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Phosphate release from Slow Release fertilizer using a mixture of Chitosan and potato Flour as a coating

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Abstract

Indonesia has a high fertilizer demand because its use is easily dissolved during watering, so the fertilization process is inefficient. On the other hand, crab shells accumulate every year because the waste is almost 50% of the initial weight. One way to overcome this problem is to make a modified fertilizer into a slow release fertilizer by adding a bio-gel layer from chitosan and potato flour. The hydrophobic properties of chitosan and potato powder were chosen in addition to the amylopectin content of potato flour more than other types of starch. Then chitosan was dissolved using acetic acid, while potato starch was dissolved by distilled water by heating 76°C. Both mixtures are added to the fertilizer then stirred until the compost is coated. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the morphology and composition of the products. Addition of thickness to the outer layer of manure reached 35.56 µm. The O-H function group is found in the spectrum of potassium and phosphorus which shows that there is a hydrogen bond in chitosan and potato flour. The most substantial swelling is obtained at the K (chitosan): P (potato flour) ratio of 3:7. The wet retention test showed that the addition of chitosan and potato flour was able to withstand soil retention. In the release test for Phosphorus shows good results at a value of 0.923 mg/L.

INTRODUCTION

The development of fertilizer technology and fertilization practices have been carried out continuously but have not entirely overcome the problem of low fertilization efficiency. The nutrient content of fertilizers such as Nitrogen, Phosphorus, and Potassium (NPK) which are volatile and readily soluble in water causes plants to get nutrients that are not optimal (Handayani, 2014). Fertilizer demand in Indonesia increases every year even in 2016 it is estimated that fertilizer demand will reach 6,589,227 tons/year. This value cannot be balanced with the amount of fertilizer production of 515,568 tons/year (Pupuk Indonesia, 2017). The savings in fertilizer use can be achieved by making slow release fertilizers that have nutrient preparations in the soil which are released according to the needs of the plants. Availability of nutrients in the land has a more extended period compared to conventional fertilizers (Tolescu & Lovu, 2010). The content of phosphates in the soil can increase the efficiency of plant nutrients and reduce the risk of water pollution.

Research on slow-release fertilizers has been carried out by previous researchers, namely making fertilizer formulations using sodium alginate (Campos et al., 2015), polyvinyl

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starch/alcohol (Han et al., 2009), polymer membranes (Dong et al, 2016), and ethyl-cellulose (Ni et al., 2009). The material used previously is not environmentally friendly and is not economical. The potential of natural ingredients such as combined chitosan with potato flour has never been used in fertilizers, although there have been many studies of starch-based coatings (Elgadir et al., 2012). Chitosan is a chitin derivative, the most abundant polysaccharide on earth after cellulose is hydrophobic and can form films and membranes (Elieh-Ali-Komi & Hamblin, 2016; Mahatmanti et al, 2017). Natural materials containing chitin are produced from crustacean animals. This study uses crab shells because this waste contains high chitosan and is easily obtained. Chitosan is used as a mixing biopolymer to improve physical properties because of the hydrogen bonds possessed by starch in amylose and amylopectin. The researcher combined chitosan and polyvinyl alcohol and observed the release mechanism of the phosphate (Jamnongkan & Kaewpirom, 2010), while the fertilizer coatings that have been widely studied were from starch (Elgadir et al., 2012). The specific purpose of this study was to test the release of phosphate in the soil for NPK fertilizer modified with chitosan and potato flour.

METHODS

Materials

The main material of this research was chitosan obtained from company in East Java, Aquadest, and Acetic Acid Pa (Merck) without further treatment, and NPK fertilizer 13-13-13.

Chitosan and Potato Flour preparation

The mixture with the ratio between chitosan and potato flour is 1: 0; 0.2: 0.8; 0.3: 0.7). A total of 3% w/w chitosan is made by dissolving chitosan powder in a solution of acetic acid (1% v/v) by stirring until evenly distributed. Potato flour is also dissolved in 8% w/v in distilled water then stirred and heated to a temperature of 76°C for 5 minutes until it becomes a gel. The two solutions were mixed with chitosan solution and potato flour gel mixed by stirring for 30 minutes at room temperature. A total of 10 grams of NPK fertilizer is taken, and the gel mixture is sufficient to coat NPK fertilizer evenly. NPK-coated fertilizers are then dried at 80ºC until the weight of NPK fertilizer is constant.

Characterization of Coating

The outer surface morphology of fertilizers and fertilizers and their coatings (chitosan and potato flour) will be investigated using Scanning Electron Microscope (SEM) with 500X magnification. The functional groups possessed by fertilizers and coating materials were evaluated using Fourier Transform Infrared (FTIR) at wave numbers 4000-450 cm^{-1}.

Water Absorbency of Gel Fertilizer (Swelling Ratio Test)

Gel coating made from chitosan and potato flour is formed into sheets on top of the glass material then dried at a temperature of 80ºC to a constant weight. Wd is a weight of the initial macrosphere that has not experienced swelling at equilibrium.

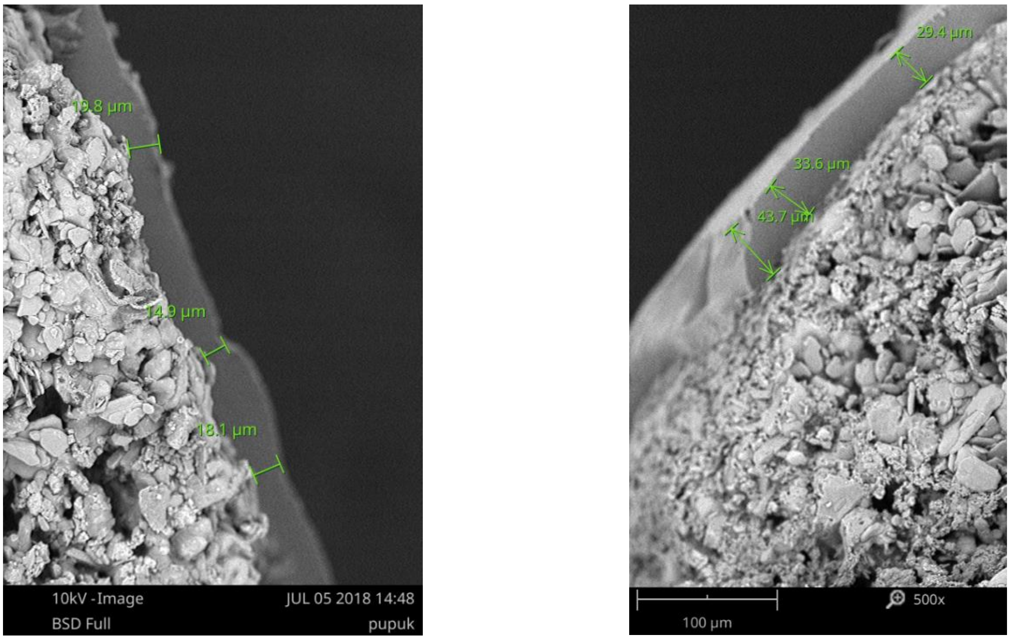
The gel with a constant weight was then soaked in distilled water until the gel was wet for 10 minutes, then removed and the surface was dried with suction paper. This is done repeatedly, and the gel is weighed every 10 minutes soaking until the gel mass is constant. The gel swelling ratio (%SR) calculated by Eq. (1). Where, Ws is the weight of the microsphere that has swelled at equilibrium.

$$\%SR = \frac{Ws - Wd}{Wd} \times 100 \quad (1)$$

Water Retention Test

Dry samples of NPK-gel fertilizer are buried in 100 g of dry sandy soil. All materials are placed in plastic cups. As much as 100 g of other dry sandy soil, without fertilizer, are placed in identical plastic cups (blank), then each cup is weighed as initial weight (Wq). A total of 50 mL of deionized water is added to each cup and the cup is re-weighed every day (Wqo). Furthermore, the storage of both glasses was carried out at the same room temperature condition and weighed every day (Wqt) for 30 days. Water retention (% WR) land is calculated using Eq. (2).

$$\%WR = \frac{Wqt - Wq}{Wqo - Wq} \times 100 \quad (2)$$



(a) (b)

Figure 1. Morphology of SEM Image (a) NPK fertilizer with gel coating (b) NPK fertilizer without gel coating.

Phosphrus Release Test

Sandy soil that has been cleaned from dirt is filtered 200 mesh so that its size is used uniformly. Fertilizer 1 gram of NPK-gel is grown in 10 grams of sandy soil in a glass with a perforated base for nutrient release testing. 30 mL of water is added to the glass. Water that has passed through the ground in the glass is collected after 3, 6, 9, 12, and 15 days, each of which is tested for the level of phophorus using the SNI standard test no 06.6989.31.2005 regarding the phosphate level at the UV-VIS Spectrophotometer at a wavelength of 880 nm.

RESULT AND DISCUSSION

Characteristics of fertilizer NPK-gel

Chitosan and potato flour as NPK coatings were observed morphologically on the surface of the sample showing additional thickness on the surface of the sample. Comparison between fertilizer given gel and without gel can be seen the addition of depth there is a coated fertilizer. There are three measurement points for the thickness of the layer. Figure 1 (a) shows NPK-gel with a width of 43.7; 33.6; and 29.4 µm. If taken on average, the thickness of the fertilizer by adding layers in the form of a gel is 35.6 µm. Figure 1 (b) shows the initial sample which indeed already has a coating on the fertilizer. NPK fertilizer has a thickness calculated at three different points, 19.8; 14.9; and 18.1 µm and if taken on average the initial fertilizer thickness was 17.6 µm. So fertilizer without adding gel has a thicker layer on the outer surface of the compost compared to the initial fertilizer. The thickness difference between the addition of conventional gel and NPK fertilizer around 18 m becomes the diffusion distance which slows the compost to the ground.

Modification in the form of chitosan and potato flour can form a layer on the surface of NPK fertilizer, so NPK fertilizer becomes thicker and more evenly distributed compared to conventional NPK fertilizer. Though the cause of NPK fertilizer quickly is not solves when added to water because the nature of the fertilizer is hygroscopic. So the function of the coating on the outer surface of NPK fertilizer is a solution to block the compost (the addition of thick) for the release of nutrients from NPK fertilizer out of the wet soil environment. A functional group analysis is performed to determine the availability of functional groups.

Functional group analysis is done to determine the availability of functional groups. The functional group analysis included the ratio of chitosan and potato flour to 3:7. There are 11 peaks presented in Figure 2 showing 11 peaks for modifying the ratio of chitosan ratio: potato flour 3:7 and for the ratio of 1:0 has 13 peaks are available.

Table 1. Characteristics of the layers of chitosan and potato flour

Functional Groups	**Wavenumber (cm^{-1})**	
	K:P (1:0)	**K+P (0.3:0.7)**
O-H overlap (vs) N-H	3367	3392
C-H aliphatic	2927	-
C≡C	2163	2151
C=O secondary amide	1639	1645
C=O carbonyl	1559	1568
C-H	1412	1417
C-O carboxylates	1257	1248
C-O amines	1154	1156
1,4-glycosidic	899	855

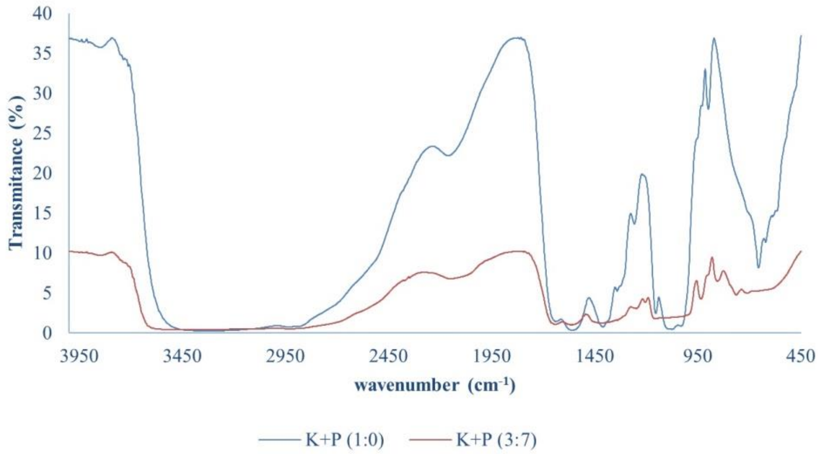


Figure 2. FTIR Spectra of NPK gel with rasio chitosan, K: potato flour, P (1:0) dan (3:7)

The infrared spectrum band characteristics of the mixture of chitosan and potato flour (1:0) and (3:7) are shown in Figure 2 and Table 1. Infrared spectrum absorption band K + P (1:0) at 3367 cm_{-1} shows the bending vibration of OH and NH functional groups. In the infrared range 3:7 ratio there is the absorption of OH and NH groups but is shorter than the rate of 1:0, because chitosan used in mixing (3:7) with potato flour is indeed less. The presence of more chitosan at a ratio of 1:0 is also shown in the absorber band 2927 cm^{-1} which indicates the presence of bending vibrations from the OH and NH_2 groups. It was also found that the stretching vibration of the wave number 1638.99 cm-1 was an absorption band from the C=O group which showed the presence of a secondary amide group at both ratios. One specific absorption characteristic of chitosan is the absorptive capacity of the area of 1650 cm^{-1} which indicates the presence of the C=O group in the bond (-$NHCOCH_3$) (Dompeipen, 2017). The absorption band 1559 cm^{-1} in the infrared spectrum ratio of 1:0 indicates a vibration stretching of C=O bonds which suggests the presence of carbonyl groups, while at a rate of 3:7 shows absorption at the same area of wave number 1567. There is a bond between C = O at a ratio of 1:0 can be indicated by symmetrical stretching vibrations, as well as a ratio 3:7. One sign of chitosan compounds is vibration at wave number 899.02 cm-1, which means the presence of glycosidic link β-1.4 found at a rate of 3:7 which has a higher absorption at a ratio of 1:0 because chitosan content is more prominent. Addition of potato flour to the layer can cause exposure to OH groups so that the OH group stretches as shown can form hydrogen bonds (Amir et al., 2013). The higher the O-H group shows, the more hydrogen bonds are formed (Zhang et al., 2018). This change is evidence of a mixture of chitosan biopolymers and potato flour chosen to function as coatings that have strong hydrogen bonds.

Swelling Ratio

The swelling ratio test is often called the swelling ratio because of the ability of a material (coating) to hold water in the document. The calculation results using Eq. (1), obtained %SR, which is presented in Figure 3. This test is carried out on coating materials with the ability of pure

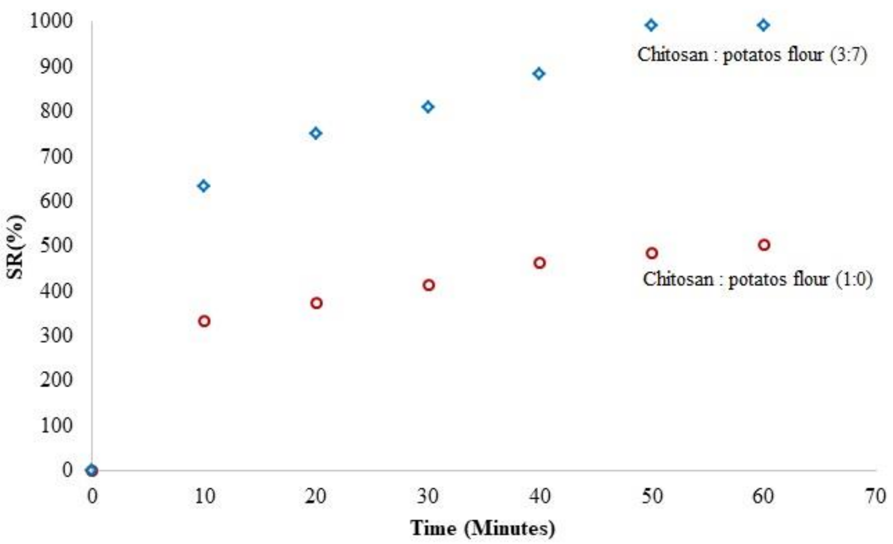


Figure 3. Effect of time on% swelling test on NPK-gel chitosan and potato flour

water until the coating on NPK has a constant mass. This shows that the gel/coating has saturated the entry of water into the surface (Majeed et al., 2015). In NPK with a ratio of 3:7 the value of %SR achieved is high, which is increased to 992% when compared with chitosan gel which only absorbs 508%. This proves that potato flour has good adsorption properties so that it can increase the development power of chitosan as a coating of NPK fertilizer. Chitosan has good fertilizer coating properties but has low water absorption caused by the presence of hydrophobic cations in chitosan (Azeem et al., 2014).

Water Retention Test

Water retention is carried out to determine the ability of fertilizers to maintain soil moisture and shown in Figure 3. The strength of water retention in soil decreases with increasing days for all samples tested, namely NPK which is given chitosan and potato flour coating (3:7) and (1: 0) and NPK fertilizer compared to soil without any manure called blank. The cause of this decline is due to evaporation due to the environment around the soil namely temperature and humidity. Samples with NPK with a 3:7 coating ratio have a higher ability to maintain greater moisture compared to all samples. Water retention behavior towards NPK gel is higher with the addition of gel in fertilizer when compared to soil with NPK only. Each represented data point is the average value of three measurements with a standard deviation of 5%. It was found that gels increase water retention. Fixed groundwater retention capacity is only 20% if just soil, but with NPK after 20 days, the soil retention decreases because NPK compounds on the ground may evaporate.

Meanwhile from the soil containing NPK and coatings each is 60% for layers with a ratio of 3:7 and 26% for a ratio of 1:0. Therefore, all gel coatings show high water retention ability to be stored. As a comparison, a fertilizer with polyvinyl chloride coating has retention water of 26% after 20 days with 2% for the land used (Jamnongkan & Kaewpirom, 2010). This is different from the water retention test after 30 days for soil with hydrogel/clinoptilolite/NPK fertilizer with a yield of 69% while the soil without fertilizer was 53% (Rashidzadeh et al., 2015).

Phophorus Release Test

Watering into a glass that already contains fertilizer for 15 days resulted in the release of phosphate. In Table 2, NPK fertilizer which is not coated with a mixture of chitosan and potato flour quickly releases P nutrient content as evidenced by the amount of concentration produced greater than 0.163 mg/L from NPK fertilizer which has been given an additional layer on the 15th day. NPK samples with chitosan coating with a ratio (1:0) can release Phosphorus elements more than NPK samples with a mixture of chitosan and potato flour coatings. Addition of ingredients such as potato flour can affect the rate of release of nutrients by slowing down. Phosphorus nutrient concentration from the beginning of the

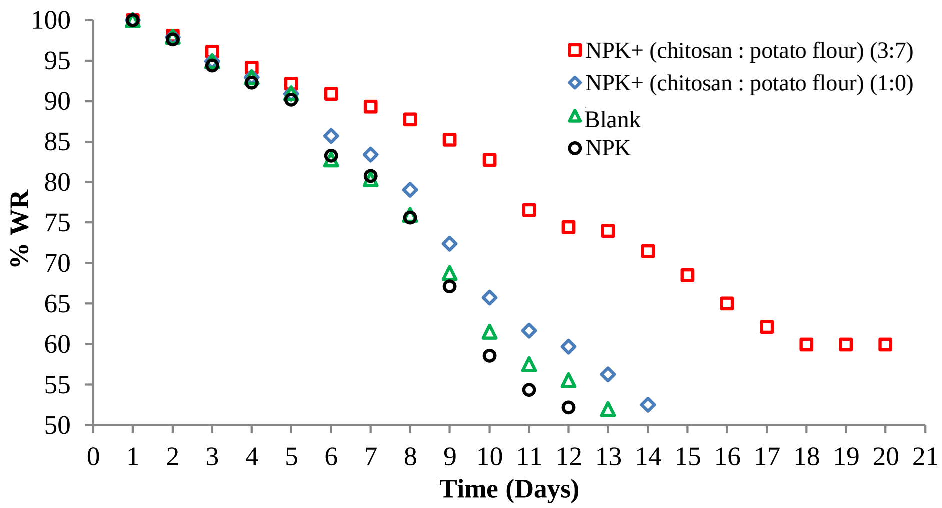


Figure 4. The relationship between % water retention with time

Table 2. Concentration element of Phosphorus release test

Sample NPK	Phosphorus release test (mg/L)					Total (mg/L)
	3 days	6 days	9 days	12 days	15 days	
No coating	0.819	0.594	0.244	0.221	0.207	2.107
Coating: chitosan: potato flour (1:0)	0.258	0.207	0.205	0.204	0.170	1.045
Coating: chitosan: potato flour (3:7)	0.207	0.197	0.194	0.169	0.163	0.923

observation, namely the 1st to 15th day. The best level used as a coating on NPK fertilizer by coating uses a ratio (3:7) with a lower total P nutrient which is smaller that is 0.923 mg/L when compared to non-coated fertilizers removing phosphorus element of 2.107 mg/L. This proves that chitosan-potato flour-gel-coated fertilizer can inhibit the release of phosphorus nutrients in the compost by 2 times. This is supported by research with coating fertilizers. This is supported by research with coating fertilizers. This is supported by research that uses a gel-based slow/controlled release fertilizer with mixed-layer coatings and synthetic materials that have effective results on nutrient release including Phosphor which reaches 2x as well (Ding et al, 2016).

CONCLUSION

The difference in concentration used between the mixture of chitosan and potato flour with a ratio of 3:7 and 1:0 affected the test results. The strength of NPK fertilizer coating with a coating ratio of 3:7 resulted in swelling rate, water retention, and phosphor release tests almost twice as good as the 1:0 ratio for the same test. Thus the addition of coatings with a mixture of 3:7 for chitosan and potato flour is superior as NPK fertilizer coatings.

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