gradient, in which urea diffuses out of the fully hydrated hydrogel matrix into a large, unlimited volume of water (Hassan and Peppas, 2000). The rapid rate of hydrogel swelling in water facilitates pore opening and accelerates the migration of urea molecules.

In contrast, in the soil medium (Figure 9), the discharge profile shows a more controlled and gradual pattern. The concentration of urea released into the soil was cumulatively lower than in water for the same period. This is due to a more complex release mechanism in the soil, which involves not only diffusion but also adsorption of soil particles, capillary water retention, and interactions with the soil matrix. Soil behaves as a semi-infinite medium with binding capacity for ions and molecules, such as urea. Soil components, such as clay and organic matter, can absorb released urea, creating a "buffer zone" that slows its immediate availability to plants (Azeem *et al.*, 2014).

In addition, the soil matrix pressure and non-uniform humidity, compared to pure water, also limit the swelling rate of the hydrogel, thereby slowing the diffusion of urea from within the matrix.

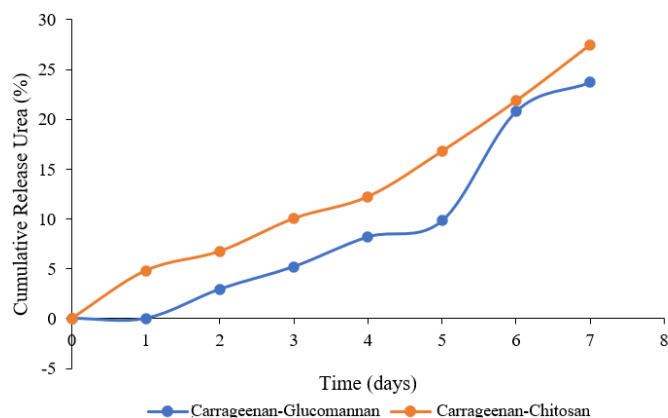


Figure 8. Urea release testing on water media.

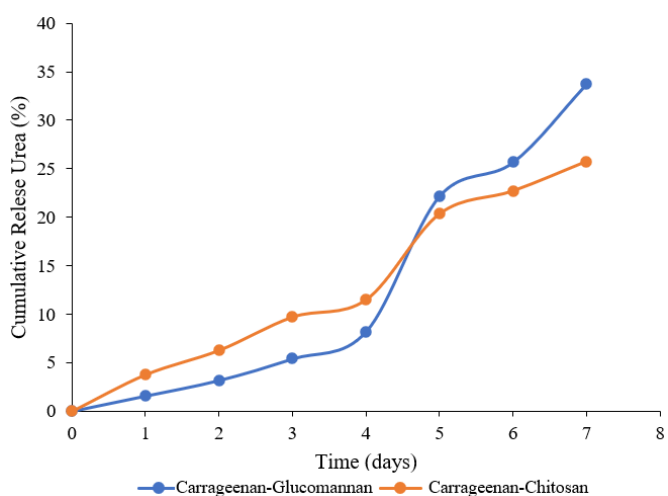


Figure 9. Urea release testing on soil media.

The performance difference between the two hydrogels in both media can be attributed to their structural characteristics. Carrageenan-chitosans, with their larger porous structure and chemical affinity between amine and urea groups, tend to release nutrients more quickly, while glucomannans-carrageenans, with a more compact matrix and crosslinks derived from hydroxyl groups, exhibit slower, more controlled release. The more stable release pattern in the soil medium of both hydrogels, especially carrageenan-glucomannan, is advantageous for agricultural applications. Too rapid release in water can lead to nutrient loss through leaching, whereas gradual release in the soil maintains nutrient availability for plants, improves fertilizer use efficiency, and minimizes environmental impact (Chen *et al.*, 2018; Trenkel, 1997). The results of these release tests confirm that both hydrogels function effectively as a release control system, with optimal performance achieved under actual application conditions (ground media). Glucomann-carrageenan hydrogels exhibit slower release characteristics, suitable for long-term applications, while carrageenan-chitosan is suitable for applications with earlier nutrient release needs.

However, as a preliminary study, this study has limitations that need to be noted, especially regarding the environmental safety of using glutaraldehyde as a crosslinking agent. The 8% glutaraldehyde concentration, proven optimal in this study, raises concerns about the toxicity of residues and their impact on soil ecosystems. Glutaraldehyde is a standard cross-binding agent in polysaccharide research (Distantina *et al.*, 2018; Jayanudin *et al.*, 2019b) because of its ability to form stable covalent bonds, such as acetal bonds (with a $-OH$ group) or Schiff bases (with $-NH_2$ groups), in polymer tissues. To minimize the risk, a strict washing procedure has been performed using 70% ethanol and repeated aqueducts to remove the unreacting free glutaraldehyde. Glutaraldehyde bound in polymer tissues is known to have lower toxicity than in its free form.

Urea Release Kinetics

The release kinetics were modeled using Equations 3 – 7 to simulate the urea release before application (Dash *et al.*, 2010). The release kinetic constant is obtained by nonlinear regression analysis. The model selection is based on the highest value of the correlation coefficient (R^2). The quantities of kinetic constants, including k_0 , k_1 , k_H , k_{KP} , and k_{HC} sourced from Equations 3 – 7 can be seen in Table 1.

Table 1. Kinetic constants from various release models.

Variable	Zero Order		First Order		Higuchi		Hixon-Crowell		Korsmeyers Peppas		
	k_0	R^2	k_1	R^2	k_H	R^2	k_{HC}	R^2	k_{KP}	n	R^2
Water Media											
Carrageenan-Glucomanan Hydrogel	0.1762	0.93	0.0019	0.96	2.2386	0.97	0.0071	0.95	0.0655	1.21	0.99
Carrageenan-Chitosan Hydrogel	0.1602	0.97	0.0015	0.98	1.94	0.99	0.0056	0.97	0.0909	1.14	0.99
Soil Media											
Carrageenan-Glucomanan Hydrogel	0.1963	0.88	0.0023	0.95	2.494	0.97	0.0085	0.94	0.0335	1.39	0.99
Carrageenan-Chitosan Hydrogel	0.1548	0.87	0.0017	0.91	1.9385	0.95	0.0063	0.91	0.0636	1.18	0.99

Analysis of urea release kinetics from both hydrogel formulations (Carrageenan-Glucomanan and Carrageenan-Chitosan) in water and soil media revealed significantly different release patterns and mechanisms. Based on the results of the calculations in Table 1, the Korsmeyer-Peppas model shows the best fit for all conditions with the highest R^2 value (0.99), indicating that the release mechanism does not follow simple kinetics such as orders of zero or one, but rather involves more complex processes (Costa and Lobo, 2001). The diffusion exponent (n) obtained from this model is in the range of 1.14 – 1.39, which, according to the criteria of Ritger and Peppas (1987), falls within the category of Super Case-II transport to anomalous transport with Case-II tendencies. This indicates that urea release is not only controlled by pure Fickian diffusion, but is also strongly influenced by the swelling and relaxation of the hydrogel polymer matrix (Oyediran *et al.*, 2025).

A comparison of water and soil media shows that environmental media significantly affect the release profile. In aqueous media, both formulations tend to have higher R^2 values, indicating more predictable release than in soil. This is due to more optimal, homogeneous swelling in water, whereas in soil, interactions with soil particles, organic content, and soil's adsorptive properties can inhibit diffusion and create non-uniform concentration gradients (Siepmann and Peppas, 2001). In addition, the discharge constant (k) of the Higuchi model and order zero are generally higher in water media, confirming that the discharge rate is faster in more homogeneous environmental conditions and less interference.

CONCLUSION

In this study, hydrogels based on carrageenan-glucomannan and carrageenan-chitosan from milkfish scale waste have been successfully synthesized as controlled-release fertilizers by crosslinking with glutaraldehyde solution. The glutaraldehyde concentration of 8% was found to be optimal for both hydrogels, resulting in the highest gel fraction structure (>90%), superior mechanical stability, and maximum urea absorption capacity, which was 8.05 g/g for carrageenan-glucomannan and 13.31 g/g for carrageenan-chitosan. Although equally effective, both hydrogels exhibit different application characteristics and performance. Carrageenan-glucomannan hydrogels, with a more compact structure and slower urea release (0.192 – 4.113% over 7 days in soil), are better suited for long-term fertilization applications. Meanwhile, carrageenan-chitosan hydrogels, with their strong affinity for urea and faster release, are suitable for earlier nutrient release. Successful controlled release is mainly achieved in soil media, where interactions with the soil matrix slow nutrient diffusion, thereby improving fertilizer efficiency and minimizing nutrient loss. Thus, this research has not only developed an effective uncontrolled fertilizer technology but also added value through the sustainable use of local fishery waste.

CONFLICT OF INTEREST

There are no conflicts of interest in this article.

AUTHOR CONTRIBUTION

AA: Conceptualization, Methodology, Funding Acquisition; DT: Data Analysis, Manuscript Draft Writing; PS: Validation, Visualization; RSDL: Supervision; JJ: Administration and Manuscript Review.

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