Fertilizers from monosodium glutamate waste encapsulated with chitosan nano-zeolite

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Abstract. Fertilizers that are safe for the environment are highly necessary to increase the agricultural productivity in handling critical land conditions, where nutrients contained in the soil are far below the normal levels of 4–5 %. This nutrient crushing occurs due to the use of synthetic chemical fertilizers, pesticides, and excessive chemical drugs. Therefore, the authors make fertilizer with a high slow release of zeolite, chitosan from the skin shell and monosodium glutamate (MSG) waste. The method used is demineralization, deproteination, and deacetylation to obtain chitosan. After that, the zeolite encapsulation was activated by chitosan and MSG waste. The product obtained is in the form of a milling solid using HEM to obtain the results of nanoparticles. These results were characterized by FTIR, SEM-EDX, XRD. XRD results refer at (angle ($2\theta$): 20) containing NH$_2$ compounds, at (angle ($2\theta$): 21–23) containing SiO$_2$, then at spectra (angles ($2\theta$): 25–28) containing LiAlSiO$_4$ compounds then at (angle ($2\theta$): 30–34) containing C and at (angle ($2\theta$): 42–44) containing FeO$_4$P. SEM results show MSG micrographs wrapped in nano-zeolite and nano-chitosan fertilizers with a sample size of 90-100nm and it is known that in MSG waste fertilizer encapsulated with nano zeolite-chitosan containing micronutrients in fertilizers such as Si as much as 10.7 %, sodium 11.8 %, nitrogen 11.8 %, 1.2 % iron, potassium 0.3 % and 0.1 % phosphorus. The FTIR results showed a peak in the fingerprint area of the MSG-zeolite-chitosan waste spectra that identified the presence of macro nutrients N, P, K, Ca, Mg and several micro elements such as Cu, and Zn in addition to other elements needed in slow release fertilizers.

Keywords: Chitosan, fertilizer, cipramin, zeolite

1. Introduction
Chili (Capsicum frutescens) is one of the agricultural commodities in Indonesia, where chili per capita consumption in Indonesia is 50,000 tons/month. However, currently the agricultural land in the archipelago is more than 60 % in critical conditions, where the nutrients contained in the soil are far below the normal levels due to the use of synthetic chemical fertilizers, pesticides and excessive chemical drugs. Therefore, in order to increase the agricultural yields, the environmentally friendly fertilizers are needed to increase agricultural productivity [1].

MSG waste contains nutrients and organic materials that can be utilized by plants and has begun to be used as fertilizer in several areas, especially in the area around the MSG plant. So that MSG waste or what is also called the amino acid process residue (Cipramin) has great potential that can be used as a fertilizer base material combined with organic waste with high NPK levels which is very potential to
be used as fertilizer [2]. However, it is necessary to control the nutrient release in plants. Therefore, innovations are needed to improve the efficiency of nutrient release. One effort to reduce nutrient losses and improve fertilizer efficiency is to modify the fertilizer to become a Slow Release Fertilizer (SRF) by mixing fertilizers from Supramin and organic waste with materials that have high cation exchange capacity (CEC) such as nano–zeolite [3].

This study focuses on testing the efficiency of nutrient release from organic waste, the combination of nano zeolite-chitosan with the substitution of monosodium glutamate which is expected to increase the ability of slow release fertilizer in fertilizers so as to increase plant growth and development.

2. Materials and method

2.1. Materials

The materials utilized in this work were Cipramin which was obtained from the by-products of food flavorings and organic waste making, shrimp shells, acetic acid (CH₃COOH), sulfuric acid (H₂SO₄), HCl, HF, AgNO₃, NaOH, distilled water, H₂O₂, TPP (Tripolyphosphate), NH₄Cl, and compost.

2.2. Making organic fertilizer with the addition of cipramin

The decomposer bacteria were diluted and added with sugar, then organic waste fertilizer was mixed with bran to form a mixture, then added 10 ml bacterial solution and 50 % water was added from the amount of organic waste used. The mixture was piled up in dry conditions and left for 8–12 days. Next was the composting process of Cipramin with a ratio of 5:2 to the weight of MSG waste with an EM4 composting solution. Then, left for 7 days and controlled every day. So that MSG waste products and organic waste were obtained.

2.3. Making nano-chitosan

The first stage in the process of purifying chitosan was the demineralization process, by smoothing the shrimp skin then adding HCl, then the mixture was heated. Then, washed with distilled water solution to remove the remaining HCl. The mineralless powder was washed with distilled water. The deproteination process was the next step, where the dried shrimp skin powder from the demineralization process was added with NaOH. Next, the shell of the shrimp was dried and then muted and stirred and then dried. The results obtained were washed with distilled water until the pH became neutral. The washed chitin was added with 70 % ethanol and continued with filtration, then washed the sediment with hot distilled water and acetone to remove the color, which was done twice. The precipitate in the form of chitin was in the form of a solid powder. The chitin yield obtained was 35 %. Deacetylation was the last stage in the making of this chitosan. The shell of the shrimp was soaked and stirred in 60 % NaOH solution, then the mixture was stirred and heated, then filtered and titrated solution using HCl to precipitate the chitosan back into the solution so that chitosan will be formed and the last HEM it for 5 hours to obtain nano-sized particles [4].

2.4. Activation of natural nano zeolites

Zeolite was immersed in 2 % HF solution for 10 min with stirring. Then, zeolite was immersed in HCl 6 M solution for 30 min, after which the zeolite was immersed with NH₄Cl 0.1 M solution. Furthermore, the zeolite was calcined and followed by characterization using Energy Dispersy Spectroscopy to determine the content of SiO₂ and Al₂O₃ which are components of zeolite.

2.5. Encapsulation process

Next was the mixing between fertilizer, zeolite and chitosan into one. In this study three variations were carried out, namely with a ratio between potassium: activated zeolite: chitosan nanoparticles were 40 %: 10 %: 50 % and 40 %: 20 % and 50 %: 20 %: 30 % which were previously dissolved in acetic acid 1 %. Mixed the ingredients then added a tween solution of 2 drops and stirred at a speed of
150 rpm for 24 h until gel was formed, then let it stand. Then, the characterization testing of nutrient content in fertilizers, release analysis in water media, analysis of Energy Dispersy Spectroscopy, release analysis in soil media were carried out.

2.6. Characterization

**SEM-EDS and SAA tests.** Characterization that will be carried out including the SEM-EDS and SAA tests. SRF fertilizers that have been previously made will be applied to agricultural land to determine the nutrients absorbed by plants. Soil taken in a composite at a depth of 0–50 cm. In the testing, the prepared planting media amounted to three media, then distinguished from the three media variations made fertilizer. In the first planting medium was given with potassium fertilizer, the second was given a combination of potassium fertilizer with zeolite nanoparticles and the third planting medium was given a combination of potassium fertilizer with zeolite-chitosan nanoparticles. The measurement time was carried out for 2 weeks. The parameters used were nutrients contained in the planting media.

**FTIR test (Fourier Transform Infra Red).** The FTIR test aimed to determine the functional groups present in the fertilizer content.

**PUP test (Fertilizer Test Device).** This analysis was carried out to determine the SRF value and nutrient content in the fertilizers by releasing the soil media.

3. Results and discussion

This study describes a convenient process for zeolite activation, modification of chitosan and encapsulation of MSG waste fertilizers (Cipramin) using an impregnation approach to load macro nutrients (primary and secondary) and micro in MSG (Cipramin) waste fertilizer encapsulated nano-zeolite and nano-chitosan. The synthesized materials (both nano-zeolite and nano-chitosan) were determined by FT-IR, SEM / EDX and XRD to gain a perception regarding the structure, morphology, chemical composition, particle size as well as thermal stability. The physical accreditation is also carried out using the standard method to find the application of modified nano-chitosan and nano-zeolite as slow release fertilizers and nutrient release studies on soil.

3.1. MSG (Ciprami) waste fertilizer encapsulated nano-zeolite and nano-chitosan

The process of purifying chitosan is the process of demineralization, the deproteinization process which will produce chitin, and deacetylation is the last step in making chitosan.

At the stage of demineralization, the deproteinized product is reacted again with 1 N HCl solution for 30 min at 60 °C. Demineralization is aimed to remove minerals, especially calcium carbonate. Demineralization is usually performed using treatment with acid by HCl, HNO₃, H₂SO₄, CH₃COOH and HCOOH [3]. Between these acids, the preferable reagent is the dilute hydrochloric acids. Demineralization is simply achieved since it covers the calcium carbonate decomposition to calcium-soluble salts by releasing the carbon dioxide. CO₂ gas bubbles in the reaction process is an indicator of the ongoing reaction of HCl with mineral salts found in shrimp skin waste which is still passing through the deproteinization process. Subsequently, many bubbles and air bubbles are formed in a quite large volume, and this lasts for approximately 5–10 min. This is caused by the formation of CO₂ and H₂O gas on the surface of the solution based on the demineralization reaction [5]. Other minerals in the shrimp skin mostly react and dissolve the salt content by the acid presence. Then, the dissolved salts can be easily isolated with the chitin solid phase screening process continued by cleansing with water [6].

The deproteinization process has a difficulty degree in regards to the strong chemical attachment among chitin and protein. Deproteinization is heterogeneously carried out with chemicals that depolymerize biopolymers as well. Overall protein extraction is highly significant for the application of biomedical, because the human population percentage known to be allergic to shellfish, the main cause
is the protein component [3]. Chemical processes are the initial approaches applied in the deproteinization. Various reagents have been checked as deproteinization chemicals, which are NaOH, Na₂CO₃, NaHCO₃, KOH, K₂CO₃, Ca(OH)₂, Na₂SO₃, NaHSO₃, CaHSO₃, Na₃PO₄ and Na₂S. The reaction conditions are greatly varied in each study. NaOH is a preferable chemical and used at concentrations ranging from 0.125 to 5.0 M, at various temperatures (up to 160 ºC) and length of process (from several min to several days). Moreover, to deproteinization, the utilization of NaOH always generates a partial deacetylation of chitin and decreases biopolymers hydrolysis.

Zeolite is a hydrated alumina silicate crystal containing alkali or alkaline cation in the form of a three-dimensional skeleton, acidic and has a molecular-sized pore. The empirical formula of zeolite is M₂n(Al₂O₃.ySiO₂) wH₂O where M = alkaline earth or alkali, n = valence alkali metal and x, y = certain numbers. Because of the unique nature of zeolite, which is atomic composition and its composition can be modified, the researchers attempted to make synthetic zeolites that have special properties according to their needs. Zeolite consists of 3 components namely interchangeable cations, skeletons alumina silicate and water content. The water content changes depending on the nature of the cations exchanged and the crystallization conditions. Water and cations in the zeolite cavity can be substituted with other molecules. As with other silica minerals, zeolite is a porous mineral. If there are several molecules entering the zeolite micropore system, molecules can be absorbed based on the polarity or interaction of molecules with zeolites. The mechanism of molecular interaction that occurs can be either by physical absorption (Van der Waals force), chemical absorption (electrostatic force), hydrogen bonding and formation of a coordination complex. The effectiveness of absorption depends on the nature of the species absorbed, ion exchange ability, acidity of zeolite solids and system moisture. Zeolites with their molecular cavities have active groups in the inter-crystal channel so that they can act as catalyst carriers. Nanoparticles from zeolite and chitosan are expected to be more reactive in their macro conditions, so that the CEC value (cation capacity) is better and nutrient release becomes more slow release, so it can be utilized in the long-term encapsulated nano-zeolite and nano-chitosan fertilizer. Besides that, the use of nanoparticles in fertilizers will make the soil pH non acidic, so the critical land in Indonesia is lower because it does not use or does not made from dangerous chemical synthesis.

MSG (Cipramin) waste fertilizer encapsulated nano-zeolite and nano-chitosan is a mixture of mixing between fertilizer, zeolite and chitosan mixed into one. An innovation was carried out to improve the efficiency of nutrient release by making the MSG (Cipramin) waste fertilizer encapsulated with nano-zeolite and nano-chitosan. One effort to reduce nutrient losses and increase fertilizer efficiency is to modify the fertilizer to become a Slow Release Fertilizer (SRF), which is by mixing fertilizers derived from Citramin materials with materials that have a high cation exchange capacity (CEC) such as nano-zeolite [1]. Zeolite as an ameliorant material which has a high CEC is expected to increase the binding capacity of the soil to nutrients. Zeolite in its use as fertilizer, so as not to be degraded or carried away by ground water, needs to be coated with compounds that are insoluble in water, namely by adding chitosan.

3.2. Characterization

Fourier transform infrared spectroscopy (FT-IR). Characteristics of the infrared spectrum absorption band of chitosan compounds from the research results. The absorption band of the infrared chitosan spectrum from the research results at wave number 3368.52 cm⁻¹, indicating the existence of vibrations bending the OH and NH groups. In the infrared spectrum of Cipramin fertilizer encapsulated nano-zeolite and nano-chitosan also absorbed at wave number 3383.46 cm⁻¹. Stretching vibration at wave number 1653.25 cm⁻¹ is an absorption band of C=O bond group which indicates the presence of secondary amide groups. This absorption band pattern is the same as that shown in the spectrum of Citramin fertilizer encapsulated nano-zeolite and nano-chitosan which is at wave number 1640.84 cm⁻¹. The existence of the bond between C–O on chitosan extracted can be shown by the symmetrical stretching vibration at wave number 1154.64 cm⁻¹ and 1074.93 cm⁻¹ (figure 1) dan the shift in the peak
in the fertilizer spectrum at the position of 662.08 cm\(^{-1}\) and 605.49 cm\(^{-1}\) (figure 2) which can be attributed to the incorporation of nutrients in the zeolite structure hence, supports the nutrient doping [4].

**Scanning electron microscopy (SEM).** The SEM analysis was carried out to gain insight into the morphology of the prepared sample. MSG micrographs encapsulated nano-zeolite and nano chitosan fertilizer (figure 2) according to the sponge properties of the samples provided the increase particle size, open porosity, and enlarge white appearance. This nanoparticle has a geometric dimension of 1 (1D) where there is a size between 1 100 nm which is included in nanometer size.

**Energy Dispersive X-Ray Analysis.** In figure 3, it is known that the MSG waste fertilizer encapsulated with nano zeolite-chitosan contains a micronutrient element such as Si as much as 10.7 %, sodium 11.8 %, nitrogen 11.8 %, 1.2 % iron and potassium 0.3 %.

**X-Ray Diffraction.** X-ray diffraction test results (figure 4) (angle (2\(\theta\))/g581) between 20–30 and 40–50, the calcite crystal phase. Refer to (angle (2\(\theta\))/g581) containing NH\(_2\) compounds, at (angle (2\(\theta\))/g581) containing SiO\(_2\), then at spectra (angles (2\(\theta\))/g581) containing LiAl SiO\(_4\) compounds then at (angles (2\(\theta\))/g581) contains C and at (angle (2\(\theta\))/g581) contains FeO\(_4\) P.

![Figure 1](image1.png) **Figure 1.** Chitosan nano chitosan FTIR spectra (yellow) and MSG (Sipramin) waste fertilizer encapsulated nano zeolite-chitosan (blue).

![Figure 2](image2.png) **Figure 2.** Scanning electron microscopy (SEM) MSG waste fertilizer encapsulated, (a) nano-zeolite 5000x and (b) nano-chitosan 35000x.
3.3. Growth in Cayenne plants

Research has been carried out on chili plants (*Capsicum sp.*) by giving MSG (Cipramin) waste fertilizer encapsulated with nano-zeolite and nano-chitosan (table 1). Data on the growth morphology of chili plants are also complemented by measurements of growth parameters. The growth parameters measured in this study included root length, number of leaves, and stem height which were influenced by treatment, namely giving MSG variants. To prove the measurement data using the Anakova test which begins with testing for normality (normality of data) using the Kolmogorov-Smirnov test and obtained the following data: the results show that MSG does not affect the plant height, leaf number and root length while still seeding, number of plant seeds chili is 24 seeds with 4 treatments namely control, A, B and C and each treatment has 6 plants, so the discussion is carried out descriptively.
The results of the observations on the average treatment after administration of MSG (Cipramin) waste fertilizer encapsulated nano-zeolite and nano-chitosan can be seen in table 2.

Based on the data in table 2, it can be seen that the administration of MSG (Cipramin) fertilizer encapsulated nano-zeolite and nano-chitosan in plant height has different mean. The plant height with control treatment had a mean of 1.25, at treatment X 1.43, at treatment Y 1.45 and at treatment Z 1.43. In the column the number of leaves with the control treatment has a mean of 1.5, on treatment X 1.5, on treatment Y 1.17 and on treatment Z 1.17. In the root length column with the control treatment it has a mean value of 3.67, at treatment X 4.03, at treatment Y 4.11 and at treatment Z 4.27. This shows that there is no similarity in the mean of each treatment, both control, X, Y and Z and on the data taken, namely plant height, number of leaves and root length. The results of the normality of the treatment test after giving MSG fertilizers (Cipramin) encapsulated nano-zeolite and nano-chitosan can be seen in table 3.

Based on the data in table 3, it can be seen that each treatment has a probability value (p-Value) which is different in each object. On the observation object of plant height with control treatment, the probability value is 0.481, treatment X probability value is 0.960, treatment Y probability value is 0.967, treatment Z probability value is 0.981. Then, on the object of observing the number of leaves with the control treatment obtained a probability value of 0.219, in treatment X the probability value is 0.580, in treatment Y the probability value is 0.582, in treatment Z the probability value is 0.733. Whereas, the root length observation object with the control treatment obtained a probability value of 0.995, in treatment X the probability value was 1.000, in treatment Y the probability value was 1.001, and in treatment Z the probability value was 0.899. Data requirements can be said to be normal if the probability value is greater than 0.05 [4]. From the above data it can be concluded that all the results of probability values in all treatments and observation objects have a value greater than 0.05 so that all data is said to be normal. Then, it can be continued to the next test. Observations on the test Homogeneity of treatment after monosodium glutamate (MSG) can be seen in table 4

From table 3 above it is known that the object of research has probability value. From these data, plant height has a probability value of 0.776. On plant height data has a probability value of 0.265.

Table 1. Element in MSG (Cipramin) Waste Fertilizer encapsulated nano-zeolite chitosan.

| Element number | Element symbol | Element name | Weight concentration | Error |
|----------------|---------------|--------------|----------------------|-------|
| 14             | Si            | Silicon      | 5.1                  | 0.8   |
| 6              | C             | Carbon       | 35.8                 | 1.6   |
| 11             | Na            | Sodium       | 7.6                  | 1.1   |
| 8              | O             | Oxygen       | 28.7                 | 1.0   |
| 7              | N             | Nitrogen     | 22.6                 | 1.5   |
| 15             | P             | Phosphorus   | 0.1                  | 3.2   |
| 26             | Fe            | Iron         | 0.1                  | 0.9   |

Table 2. Growth in Cayenne plants.

| Treatment | Plant height | Number of leaves | Root length |
|-----------|--------------|------------------|-------------|
| Control   | 1.25         | 1.5              | 3.67        |
| X         | 1.43         | 1.5              | 4.03        |
| Y         | 1.45         | 1.17             | 4.11        |
| Z         | 1.43         | 1.17             | 4.27        |
Table 3. Summary of the results of the normality test using Kolmogorov-Smirnov.

| Data   | Probability value | Information |
|--------|-------------------|-------------|
| Stem   | 0.776             | Homogen     |
| Leaf   | 0.265             | Homogen     |
| Root   | 0.557             | Homogen     |

Table 4. Summary of data homogeneity test results.

| Data               | Treatment | Probability value | Information |
|--------------------|-----------|-------------------|-------------|
| Plant height       | Control   | 0.481             | Normal      |
|                    | X         | 0.960             | Normal      |
|                    | Y         | 0.967             | Normal      |
|                    | Z         | 0.981             | Normal      |
| Number of leaves   | Control   | 0.219             | Normal      |
|                    | X         | 0.580             | Normal      |
|                    | Y         | 0.582             | Normal      |
|                    | Z         | 0.733             | Normal      |
| Root length        | Control   | 0.995             | Normal      |
|                    | X         | 1.000             | Normal      |
|                    | Y         | 1.001             | Normal      |
|                    | Z         | 0.899             | Normal      |

And the root length data has a probability value of 0.557. A data can be said to be homogeneous if the probability value is greater than 0.05 [4]. In the observation data above it can be concluded that all the data presented in the table has a probability value all of which are above 0.05. Thus all of these data meet homogeneous assumptions.

4. Conclusion
Monosodium glutamate encapsulated nano chitosan-zeolite waste can be used as a fertilizer that can increase the plant growth. Where the best fertilizer modification is in variation 1 with the ratio of MSG waste: zeolite: chitosan = 40%; 10% and 50% which causes the effectiveness of waste fertilizer MSG encapsulated in zeolite-chitosan reached 76.99%.

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