# Vinasse-Based Slow-Release Organo-Mineral Fertilizer with Chitosan-Bentonite Matrix

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# Vinasse-Based Slow-Release Organo-Mineral Fertilizer with Chitosan-Bentonite Matrix

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| Article Info | Abstract |
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| | Controlling the release rate of the nitrogen-phosphorus-potassium (NPK) for the soil fertilized can enhance the fertilizer efficiency and reduce the drawback for the environmental. In this work, a novel slow-release organo-mineral fertilizer was produced from the vinasse, which was blended with the NPK and the chitosan-bentonite matrix. The NPK used as additional nutrients source and the chitosan-bentonite matrix was performed as a barrier to prevent the nitrogen, phosphorus, and potassium from a rapid dissolving. The NPK release rate was measured and analyzed after 3, 6, 9, and 12 days using the incubation method and leaching test. The most efficient release rate was obtained when a 1% vinasse mixed with 9% NPK and 5% chitosan-bentonite matrix with the ratio of 8:2. The vinasse-based slow-release of organo-mineral fertilizer (SR-OMF) was compared to the vinasse organo-mineral fertilizer (OMF). The result indicated that the NPK release rate in the vinasse-based SR-OMF was lower compared to that in the vinasse OMF. |

## INTRODUCTION

In recent years, the utilization of biomass or bioproduct waste becoming important global issues due to its increasing number of wastes (Feo et al., 2019). The advantages of waste utilization are minimizing the waste quantity and producing the value-added product. Vinasse is one of the liquid wastes produced from the bioethanol industry with the amount generated is 9-14 L/L ethanol (Kose et al., 2018). Vinasse is a potential raw material for the fertilizer due to its nutrient content such as nitrogen, phosphorus, and potassium, which can support agriculture crops growth (da Silva Paredes et al., 2014) (Kusumaningtyas et al., 2017). The

utilization of vinasse as a fertilizer is gaining interest in the sugarcane biorefinery (da Silva Paredes et al., 2014). Unfortunately, direct use of vinasse to the soil can cause serious environmental problems because of high content organic matter (COD and BOD), low pH, and other contaminants that will pollute the soil and water (Christofoletti et al., 2013). Moreover, it can cause an inefficient use of nutrients named soil overfertilization (Fuess et al., 2017). The use of vinasse with the controlled nutrient release to the soil becomes critical to enable the effective use of the nutrient. N losses, and P, K overfertilization can occur in the soil fertilization caused by the conventional organic and inorganic fertilizers.

One of the vital nutrients required in agriculture production is nitrogen (N) (Qiu et al., 2018). N fertilizer is commonly used to improve crop production. Therefore, it is produced in a huge amount to fulfill the demand of agricultural production worldwide. The conventional use of N fertilizer becomes inefficient since more than 42-47% of N fertilizer will be leached, denitrified, or volatile (Bouwman et al., 2017; Siva et al., 1999; Zhang et al., 2015; Zhu et al., 2018). Other nutrients called potassium and phosphorus are also key nutrients which play an important role in the plant photosynthesis (Khan et al., 2019). Controlling of P and K release is also important to optimize the use of the nutrient because P and K are not available in abundant sources in nature. Moreover, the accumulation of the nutrients in the soil can pollute the water followed by the economic losses due to inefficient use of the nutrients. Thus, optimization of P and K in agriculture fertilization become one of the most important issues.

Developing the N, P, and K loss strategies have been the main concern nowadays due to its important effect on fertilizer optimization and the environmental impact. The N loss through ammonia volatilization can be successfully reduced by the addition of the biochar with the urea (Zhu et al., 2018). Moreover, N loss through leaching can be declined with the method of combining biochar and water treatment (Zhu et al., 2018). A significant amount of N can be saved to prevent the N loss through leaching and ammonia emission by using urea in the form of a slow-release fertilizer, which can produce a high amount of crop (Tian et al., 2018; Yang et al., 2017). The extended-release mechanism was produced through The Flavonol Polymer Technology, which acts as an encapsulation agent for the phosphorus fertilizer. (Masri et al., 2019). Potassium fertilizer was also successfully coated with the humic substances to optimize the use of fertilizer and minimizing water pollution. (Khan et al., 2019). A controlled-urea fertilizer with improving the efficiency and minimizing the environmental impact was produced through a novel coating material called poly-(eugenol sulfone) (Liu et al., 2020). The N, P, and K release rate in the fertilizer was decreased by less than 50% when coated by superabsorbent polymer (SAP) compared to the uncoated (Ahmed Khan et al., 2020).

One of the important strategies to increase the efficiency of the fertilizer is using Organo-

mineral fertilizer (OMF). OMF can be useful to prevent fertilizer loss because it has a slow-release mechanism. It also can enhance crop production and maintain the soil condition (Buss et al., 2019). The use of OMF can accommodate the nutrients continuously through a control release mechanism. OMF consists of the phosphate nutrient with nutrients release control, which can enhance more crop production compared to the conventional phosphate-based fertilizer (Buss et al., 2019). OMF of nitrogen-based can increase the efficiency of the nutrients uptake, plant photosynthesis, and N presence in the crop's life cycle compared to the conventional nitrogen-based fertilizer (Nguyen et al., 2017). Sewage-sludge was used as an organo-mineral fertilizer, which showed the slow release nutrients behavior of nitrogen and phosphorus (Kominko et al., 2017, 2018). The slow-release of OMF which consists of brown coal mixed with urea can decrease N losses and enhance the crop yield (Saha et al., 2019). The slow-release fertilizer also can be produced from the mix of mono-ammonium phosphate, triple superphosphate, and phosphoric acid with and without magnesium oxide. The results show a promising a control release mechanism of P nutrients (Lustosa Filho et al., 2017). Organo-mineral fertilizer of biochar-ash composite can reduce the pollution of Cr, salinity, and leaching of potassium in the soil (Buss et al., 2019). Biobased matrix of slow-release fertilizer is one of the main factors to produce the desired fertilizer with slow-release behavior. Chitosan is one of the biobased materials which has a high potential to be used as a matrix in the slow-release fertilizer. Multilayer chitosan mixed with alginate, pectin, and sodium tripolyphosphate (TPP) produced a nitrogen release controlling mechanism (Kusumastuti et al., 2019). Chitosan blended with montmorillonite clay (MMt) microparticles were capable to maintain the concentration of the potassium release in the soil (Messa et al., 2019). Bentonite was also equipped as a good substrate for superabsorbent polymers, which was used in agricultural water-managing materials, because of its biodegradability, a high specific surface area, and swelling capacity properties (Wen et al., 2017). On the other hand, the slow-release organo-mineral fertilizer form vinasse with the chitosan-bentonite matrix has not been examined in the open literature.

In this study, slow-release organo-mineral fertilizer from vinasse with the chitosan-bentonite matrix was developed to investigate the

phosphorus-potassium release performance in soil fertilized, which was the continuing study from our previous work in the nitrogen release performance.

## MATERIALS AND METHODS

### Materials

A fresh sugarcane vinasse of 3 kg was collected directly in one period of time from a local bioethanol refinery (PT Madubaru, Yogyakarta). The vinasse was used as a raw material for the slow-release organo-mineral fertilizer without further purification. A granular NPK as a mixture agent of fertilizer was taken from a local chemical store in Semarang, Indonesia, which consists of nitrogen (N) as ammonium nitrate ($NH_4NO_3$), phosphorus as phosphate ($P_2O_5$), and potassium (K) as potash ($K_2O$) with each composition of 15%. Sodium hydroxide (NaOH) with a mass purity of 40% was taken from a local chemical store in Semarang, Indonesia. Chitosan and a natural bentonite as matrix agents with a mass purity of 94.88% and 90%, respectively, were obtained from a local chemical store in Semarang and Indramayu, Indonesia. Chitosan-bentonite matrix was used as a control agent in the nutrients release rate because of its eco-friendly and biodegradable properties. The technical grade of acetic acid ($CH_3COOH$) was prepared in our laboratory. Polysorbate 80 was obtained from the local chemical store in Semarang, Indonesia and used as provided. The surfactant of Polysorbate 80 was used in the matrix preparation to stabilize the particle emulsion and to prevent the agglomeration.

### Methods

#### Preparation of the Slow Release Organo-mineral Fertilizer

The preparation method to obtain the slow release organo-mineral fertilizer was conducted as clearly described in our previous work (Kusumaningtyas et al., 2020). The method consists of the following steps:

**a. Preparation of Vinasse-Based OMF**

NaOH was added into 100 g of vinasse to maintain the neutral pH of vinasse. The water content of up to 80% in the mixture was removed through the evaporation at the temperature range of 80-90 °C for 30 minutes. The NPK nutrients were added to the concentrated vinasse. The mixture was stirred with a constant speed to obtain the completely dissolved-NPK. The mixture of NPK and concentrated vinasse was heated properly at the temperature of 110 °C to remove the water content until the weight of the mixture remain constant.

**b. Preparation of 1% Chitosan**

Chitosan of 1 g was dissolved in the acetic acid of 100 mL (2% w/v) and stirred with a constant speed at a temperature of 25 °C for 30 minutes to obtain the chitosan solution (1% w/v).

**c. Preparation of Chitosan-Bentonite Matrix Composite**

Bentonite of 2, 3, and 5 grams were dissolved in the chitosan solution and stirred for about 5 hours at atmospheric temperature. Two drops of surfactant (Polysorbate 80) were added into the solution with 1 hour stirring process at a constant speed to obtain the chitosan-bentonite matrix with the concentration of 1%, 2%, 3%, and 5%.

**d. Preparation of Vinasse-Based Slow release OMF**

OMF with the NPK content of 9% was mixed with the chitosan-bentonite matrix in a ratio of 8:2 to obtain 100 gram of slow-release OMF followed by the stirring process for 2 hours at atmospheric temperature. Then, the solution was heated at a temperature of 100 °C until the weight of the solution remains constant. The concentrations of N, P, K, and C/N ratio were identified in the SR-OMF, which formed from mixed the vinasse-OMF with a chitosan-bentonite matrix with the ratio 8:2. The vinasse-based SR-OMF was prepared in four formulations, viz. SR-OMF A, SR-OMF B, SR-OMF C, and SR-OMF D, which consistsed of a chitosan-bentonite matrix of 1 %, 2%, 3%, and 5%, respectively.

#### Nutrients Release Testing

The incubation method in the atmospheric condition was used to measure the nutrients release rate. Low-density polyethylene tubes with the dimension of 0.6 cm of diameter and 6.70 cm of height were used as a vessel. Dry soil was filtered using a 2 mm sieve to remove the impurities. The 113.79 g of dry soil mixed with 1 g of SR-OMF was placed in each tube. The nutrients leaching test experiment was performed through the watered method during was analyzed at 3, 6, 9, and 12 days as modified from literature (Purnomo et al., 2018).

The Kjeldahl method was used to analyze the composition of nitrogens in the water. The UV/Vis spectrophotometer was used to identify the carbon and the phosphorus composition, while Inductively Coupled Plasma (ICP) was used to determine the composition of the potassium.

## RESULTS AND DISCUSSION

### Raw Material Analysis

According to the PT Madubaru, the vinasse compositions consists of 29% of mineral, 11% of reducing sugar, 21% of Gum, and 17% of phenol and lignin (PT Madubaru, 2015). It has low pH with a brown colour-liquid phase. The results of this work alsoed show that the vinasse consisted of water content, total nitrogen, total organic carbon, C/N ratio, and phosphorus of 73.10%, 0.55%, 19.95%, 36.27, and 662.05 ppm, respectively.

### N, P, K and C/N Ratio Analysis

The concentrations of N, P, and K in each formulation of vinasse-based SR-OMF were provided in Figures 1-3. The concentration of nitrogen was taken from our previous work (Kusumaningtyas et al., 2020) to compare the behavior of the addition of chitosan-bentonite matrix concentration in N, P, K, and C/N ratio. The figures are clearly described that the addition of chitosan-bentonite matrix concentration will increase the total amount of N, P, and K. The chitosan-bentonite matrix concentration added were 1, 2, 3, and 5 %w/v which produced nitrogen content of 0.5, 1.51, 1.66, 1.91, and 2.10 %w/w, respectively (Kusumaningtyas et al., 2020), phosphorus content of 0.066, 0.090, 0.105, 0,112, 0.118, respectively, and potassium content of 19.95, 22.82, 26.19, 27.18, and 28.13, respectively. The effect of a chitosan-bentonite matrix concentration on the C/N ratio was shown in Figure 4. It shows that the C/N ratio was decreased with the increase of chitosan-bentonite matrix concentration. It is also demonstrated that the chitosan-bentonite matrix concentration of 0, 1, 2, 3, and 5 %w/v yielded the C/N ratio of 36.27, 15.11, 15.78, 14.23, and 13.40, respectively. Based on the N, P, K, and C/N ratio results, it can be inferred that the vinasse-based SR-OMF D with the chitosan-bentonite matrix concentration of 5 %w/v provided the best results compared to other formulation. The vinasse-based SR-OMF D can meet the requirements of Indonesia Standard for fertilizer (SNI 19-7030-

2004) which has the minimum concentrations of N, P, K, and C/N ratio of 0.4%, 0.1%, 0.2%, and 10, respectively (BSN, 2004).
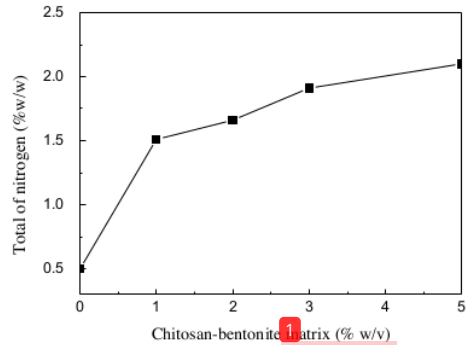


Figure 1. Total of nitrogen in a vinasse-based SR-OMF mixed with the chitosan-bentonite matrix. (Kusumaningtyas et al., 2020).
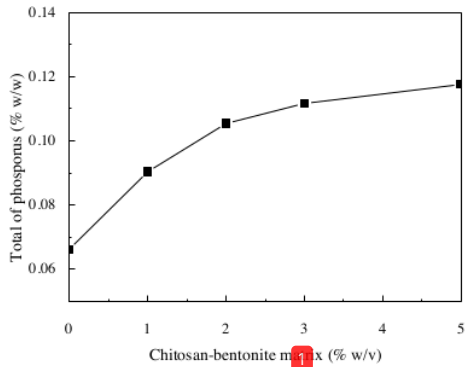


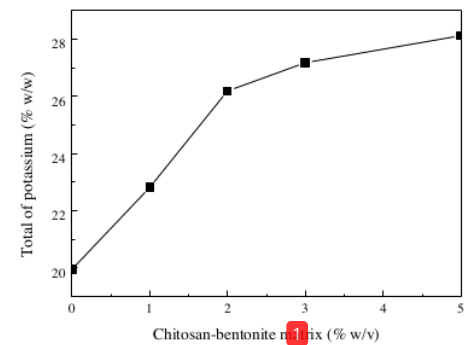Figure 2. Total of phosphorus in a vinasse-based SR-OMF mixed with the chitosan-bentonite matrix.



Figure 3. Total of potassium in a vinasse-based SR-OMF mixed with the chitosan-bentonite matrix.

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**Table 1.** The release rate of the nutrient in a vinasse-based SR-OMF D and vinasse-based OMF.

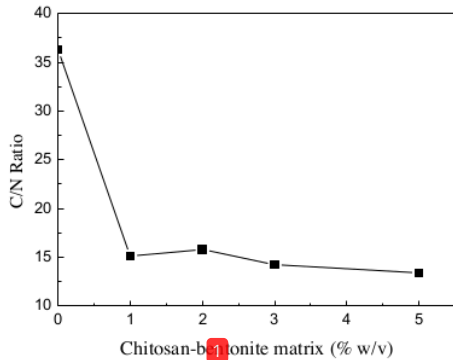| Time/days | Concentration (% w/w) | | | | | |
|---|---|---|---|---|---|---|
| | N* | | P | | K | |
| | SR-OMF D | OMF | SR-OMF D | OMF | SR-OMF D | OMF |
| 3 | 0.008 | 0.011 | 0.001 | 0.002 | 0.025 | 0.032 |
| 6 | 0.005 | 0.01 | 0.001 | 0.001 | 0.014 | 0.017 |
| 9 | 0.001 | 0.008 | 0.0003 | 0.001 | 0.009 | 0.011 |
| 12 | 0.0009 | 0.006 | 0.00007 | 0.0007 | 0.008 | 0.010 |

*taken from (Kusumaningtyas et al., 2020)



Figure 4. C/N ratio in a vinasse-based SR-OMF mixed with the chitosan-bentonite matrix.

**Nitrogen, Phosphorus, and Potassium Release Pattern**

The release rate of the nutrients (nitrogen, phosphorus, and potassium) contained in vinasse-based SR-OMF to the soil was identified using incubation method and leaching test. Nutrients concentration (N, P, K) remaining in the vinasse-based SR-OMF D during the leaching were analyzed and compared with those in the vinasse-based OMF as shown in Table 1. The OMF was a non slow-release fertilizer without a chitosan-bentonite matrix. The results revealed that the SR-OMF D has a less nutrient release for N, P, and K compared to the OMF because the chitosan mixed with bentonite used as a matrix can coat the fertilizer effectively and hard to dissolve in the water. Thus, the nutrient release to the water can be controlled. The nitrogen, phosphorus, and potassium release rate in SR-OMF D compared with OMF shown in Figures 5-7. As described in our previous work that the amount nitrogen dissolved in water for the vinasse-based SR-OMF D was less compared to the vinasse-based OMF [28]. The results for phosphorus and potassium release rate also had a similar pattern, in which vinasse-based SR-OMF D exhibited the lower nutrient release rate compared to the vinasse-based OMF

nutrient release rate. This phenomenon was caused by the ion exchange occurred in the chitosan. Chitosan has a positive charge and hydrophobic character. It will be replaced by $Ca^{2+}$ and $Na^{2+}$ cations from the bentonite, which has a hydrophilic character. Hence, vinasse-based SR-OMF D can hold a better water retention capacity and swelling power compared to vinasse-based OMF. Finally, the vinasse-based SR-OMF D release rate can be controlled effectively. The release rate profile of all nutrient was provided in Figure 8. It clearly shows that all nutrients have similar trend for the decreasing release rate.
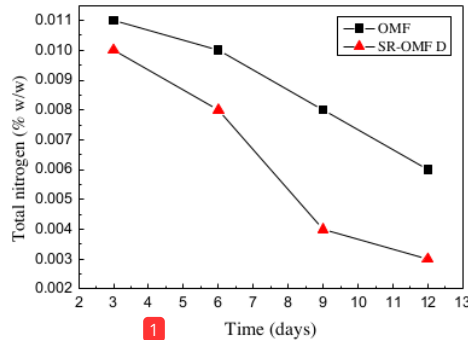


Figure 5. The release rate of nitrogen for a vinasse-based SR-OMF D and vinasse-based OMF (Kusumaningtyas et al., 2020).
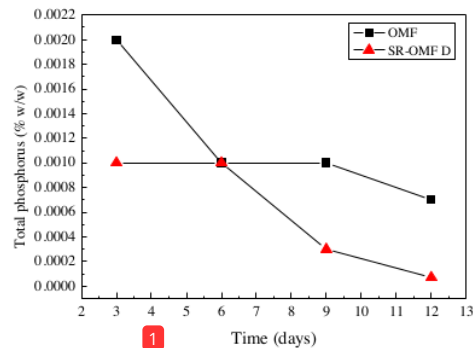


Figure 6. The release rate of phosphorus for a vinasse-based SR-OMF D and vinasse-based OMF.
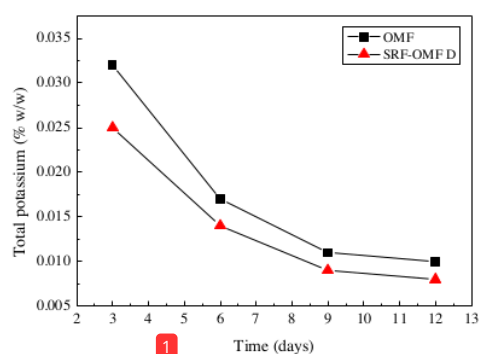
Figure 7. The release rate of potassium for a vinasse-based SR-OMF D and vinasse-based OMF.
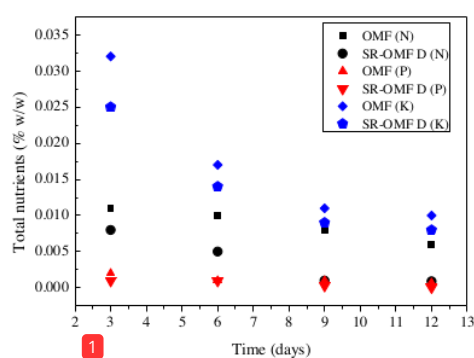


Figure 8. The release rate comparison of three nutrients for a vinasse-based SR-OMF D and vinasse-based OMF (N profile taken from (Kusumaningtyas et al., 2020)).

## CONCLUSION

The novel slow-release organo-mineral fertilizer from vinasse with the chitosan-bentonite matrix was studied in this work. The vinasse based slow-release organo-mineral fertilizer with four formulas were used in this work, namely vinasse-based SR-OMF A, B, C, and D with the chitosan-bentonite matrix of 1%, 2%, 3%, and 5%, respectively. The best performance was showed by vinasse-based SR-OMF D which the nutrients contents can fulfill the Indonesia Standard of fertilizer. This formulation resulted in phosphorus concentration, potassium concentration, and the C/N ratio of 0.118 (% w/w), 28.13 (% w/w), and 13.40, respectively. The characterizations of the nutrients release rate were measured using the incubation method. The nutrients release rate of

SR-OMF D compared to the OMF. The results show that the nutrients release rate of the vinasse-based SR-OMF D was lower than the vinasse-based OMF. It demonstrated that vinasse-based SR-OMF D can control the nutrients release rate effectively. Moreover, the release rate pattern for each nutrient in vinasse-based SR-OMF D had a similar trend to each other. Therefore, the SR-OMF from vinasse can be a potential slow-release organo-mineral fertilizer which can meet the requirement of the optimal agricultural fertilizer.

## ACKNOWLEDGEMENT

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