ISSN: 1410-8917
Jurnal Kimia Sains & Aplikasi
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 27 (10) (2024): 470-476
Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry
Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Development and Characterization of a Chitosan and Polyvinyl Alcohol (CS/PVP)-Based Slow-Release Urea Fertilizer Membrane

Retno Ariadi Lusiana [1,*], Khabibi [1], Rahmad Nuryanto [1], Muhammad Ridho Shofwan Al Aziz [1]

[1] Chemistry Department, Faculty of Sciences and Mathematics, Diponegoro University, Jl. Prof. Soedarto, SH., Tembalang, Semarang, Indonesia

* Corresponding author: retno.lusiana@live.undip.ac.id

https://doi.org/10.14710/jksa.27.10.470-476

Article Info

Article history:

Received: 18th August 2024
Revised: 21st October 2024
Accepted: 28th October 2024
Online: 30th October 2024

Keywords:
SRF membrane; chitosan; polyvinyl pyrrolidone K30; slow-release urea

Abstract

A slow-release test of urea fertilizer was conducted using chitosan-urea (CS-U) and chitosan/polyvinyl pyrrolidone K30-urea (CS/PVP-U) membranes. The urea membrane synthesis involved a blending method, with PVP K30 added as a component. The slow-release capabilities of CS-U, CS/PVP1-U, CS/PVP2-U, CS/PVP3-U, and CS/PVP4-U membranes were compared. FTIR results showed an increased intensity of the primary NH double peak at 1587 cm^{-1} and 1640 cm^{-1}, while the C=O spectrum shifted from 1640 to 1647 cm^{-1} and the -OH group from 3354 cm^{-1} to 3362 cm^{-1}, indicating hydrogen bond formation in CS/PVP-U. XRD analysis confirmed the membrane's amorphous structure, and FE-SEM and AFM studies revealed morphology and roughness differences, with CS/PVP4-U having the largest cross-sectional diameter. The release study showed that PVP-modified chitosan membranes increased urea release, achieving 60 ppm/2 days for the first 16 days, then decreasing to about 55 ppm through day 30, with partial urea release controlled over time. This suggests that SRF fertilizer can effectively control urea release into the environment.

1. Introduction

Fertilizer plays a crucial role in enhancing agricultural productivity, with urea fertilizer being one of the most commonly used types due to its function as a nitrogen source [1, 2]. Nitrogen is an essential nutrient for plants, promoting vegetative growth, leaf development, and increased yield. However, conventional urea fertilizer faces a significant challenge: low usage efficiency. Granular urea is highly soluble in water, leading to a rapid, often excessive, nitrogen release. Plants can absorb only about 30% of the nitrogen provided, while much of it is lost through ammonia volatilization or leaching. These losses reduce fertilizer efficiency, raise production costs, and have environmental consequences, such as water pollution and greenhouse gas emissions [3].

To address this issue, slow-release urea fertilizer (SRF) was developed. SRF is designed to release nutrients gradually into the soil, allowing plants to absorb them over an extended period at a more consistent rate. This controlled release matches the plants' nutrient needs more effectively and minimizes nutrient loss to the environment. Unlike conventional fertilizers, which typically release nutrients quickly after application—leading to significant losses through leaching or volatilization—SRF reduces the risk of nitrogen loss, thus enhancing fertilizer efficiency. This approach ultimately improves nutrient availability to plants and lowers environmental impact [4, 5].

Slow-release urea fertilizers are typically produced by coating the urea granules with materials like polymers or sulfur, which help regulate water contact and slow nitrogen release. This controlled release not only reduces nutrient loss but also improves plant resilience to challenging environmental conditions, such as drought, by ensuring a more consistent nitrogen supply.

Various coating materials have been explored for the encapsulation of SRF, including durable polymers like polysulfone [6] and polyacrylonitrile [7], as well as biodegradable options like polyurethane [8], polystyrene [9, 10], and biopolymers such as lignin, gelatin, chitosan, polylactic acid, carboxylic cellulose, and starch [11]. Beyond composition, factors like coating thickness, layering, porosity, and hydrophilicity play crucial roles in the effectiveness of SRF nutrient release. For instance, NPK fertilizer granules coated with poly(acrylic acid co-acrylamide) cross-linked chitosan demonstrated a 30- day nutrient release profile of 84±18% for nitrogen, 63±12% for phosphorus, and 36±15% for potassium in water [12, 13].

The significance of the constituent materials in SRF fertilizer production has led researchers to focus heavily on exploring various options. In efforts to minimize environmental impact, biopolymers have become a preferred choice for SRF fertilizers [11]. This study focuses on developing SRF fertilizer using chitosan and PVP K30 as urea coating materials. Chitosan, a widely abundant biopolymer, is biodegradable, non-toxic, and hydrophilic. It is also easy to form into thin membranes and can interact with other compounds through its hydroxyl (-OH) and amine ($-NH_2$) groups, allowing the creation of materials with specific functions.

Blending chitosan with other polymers enhances its performance, and one such polymer used in this blend is PVP. PVP is a non-toxic, hydrophobic, degradable synthetic polymer that acts as a membrane porogen and is commonly used in biomedical applications. Adding PVP improves the hydrophilicity and porosity of the membrane, helping to organize the cavity structure within the chitosan membrane. The combination of chitosan and PVP works synergistically to coat urea, maintaining controlled contact with water, which regulates the dissolution of urea into the environment [14].

Several researchers have developed SRF fertilizers in granular form, but studies have shown that this form has limitations due to agglomeration, which leads to an uneven surface and clogged pores, impairing the performance of the fertilizer [15]. To address this, an innovative approach is needed, such as creating SRF fertilizer in membrane form. This method is expected to enhance the manufacturing process, improve application efficiency, and be more effective. The membraneization process is carried out in situ by reacting CS and PVP K30 to coat urea, ensuring even dispersion within the membrane and regulating a slow release of urea.

2. Experimental

2.1. Materials

The tools used in this study include beaker glass (Herma and Pyrex), 100 mL vial bottle, measuring cup (Herma), volume pipette (Pyrex), dropper pipette, spatula, petri dish (Sterilplan), stirrer, ruler, digital analytical balance (OHAUS), thickness meter (Mitutoyo), magnetic stirrer (Biomega and Jenway), oven, pH meter, FTIR spectrophotometer (Spektrum 100-Perkin Elmer), UV-Vis spectrophotometer (PG 60), and SEM instrument (JEOL JSM-6510LA). The materials used were chitosan (MW = 132,000, DD = 87%, Biotech Surindo Co., Indonesia), urea fertilizer, 4-(Dimethylamino) benzaldehyde/DMAB (BM Merck), ethanol (Smart-Lab), HCl (Merck), PVP K30 (BM = 30,000 g/mol, Merck), acetic acid (BM = 60 g/mol, Merck), distilled water (Diponegoro University Integrated Laboratory), and NaOH (BM = 40 g/mol, Merck).

2.2. Synthesis of Chitosan-PVP K30 (CS/PVP)

A total of 1.5 g of chitosan was dissolved in a 1% acetic acid solution and stirred at room temperature for 24 hours to ensure homogeneity. Separately, 1.5 g of PVP K30 was dissolved in water at 60°C and stirred until fully dissolved. The two solutions were then combined in varying concentration ratios of CS:PVP, specifically 1.5:0, 1.5:0.25, 1.5:0.5, 1.5:1, and 1.5:1.5, maintaining a consistent volume ratio of 1:1 (v/v) (Table 1). This mixture was subsequently sonicated to remove any air bubbles formed during stirring.

2.3. Fabrication of CS/PVP-U (SRF) Membrane

The SRF membrane was prepared using the sandwich/coating method. First, 2 mL of the Chitosan/PVP K30 mixture was poured into a petri dish and dried at 40°C for 4 hours. Next, 1 mL of a 400 ppm urea solution was added and air-dried, followed by another 2 mL of the Chitosan/PVP K30 solution to coat the top layer. Table 1 details the membrane composition. The membrane was then dried again at 40°C for 20 hours. Once formed, the membrane was soaked in a 2% NaOH solution until it separated from the petri dish, washed with distilled water until a neutral pH was achieved, and finally air-dried at room temperature. The mechanism reaction can be seen in Figure 1.

2.4. Analytical Methods

The successful formation of functional groups from the reaction products was analyzed using an FTIR spectrophotometer (Shimadzu) within a range of 700– 4000 cm^{-1}. The membrane's crystallinity was assessed using XRD. The surface and interior morphology of the membrane were examined via FESEM at 2,500× magnification and 20 kV energy. Additionally, AFM was employed to analyze the membrane's surface roughness.

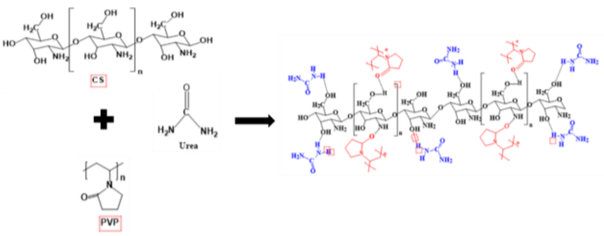

Figure 1. Preparation reaction and chemical structure of CS/PVP-U

Table 1. Composition of modified chitosan membranes

Membrane type	Chitosan (%)	PVP K30 (%)	Urea (%)
CS-U	80	0	20
CS/PVP1-U	68	12	20
CS/PVP2-U	60	20	20
CS/PVP3-U	48	32	20
CS/PVP4-U	40	40	20

2.5. Membrane Weight and Thickness Test

The membrane weight was determined using an OHAUS analytical balance, with each sample weighed three times. The membrane thickness was measured using a Mitutoyo thickness gauge, with five measurements taken at random locations for each sample.

2.6. Porosity and Swelling Test (Swelling)

The membrane porosity was measured by immersing each membrane in 10 mL of distilled water for 24 hours. After immersion, the membranes were gently dried with absorbent paper and weighed to obtain the wet weight (W_w). Each membrane was then dried at 100°C for 6 hours until fully dry, cooled, and weighed again to determine the dry weight (W_d). The membrane porosity percentage was calculated using Equation (1) [16].

$$\varepsilon = \frac{(W_w - W_d)}{(V_{\rho w})} \times 100\% \quad (1)$$

Where, ρw is the density of water (1.0 g/cm^3).

For the swelling test, the initial diameter (I_o) of each membrane variation was measured, followed by immersion in 10 mL of distilled water for 24 hours. After immersion, the final diameter (I_t) was recorded. The degree of swelling was then calculated using Equation (2).

$$SD\ (\%) = \frac{l_t}{l_o} \times 100 \quad (2)$$

Where, l_o is the initial membrane diameter (cm), and l_t is the membrane diameter during expansion.

2.7. Slow-Release Fertilizer in Water

To simplify calculations, a urea standard curve was generated using urea solutions with concentrations of 0, 100, 200, 300, 400, and 500 ppm. Using this standard curve, the amount of urea released was calculated. Each membrane variation sample was immersed in a vial containing 100 mL of pH 7 distilled water. Every 2 days over a 30-day period, the solution from each vial was sampled to measure the urea released from the membrane. Based on wavelength scanning of the urea solution (400–440 nm), the highest absorbance was observed at 425 nm, and thus, urea concentration measurements were conducted at this wavelength.

3. Results and Discussion

3.1. FTIR Analysis

Based on Figure 2, the specific absorption bands of chitosan at 1587 cm^{-1} and 1640 cm^{-1} indicate NH bending from primary amines and C=O stretching from amide II, respectively. The absorption band at 1028 cm^{-1} indicates CO stretching from the C-OH groups. Symmetrical and asymmetrical CH stretching, characteristic of polysaccharides, is observed at 2877 cm^{-1}. The intermolecular OH bond is represented by an absorption band at 3354 cm^{-1}. All these absorption bands are consistent with those reported in the spectra of chitosan samples by Lustriane *et al.* [17].

Pure PVP K30 exhibits a CN absorption band at 1289 cm^{-1}, which is absent in chitosan. Absorption bands at 3391 cm^{-1}, 2952 cm^{-1}, and 1640 cm^{-1} are shared with chitosan, while two bands around 1450–1500 cm^{-1} indicate symmetric and asymmetric CC stretching. These absorption bands in the spectra of PVP K30 samples were also observed in the study by Hashim Abed Almwli *et al.* [18].

The specific spectrum of urea shows NH bending at 1558 cm^{-1}, NH stretching at 3455 cm^{-1}, and CN stretching at 1454 cm^{-1} [16]. The successful blending of CS, PVP K30, and urea (CS-U, CS/PVP1-U, CS/PVP2-U, CS/PVP3-U, and CS/PVP4-U) is evidenced by the appearance of CN absorption bands at 1289 cm^{-1} and 1587 cm^{-1}. The C=O stretching of amide I shifted from 1640 cm^{-1} to 1647 cm^{-1}, accompanied by increased transmittance intensity. The peak at 3354 cm^{-1} in pure chitosan shifted to 3362 cm^{-1}, indicating the presence of hydrogen bonds between chitosan and PVP. These hydrogen interactions cause the distance between chitosan polymers in the membrane structure to become more regular, forming uniform cavities within the membrane. The presence of these cavities, which act as pores, suggests that the more hydrogen bonds formed between chitosan and PVP, the more porous the membrane becomes.

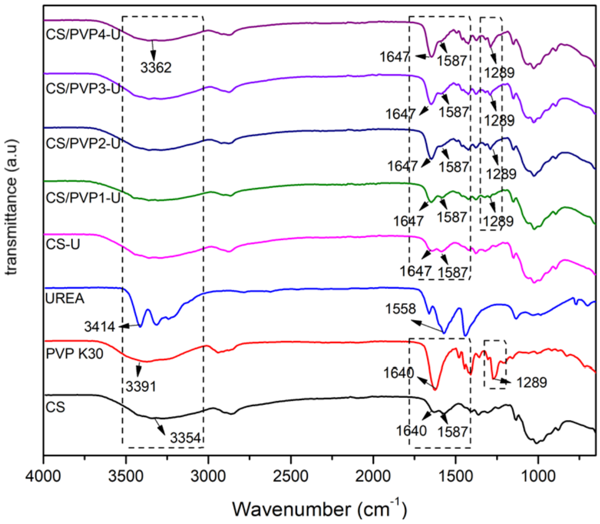

Figure 2. FTIR spectra of membranes

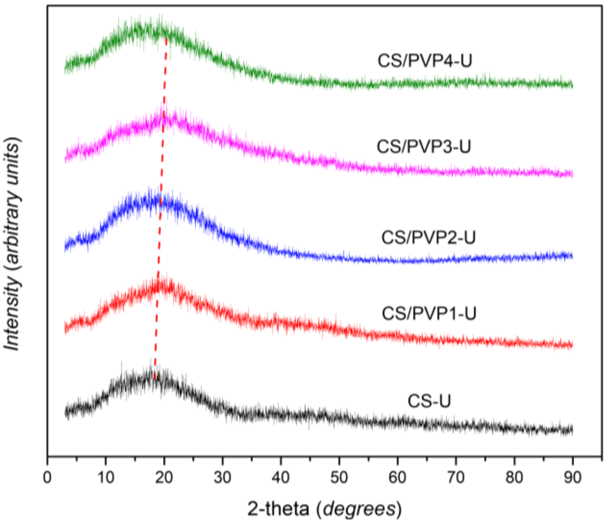

Figure 3. XRD pattern of the membranes

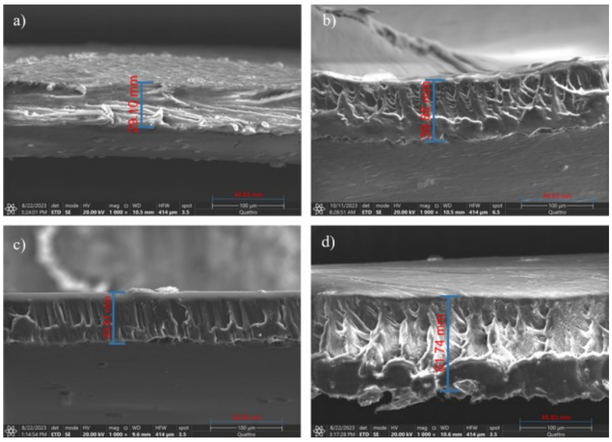

Figure 4. FE-SEM images of (a) CS membrane, (b) CS/PVP4 membrane, (c) CS-U membrane, and (d) CS/PVP4-U membrane

3.2. XRD

The diffraction pattern in Figure 3 confirms the successful synthesis of the chitosan-urea membrane, as indicated by the characteristic peaks of chitosan and urea at 11.43°, 21.1°, 22.5°, 24.18°, and 30.16°. The addition of PVP K30 results in a reduction of the peak at $2\theta = 20°$ and a shift in the 2θ position, as shown in Figure 3. These results suggest that chitosan exhibits good compatibility with PVP, promoting the formation of a porous membrane. The XRD pattern further reveals that all membrane types exhibit an amorphous structure [19].

3.3. FESEM

SEM observations revealed significant differences in the sub-layers of CS and CS/PVP4 membranes (Figure 4). The CS membrane exhibited an irregular transverse structure with sparse and inconsistent pore distribution, consistent with findings by Cahyaningrum *et al.* [20], who noted that pure chitosan tends to have a higher particle density, resulting in lower porosity. In contrast, the CS/PVP4 membrane showed a more regular transverse structure with a higher pore density. Compared to the CS membrane, the CS/PVP4 displayed a thinner overall thickness than the CS-U and CS/PVP4-U membranes, which was increased by adding urea. Based on the FE-SEM scale, a length of 46.83 mm in the image corresponds to 100 µm in reality. The measured thicknesses were 62.14 µm for the CS membrane, 71.57 µm for CS-U, 85.12 µm for CS/PVP4, and 131.84 µm for CS/PVP4-U. The observed membrane morphology aligns with porosity test results, indicating that the chitosan membrane has the lowest porosity, while CS/PVP4-U has the highest porosity, potentially enhancing urea release efficiency.

3.4. AFM

Three-dimensional AFM image analysis, shown in Figure 5, revealed distinct surface roughness characteristics among the membranes. The CS membrane displayed fewer and lower surface nodules, while the CS- U membrane showed an increase in both the number and height of nodules, indicating greater roughness. The addition of urea to the chitosan solution contributed to this change, with urea deposits on the membrane surface increasing the roughness of the CS-U membrane. The CS/PVP4 membrane exhibited fewer and lower nodules than the CS/PVP4-U membrane, suggesting that the addition of PVP K30 enhanced membrane hydrophilicity, facilitating urea solubilization. As a result, the CS/PVP4- U membrane presented with fewer and lower nodules, aligning with the findings of Xiong *et al.* [21], who noted that modifications to increase membrane hydrophilicity can reduce surface roughness.

3.5. Membrane Weight and Thickness

As shown in Table 2, modifying chitosan membranes by adding PVP and urea contributed to a decrease in membrane mass and thickness. During fabrication, all membranes were prepared with the same solution volume and concentration and cast on an area of 5 cm². Chitosan, with a molecular weight of 132.812 g/mol, contributed the highest mass per unit area to the membrane. The inclusion of PVP K30, with a molecular weight of 30,000 g/mol, reduced the total mass per unit area, resulting in a lighter membrane than pure chitosan. This thinner membrane structure is anticipated to improve urea release efficiency [20].

3.6. Porosity and Swelling of Membranes

Porosity reflects the amount of empty space within the membrane structure. According to the data, the CS-U membrane has a porosity of 7.95%. The addition of PVP at various concentration ratios increases membrane porosity to as high as 35.60%. Hydrogen bonding between chitosan and PVP promotes uniform spacing within the membrane, creating consistent cavities throughout. Furthermore, the presence of hydrophilic groups, such as C=O and C–N from PVP K30, enhances the membrane's water-attracting ability, slowing the solidification process. This slower process allows for the formation of larger and more numerous pores, increasing overall membrane porosity [22, 23]. The membrane porosity measurement results are presented in Figure 6a.

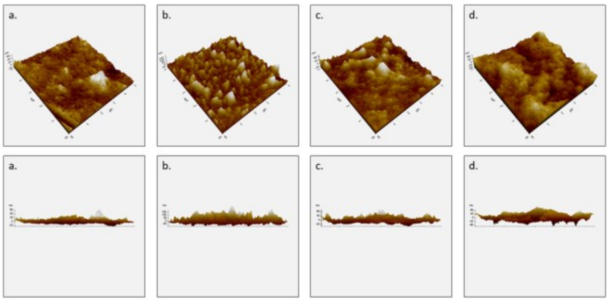

Figure 5. Three-dimensional AFM images of (a) CS, (b) CS-U, (c) CS/PVP4, and (d) CS/PVP4-U membranes

Table 2. Membrane weight and thickness measurement results

Membrane type	Thickness ($\times 10^{-2}$ mm)	Weight (g)
CS-U	8.5	0.180
CS/PVP1-U	6.4	0.142
CS/PVP2-U	5.8	0.154
CS/PVP3-U	5.7	0.172
CS/PVP4-U	4.4	0.175

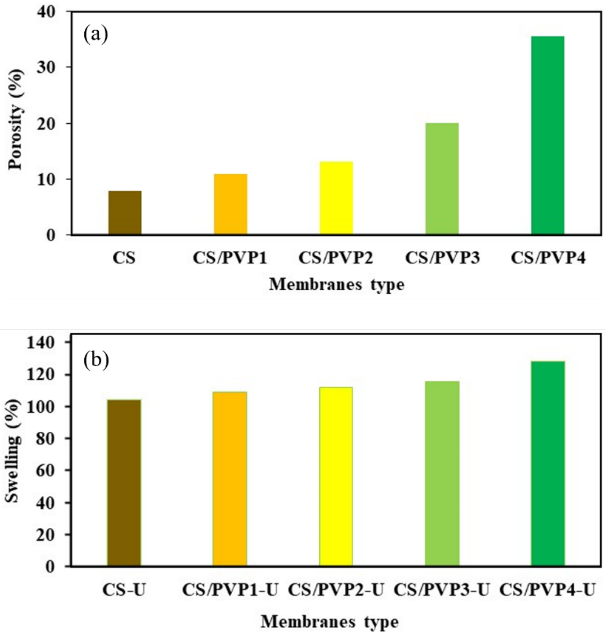

Figure 6. (a) membrane porosity and (b) membrane swelling capacity

The membrane's expansion capacity reflects the extent to which it can expand upon exposure to water. This measurement is obtained by comparing the membrane diameter before and after water immersion. As shown in Figure 6b, the CS-U membrane exhibits the lowest expansion value at 104.22%. The expansion value increases by 24% with the addition of PVP to the chitosan matrix. This increase is attributed to the hydrophilic C=O and C–N groups within the membrane structure, which attract water molecules. Consequently, adding PVP K30 to the polymer matrix increases the volume and number of cavities in the membrane, resulting in a higher expansion rate [21].

3.7. Slow-Release Application

Testing the membrane's capability for slow urea release in water is essential for evaluating its release efficiency. By periodically monitoring urea levels every 2 days, the membrane's effectiveness in controlling nutrient release can be assessed. The results, shown in Figure 7, provide insights into the membrane's performance under simulated real-world conditions.

Figure 7 is divided into two zones (A and B). In all membranes, the urea release slope in Zone A is steeper than in Zone B, indicating a relatively fast initial release (first 16 days in Zone A) at an average rate of 65 ppm per 2 days, followed by a slower release from days 16 to 30 in Zone B, averaging 55 ppm per 2 days. For instance, the CS-U membrane shows a 50% release fraction in Zone A over 16 days but only a 16% release fraction in Zone B over the subsequent 14 days. By day 30, cumulative urea release reached 664 ppm for the CS-U membrane, 728 ppm for CS/PVP1-U, 734 ppm for CS/PVP2-U, 698 ppm for CS/PVP3-U, and 797 ppm for CS/PVP4-U. These findings suggest that urea release occurs gradually via diffusion in a controlled manner. Overall, incorporating PVP into the chitosan structure increases urea release.

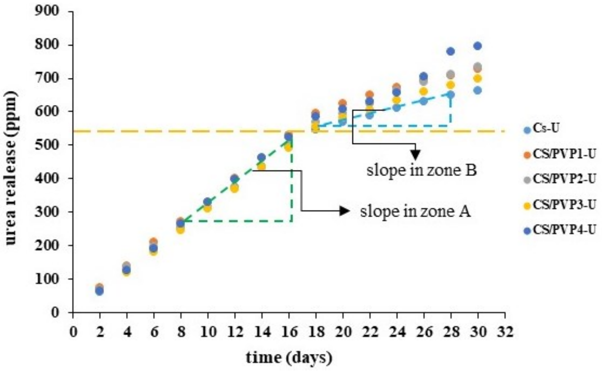

Figure 7. Fractional release of urea as a function of time

As noted by Chen *et al.* [24], the hydrophilic nature of PVP K30 promotes enhanced water–membrane interactions, as the electrostatic bond between water molecules and urea is stronger than that between urea and the membrane, facilitating easier urea release. This behavior confirms urea's hygroscopic nature, which significantly influences its environmental release.

4. Conclusion

The synthesis of a chitosan-PVP membrane with urea for slow-release applications aims to develop an efficient controlled-release urea system. Chitosan, as a natural polymer, serves as the membrane matrix, offering biodegradability and biocompatibility. The addition of PVP enhances membrane flexibility and promotes a more uniform pore structure, while urea acts as the active component, gradually released through diffusion from within the membrane. This technique enables the controlled, slow release of urea, reducing leaching losses and increasing utilization efficiency, particularly in agricultural applications. This slow-release system helps provide nutrients to plants sustainably, reducing the need for frequent fertilization and minimizing environmental impact. Overall, the chitosan-PVP-urea membrane shows promising potential as a material for slow-release urea, with benefits in extending release duration and enhancing urea utilization efficiency in soil.

Acknowledgment

The authors would like to thank the Faculty of Sciences and Mathematics, Diponegoro University, for their financial support through the 'Implementation of Research Activities from Funding Sources Other than the APBN within the Faculty of Science and Mathematics, Diponegoro University for the Fiscal Year 2023,' under contract number 21.B/UN7.F8/PP/II/2023.

References

[1] Bilal Beig, Muhammad Bilal Khan Niazi, Zaib Jahan, Munir Zia, Ghulam Abbas Shah, Zahid Iqbal, Inamullah Douna, Facile coating of micronutrient zinc for slow release urea and its agronomic effects on field grown wheat (*Triticum aestivum* L.), *Science of The Total Environment*, 838, (2022), 155965 https://doi.org/10.1016/j.scitotenv.2022.155965

[2] Christian O. Dimkpa, Maria G. N. Campos, Job Fugice, Katherine Glass, Ali Ozcan, Ziyang Huang, Upendra Singh, Swadeshmukul Santra, Synthesis and

characterization of novel dual-capped Zn–urea nanofertilizers and application in nutrient delivery in wheat, *Environmental Science: Advances*, 1, 1, (2022), 47-58 https://doi.org/10.1039/D1VA00016K

[3] Curtis J. Ransom, Von D. Jolley, Trenton A. Blair, Lloyd E. Sutton, Bryan G. Hopkins, Nitrogen release rates from slow- and controlled-release fertilizers influenced by placement and temperature, *PLOS ONE*, 15, 6, (2020), e0234544 https://doi.org/10.1371/journal.pone.0234544

[4] Babar Azeem, KuZilati KuShaari, Zakaria B. Man, Abdul Basit, Trinh H. Thanh, Review on materials & methods to produce controlled release coated urea fertilizer, *Journal of Controlled Release*, 181, (2014), 11-21 https://doi.org/10.1016/j.jconrel.2014.02.020

[5] Jinhui Yang, Tai Liu, Hongbin Liu, Limei Zhai, Man Wang, Yonggang Du, Yanxue Chen, Cheng Yang, Huining Xiao, Hongyuan Wang, Dimethylolurea as a Novel Slow-Release Nitrogen Source for Nitrogen Leaching Mitigation and Crop Production, *Journal of Agricultural and Food Chemistry*, 67, 27, (2019), 7616-7625 https://doi.org/10.1021/acs.jafc.9b01432

[6] Maria Tomaszewska, Anna Jarosiewicz, Use of Polysulfone in Controlled-Release NPK Fertilizer Formulations, *Journal of Agricultural and Food Chemistry*, 50, 16, (2002), 4634-4639 https://doi.org/10.1021/jf0116808

[7] Alummoottil N. Jyothi, Swetha S. Pillai, Mancharyamkunnath Aravind, Salma A. Salim, Susan John Kuzhivilayil, Cassava starch-graft-poly(acrylonitrile)-coated urea fertilizer with sustained release and water retention properties, *Advances in Polymer Technology*, 37, 7, (2018), 2687-2694 https://doi.org/10.1002/adv.21943

[8] Qian Wang, Fuping Dong, Jun Dai, Qingpo Zhang, Meng Jiang, Yuzhu Xiong, Recycled-Oil-Based Polyurethane Modified with Organic Silicone for Controllable Release of Coated Fertilizer, *Polymers*, 11, 3, (2019), 454 https://doi.org/10.3390/polym11030454

[9] Yue-chao Yang, Min Zhang, Yuncong Li, Xiao-hui Fan, Yu-qing Geng, Improving the Quality of Polymer-Coated Urea with Recycled Plastic, Proper Additives, and Large Tablets, *Journal of Agricultural and Food Chemistry*, 60, 45, (2012), 11229-11237 https://doi.org/10.1021/jf302813g

[10] Bruno R. Araújo, Luciane P. C. Romão, Marta E. Doumer, Antonio S. Mangrich, Evaluation of the interactions between chitosan and humics in media for the controlled release of nitrogen fertilizer, *Journal of Environmental Management*, 190, (2017), 122-131 https://doi.org/10.1016/j.jenvman.2016.12.059

[11] Weijie Yuan, Sihan Li, Haohui Guan, Shuai Zhang, Yaoxiang Zhang, Min Zhang, Yi Yu, Xiangyi Chen, Preparation and Properties of a Novel Biodegradable Composite Hydrogel Derived from Gelatin/Chitosan and Polylactic Acid as Slow-Release N Fertilizer, *Polymers*, 15, 4, (2023), 997 https://doi.org/10.3390/polym15040997

[12] Supaporn Noppakundilograt, Natthaya Pheatcharat, Suda Kiatkamjornwong, Multilayer-coated NPK compound fertilizer hydrogel with controlled nutrient release and water absorbency, *Journal of Applied Polymer Science*, 132, 2, (2015), 41249 https://doi.org/10.1002/app.41249

[13] Rasha E. El-Mekawy, Heba A. Elhady, Hossa F. Al-Shareef, Highly stretchable, smooth, and biodegradable hydrogel films based on chitosan as safety food packaging, *Polymers and Polymer Composites*, 29, 6, (2021), 563-573 https://doi.org/10.1177/0967391120926892

[14] Lisendra Marbelia, Muhammad R. Bilad, Ivo F. J. Vankelecom, Gradual PVP leaching from PVDF/PVP blend membranes and its effects on membrane fouling in membrane bioreactors, *Separation and Purification Technology*, 213, (2019), 276-282 https://doi.org/10.1016/j.seppur.2018.12.045

[15] Liang Zhuang, Xiujuan Zhi, Bin Du, Sichun Yuan, Preparation of Elastic and Antibacterial Chitosan–Citric Membranes with High Oxygen Barrier Ability by in Situ Cross-Linking, *ACS Omega*, 5, 2, (2020), 1086-1097 https://doi.org/10.1021/acsomega.9b03206

[16] Retno Ariadi Lusiana, Nurwarrohman Andre Sasongko, Vivi Dia A. Sangkota, Nor Basid Adiwibawa Prasetya, Parsaoran Siahaan, Agung Abadi Kiswandono, Mohd Hafiz Dzarfan Othman, In-Vitro Study of Polysulfone-polyethylene glycol/chitosan (PEG-PSf/CS) Membranes for Urea and Creatinine Permeation, *Jurnal Kimia Sains dan Aplikasi*, 23, 8, (2020), 283-289 https://doi.org/10.14710/jksa.23.8.283-289

[17] Cita Lustriane, Fenny M. Dwivany, Veinardi Suendo, Muhammad Reza, Effect of chitosan and chitosan-nanoparticles on post harvest quality of banana fruits, *J Plant Biotechnol*, 45, 1, (2018), 36-44 https://doi.org/10.5010/JPB.2018.45.1.036

[18] Hanan Hashim Abed Almwli, Seyed Mahmoud Mousavi, Shirin Kiani, Preparation of poly(butylene succinate)/polyvinylpyrrolidone blend membrane for pervaporation dehydration of acetone, *Chemical Engineering Research and Design*, 165, (2021), 361-373 https://doi.org/10.1016/j.cherd.2020.10.033

[19] Santosh Kumar, Joonseok Koh, Physiochemical, Optical and Biological Activity of Chitosan-Chromone Derivative for Biomedical Applications, *International Journal of Molecular Sciences*, 13, 5, (2012), 6102-6116 https://doi.org/10.3390/ijms13056102

[20] Sari Edi Cahyaningrum, Retno Ariadi Lusiana, Taufik Abdillah Natsir, Fitriari Izzatunnisa Muhaimin, Andika Pramudya Wardana, Amalia Putri Purnamasari, Misni Bin Misran, Synthesis and characterization of chitosan-modified membrane for urea slow-release fertilizers, *Heliyon*, 10, 15, (2024), e34981 https://doi.org/10.1016/j.heliyon.2024.e34981

[21] Zhu Xiong, Yun Zhong, Haibo Lin, Fu Liu, Tiantian Li, Jinglong Li, PDLA/PLLA ultrafiltration membrane with excellent permeability, rejection and fouling resistance via stereocomplexation, *Journal of Membrane Science*, 533, (2017), 103-111 https://doi.org/10.1016/j.memsci.2017.03.028

[22] Retno Ariadi Lusiana, Putri Widiarti Mariyono, Hasan Muhtar, Sari Edi Cahyaningrum, Taufik Abdillah Natsir, Lisna Efiyanti, Environmentally friendly slow-release urea fertilizer based on modified chitosan membrane, *Environmental*

Nanotechnology, Monitoring & Management, 22, (2024), 100996 https://doi.org/10.1016/j.enmm.2024.100996

[23] Tianrong Zhu, Yunbai Luo, Yanwen Lin, Qin Li, Ping Yu, Ming Zeng, Study of pervaporation for dehydration of caprolactam through blend NaAlg–poly(vinyl pyrrolidone) membranes on PAN supports, *Separation and Purification Technology*, 74, 2, (2010), 242-252 https://doi.org/10.1016/j.seppur.2010.06.012

[24] Songling Chen, Ming Yang, Chuang Ba, Susu Yu, Yifei Jiang, Hongtao Zou, Yulong Zhang, Preparation and characterization of slow-release fertilizer encapsulated by biochar-based waterborne copolymers, *Science of The Total Environment*, 615, (2018), 431-437 https://doi.org/10.1016/j.scitotenv.2017.09.209