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Effect of Urea Variation Concentration on Slow Release Fertilizer (SRF) Based Chitosan/NaTPP/Calcium

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Abstract: Environmental pollution due to urea can negatively impact the environment and its surroundings. Efforts to prevent environmental pollution include encapsulating urea made of chitosan/NaTPP/Ca, which aims to determine its physical and chemical properties. This study crosslinks chitosan 1.66%, with NaTPP 3.33%, CaO, with variations in the addition of urea concentrations of 0.05%, 0.1%, 0.15%, 0.2%, and 0.25%. The results of FTIR characterization showed that there were functional groups OH-, C-H, Ca-O, NH, and P=O. The membrane weight yield ranges from 0.14-0.16 grams, while the average membrane thickness is 0.15-0.35 mm. The water absorption test is 1.86-2.64%, and the membrane porosity result is 0.91-2,25%. This shows that the membrane with a base material of 1.66% chitosan and 3.33% NaTPP is the best.

Keywords: Chitosan; Fertilizer; NaTPP; Urea.

Introduction

Urea fertilizer contains Nitrogen (N) [1]. Nitrogen has the most important function in plant growth because it is for nutrients in plants and is also very important in food production and maintaining global food security [2], especially growth in leaves and stems. Most of the nitrogen in the soil is found in relatively small amounts in the form of ammonium and nitrate. Applying urea fertilizer in the right dosage makes the plant fertile and does not pollute the environment. The dose of urea must be appropriate because excess urea causes toxicity to plants, namely, causing plants to collapse easily, be easily attacked by pests/diseases, and damage the environment. In contrast, lacking fertilizer causes a deficit or nutrient deficiency [3]. So far, the use of urea fertilizer is considered less effective because of the large amount of urea fertilizer that pollutes the environment because the absorption in plants is at the maximum limit.

Several studies have been conducted to improve the urea fertilizer release process. One of them is making slow-release fertilizers. Slow release is controlled according to the needs of use and increases fertiliser use efficiency [4]. Urea fertilizer with the slow-release method has many advantages, such as maximizing nutrients in plants, reducing potential negative impacts, reducing fertilizer pollution, and making the use of fertilizer more efficient because of the constrained release [2][4][21].

There are also many modifications to the manufacture of *slow-release fertilizers*, and each modification has its advantages and disadvantages [23]. This study showed that slow-release NPK is in the form of granules. The shallot plant test in Brebes, Central Java, can increase the yield by about 14% compared to the use of ordinary NPK fertilizer and save up to 50% of fertilizer. Applying plant fertilization using *a slow-release system fertilizer* is enough to fertilize once during the planting period. Slow-release fertilizer can control the release of nutrient elements well, according to the results of the water dissolution test. Visually, it can be seen that the shallots produced are better with a larger bulb size and bright red color [5].

In this study, urea fertilizer is used because it is widely used in Indonesian agriculture. Urea fertilizer also has a % nitrogen content of 46% [1]. This content is indispensable for plants, especially during growth [6].

In the research on modifying slow-release fertilizer production, in addition to granularity, the encapsulation process for making slow-release fertilizer is used as a membrane. The membrane has the advantage of having a large cross-sectional area so the roots can reach the membrane more easily. The membrane can also store more water than the granular form. In addition, the membrane can selectively hold other components [7]. In addition to effectively holding components, membranes can pass other components based on diffusion coefficients, electrical charges, and solubility differences [8][24].

Modification of chitosan as a component of cross-linking agents is widely carried out [27][29] as an example in the research of [2], which crosses chitosan with sodium alginate. In this study, alginate dissolved with CaCl2 and the form of a hydrogel cross-linked between Sodium Alginate/Propyl Chitosan Chloride/Urea (Alg/HTACC/Urea) into the soil can increase water retention, reduce urea loss, inhibit the growth of harmful microbes, and increase crop yield. This study used a cross-link between chitosan and Sodium Tripolyphosphate (NaTPP). The advantage of cross-linking with sodium tripolyphosphate is that the method and reaction are simple, and there is no need to use organic solvents [7].

In the study of [9] Crosslinking chitosan with succinate/polyvinyl alcohol-polyethylene glycol (PVA-PEG). The results of the analysis showed that succinate had reacted with chitosan. Modifying chitosan through cross-

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linking and polymer alloys increases the tensile strength and strain of the membrane better than pure chitosan membranes, where the increasing percentage of elongation also increases the tensile strength (Mpa). In addition, modified membranes also have higher water absorption and hydrophilicity values than unmodified membranes, which has implications for the membrane's ability to permeate creatinine. This research aims to provide information on agricultural studies, especially on the application of urea case studies which pollute the environment.

Research Methods

In the study, several tools were used: Duran 250 ml beaker, 100 ml measuring flask, 500 ml measuring flask, 100 ml Iwaki beaker, 10 ml Iwaki measuring cup, watch glass, magnetic stirrer, 100 ml Iwaki measuring cup, analytical balance, drop pipe, spatula, small petri dish, aluminium foil, filter paper, oven, pestle mortar, and Plant pot. For characterization, Fourier Transform Infra-Red (FTIR), Scanning Electron Microscope (SEM), and Ultraviolet-Visibel (UV-Vis) instruments were used. The materials used for the manufacture of Kt/NaTPP/Ca/Urea membranes are used aquades, glacial acetic acid, Chitosan, CaO, Urea, Sodium Tripolyphosphate (NaTPP), Para-Dimethylaminobenzaldehyde (p-DAB), HCl, NaOH 1M, and corn plants.

Preparation of chitosan solution 1.66%

A total of 1.66 grams of chitosan in a chemical glass. Next, it is added with 100 mL of 1% glacial acetic acid and stirred with a magnetic stirrer with a temperature of 60-80oC for ±24 hours or until homogeneous [10].

Preparation of NaTPP solution 3.33%

A total of 3.33 grams of NaTPP powder with 100 mL of aquades was stirred with a magnetic stirrer until homogeneous.

Membrane solution manufacturing

The manufacture of the membrane solution was carried out by putting 90 mL of chitosan solution into a 100 mL beaker and adding 10 mL of 1.66% Sodium Tripolyphosphate solution drop by drop and then stirring with a magnetic stirrer with a temperature of 55oC ± 4 hours until homogeneous. Chitosan absorbs water very quickly and has a high degree of swelling in the aquatic environment, so agricultural applications such as fertilizer transmission and discharge systems are less favourable. Therefore, NaTPP must be added to produce chitosan derivatives with increased swelling biocompatibility and a very high swelling [11]. Next, 0.01 grams of CaO powder is added to the solution and stirred at low speed with *a magnetic stirrer* for ± 2 hours until homogeneous. Next, sonication is carried out at 30^{o}C for 15 minutes. The purpose of sonication is to lower the molecular weight with the increasing duration of the ultrasonic wave administration [12].

Then urea is added with variations (0.05, 0.1, 0.15, 0.2, and 0.25) %. After that, continue stirring with a magnetic stirrer for ± 2 hours until homogeneous. After that, sonication is carried out at a temperature of 30^{o}C for 10 minutes. A yellowish-white membrane solution formulation was produced.

Next, the drying stage of the solution is carried out by putting 10 mL of solution into a petri dish with a diameter of 6 cm and putting it in an oven with a temperature of 35-40oC or room temperature and drying the membrane solution at an oven until it dries and produces a dry membrane.

The next stage is to insert the dry membrane into the NaOH 1M solution and soak it until it is completely lifted or floating. The purpose of immersion is that NaOH is used during the immersion process to activate functional groups on the chitosan membrane, thus allowing cross-linking reactions with sodium tripolyphosphate (NaTPP) [13]. Membrane washing is carried out by inserting the dry membrane into a 100 mL beaker, adding 10 mL of aquaade, and repeating until the pH is neutral. Membrane formulations are F0, F1, F2, F3, F4, F5.

Characterization of Physics and Chemistry

Physical characterization for membranes, i.e. measurement of membrane mass, is carried out using the OHAUS analytical balance by weighing each sample. In addition, the measurement of membrane thickness was carried out with a thickness meter with five repetitions at different points at random and calculated on average. This thickness test aims to determine the effect of variations in the composition of the number of mass constituent membranes in the same unit of area [14]. The water absorption test was carried out by weighing the initial weight of the membrane sample, then soaked with 10 mL aqueous for 6 hours. After washing, the membrane is weighed again. The initial weight and weight after immersion are used to determine the percentage of water absorption of the membrane. The membrane porosity test was carried out by immersing the membrane in 10 mL of aqueous solution simultaneously (6 hours). After that, each membrane is weighed so that the wet weight of the membrane is obtained. Then, the membrane is heated in an oven at 100^{O}C for 24 hours. After 24 hours, the membrane is weighed again so that the dry weight of the membrane is obtained. The membrane morphology test was carried out using a scanning electron microscope (SEM) instrument. Chemical characterization was performed with functional group tests using Fourier Transform Infra Red (FTIR) instruments. The pH check is carried out using a pH meter calibrated with a standard buffer solution. Dip the pH meter in the membrane formulation wash solution for a few minutes until the number comes out. Measurements are taken at room temperature. The pH observation aims to determine whether the membrane is pH neutral.

Results and Discussion

Chitosan Characterization

The chitosan solution was then characterized using FTIR to analyze the functional group at a 4000-400 cm-1 wave number. The following are the FTIR spectra of the chitosan used and the standard chitosan FTIR spectra.

The chitosan sample used in the study had six peaks of 4000-500 cm^{-1}, namely 3429.58, 2922.25, 2856.67, 1643.40, 1437.01, and 875.71 cm^{-1}. The analysis of the FTIR sample chitosan characteristics compared to the standard chitosan spectra showed that the two spectra had no significant difference or that all the uptake in the standard chitosan was also possessed in the sample chitosan. This indicates that the compound used in this study is chitosan. The results of the characterization of chitosan align with research that states that there is a typical functional group of chitosan, namely OH^-, C=O, C-H, and NH. [16][26].

Characterization of NaTPP

The NaTPP solution was then characterized using FTIR to analyze the functional group at a 4000-400 cm-1 wave number. The following are the FTIR spectra of the NaTPP used and the standard NaTPP FTIR spectra.

The NaTPP sample used in the study had seven peaks in the range of 4000-500 cm^{-1}, namely 3525.99, 3504.77, 1685.84, 1514.17, 1213.26, 1166.97, and 896.99 cm^{-1}. The functional groups in the FTIR spectrum are visible: the P-O, P=O, and P-OH [17][25].

CaO Characterization

CaO powder was then characterized using FTIR to analyze the functional group at a wave number of 4000-400 cm^{-1}. The following are the FTIR spectra on the CaO and the standard FTIR CaO spectra.

The CaO sample used in the study had one peak in the 4000-500 cm-1 range, 1433.15 cm^{-1}. This is in line with research that shows the FTIR spectra of CaO are similar to the FTIR spectra of CaO. [18][30]

Urea Characterization

The urea grains were then characterized using FTIR to analyze the functional group at a 4000-400 cm-1 wave number. The following are the FTIR spectra on the urea used and the FTIR spectrum of standard urea.

The urea sample used in the study had seven peaks in the range of 4000-500 cm^{-1}, namely 3443.05, 3380.10, 1674.26, 1627.94, 1622.18, 1462.09, and 1153.47 cm^{-1}. Research by [19] showed that the FTIR spectra of urea were similar to the FTIR spectra of urea above.

Membrane characterization

The membrane solution was then characterized using FTIR to analyze the functional group at a wave number of 4000-400 cm^{-1}. The following are the FTIR spectrum on the membrane solution and the standard urea FTIR spectra.

The urea sample used in the study had nine peaks in the range of 4000-500 cm^{-1}, namely 3466.19, 2924.18, 2852.81, 1658.83, 1541.17, 1647, 1585.89, 1153.47 and 878.96 cm^{-1}.

The membrane is then characterized by FTIR at a wave number of 4000-400 cm^{-1}, resulting in the following FTIR spectrum.

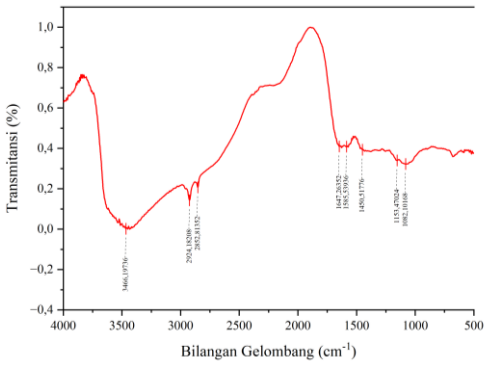

Figure 1. Spectra FTIR Kt/NaTPP/Ca/Urea

Based on Figure 1 on the Chitosan/NaTPP/Ca/Urea spectra, no new groups indicate no reaction with each other. This is following research conducted [8] and [15]

The formation mechanism is shown in Figure 2. Protonation in chitosan aims to react with other compounds and can be used in various applications. In this structure, positive ions of the amine group in the chitosan molecule are produced, which will be cross-linked with negative ions from TPP. NaTPP is dissolved in water. It forms hydroxyl ions ($-OH^-$) and Tripolyphosphate ions ($P_3O_{10}^{5-}$, $P_3O_{10}^{4-}$ and $H_3P_3O_{10}^{2-}$). The reaction is as follows:

$Na_5P_3O_{10} + 5H_2O \rightarrow 5Na^+ + H_5P_3O_{10} + 5OH^-$

$H_5P_3O_{10} + OH^- \rightarrow H_4P_3O_{10}^- + H_2O$

$H_4P_3O_{10}^- + OH^- \rightarrow H_3P_3O_{10}^{2-} + H_2O$

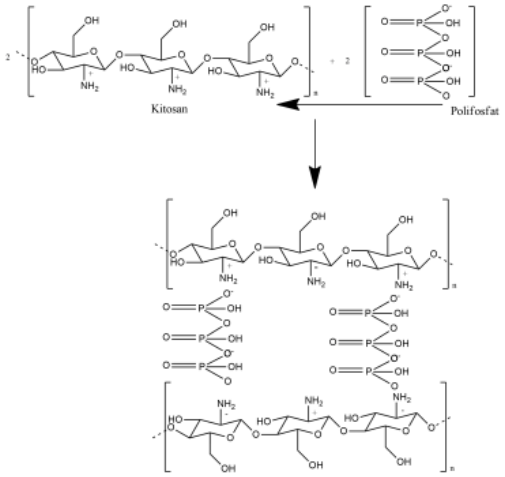

Figure 2. Cross-Link Mechanism between Chitosan and TPP

Deprotonation is experienced in TPP solutions in alkaline conditions. Deprotonation is when ions or molecules lose one or more protons. Therefore, cross-linking between chitosan and TPP will occur. Hydroxyl ions and TPP will compete to react ionically with the -NH3+ group in chitosan by forming ionic crosslinking between chitosan and TPP [20]. The mechanism is illustrated in the figure 2

The membrane is then physically characterized, which is then measured by the membrane weight, membrane thickness, water absorption test, and membrane porosity test presented in the following table.

Table 2. Membrane Physical Test Data

F	Membrane weight (gram)	Average membrane thickness (mm)	Water absorption test (%)	Membrane porosity test (%)
F0	0.15	0.15	1.86	1.17
F1	0.14	0.18	1.98	1.99
F2	0.15	0.18	2.27	1.50
F3	0.16	0.18	2.30	2.25
F4	0.14	0.19	2.36	2.06
F5	0.15	0.35	2.64	0.91

The membrane samples show that the higher the urea concentration [8], the heavier the membrane mass. This thickness test aims to determine the effect of variations in the composition of the amount of membrane mass in the same unit area [22]. The thickness of the membrane sample shows that the greater the urea concentration, the thicker the membrane sample.

The membrane absorption test aims to determine whether the membrane can bind to the water around the membrane. In this test, the percentage of water absorption tests on the membrane is expected to be higher than the water absorption test with only chitosan. In the membrane, the increasing number of electronegative groups, such as -O- from TPP in the chitosan structure, increases the ability to absorb water [15][28]. Then, porosity tests are carried out to determine the amount of space in the membrane, as well as to determine the pores in the membrane.

Conclusion

The SRF Chitosan/NaTPP/Ca/Urea membrane shows characterization in chemistry, physics, urea release, and plant tests. The results of FTIR characterization showed the presence of OH-, C-H, Ca-O, NH, and P=O functional groups. The result of membrane weight ranges from 0.14-0.16 grams, while the average membrane thickness is 0.15-0.35 mm. The water absorption test was in the range of 1.86-2.64 %, and the result of membrane porosity was in the range of 0.91-2.25 %

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