



Research article

Environmentally friendly membrane based on chitosan, citric acid, and calcium for slow-release fertilizer

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ABSTRACT

In agriculture, fertilizers are important for plant growth. Among them, conventional fertilizers, particularly urea fertilizers, are popular owing to their low cost and high nitrogen content. However, their use often leads to uneven nitrogen absorption and environmental pollution. Slow-release fertilizers (SRFs), particularly those based on chitosan, offer a solution. This research aims to produce biodegradable chitosan/citric acid/calcium-urea (CS/St/Ca-urea) films to increase the absorption efficiency and use of artificial nitrogen fertilizers (especially urea). Herein, chitosan/citric acid/calcium (CS/St/Ca) films were synthesized and applied as SRFs. Chitosan was dissolved in 1 % acetic acid and added to citric acid at 55 °C for 24 h. Then, calcium oxide (CaO) and urea were added to the CS/St mixture and stirred until homogeneous. Subsequently, the membrane product was characterized by ATR-IR, SEM-EDX, and elemental analysis and its nitrogen solubility was determined using a UV-vis spectrophotometer. The physical properties of the CS/St/Ca were investigated via swelling, hydrophobicity, and tensile strength tests. Results showed that a CS/St at weight ratio of 1:1 can increase the tensile strength by up to 13.6 %. The addition of a filler with a Ca additive, as well as the addition of CaO, can increase the mechanical strength of the membrane. The CS/St/Ca film membranes can function optimally as a urea SRF coating material with a release rate of 3.37–9.46 ppm day⁻¹. The applied kinetic model follows the Higuchi kinetic model, with an R² value of 0.9505.

1. Introduction

Fertilizers have been an important part of agriculture. Among them, conventional fertilizers, notably urea fertilizers, have been widely used as a nitrogen supplement for plant growth because of their low cost and rich nitrogen content of up to 46 % [1]. However, nitrogen absorption from these fertilizers is not evenly distributed, resulting in poor plant growth. In addition, the use of conventional fertilizers causes the accumulation of excess nitrogen levels in the soil, thereby polluting the environment. Therefore, the efficient use of fertilizers is needed to overcome these problems. Slow-release fertilizers (SRFs) are proposed as alternatives to conventional fertilizers. Chitosan, a biomaterial, can be used as an SRF.

Chitosan can be used as a slow-release matrix due to its amino groups, which can form complexes with various compounds. In

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addition, chitosan is cheap and environmentally friendly. SRF materials based on chitosan have been developed, such as chitosan/citric acid [2], chitosan/silica/glutaraldehyde [3], chitosan/kaolinite [4], and chitosan/NPK [5]. In addition, chitosan has characteristics of nontoxicity, biodegradability, biocompatibility, and antibacterial capabilities [4], making it suitable as SRFs.

Chitosan-based SRF coatings cannot be synthesized using only pure chitosan because the functional groups available in chitosan are not reactive enough to provide sufficient interaction with the target compound, i.e., urea. To overcome its disadvantages, chemical modification of pure chitosan needs to be performed to effectively change the charge of the active site, attach active groups to the membrane, and increase the hydrophilicity of the membrane by cross-linking.

Several methods for modification of chitosan as an SRF matrix have been reported, such as cross-linking [1], blending with polymers or other materials [6], incorporation of nanoparticles or bioactive compounds [7], and microencapsulation [8]. Recently, chitosan modified with cross-linked citric acid and calcium has been reported to increase the mechanical strength of biodegradable films [9]. However, the application of chitosan modified with cross-linked citric acid and calcium as an SRF matrix has not yet been investigated.

Herein, we investigated the preparation of chitosan film membranes by adding citric acid as a cross-linking agent, calcium for mechanical strengthening, and urea as a filler material to provide nutrients for urea-based fertilizers. To the best of our knowledge, this is the first report of using chitosan-based membranes as SRFs, making this study a valuable reference for environmental science and promoting sustainable development, thereby contributing to the efficient and eco-friendly use of chitosan as a coating material for urea SRFs.

2. Experimental methods

2.1. Materials

Chitosan (MW = 40,000 g/mol, DD = 87 %) was obtained from Biotech Surindo, Indonesia. Citric acid ($C_6H_8O_7$, MW = 192 g/mol), urea (CH_4N_2O , MW = 60 g/mol), acetic acid (CH_3COOH , MW = 60 g/mol), NaOH (MW = 40 g/mol), *p*-dimethylaminobenzaldehyde (p-DMAB, MW = 149.19 g/mol), 96 % ethanol, and 37 % HCl were purchased from Merck.

2.2. Synthesis of cross-linked chitosan–citric acid (CS/St/Ca–urea)

A total of 1.5 g of chitosan was dissolved in 90 mL of 1 % acetic acid (v/v). The solution was stirred for 24 h. Dissolved citric acid was added to the chitosan solution with different chitosan/citric acid mass ratios of 1:1, 1:2, and 1:3. The solution was stirred for 4 h at 50 °C. Afterward, the solution was heat printed at 60 °C for 24 h so that a CS/St membrane was formed. Then, 0.03 and 0.04 g of calcium oxide (CaO) were added to the as-prepared CS/St membrane and stirred for 4 h at a temperature of 50 °C. Subsequently, the solution was sonicated for 20 min at room temperature. The solution was then heat printed at 60 °C, obtaining a CS/St/Ca membrane. Then, 0.1 g of urea was added to the as-prepared CS/St/Ca solution and stirred for 2 h. Thereafter, the solution was sonicated for 15 min at room temperature. The solution was then heat printed at 60 °C for 24 h, forming a CS/St/Ca–urea membrane. Each membrane was soaked in 1 M NaOH solution and washed until neutral. The membranes were characterized by FTIR (Shimadzu IR Prestige-21), SEM–EDX (Hitachi SU 3500 at 5000 V voltage and 13.9700 nA emission current), and elemental analysis (Thermo Scientific FlashSmart CHNS/O). The physiochemistry of the membranes was investigated by swelling, hydrophobicity, and tensile strength tests (Pearson Panke Equipment Ltd., model WDW-1/2/3/5).

2.3. Testing membranes as SRF

The nitrogen release test was conducted by immersing the CS/St/Ca–urea membrane in 10 mL of distilled water. Then, a complexing solution was made by mixing 1 g of p-DMAB, 50 mL of ethanol, and 10 mL of HCl. At a certain time, 2 mL of the membrane solution was taken and 3 mL of the complexing solution was added. Subsequently, the mixed solution was analyzed using a UV–Vis spectrophotometer (Hanna Iris Spectrophotometer H1801). The interaction between urea and p-DMAB produced a yellowish complex, which was then analyzed using a UV–Vis spectrophotometer at a wavelength of 420–430 nm [10,11].

2.4. Hydrophobicity test

The hydrophobicity test was conducted by cutting the sample with size 2×2 cm and obtaining the initial weight (W_0). Then, the sample was placed in a glass beaker filled with 20 mL of water and left to stand for 24 h. Afterward, the membrane was weighed to obtain the final mass. The amount of water absorbed by the sample was calculated using the following equation:

$$\text{Water absorption (\%)} = \frac{W - W_0}{W_0} \times 100\%, \quad (1)$$

where W_0 is the dry sample weight and W is the wet sample weight.

Afterward, the percentage of water absorbed was calculated using the following equation:

$$\text{Hydrophobicity (\%)} = 100\% - \text{Water absorption (\%)}. \quad (2)$$

3. Results and discussion

3.1. Influence of citric acid

The physical appearance of the chitosan membrane and its modifications are shown in Fig. 1. It is observed that increasing the amount of citric acid added to the membrane causes further damage to the membrane shape. It is known that citric acid can engage in electrostatic interactions with the positively charged amino groups present in the chitosan chains, leading to the formation of ionically cross-linked networks [12]. However, an excess of citric acid breaks down the membrane and may reduce the intermolecular forces between polymer chains, resulting in unstable interactions that prevent membrane formation [12]. This result was corroborated by the FTIR spectra shown in Fig. 2.

The FTIR spectra of chitosan and citric acid cross-linking are shown in Fig. 2. In the spectrum of citric acid cross-linked chitosan

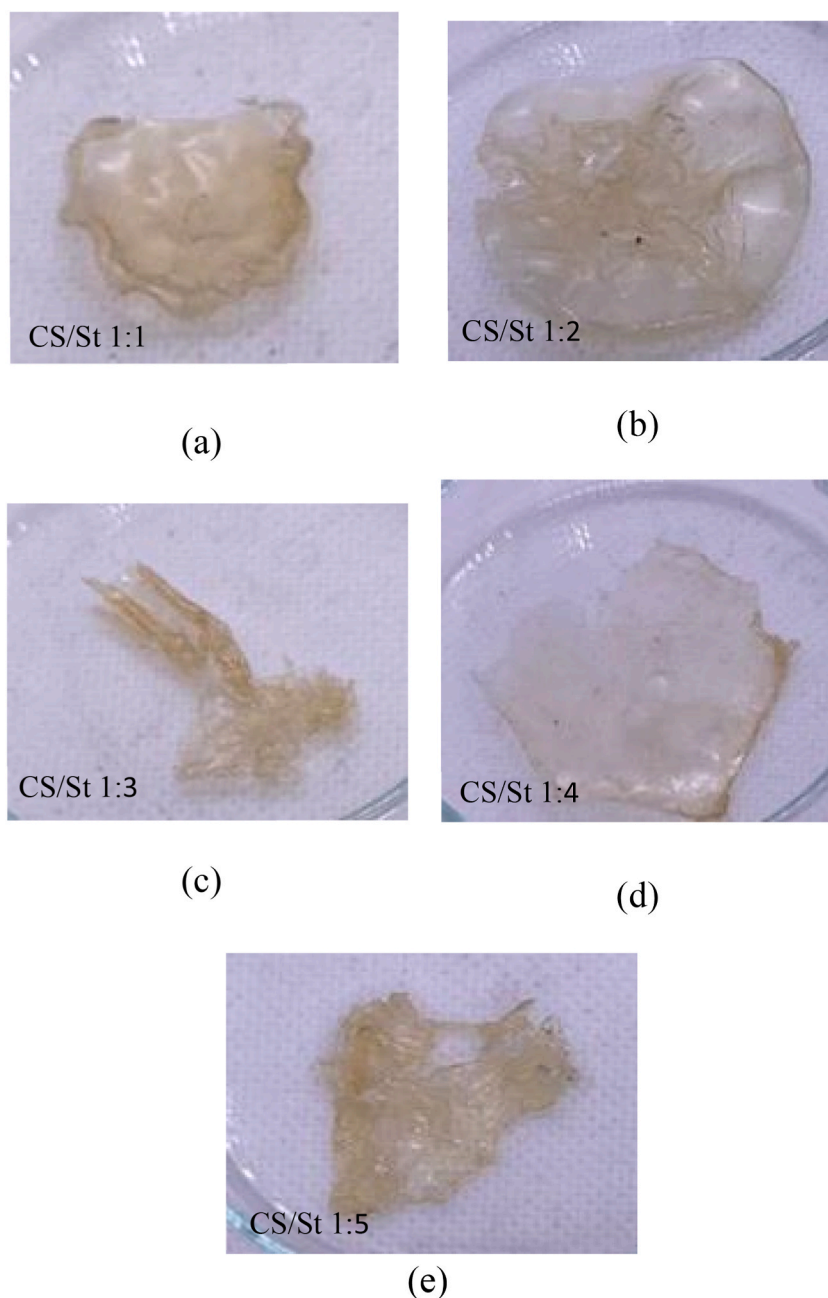


Fig. 1. Physical appearance of the (a) CS/St 1:1, (b) CS/St 1:2, (c) CS/St 1:3, (d) CS/St 1:4, and (e) CS/St 1:5 membranes.

(CS/St), a new peak at wavenumber 1640 cm^{-1} appears, which is attributed to the interaction between COOH and NH_3 via amidation reaction [12], indicating the successful cross-linking of chitosan with citric acid. In addition, the peak at 1572 cm^{-1} shifts to a higher wavenumber, indicating that the NH_2 in CS is protonated to NH_3^+ and the sample is essentially in acetate form [13]. Consequently, ionic interactions are confirmed to exist in chitosan–citric acid. The difference in the intensity of the OH peak at approximately 3429 cm^{-1} indicates that cross-linking is also formed by a large number of hydrogen bonds [14,15]. A higher amount of citric acid causes a relative decrease in intensity of the OH peak at CS/St 1:2 and 1:3, leading to disruption of the chitosan–citric acid interaction.

The variation in the tensile strength of citric acid in CS/St membranes is illustrated in Fig. 3(a). Incorporating citric acid to chitosan with a ratio of CS/St = 1:1 enhances the tensile strength. This improvement arises from cross-linking facilitated by a significant number of hydrogen and covalent bonds, contributing to the mechanical response of membrane's soft elasticity [12,14,15], as observed in the FTIR spectra. However, increasing citric acid content further, at CS/St ratios of 1:2 and 1:3, results in a decrease in tensile strength. This decline is attributed to the disruption of cross-linking and the excessive formation of citrate complexes, which adversely affect the mechanical properties of the membrane. Therefore, the optimal condition for membrane formation is achieved at CS/St = 1:1, serving as the basis for further variation.

Fig. 3(b) shows that CS/St with ratios of 1:1 and 1:2 have a high degree of membrane development, indicating that the addition of citric acid can increase the volume of cavities in the membrane. The cavities in the membrane will hold water and increase the diameter of the membrane. A higher water absorption leads to a high degree of membrane development [16]. However, a higher amount of citric acid added to the membrane impedes membrane development because of the disruption of the membrane and the formation of citrate complexes. This result is consistent with tensile strength results discussed above. In addition, a higher amount of citric acid added to the membrane increases the hydrophobicity (Fig. 3(c)). The utilization of hydrophilic groups in the amidation reaction will lead to a reduction in the hydrophilic nature of the composite film. Consequently, the hydrophobicity of the cross-linked film is enhanced [12].

Exposure of the CS/St membrane to various pH solutions is needed to assess the stability of the membranes when applied to the environment. Our study showed the superiority of CS/St 1:1 and 1:2 under various pH conditions, i.e., from pH 3 to pH 11, even up to 30 days. The morphology of the membranes is still intact because of the reorganization of the polymer under the effect of deprotonation [17]. Although the morphology of CS/St 1:1 and 1:2 under various pH conditions exhibited superiority, its tensile strength after 30 days decreased to $1\text{--}2\text{ N/mm}^2$. This result indicated that the membrane degraded over time. Meanwhile, the CS/St 1:3, 1:4, and 1:5 membranes underwent the degradation process, indicating low resistance to strong acid and alkaline solutions. At low pH, the CS/St 1:3, 1:4, and 1:5 membranes degraded at 20, 15, and 10 days, respectively. The addition of more citric acid accelerates the degradation of the membrane and weakens the interaction between citric acid and chitosan because citric acid could act as a plasticizer rather than as a cross-linker [10,18]. Therefore, the phenomenon is linked to the characteristic solubility of CS in dilute organic acids. Under alkaline conditions (pH 11), the CS/St 1:3, 1:4, and 1:5 membranes degraded rapidly in 5 days. The weak interaction between CS and citric acid causes the deacetylation of CS [19].

CS/St = 1:1 and CaO (CS/St/Ca) were added to increase the mechanical strength and thermal stability of chitosan. In addition, the Ca in CaO could increase the resistance of the membrane coatings formed [20]. Then, the formed membrane (CS/St/Ca) was characterized by FTIR, and the results are shown in Fig. 4. It can be observed that the FTIR spectrum of the CS/St/Ca membrane shows no notable differences from that of the CS/St membrane, indicating that CaO was detected by FTIR because of the low amount of calcium present. Therefore, EDX was applied to confirm the presence of calcium in the membrane, and the results are listed in Table 1.

Based on Table 1, Ca is present at 0.13 % in the CS/St/Ca 1:1 membrane, indicating the successful addition of CaO to the membrane. This finding is further supported by a 2.91 % increase in the content of O (i.e., from 44.09 % to 47 %) in the CS/St/Ca membrane compared with that in the CS/St membrane. The presence of Na in both CS/St and CS/St/Ca membranes is attributed to residual Na on

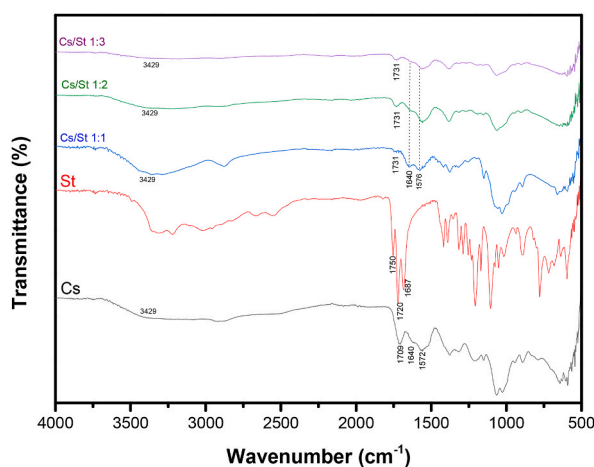


Fig. 2. FTIR spectra of pure chitosan, pure citric acid, and chitosan and citric acid cross-linking (CS: chitosan; St: citric acid).

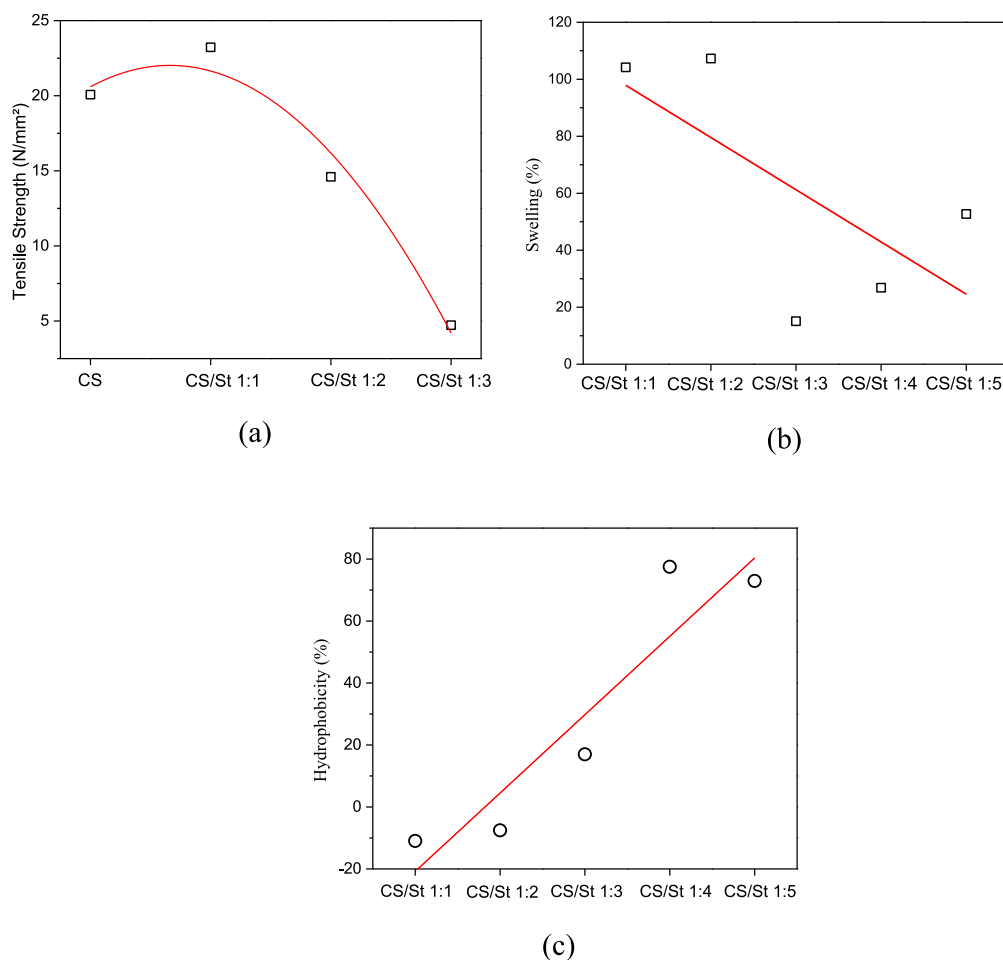


Fig. 3. (a) Tensile strength, (b) swelling, and (c) hydrophobicity of CS/St membranes.

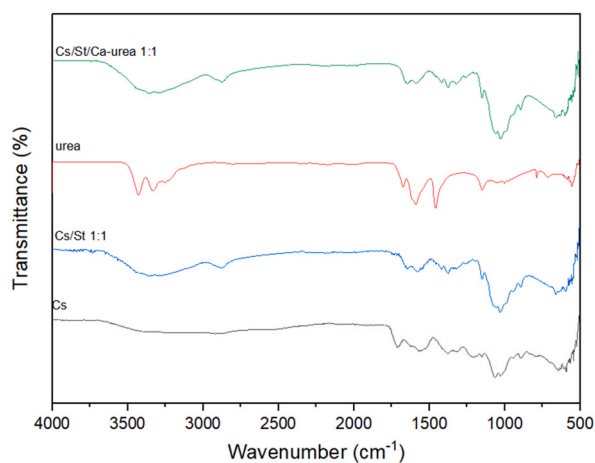


Fig. 4. FTIR spectra of CS/St/Ca-urea 1:1, urea, CS/St 1:1, and CS.

the membrane from the use of NaOH to release the membrane from its mold. The influence of Ca on the membrane was also investigated by differential scanning calorimetry (DSC) analysis, and the results are shown in Fig. 5(a). The CS/St/Ca membrane showed a shift in the exothermic peak to a lower temperature compared with the CS/St membrane, as shown in Fig. 5(a), indicating that Ca

Table 1

Elemental analysis of the membrane.

Sample	% Mass				
	C	N	O	Na	Ca
CS/St 1:1	37.86	17.91	44.09	0.14	–
CS/St/Ca 1:1	36.26	16.35	47.00	0.25	0.13

affects the amine functional group of CS. The interaction between calcium ions and the nitrogen atoms in the amine groups influences the formation or rearrangement of the polymer chains as they cool down and establish a more stable, organized structure after melting [35]. However, the interaction between Ca and the amine functional group cannot be detected by FTIR, as discussed previously. CS typically exhibits a broad endothermic peak in the DSC curve at approximately 70 °C–100 °C, which is associated with the evaporation of water bound to the polymer. Another significant thermal event is observed at higher temperatures, usually between 250 °C and 300 °C, corresponding to the thermal degradation of the amine functional groups of CS [21].

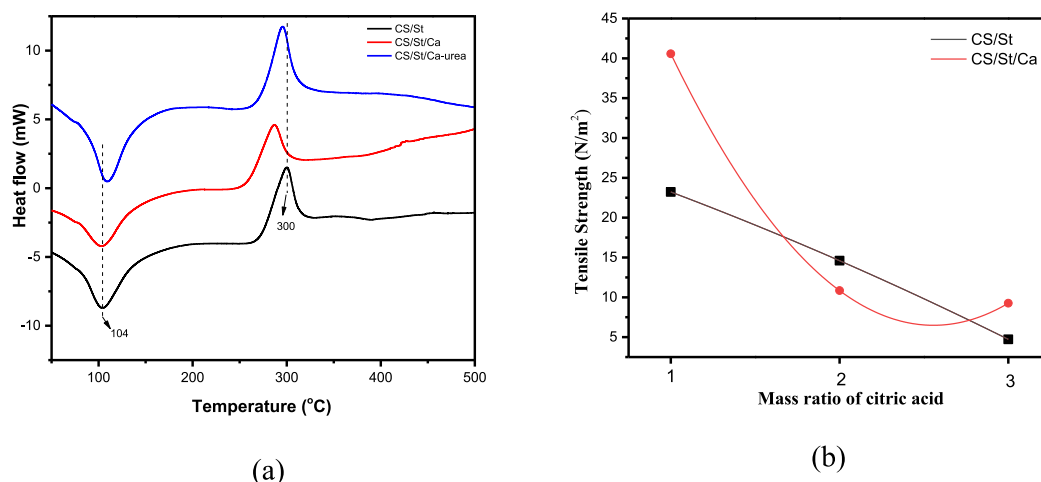
The addition of Ca to CS/St significantly affects the tensile strength of the modified chitosan membrane [22], as shown in Fig. 5(b). CS, a polymer characterized by its hydrophilic nature and NH₂ and OH functional groups, can encapsulate CaO nanoparticles through hydrogen bonding, leading to the formation of nanocomposites with unique properties, such as enhanced tensile strength. Intramolecular and intermolecular hydrogen bonds are formed by the –OH and –NH₂ groups, which significantly impede the rotation and mobility of the molecular chain. The introduction of CaO weakens the intermolecular hydrogen bonds and leads to the formation of new hydrogen bonds between CS and CaO, which facilitate the rotation and movement of the molecular chain, resulting in a marked improvement in both tensile strength and elongation at break of the composite membranes [23,24].

The appearance of the membrane was examined both from the surface side and cross section, as shown in Fig. 6. The CS/St membrane (Fig. 6(a) and (d)) has a dense structure with small pores. By contrast, CS/St/Ca (Fig. 6(b) and (e)) exhibits a dense structure with a smooth and porous surface, which can be attributed to the citric acid and Ca additives diffusing well into the membrane [25].

The CS/St/Ca membrane was treated with urea to simulate the use of fertilizers. Urea was added to the CS/St/Ca membrane through the blending method to ensure its proper integration. However, FTIR analysis did not detect the presence of urea in CS/St/Ca, as shown in Fig. 4. The absence of urea in the FTIR analysis is probably due to the low amount of urea in the membrane. Therefore, the membrane was further characterized by elemental analysis, and the results are presented in Table 2.

Based on Table 2, the mass percentage of nitrogen in the CS/St/Ca–urea membrane has significantly increased compared with that in the CS/St/Ca membrane, indicating that the addition of urea was successful [26]. This finding is further supported by the increased mass percentages of carbon and hydrogen. Furthermore, the addition of urea has slightly influenced the morphology of CS/St/Ca, as shown in Fig. 6(c) and (f). The pores in CS/St/Ca–urea appear slightly denser than those in CS/St/Ca, indicating the incorporation of urea in the pores of CS/St/Ca–urea.

The impact of adding CaO in the membrane was examined with varying masses of 0.01, 0.02, 0.03, 0.04, and 0.05 g, which are denoted as CS/St/Ca (1) to CS/St/Ca (5), respectively. The findings indicate that increasing Ca content in the membrane decreases its tensile strength. Additionally, Ca addition enhances the membrane's hydrophilic properties, as evidenced by a reduction in the water contact angle on the membrane surface, as shown in Fig. 7. With increasing CaO mass, the water contact angles were calculated to be 74.62°, 73.30°, 71.94°, 70.39°, and 58.75°. This aligns with Hosseini et al. (2022), who reported that adding metal additives to membranes can lower the water contact angle [33]. Membranes with high hydrophilicity due to the incorporation of metal additives help reduce membrane fouling [34]. High hydrophilicity allows water to penetrate the membrane pores and gradually release urea

**Fig. 5.** (a) DSC analysis of membranes and (b) tensile strength with the addition of Ca.

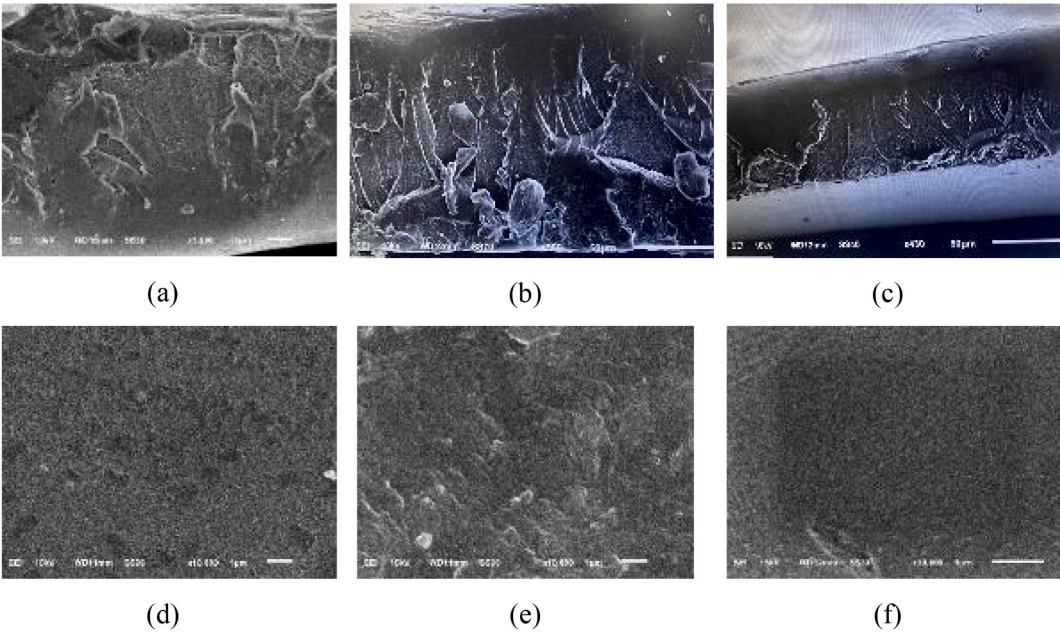


Fig. 6. Membrane morphologies of the cross sections of (a) CS/St, (b) CS/St/Ca, and (c) CS/St/Ca-urea and surfaces of (d) CS/St, (e) CS/St/Ca, and (f) CS/St/Ca-urea.

Table 2
Elemental analysis of the characterization results of CS/St/Ca-urea.

Sample	% Mass		
	C	H	N
CS/St 1:1	39.73	7.21	6.96
CS/St/Ca 1:1	42.05	7.37	7.18
CS/St/Ca-urea 1:1	45.27	8.07	8.25

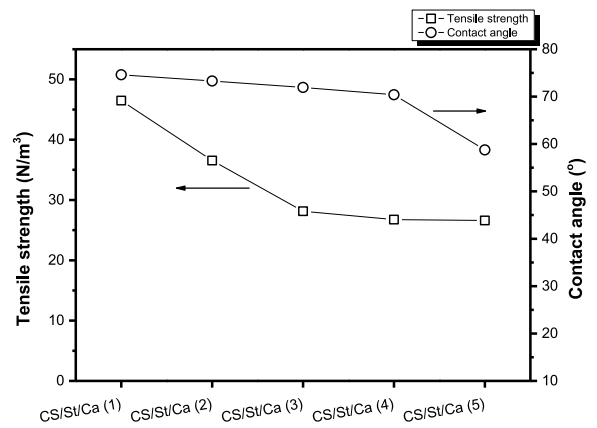


Fig. 7. Effect of Ca on the tensile strength and hydrophilicity of membranes.

content.

3.2. Urea release test

Based on Fig. 8, the release of urea corresponds to the duration of time. Urea dissolves well in water through hydrogen bonding interactions. As the soaking time of the membrane increases, the interaction between urea and water intensifies, resulting in the rapid

release of urea. All five membranes exhibit similar urea release profiles, characterized by a slowed release. The results show that CS modification can effectively serve as a coating for urea fertilizer, leading to an SRF with variable average release rates and time delays. In Table 3, urea release on the CS/St/Ca-urea membrane has average release rates of 3.37–9.46 ppm day⁻¹ or 0.7–1.7 % w/w.

One of the definitions of SRF proposed by the European Committee for Standardization (CEN) is that no more than 15 % of the nutrients in a fertilizer are released within 24 h [27]. Based on the application of CS/St/Ca-urea membranes, only 0.7–1.7 % of nitrogen or 3.4–9.46 ppm urea was released within 24 h, as per the definition of SRF proposed by the CEN.

The effectiveness of the CS/St/Ca-urea membrane for SRF is shown in Table 4. The CS/St/Ca-urea membrane exhibited good performance compared to the other membranes. The average N release was 0.7 % day⁻¹, i.e., releasing 7 % of urea over 10 days using the CS/St/Ca (3)-urea membrane. Meanwhile, the other membranes released N in the range of 3.18–48 % on the first day.

To determine the urea release from the CS film cross-linked with citric acid and calcium, several kinetic models, namely, first-order, Higuchi, and Korsmeyer–Peppas models, were used. The results are presented in Table 5. Based on the linearity of the curves shown in Table 5, the kinetics of urea release tend to follow the Higuchi kinetic model, with an R^2 value of 0.9505. This type of reaction kinetic occurs in SRFs in the form of a thin film membrane CS/St/Ca (3)-urea. It presumes that urea dissolves quickly relative to the diffusion process, making diffusion the slowest step. The urea concentration gradient is uniform, and the matrix functions as an ideal sink, implying that the urea concentration in the surrounding medium is minimal. The use of citric acid and calcium as binders enables the slow-release of urea from the membrane, indicating that the CS/St/Ca membrane can be optimally utilized as a coating for SRFs [32].

4. Conclusion

Based on the results, we can conclude that chitosan membrane modification with citric acid and CaO provides improved membrane characteristics, including degree of development, hydrophobicity, membrane stress, and nitrogen release on the membrane. The CS/St ratio of 1:1 shows high stability under acid and base conditions, high strength tensile, and swelling. The modified CS/St/Ca-urea membrane can function effectively as an SRF, following the Higuchi kinetic model. The average N release is 0.7 % day⁻¹, i.e., releasing 7 % of urea over 10 days using the CS/St/Ca-urea membrane.

CRedit authorship contribution statement

Taufik Abdillah Natsir: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Alvina Mita Iknawati:** Writing – original draft, Formal analysis, Data curation. **Iqbal Dian Wanadri:** Investigation, Data curation. **Dwi Siswanta:** Supervision, Formal analysis. **Retno Ariadi Lusiana:** Supervision, Methodology. **Sari Edi Cahyaningrum:** Supervision, Methodology, Conceptualization.

Ethical statement

This study did not involve human or animal subjects, and thus, no ethical approval was required.

Data availability statement

The datasets generated within the scope of the current study are available from the corresponding author on reasonable request.

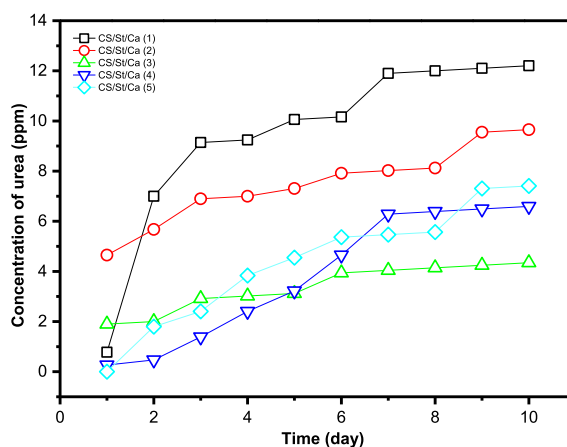


Fig. 8. Release rates of urea in water.

Table 3

Release rates of urea from the chitosan modified membranes.

Membranes	Average daily urea release rate (ppm)	Percentage of N release (% w/w)
CS/St/Ca (1)-urea	9.46	1.7
CS/St/Ca (2)-urea	7.48	1.3
CS/St/Ca (3)-urea	3.37	0.7
CS/St/Ca (4)-urea	3.82	0.8
CS/St/Ca (5)-urea	4.37	0.9

Table 4

Performances of our membrane and various reported membranes for urea SRF.

Membrane	Performance	Reference
Chitosan/citric acid/calcium-urea	Average N release of 0.7 % day ⁻¹ or released 7 % of urea in 10 days	This study
Chitosan-humic acid-urea (CHAU)	Released 44 % of urea on the first day	[28]
Chitosan-peat-urea (CPTU)	Released 48 % of urea on the first day	[28]
Chitosan-humin-urea (CHMU)	Released 67 % of urea on the first day	[28]
Salicylimine-chitosan hydrogel	Prolonged released 45 % of urea on the first to fifth day	[29]
	Released 100 % of urea on the 35th day	
Sodium alginate/carboxymethyl starch sodium/polydopamine/urea (SCPU)	Released 79.7 % of urea on the 25th day	[30]
Chitosan-NPK	Released 14.7 % of N on the third day	[5]
	Released 19.2 % of N on the fifth day	
Sulfur-coated urea	Released 2.94 mol/L urea on the fifth day	[31]
Sulfur-gypsum-GML	Released 3.63 mol/L urea on the fifth day	[31]

Table 5

Different reaction kinetic models: (a) first-order, (b) Higuchi, and (c) Korsmeyer-Peppas.

First-order		Higuchi		Korsmeyer-Peppas		
R ²	K ₁ (day ⁻¹)	R ²	K _H (day ^{1/2})	R ²	K (day ⁻ⁿ)	n
0.8733	0.0944	0.9505	0.1258	0.9422	1.7565	0.4052

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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