Research article

Synthesis and characterization of chitosan-modified membrane for urea slow-release fertilizers

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ABSTRACT

Background: Urea is a fertilizer widely used by farmers, especially vegetable farmers, due to its high nitrogen content, around 46 %. However, plants only use a small amount of nitrogen, a maximum of 35 %, while the remaining nitrogen is wasted and released into the environment. Undeniably, it causes increases production costs and environmental problems. A slow-release urea fertilizer (SRF) has been formulated to resolve these issues.
Methods: In this study, the membrane was made of chitosan with several crosslinking agents such as Tripolyphosphate (TPP). In addition, calcium ion bonds are expected to increase the interaction with urea fertilizer through the encapsulation process.
The results: Our data showed that urea slow-release fertilizer (SRF) with the chitosan/TPP/Ca membrane, was successfully synthesized. This membrane has the characteristics of a thin white layer that is transparent. The physical and chemical characterization of SRF membranes with various coating membrane variations showed that the chitosan/TPP/Ca-urea membrane has Young's modulus of 7.75–22.05 N/mm2, swelling of 109.52–132.62 % and porosity of 0.756–1.06 %. Functional group analysis shows that several spectral changes indicate the presence of crosslinking process between the chitosan functional groups and TPP. The urea release results show that the membrane is released through a diffusion mechanism. Furthermore, SEM results show that these membranes have pores with various shapes and sizes.
Conclusion: Based on the result, it can be concluded that chitosan membrane modification with the addition of TPP and calcium oxide provides improved membrane characteristic cs including degree of development, hydrophobicity, membrane stress, and nitrogen release on the membrane. This membrane shows is indicating suitability as a slow-release fertilizer.

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1. Introduction

Urea is the most common crop fertilizer due to its high nitrogen content (±46 %). Nitrogen is one of the macronutrients needed by plants, which can only be used in limited amounts (30–35 %) due to evaporation, denitrification, mobilization, volatilization, and leaching processes [1–3]. Nitrogen losses can be reduced by re-fertilizing in one growing season; however, this technique is inefficient due to the high cost for the farmers and the increased chance of water and soil pollution [4,5]. Besides its benefits, using nitrogen is found to cause a decrease in soil quality and fertility, toxicity to the ecosystem, and soil and water pollution [6–9]. An alternative method is a slow-release urea system (SRF) that is found to improve the efficiency of fertilizer use to sustain the needs of plants for nitrogen, limit the environmental impacts [10], and reduce the frequency of urea fertilizer application [11].

Urea fertilizer in the form of tablets or granules is coated with a coating or biodegradable material that is hard to dissolve in water [12]. These fertilizers are manufactured using coating or encapsulating conventional soluble fertilizers with a water-insoluble and porous membrane to control water penetration and nutrient dissolution rates [5,13,14]. Several studies have reported improving plant growth, harvest yield, and nutrient concentrations using the encapsulated urea fertilizer with an inert carrier [15,16]. The slow release of coated urea is controlled by diffusion through the coating; the coated urea with sulphur, polyethylene, and superphosphate are typical examples [3,17,18]. Some studies show that the urea coating process provides longer release times and higher utility rates and is mainly used in developed countries. The technology is not yet widespread in developing countries due to higher costs. Meanwhile, developing countries have a high demand for nitrogen fertilizer with nitrogen efficiency use of 20–35 % [5,11].

A double-layer, slow-release, water-retention urea fertilizer is made by crosslinking poly (acrylic acid) containing urea (outer layer), polystyrene (PS) (inner layer), and urea granules (core) [19,20]. Elemental analysis results showed that the product's nitrogen content was 33.6 % by weight [21,22]. The outer layer regulates the rate of nitrogen release and protects the inner layer from damage. It was found that the percentage of coating, temperature, and moisture absorption significantly affected nitrogen release [13,23]. However, the pH has no effect. The results show that the product has good slow-release properties and excellent water retention capacity, which can effectively improve the utilization of fertilizer and water resources. This research indicates that slow-release fertilizer can be applied in agriculture and horticulture, especially in drought-prone areas [24–26].

Another option as a carrier is chitosan, a natural polymer that can be isolated from shrimp shell waste. Chitosan is biodegradable, non-toxic, and a natural polymer rich in nitrogen. Chitosan can be used as a slow-release matrix because it can reduce production costs and is environmentally friendly [27,28]. Chitosan has been intensively researched in biomedicine, elastic hydrogel, water treatment, bio membranes, and active food packaging due to its non-toxic, biodegradable, biocompatibility, and antibacterial abilities [29]. Several researchers have made SRF fertilizers in granule form using chitosan as its coating. Previous findings have shown that the granule form has limitations of agglomeration, causing rough surface formation. Some pores are closed, thus disrupting the performance of SRF fertilizer [1,13,23]. Innovation is required to address this problem by producing SRF fertilizer in membrane form, which is anticipated to make things more effective, efficient, and straightforward to manufacture and use [30,31]. Previously, membranes for SRF fertilizer were formulated with various coatings, including starch with an acrylate crosslinking agent, starch with the borax crosslinking agent, chitosan with PVA, chitosan with polyester crosslinking agent, chitosan with acrylamide crosslinking agent, etc [13,32]. Several studies have shown that only two materials are used, for example, starch and acrylate; chitosan with PVA means that the encapsulated or coated fertilizer will easily come off, so to overcome this, technological innovation needs to be carried out by adding material to bind the fertilizer [31,33].

In this research, SRF will be developed to form a chitosan-based membrane modified with several Tripolyphosphate (TPP) and Calcium oxide cross-linking materials. The addition of calcium ions from calcium oxide is expected to improve the encapsulation process when interacting with urea fertilizer.

2. Materials and methods

All chemicals used in the pro-analysis conditions were obtained from Merck, including chitosan (molecular weight = 40.000 g/mol), NaTPP (molecular weight = 367,86 g/mol), CH_4N_2O (molecular weight = 60 g/mol), acetic acid (CH_3COOH, molecular weight = 60 g/mol), and NaOH (molecular weight = 40 g/mol), aquades, *p*-dimethylamine benzaldehyde (*p*-DMAB BM = 149,19 g/mol), ethanol p. a 96 %, and HCl 37 %.

Table 1
Membrane composition.

No.	Membrane formula	Composition			
		Chitosan	NaTPP	CaO	Urea
1	FA	90 mL 1.66 %	0	0	0
2	FB	90 mL 1.66 %	10 mL 1.66 %	0	0
3	FC	90 mL 1.66 %	10 mL 1.66 %	0.01 g	0
4	FD	90 mL 1.66 %	10 mL 1.66 %	0.01 g	0.1 g
5	FE	90 mL 1.66 %	10 mL 3.22 %	0.01 g	0.1 g
6	FF	90 mL 1.66 %	10 mL 4.98 %	0.01 g	0.1 g

2.1. Synthesis CS/TPP/CA-urea membrane

The membrane compositions including chitosan, Na-TPP, CaO, and urea with various combination were used (Table 1). Each mixture was homogenized for ±2 h and followed by ultrasonics for 15 min at a temperature of 30 °C (Fig. 1). The mixture was then dried for ±3 h at 50 °C. The membrane formed was then soaked in 1 M NaOH and rinsed with distilled water until the pH was neutral.

2.2. Characterization OF CS/TPP/CA-urea membranes

Functional groups from the CS/TPP/CA-Urea membrane were identified e using FTIR (PerkinElmer Frontier) and, membrane thickness was measured using a Mitutoya Thickness Meter. Testing membrane positivity and surface morphology using Hitachi Flex SEM 100.

2.3. Membrane swelling

The membrane was dried at 40 °C for 30 min for swelling experiments and weighed (Wd). Subsequently, the membrane was soaked in distilled water for 24 h at 25 °C. A constant weight experiment ensured the swollen membrane reached an equilibrium state. The swollen membrane was carefully cleaned with tissue paper to eliminate excess surface water, and then its weight was measured using a mass balance. The swelling index was calculated by using formula below:

$$\%Swelling = \frac{Wa - Wb}{Wb} X100$$

where, Wa and Wb represent the weight of swollen and dry samples, respectively.

2.4. Porosity

The membrane was immersed in 10 mL of distilled water for 24 h. The membrane is dried and weighed to obtain the W0 (g) value as the initial wet weight of the membrane. The membrane was then dried in an oven at 100 °C until dry, cooled, and weighed to obtain the
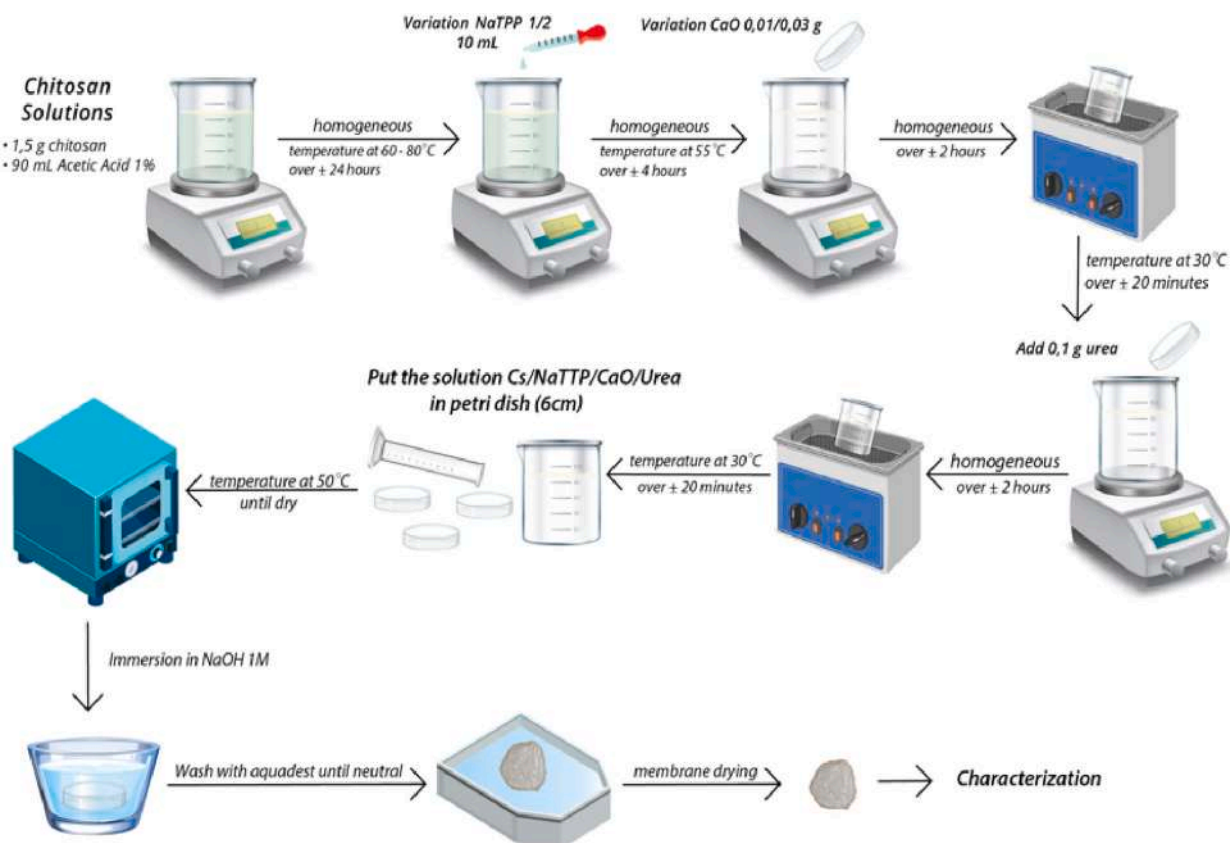

Fig. 1. Fabrication scheme of membrane SRF.

W1 (g) value as the dry weight of the membrane. The process was repeated five times, then dried using tissue paper quickly to obtain the percent membrane porosity value. The membrane porosity Ɛ (%) was calculated by using gravimetric method [34].

$$\varepsilon = \frac{\omega w - \omega d}{\rho \times a \times I}$$

ω_w, ω_d are the weights of wet and dry membrane samples, respectively; a is the membrane effective area (m^2), l is the membrane thickness (m), and ρ is the water density (0.998 g/cm^3).

2.5. Slow-release method

Slow-Release (SRF) application is carried out by two methods: aqueous release and deep release land with vegetable plants (kale). To assess urea release, a urea standard curve was initially created specified, includes concentrations of 0, 100, 200, 300, 400, and 500 ppm. In water release the method, 100 mL of distilled water is placed in a container with an SRF membrane. Every 10 h, 2 mL the solution was extracted, complexed using DMAB reagent, and its absorption was measured using UV–Vis spectrophotometry at a wavelength of 425 cm-1. For the soil release method, observations were extended to 10 days of kale plant growth. Every variation of membrane is incorporated into it land where kale plants are cultivated. Every day, 1 g of soil around the plants is dissolved in 10 mL of distilled and filtered water. Urea levels are measured by complexing the filtering results water using DMAB. Measurements were carried out on a UV–Vis spectrophotometer at wavelengths 425 cm-1. The urea release data were analyzed using the following mathematical models to investigate the mode of urea release from the membrane.

Zero Order Kinetics

$$Qt = Ko\ t$$

First order Kinetics

$$log\left(\frac{Qt}{Qo}\right) = -\frac{K1t}{2.303}$$

Korsmeyer and Peppas equation

$$Qt = K_{kp}t^n$$

Higuchi's equation

$$Qt = K_H t^{1/2}$$

Where, K_0, K_1, K_{HC}, K_{KP} and K_H are the coefficients of Zero order, First order, Korsmeyer-Peppas and Higuchi's equations and Qt is the percent of drug released at times' t.

3. Results and discussion

3.1. The characterization of membrane

Chitosan modification has been widely carried out by crosslinking reaction with the crosslinking agent sodium tripolyphosphate (NaTPP). The resulting membrane is shown in Fig. 2.

Bhumkar and Pokharkar study of NaTTP in the engineering process has found that ionic crosslinking of chitosan-NaTPP can facilitate kinetic binding of chitosan with aqueous medium under physiological conditions [9]. In this research, several membrane compositions were used (Table 1) and synthesized with ionic gelation (ionotropic gelation) method. Here, the interaction occurs

Fig. 2. Synthesized membrane: Cs (FA); 1 (FB); 2 (FC); 3 (FD); 4 (FE) and 5 (FF).

between the negative charge of the crosslinking agent (TPP) and the positive charge of the amine group on the chitosan molecule formed. The advantage of this method is that it is a simple reaction at a relatively low temperature and does not need to use organic solvents [15]. It was known that including TPP in the chitosan structure increases the pore radius, which increases membrane hydrophilicity (Fig. 3) [5].

The membrane that has been formulated was characterized by thickness and mass. Our results have shown that the membrane composition variations cause the difference in the membrane thickness. The thickness of the membrane tends to increase when the variation of membrane composition is higher (Fig. 3). It can be seen that the addition of NaTPP affects the thickness of the membrane as well as the physical and chemical characteristics of the membrane.

In Fig. 4, it can be seen that increasing the amount of NaTPP affects the membrane thickness. Modification of the chitosan membrane with the addition of NaTPP causes an increase in the mass (Fig. 5) and thickness of the membrane. This is related to density, where the denser the components that make up the membrane, the weight and thickness of the membrane will increase. The greater the amount of NaTPP added, the greater the weight and thickness of the membrane. The addition of additives will produce denser and thicker membranes, as well as increasing membrane selectivity [34]. NaTPP functions as a cross-linking agent which of course affects the composition and thickness of the membrane [34].

The data in Table 2 shows that the mechanical properties of the membrane were analyzed, including tensile strength (load), elongation (strain), and elasticity (Young's modulus). The load value is the value that shows the tensile strength at break, and the elongation value is the value that shows the amount of strain at break that the chitosan - TPP membrane has. Young's modulus assessment is used as a reference to determine the mechanical strength of the membrane.

It was found that the load value and elongation value are inversely proportional. The chitosan-TPP-Ca Urea-Ca Urea membrane with a ratio of 3:1 has a Young's modulus value more significant than the chitosan-TPP membrane. Additional chitosan in the improves improve the mechanical properties of the membrane improve with adding chitosan in the mixture. Its dense structure causes the distance between the molecules in the membrane to become closer. Conversely, the addition of TPP in the mixture can cause the mechanical properties of the chitosan-TPP membrane to become brittle [6]. The greater the Young's modulus value, the better the ability to prevent damage caused by external forces, resulting in a strong chitosan-TPP membrane [11].

The subsequent measurement that was conducted was the relation between the porosity and swelling degree of expansion as seen in Fig. 6, which are related, both of which refer to the amount of empty space in the membrane. Increasing the addition of TPP creates porosity but does not increase membrane porosity (Fig. 7). It was indicated from the presence of the best or optimal distance for the modified compound when TPP was added to chitosan. The best distance is needed in the permeation process, allowing the active side of the membrane to bind to the species that will be separated. These values are possible with the inclusion of TPP into the membrane structure, the groups capable of interacting with water increase. Furthermore, the water that has formed hydrogen bonds with the functional groups in the membrane structure leaves empty cavities similar to pores. Increasing the porosity of the membrane will cause the membrane to have adequate and regular cavity spacing, allowing the diffusion of water to pass through the membrane easily.

Next, functional groups on the chitosan membrane - chitosan-TPP-Ca Urea were determined and the possibility of reactions occurring that are characterized by the emergence of new functional groups that were previously undetectable or a shift, increase, and decrease in intensity. The success of the crosslinking reaction will be proven by the FT-IR spectra (Fig. 8). The chitosan-TPP-Ca Urea spectra shows C–H bond vibrations in the absorption area of 2922 cm^{-1}. The presence of absorption in the 1647 and 1422 cm^{-1} areas indicates the formation of new bonds between ammonium ions and phosphate ions. The absorption of 1156 cm^{-1} indicates the
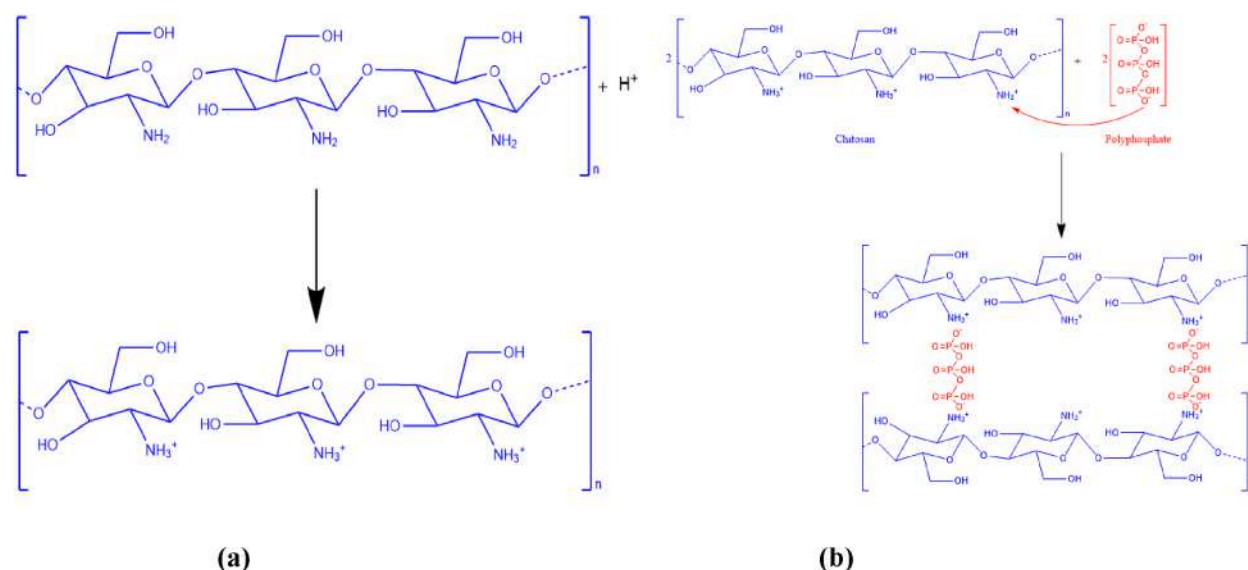

Fig. 3. Hypothetic interaction of chitosan with Tripolyphosphate [10]. (a) Chitosan protonation, (b) Crosslink agent process.
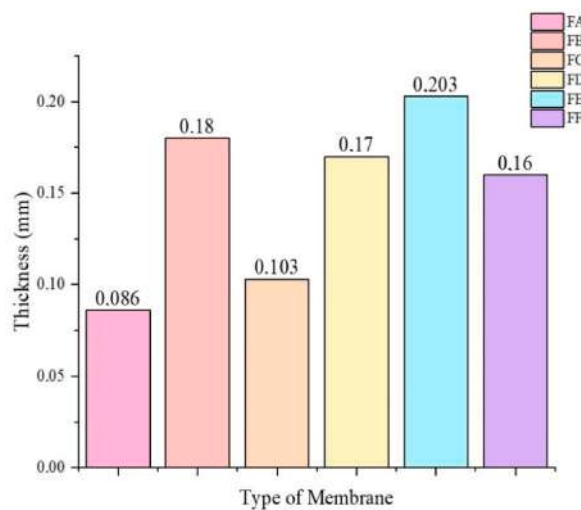
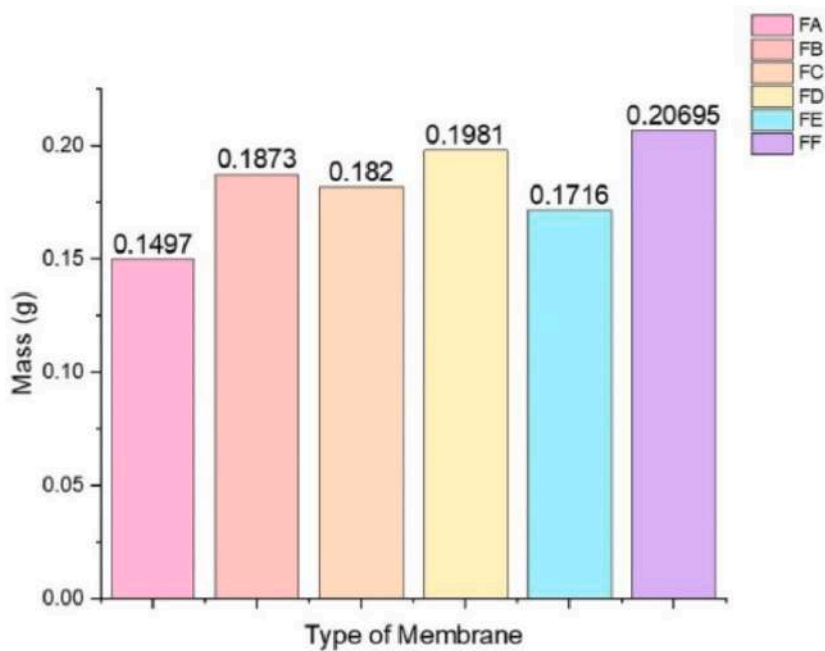**Fig. 4.** The results from membrane thickness measurement.

Fig. 5. The mass of the membrane.

Table 2
Mechanical test of properties of Chitosan –TPP-Ca-Urea Membrane.

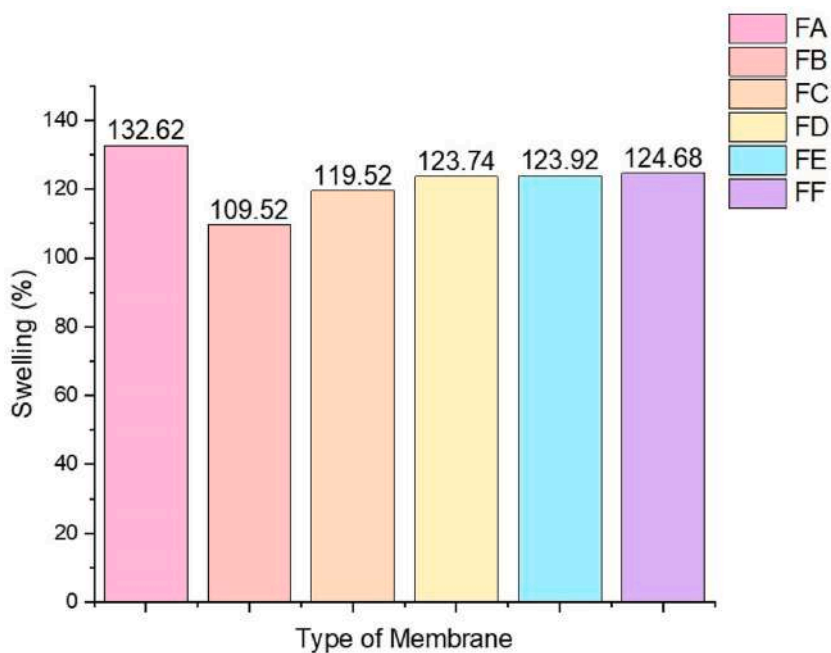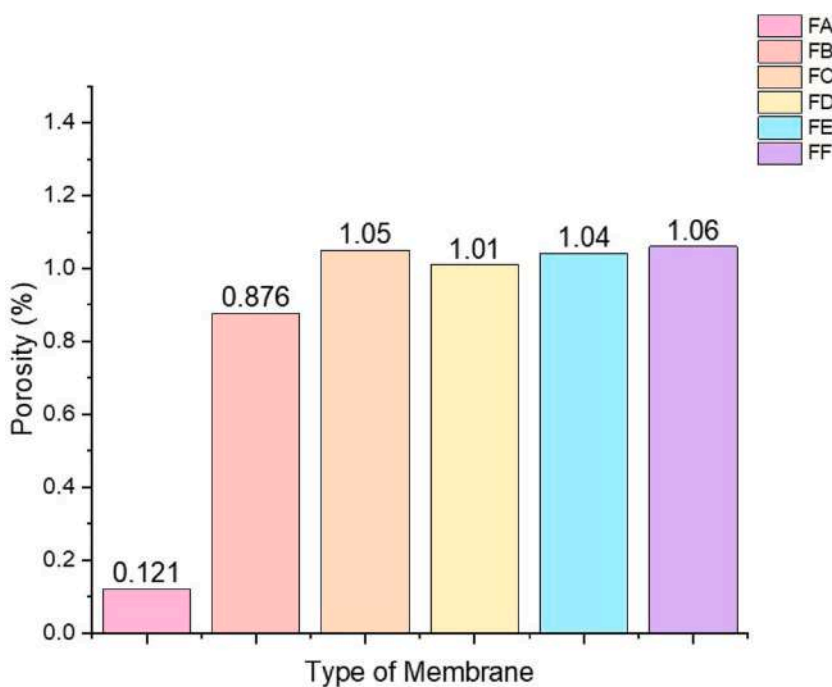| Membrane	Load (N/mm^2)	Elongation (%)	Modulus Young (N/mm^2)
FA	31.33	4.04	7.75
FB	54.83	3.40	16.12
FC	58.67	3.20	18.33
FD	60.67	3.40	19.92
FE	61.89	4,55	20.23
FF	62.98	5,87	22.05

Fig. 6. The swelling of the membrane.

Fig. 7. The porosity of the membrane.

stretching of the PO_2 group in phosphate which in line with previous findings [35].

3.2. Kinetic release of urea from membrane

Chitosan membrane crosslinked with sodium tripolyphosphate produces a strong and porous membrane. The addition of Ca ions will strengthen the membrane structure, especially on the membrane surface. Crosslinking can occur well so as to minimize the
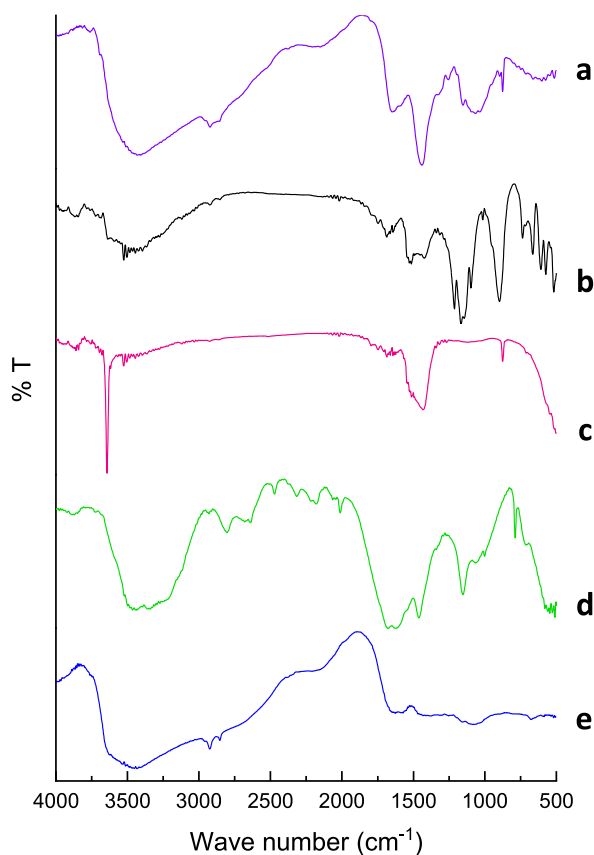
Fig. 8. FTIR spectra of (a) chitosan, (b) NaTPP, (c) Cao, (d) Urea and (e) chitosan/TPP/Ca Urea membranes the phosphate.

controlled release of urea in both water and soil media. The dropping stage with CaO solution is intended to form crosslinks in the TPP chitosan so that the particles tend to cluster and form intermolecular hydrogen bonds between the chitosan. The release profile of urea can be determined by passing a dissolution test. The results of the dissolution test were then analyzed into the zero-order, first-order, Higuchi & Korsmeyer-Peppas drug release kinetics model Tables 3 and 4). The table shows that urea release is dominant in the Korsmsyer-Peppas kinetic model in both water and soil media. Based on the n values obtained, all formulas have n between 0.45 and 0.89 which indicates that the mechanism of urea release after the release is diffusion. This shows that the mechanism of urea release is through a of diffusion mechanisms. This release occurs due diffusion of the membrane matrix. This result is the same as the release result of the drug encapsulated in the polymer [36] For the result indicated that these slow-release fertilizers bear all the essential properties to be efficiently used in agricultural practices. They are one of the most effective ways of nutrient delivery in plants because they can be formulated to release nutrients slowly and restrictively [27,37,36].

It is observed the urea released in the soil media was 18.7 % for the chitosan membrane alone and a maximum of 13.8 % for the Cs/NaTPP/Ca membrane (Fig. 9a). Meanwhile, for urea released in the water medium, the membrane containing only chitosan released 97.7 % of the urea, while the CS/NaTPP/Ca membrane released the most 95.6 % (Fig. 9b). Previous studies observed the Sodium Alginat Beads and Coated Sodium Alginate Beads samples released in a water test for 7 days at 57 % and 43 %, respectively [34,38]. In the soil test, the urea release from SAB and CSAB samples was monitored for 7 days at 19 % and 16 %, respectively [39].

3.3. Morphology surface of membrane

The data in Fig. 10 shows about membrane surface morphology using Scanning Electron Microscopy (SEM) which can provide information about the morphological structure of the membrane. With SEM, data can also be obtained regarding the pore size of the membrane, so that from these results, a standard of membrane structure uniformity can be determined that can be used.

The physical characteristics of the membrane were analyzed both in terms of surface morphology (Fig. 10(a–f)) and cross section (Fig. 11(a–f)). Making a chitosan membrane cross-linked with sodium tripolyphosphate produces a strong and porous membrane. The resulting membrane has pores of various sizes as seen in Fig. 10(a–f). The results of surface morphology analysis also show that there is no agglomeration that can close pores and inhibit membrane performance. The addition of Ca ions will strengthen the membrane structure, especially on the membrane surface. Cross-linking can occur properly so as to minimize the controlled release of urea in both water and soil media. The dropping stage with a CaO solution is intended to form cross-links in the chitosan -TPP, thereby producing

Table 3
Dissolution Kinetic Urea in the water medium.

Membrane	Zero order		First order		Higuchi		Korsmeyer-peppas		
	R^2	Ko (min^{-1})	R^2	K_1 (min^{-1})	R^2	K_H ($min^{-1/2}$)	R^2	K_{KP} (min^{-n})	n
FA	0.7375	0.0125	0.7358	0.0001	0.6787	0.3355	0.9203	0.8875	0.4666
FB	0.8437	0.0453	0.7686	0.0002	0.7649	0.4542	0.8975	0.9892	0.4675
FC	0.7877	0.0385	0.7862	0.0006	0.7851	0.4551	0.9238	0.9674	0.4875
FD	0.8325	0.0584	0.7192	0.0008	0.7573	0.3278	0.9194	1.0235	0.5674
FE	0.8438	0.0592	0.8025	0.0003	0.7882	0.5388	0.9328	1.1044	0.5724
FF	0.8779	0.0677	0.7843	0.0006	0.8334	0.4367	0.9188	1.0516	0.5902

Table 4
Dissolution Kinetic Urea in the soil medium.

| Membrane	Zero order		First order		Higuchi		Korsmeyer-peppas		
	R2	Ko (min-1)	R2	K1 (min-1)	R2	KH (min-1/2)	R2	KKP (min-n)	n
FA	0.0735	0.0124	0.0366	0.0001	0.5779	0.6347	0.9204	0.9875	0.4562
FB	0.0423	0.0361	0.0655	0.0002	0.5324	0.9875	0.8892	1.0233	0.5468
FC	0.0695	0.0331	0.0531	0.0004	0.5109	0.9983	0.9104	1.0674	0.5874
FD	0.0488	0.0277	0.0642	0.0001	0.4891	0.9295	0.9387	1.0563	0.5908
FE	0.0533	0.0981	0.0555	0.0003	0.5089	0.9542	0.9428	1.1033	0.6784
FF	0.0286	0.0669	0.0461	0.0005	0.5287	0.9919	0.9675	1.1255	0.7865
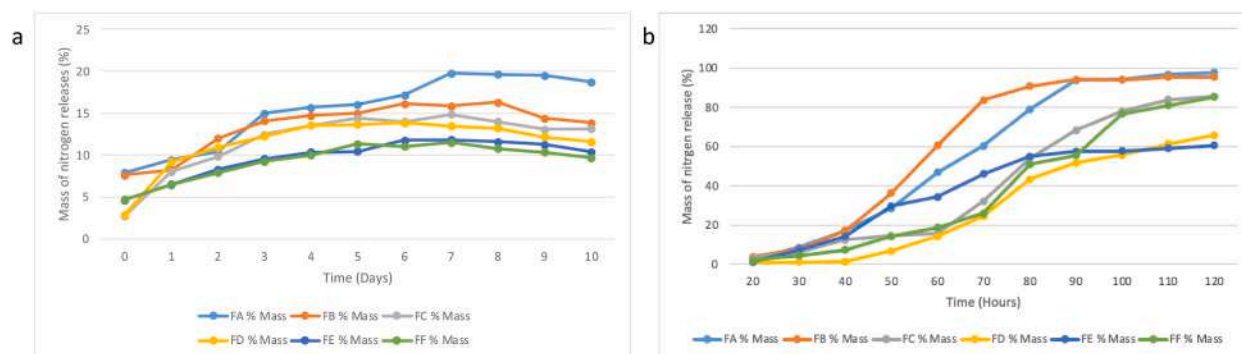
Fig. 9. The percentages of mass of nitrogen release in (a) soil and (b) water.

particles that tend to cluster and form intermolecular hydrogen bonds between the chitosan. It was found that the Cs/TPP3/Ca/Urea membrane showed a dense microstructure with a smooth surface and visible pores (Fig. 11). Coating with Ca^{2+} makes the membrane rougher, exposing a layer of compound on its surface.

4. Conclusions

Urea slow-release fertilizer (SRF) with a modified chitosan-based coating membrane, namely the chitosan/TPP/Ca/Urea membrane, was successfully synthesized. The results of the physical and chemical characterization of SRF membranes with various coating membrane variations show that the chitosan/TPP/Ca-urea membrane has a Young's modulus of 7.75–22.05 N/mm2, a Swelling of 109.52–132.62 % and a porosity of 0.756–1.05 %. Functional group analysis shows that there are several spectral changes indicating that a cross-linking process has occurred between the chitosan functional groups and TPP. The results of urea release and calculation of urea release kinetics show that urea is released from the membrane through a diffusion mechanism. SEM results show that the cross-section of the membrane has pores and an asymmetrical pattern, while the surface morphology is almost entirely porous with varying shapes and sizes and no agglomeration. Future research needs to carry out SRF trials to extend the release time in the soil and observe its effect on plants.

There are no conflicts to declare.

Data availability statement
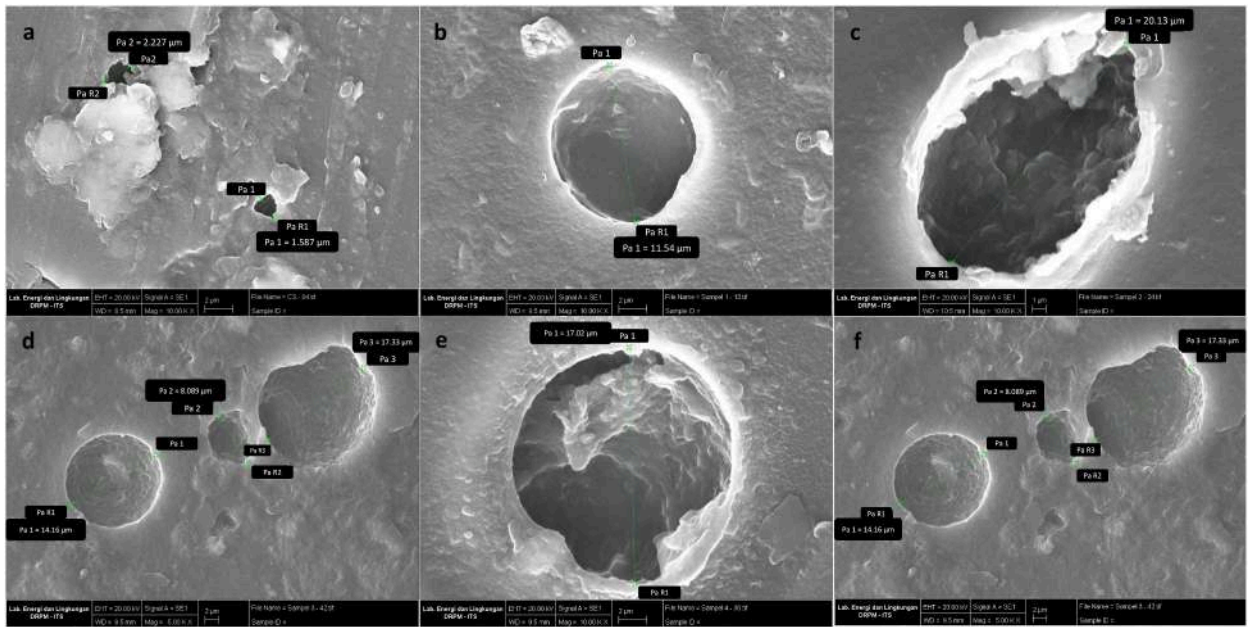
No addition information is available for this paper.

Fig. 10. Chitosan membrane surface morphology: (a) FA, (b) FB, (c) FC, (d) FD, (e) FE and (f) FF.
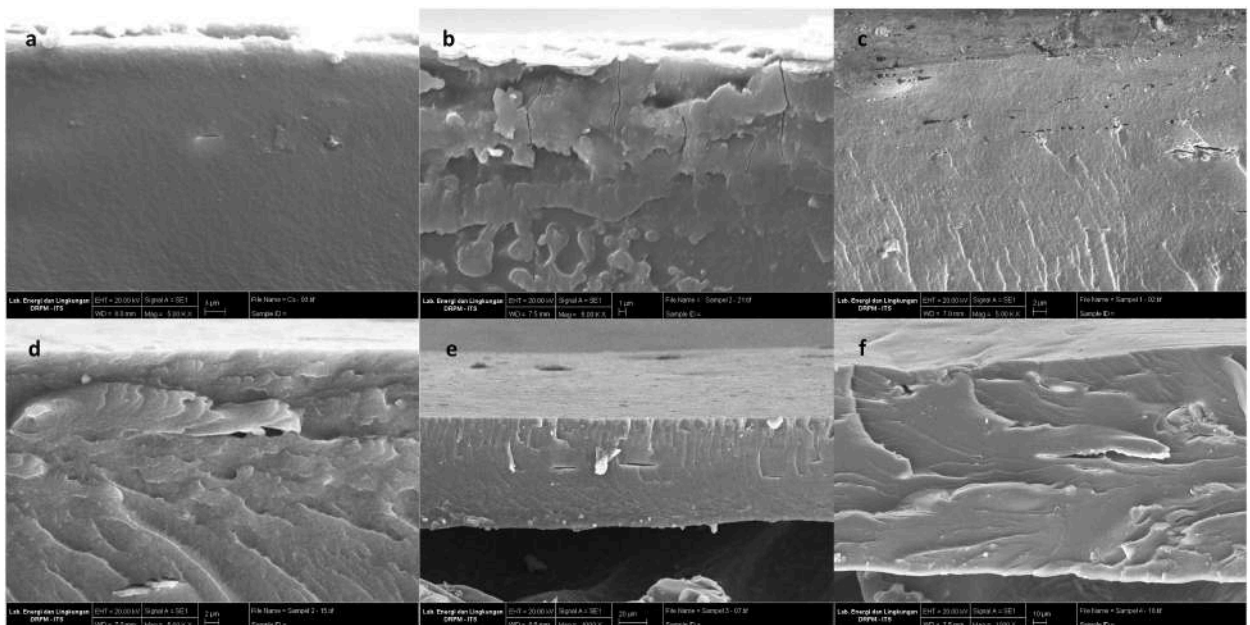

Fig. 11. Cross section of chitosan membrane: (a) FA, (b) FB, (c) FC, (d) FD, (e) FE and (f) FF.

CRediT authorship contribution statement

Sari Edi Cahyaningrum: Writing – review & editing, Methodology, Investigation, Conceptualization. **Retno Ariadi Lusiana:** Writing – original draft, Methodology, Data curation. **Taufik Abdillah Natsir:** Writing – original draft, Validation, Formal analysis. **Fitriari Izzatunnisa Muhaimin:** Project administration, Methodology, Investigation, Funding acquisition. **Andika Pramudya Wardana:** Project administration, Methodology, Investigation, Funding acquisition. **Amalia Putri Purnamasari:** Visualization, Validation, Supervision, Software, Resources. **Misni Bin Misran:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

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References

[1] S. Bi, V. Barinelli, M.J. Sobkowicz, Degradable controlled release fertilizer composite prepared via extrusion: fabrication, characterization, and release mechanisms, Polymers 12 (2) (Feb. 2020) 301, https://doi.org/10.3390/polym12020301.

[2] X. Yang, B. Yu, Z. Zhong, B. Guo, Y. Huang, Nevirapine-polycaprolactone crystalline inclusion complex as a potential long-acting injectable solid form, Int. J. Pharm. 543 (1–2) (May 2018) 121–129, https://doi.org/10.1016/j.ijpharm.2018.03.043.

[3] B. Beig, et al., Slow-release urea prills developed using organic and inorganic blends in fluidized bed coater and their effect on spinach productivity, Sustainability 12 (15) (Jul. 2020) 5944, https://doi.org/10.3390/su12155944.

[4] M.K. Souri, M. Naiji, M.H. Kianmehr, Nitrogen release dynamics of a slow release urea pellet and its effect on growth, yield, and nutrient uptake of sweet basil (Ocimum basilicum L.), J. Plant Nutr. 42 (6) (Apr. 2019) 604–614, https://doi.org/10.1080/01904167.2019.1568460.

[5] W. Tanan, J. Panichpakdee, P. Suwanakood, S. Saengsuwan, Biodegradable hydrogels of cassava starch-g-polyacrylic acid/natural rubber/polyvinyl alcohol as environmentally friendly and highly efficient coating material for slow-release urea fertilizers, J. Ind. Eng. Chem. 101 (Sep. 2021) 237–252, https://doi.org/10.1016/j.jiec.2021.06.008.

[6] M.A. Sutton, O. Oenema, J.W. Erisman, A. Leip, H. van Grinsven, W. Winiwarter, Too much of a good thing, Nature 472 (7342) (Apr. 2011) 159–161, https://doi.org/10.1038/472159a.

[7] M.M. Mekonnen, A.Y. Hoekstra, A global assessment of the water footprint of farm animal products, Ecosystems 15 (3) (Apr. 2012) 401–415, https://doi.org/10.1007/s10021-011-9517-8.

[8] A. Abbasi, et al., Agricultural pollution: an emerging issue, in: Improvement of Crops in the Era of Climatic Changes, New York, NY, Springer, New York, 2014, pp. 347–387, https://doi.org/10.1007/978-1-4614-8830-9_13.

[9] B. Gu, M.A. Sutton, S.X. Chang, Y. Ge, J. Chang, Agricultural ammonia emissions contribute to China's urban air pollution, Front. Ecol. Environ. 12 (5) (Jun. 2014) 265–266, https://doi.org/10.1890/14.WB.007.

[10] Y. Shen, et al., Synthesis and characterization of double-network hydrogels based on sodium alginate and halloysite for slow release fertilizers, Int. J. Biol. Macromol. 164 (Dec. 2020) 557–565, https://doi.org/10.1016/j.ijbiomac.2020.07.154.

[11] B. Azeem, K. KuShaari, Z.B. Man, A. Basit, T.H. Thanh, Review on materials & methods to produce controlled release coated urea fertilizer, J. Contr. Release 181 (May 2014) 11–21, https://doi.org/10.1016/j.jconrel.2014.02.020.

[12] P. Vejan, T. Khadiran, R. Abdullah, N. Ahmad, Controlled release fertilizer: a review on developments, applications and potential in agriculture, J. Contr. Release 339 (Nov. 2021) 321–334, https://doi.org/10.1016/j.jconrel.2021.10.003.

[13] H.-M. Ye, et al., Degradable polyester/urea inclusion complex applied as a facile and environment-friendly strategy for slow-release fertilizer: performance and mechanism, Chem. Eng. J. 381 (Feb. 2020) 122704, https://doi.org/10.1016/j.cej.2019.122704.

[14] M. Chen, et al., Mechanochemical transformation of apatite to phosphoric slow-release fertilizer and soluble phosphate, Process Saf. Environ. Protect. 114 (Feb. 2018) 91–96, https://doi.org/10.1016/j.psep.2017.12.008.

[15] M.K. Souri, M. Naiji, M.H. Kianmehr, Nitrogen release dynamics of a slow release urea pellet and its effect on growth, yield, and nutrient uptake of sweet basil (Ocimum basilicum L.), J. Plant Nutr. 42 (6) (Apr. 2019) 604–614, https://doi.org/10.1080/01904167.2019.1568460.

[16] C. Lu, H. Tian, Global nitrogen and phosphorus fertilizer use for agriculture production in the past half century: shifted hot spots and nutrient imbalance, Earth Syst. Sci. Data 9 (1) (Mar. 2017) 181–192, https://doi.org/10.5194/essd-9-181-2017.

[17] M.E. Trenkel, Impr. Point 44, Slow- and Controlled-Release and Stabilized Fertilizers : an Option for Enhancing Nutrient Use Efficiency in Agriculture. IFA, International Fertilizer Industry Association, 2010.

[18] S.M. Al-Zahrani, Utilization of polyethylene and paraffin waxes as controlled delivery systems for different fertilizers, Ind. Eng. Chem. Res. 39 (2) (Feb. 2000) 367–371, https://doi.org/10.1021/ie980683f.

[19] S.O. Dozie-Nwachukwu, Y. Danyuo, J.D. Obayemi, O.S. Odusanya, K. Malatesta, W.O. Soboyejo, Extraction and encapsulation of prodigiosin in chitosan microspheres for targeted drug delivery, Mater. Sci. Eng. C 71 (Feb. 2017) 268–278, https://doi.org/10.1016/j.msec.2016.09.078.

[20] D.F. da Cruz, R. Bortoletto-Santos, G.G.F. Guimarães, W.L. Polito, C. Ribeiro, Role of polymeric coating on the phosphate availability as a fertilizer: insight from phosphate release by Castor polyurethane coatings, J. Agric. Food Chem. 65 (29) (Jul. 2017) 5890–5895, https://doi.org/10.1021/acs.jafc.7b01686.

[21] A.S.M. Ghumman, et al., Degradable slow-release fertilizer composite prepared by ex situ mixing of inverse vulcanized copolymer with urea, Agronomy 12 (1) (Dec. 2021) 65, https://doi.org/10.3390/agronomy12010065.

[22] A.S.M. Ghumman, et al., A degradable inverse vulcanized copolymer as a coating material for urea produced under optimized conditions, Polymers 13 (22) (Nov. 2021) 4040, https://doi.org/10.3390/polym13224040.

[23] C. Xue, L.D. Wilson, Kinetic study on urea uptake with chitosan based sorbent materials, Carbohydr. Polym. 135 (Jan. 2016) 180–186, https://doi.org/10.1016/j.carbpol.2015.08.090.

[24] B. Azeem, et al., Production and characterization of controlled release urea using biopolymer and geopolymer as coating materials, Polymers 12 (2) (Feb. 2020) 400, https://doi.org/10.3390/polym12020400.

[25] H. Yan, et al., Porous geopolymer based eco-friendly multifunctional slow-release fertilizers for promoting plant growth, Colloids Surf. A Physicochem. Eng. Asp. 631 (Dec. 2021) 127646, https://doi.org/10.1016/j.colsurfa.2021.127646.

[26] M.Y. Naz, S.A. Sulaiman, Attributes of natural and synthetic materials pertaining to slow-release urea coating industry, Rev. Chem. Eng. 33 (3) (Jan. 2017), https://doi.org/10.1515/revce-2015-0065.

[27] M.S. Haydar, D. Ghosh, S. Roy, Slow and controlled release nanofertilizers as an efficient tool for sustainable agriculture: recent understanding and concerns, Plant Nano Biology 7 (Feb. 2024) 100058, https://doi.org/10.1016/j.plana.2024.100058.

[28] A. Dubey, D.R. Mailapalli, Zeolite coated urea fertilizer using different binders: fabrication, material properties and nitrogen release studies, Environ. Technol. Innov. 16 (Nov. 2019) 100452, https://doi.org/10.1016/j.eti.2019.100452.

[29] M.D. Gumelar, Moh Hamzah, A.S. Hidayat, D.A. Saputra, Idvan, Utilization of chitosan as coating material in making NPK slow release fertilizer, Macromol. Symp. 391 (1) (Jun. 2020), https://doi.org/10.1002/masy.201900188.

[30] H.-M. Ye, et al., Degradable polyester/urea inclusion complex applied as a facile and environment-friendly strategy for slow-release fertilizer: performance and mechanism, Chem. Eng. J. 381 (Feb. 2020) 122704, https://doi.org/10.1016/j.cej.2019.122704.

[31] M. Salimi, B. Channab, A. El Idrissi, M. Zahouily, E. Motamedi, A comprehensive review on starch: structure, modification, and applications in slow/controlled-release fertilizers in agriculture, Carbohydr. Polym. 322 (Dec. 2023) 121326, https://doi.org/10.1016/j.carbpol.2023.121326.

[32] X. Yang, B. Yu, Z. Zhong, B. hua Guo, Y. Huang, Nevirapine-polycaprolactone crystalline inclusion complex as a potential long-acting injectable solid form, Int. J. Pharm. 543 (1–2) (May 2018) 121–129, https://doi.org/10.1016/j.ijpharm.2018.03.043.

[33] C. Wang, et al., Biochar-based slow-release of fertilizers for sustainable agriculture: a mini review, Environmental Science and Ecotechnology 10 (Apr. 2022) 100167, https://doi.org/10.1016/j.ese.2022.100167.

[34] H. Padinjarathil, et al., Design of an antibiotic-releasing polymer: physicochemical characterization and drug release patterns, Membranes 13 (1) (Jan. 2023), https://doi.org/10.3390/membranes13010102.

[35] R.A. Lusiana, D. Siswanta, T. Hayashita, 262 THE INFLUENCE OF PVA.cl.CITRIC ACID/CHITOSAN MEMBRANE HYDROPHICILITY ON THE TRANSPORT OF CREATININE AND UREA. https://doi.org/10.22146/ijc.21286, 2013.

[36] H. Zhang, H. Liang, L. Xing, W. Ding, Z. Geng, C. Xu, Cellulose-based slow-release nitrogen fertilizers: synthesis, properties, and effects on pakchoi growth, Int. J. Biol. Macromol. 244 (Jul. 2023) 125413, https://doi.org/10.1016/j.ijbiomac.2023.125413.

[37] H. Zhang, et al., Preparation and characterization of biochar-based slow-release nitrogen fertilizer and its effect on maize growth, Ind. Crops Prod. 203 (Nov. 2023) 117227, https://doi.org/10.1016/j.indcrop.2023.117227.

[38] W. Tanan, J. Panichpakdee, P. Suwanakood, S. Saengsuwan, Biodegradable hydrogels of cassava starch-g-polyacrylic acid/natural rubber/polyvinyl alcohol as environmentally friendly and highly efficient coating material for slow-release urea fertilizers, J. Ind. Eng. Chem. 101 (Sep. 2021) 237–252, https://doi.org/10.1016/j.jiec.2021.06.008.

[39] N. Phansroy, et al., Innovative environment-friendly liquid fertilizer bead from sodium alginate coating with IPN membrane derived from natural rubber and cassava starch, J. Polym. Res. 31 (3) (Mar. 2024), https://doi.org/10.1007/s10965-024-03925-5.