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Utilization of shrimp shell waste as matrix controller by using ionotropic gelation method in slow release fertilizer based on environmental conservation

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Abstract. The Availability of shrimp waste in Indonesia is huge, especially in shrimp pond areas. However, it has not been utilized optimally and caused environmental pollution. The weight of shrimp waste reaches 30%-40% of its weight. Most of the shrimp waste is dominated with shrimp shells. Shrimp shells containing 60% -70% chitin. It will produce 15-20% yield of chitosan synthesized from chitin. On the other hand, the use of fertilizer continues to increase. Fertilizer is an essential nutrient for plants if lack nutrients to make plants can't grow normally. Preparation of chitosan as matrix controller begins from shrimp shell synthesis which is obtained by deacetylation method with the highest deacetylation degree of 74.5% and the optimum deacetylation is 71.2%. The SEM test which shows the thickening and rougher structure of the fertilizer surface, fertilizer coated by microspheres has a thickener and coarser surface so as to inhibit the release of elements inside. The shrimp shell waste based coating is able to inhibit the release of NPK contained in the fertilizer. The occurrence of ionic crosslinking shown by the presence of N-H groups and -P=O on material.

2 I. Introduction

Chitosan is a biopolymer material that consist of β -(1-4) D-glucosamine units obtained by chemical or enzymatic synthesis, by a deacetylation process of the amino acid polysaccharide contained in chitin. Chitin compounds are generally found as structural compounds of arthropods (eg, lobster and shrimp) and are formed from β - (1-4) units of N-acetyl D-glucosamine. Chitosan has biocompatibility and biodegradation in the environment, is non-toxic and has excellent absorption properties when compared to materials made from synthetic plastics [1]. Chitosan has many benefits in the industry, including the food industry, agriculture, water treatment, medical device manufacturing and medicine, synthetic tissue and synthetic membranes, cosmetics, antifungal and antibacterial products [2].

In the fishery sector, the processing industry produces shrimp shell waste. Shrimp shell waste has not been optimally utilized. Waste is only used as a mixture of making shrimp paste and animal feed mixture. Utilization is only able to overcome a small part of the total amount of shrimp waste and has a very small economic value. According to the Badan Pusat Statistik in 2012 noted that shrimp production in Indonesia increased by 5% every year. The Ministry of Marine Affairs and Fisheries also reported that shrimp export volume in 2010-2014 increased from 113 937.0 tonnes to 148 519.4 tonnes, with the foreign exchange value of USD 1 706 784.4 in 2014. However, there are major problems in shrimp processing industry, which produces waste in a very large amount. The waste contains proteins

7 (35-50%), chitin (15-25% of dry weight) and inorganic compounds (calcium carbonate) considered to be the main cause of environmental pollution.

Shown in figure 1 that describing needs and production of NPK fertilizer in Indonesia from 2007 until 2015. It is necessary to save the use of fertilizer to reduce the increase in the number of fertilizer needs, one way to overcome it is to create innovations in fertilizer, which is making slow release fertilizer. Slow release fertilizer is a fertilizer capable of controlling the speed of release of nutrient elements lost due to dissolve in water, evaporate and the denitrification process against the fertilizer itself. Increasing the effectiveness of the fertilizer by modifying the product into a slow-release fertilizer. Fertilizer of slow modification 10 made by using chitosan obtained from shrimp waste synthesis as a coating on fertilizer. Thus the release rate of soil nutrients can be adapted to the needs of the plant. In addition to the innovation of low-fertilizer can reduce the amount of fertilizer consumption. The innovation of slow-release fertilizer is made from chitosan, besides can be made using zeolite [3], bentonite and alginate [4], starch-polyvinyl alcohol [5], polymers [6], [7] using kraft lignin pine trees, [8] with acrylamide copolymers, [9] using softwood kraft lignin for coating urea, [10] using sodium alginate and biochar for superabsorbent slow-release fertilizer. Utilization of shrimp shells that are synthesized into chitosan expected to solve the problem of waste shrimp while enhancing the economic value of shrimp shells. In addition, shrimp shells used as a control of soil nutrient release can improve the effectiveness and efficiency of fertilizers. The method used in the manufacture of fertilizer is slow-release is the ionotropic gelation method other than the ionotropic gelation method there are other methods such as matrix hydrophilic, and hydrophobic [11]. [12] encapsulated by starch-based superabsorbent polymer. The basic innovation of this research is that many coatings of fertilizers using polymers are not biodegradable to the detriment of the environment. In addition, the production cost used is also relatively large. The use of ionotropic gelation method is assumed to avoid the possibility of soil contamination.

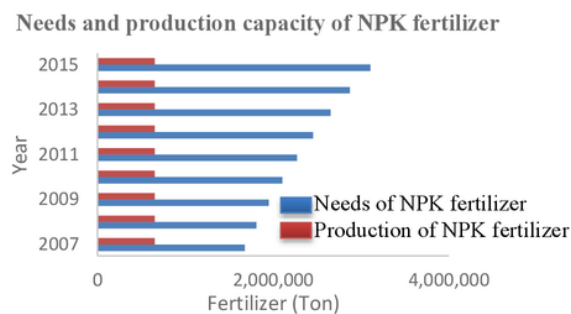


Figure 1. Needs and production capacity of NPK fertilizer.

2. Materials and method

2.1. Materials

Shrimp shell, HCl 5%, NaOH, pH indicator, acetic acid 1% v/v, potato starch flour, sodium tripolyphosphate 1% wt/wt, NPK fertilizer, aquadest.

2.2. Preparation of slow release fertilizer 5

11 Shrimp shells are cleaned and then 5 soaked in 0.5% NaOH solution for 24 hours, wash with water until neutral pH deproteination using 5% NaOH solution for 24 hours, wash water using until neutral pH demineralization with 5% HCl solution for 24 hours, wash again until pH neutral, dry at room temperature then formed chitin, to change chitin into chitosan need to do various stages as follows: soak chitin in 50% NaOH solution, at room temperature for 1 week, done stirring then wash with water until neutral pH dry in room temperature puree. In making Macrospheres by Making chitosan solution

of chitosan first 3 grams dissolved in 1% acetic acid as much as 100 mL chitosan solution stirred using magnetic stirrer followed by making potato starch gel, potato starch as much as 8 grams in 100 mL of aquadest, do stirring by using magnetic stirrer and heated until the temperature reaches 76 °C. Preparing STTP solution is done by dissolving STTP as much as 1 gram in 100 mL of aquadest measuring pH to reach pH 8.6. Makes microspheres coating by mixing chitosan solution with potato starch gel, stirring until homogeneous solution, storing mixture at room temperature for 30 minutes make SRF fertilizer by dipping NPK fertilizer with macrosphere, stirring until homogeneous, mixing macrosphere coated fertilizer with STTP then do stirring 2 hours of draining SRF fertilizer at 85°C for 48 hours up to constant.

The manufacture of matrix controller on NPK fertilizer is made by using chitosan feedstock which is distilled from shrimp waste. The coating of fertilizer with several variables such as chitosan, starch, with the addition of STTP and without the addition of STTP with a certain concentration as follows at Table 1.

Table 1. Variabel used in research.

Chitosan	Potato Starch	Coating (time)			STTP		Fertilizer
1	0	1	2	3	Without STTP	With STTP	NPK
1	1	1	2	3	Without STTP	With STTP	NPK
1	2	1	2	3	Without STTP	With STTP	NPK
1	3	1	2	3	Without STTP	With STTP	NPK

2.3. SEM and EDX characterization

Macrospheres chitosan and chitosan are mounted on aluminum with double tape adhesive and coated with gold. The surface morphology is examined by SEM devices with gun emissions which are operated at 3 kV. The micrograph is taken from an enlargement between 500 X and 15000 X.

2.4. FTIR characterization

The chitosan-starch FTIR spectrum without STTP and chitosan with STTP microspheres were recorded on FTIR spectrophotometers operating in the range of 4000-400 cm⁻¹ at a resolution of 4 cm⁻¹. The samples were mixed thoroughly with potassium bromide at 1:20 gm (KBr sample) mass ratio. KBr discs are composed by compressing the powder mixture with hydraulic pressure.

3. Result and discussion

3.1. SEM characterization

SEM analysis is used to determine the topography that is the surface characteristics of texture, morphology, and microspheres composition. Here is a micrograph analysis was taken from an enlargement of 500X to 15000X.

SEM test result known a surface difference between coating fertilizer show in figure 2 and without coating fertilizer show in figure 3. Coating fertilizer at magnification 500 (figure 2a) and 1000 (figure 2b) formed shaped granule-shaped granules that indicate the coating on the layer of fertilizer, this layer is able to inhibit the release of nutrients in the fertilizer. While in the coating without coating shown in figure 3 is not formed a layer of granule-shaped granules or coating surface so that there is no inhibition of release of elements in it. At magnification 10000 (figure 2c) and 15000 (figure 2d) can be observed in more detail coating fertilizers show a surface with a thicker texture and morphology when compared with a coating without coating.

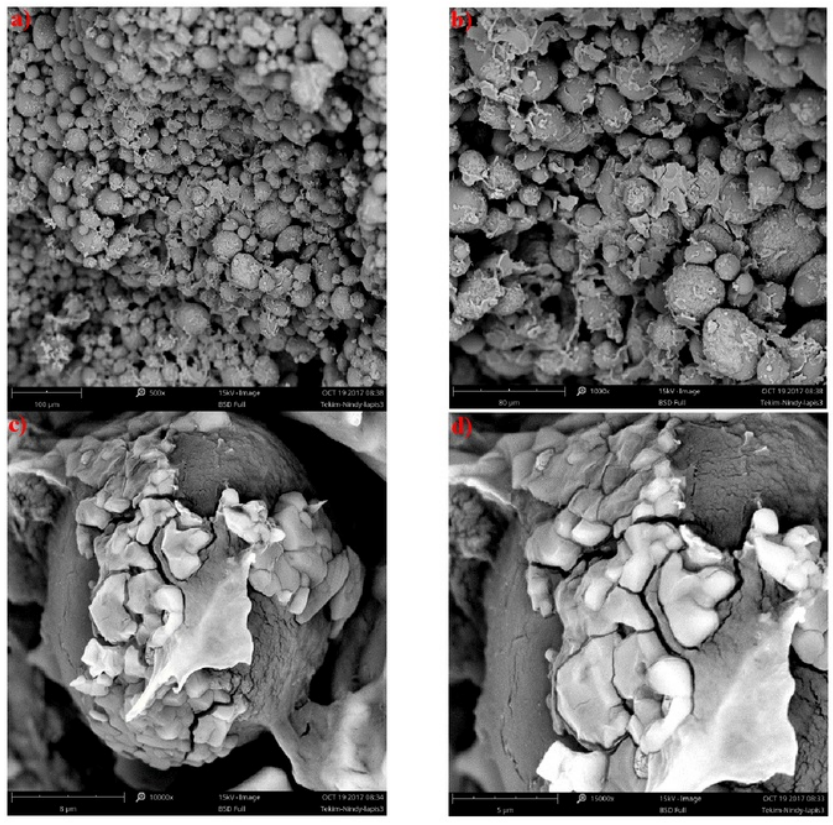
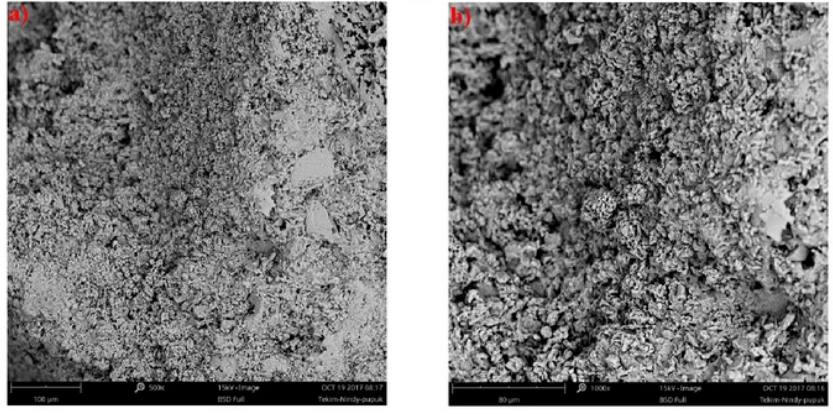


Figure 2. SEM test analysis of fertilizer sample with coating. a) 500X b) 1000X c) 10000X d) 15000X.



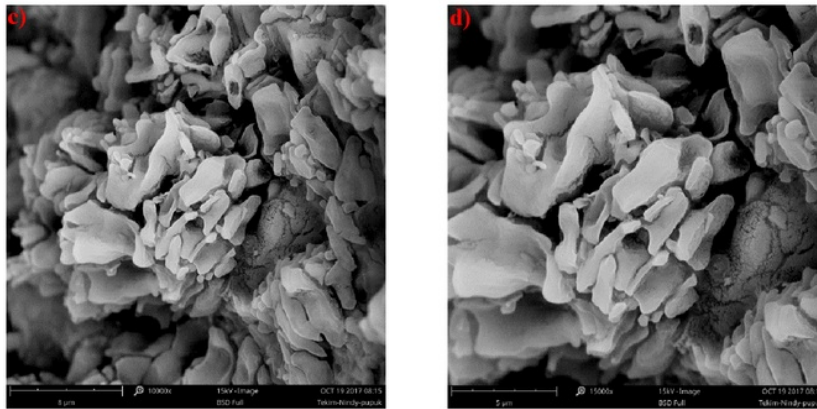


Figure 3. SEM test analysis of fertilizer sample without coating. a) 500X b) 1000X c) 10000X d) 15000X.

3.2. EDX characterization

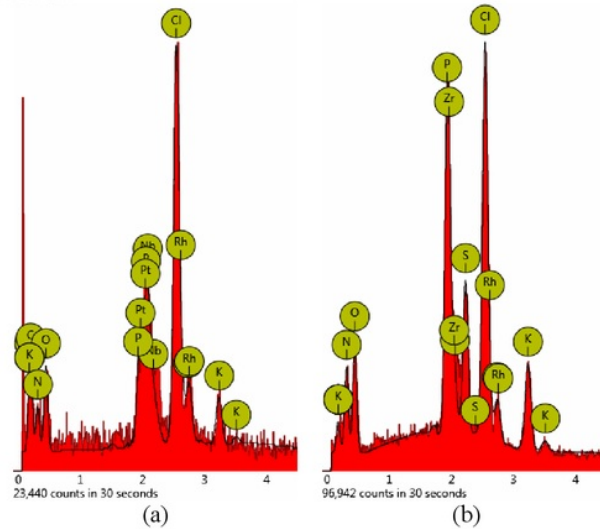


Figure 4. NPK content analysis on fertilizer a) with coating b) without coating.

Based on figure 4 the results of analysis of fertilizer is presented in the following Table 2 and Table 3 show the difference of NPK content found on the surface of with coating fertilizer and on the surface of the fertilizer without coating, presented in the following Table 4. It can be concluded that the content of NPK contained in the surface of with coating fertilizer is smaller when compared with fertilizer without coating so that the release of the elements contained in the fertilizer can be inhibited. Inhibition of release on the fertilizer can be calculated using the ratio value of 3.32 to 5.17 so that the release of elements in the fertilizer can be inhibited \pm 3-5 times.

Table 2. Result of analysis of fertilizer with coating

Element Number	Element Symbol	Element	Weight Concentration	Error %
15	P	Phosphorus	1.2	2.6
19	K	Potassium	1.3	0.5
7	N	Nitrogen	6.9	0.5

Table 3. Result of analysis of fertilizer without coating

Element Number	Element Symbol	Element	Weight Concentration	Error %
15	P	Phosphorus	6.2	0.2
19	K	Potassium	4.2	0.2
7	N	Nitrogen	30.3	0.8

Table 4. Differences of NPK content found on the surface of with coating fertilizer and on the surface of the fertilizer without coating.

Element	Fertilizer with coating	Fertilizer without coating	Ability to inhibit element release
N	6.9	30.3	4.39
P	1.2	6.2	5.17
K	1.3	4.2	3.23

3.3. FTIR characterization

Tests using FTIR tools were performed to gain an understanding of the macrosphere structural changes obtained after the addition of coatings on NPK fertilizers. The spectrum of potato starch FTIR [9] shows a common feature of polysaccharides. In Figure 5 (a) and (b) shows an intense band at 1022 cm^{-1} and 1736 cm^{-1} corresponds to the stretch areas C-O and C-H [13]. Shown in Figure 5(a) FTIR test result of the sample with STTP, the pure chitosan spectrum presents the characteristic bands at 3370 cm^{-1} that are associated with the overlap of the stretching vibrations of the -NH₂ and -OH groups [14]. Macrospheres prepared with chitosan only shows the shoulder at 1240 cm^{-1} , which can be given at the stretching vibration of P=O, indicating the presence of phosphate groups as a consequence of ionic crosslinking [15] which a sample is with STTP. A samples using STTP occurs ionic crosslinking. On figure 5(a) The FTIR spectrum of the matrix obtained from the mixture also revealed the shoulders at 1240 cm^{-1} , indicating the presence of the P-O group and indicating that crosslinking occurs through ionic interactions between the negatively charged group P=O and NH₃⁺ groups in chitosan.

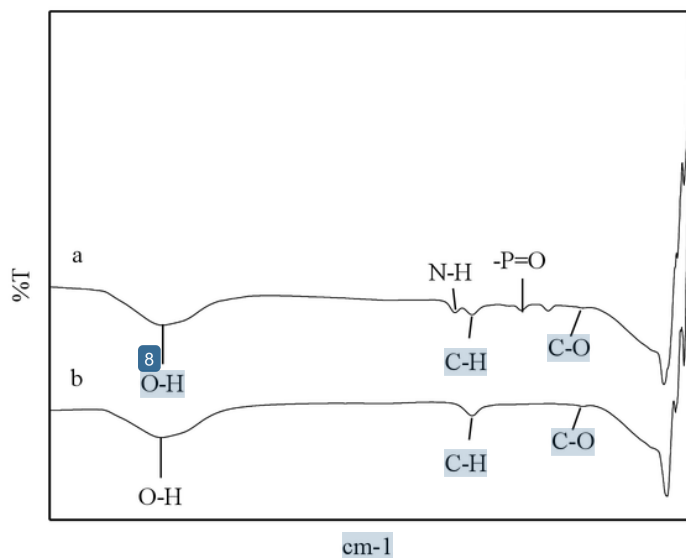


Figure 5. FTIR test result of sample (a) with STTP (b) without STTP.

4. Conclusions

Making chitosan as a matrix controller begins with the synthesis of shrimp shells by deacetylase method. After chitosan was formed making microspheres by dissolving chitosan and stirring process. The mass of the dry beads is calculated to determine the soluble fraction. Before the test release on fertilizer, the product that has been formed is characterized by various methods such as Scanning Electron Microscope (SEM) test to find out the morphology of the product, there are some other tests to know the characteristics such as FTIR test and EDX after testing is done release test. From the test proved the existence of slow release (slow release) nutrient decomposition on the fertilizer.

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Acknowledgments

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