The Effects of Zeolite-Based Slow-Release Nitrogen Fertilizer and Sulfur on the Dynamics of N, P, K, and S Soil Nutrients, Growth and Yield of Shallot (*Allium cepa L.*)

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Abstract—Shallot or red onion is one of the horticultural commodities that has good economic value as it is needed for almost every cuisine. The aims of the research were to determine 1) the effect of nitrogen slow-release zeolite-based NZEO-SR fertilizer and elemental sulfur on the dynamics of soil main nutrients N, P, K, and S; 2) the effect of slow-release N fertilizer on the growth and yield of shallots; 3) the effect of S fertilizer on the growth and yield of red onion and 4) the interaction of slow-release N fertilizer and S soil nutrient dynamics and the growth and yield of shallots. The research was conducted in a greenhouse using Inceptisols. Soil analysis was carried out in the the Land Resource Laboratory, Faculty of Agriculture, Jenderal Soedirman University, Indonesia. The design of this study was a Randomized Block Design (CRBD) with two factors i.e. slow-release nitrogen fertilizer NZEO-SR and elemental sulfur. The test plant used was shallot Bauji variety. The slow release nitrogen fertilizer were applied at 0, 100, 200, dan 300 kg ha⁻¹, while the rates of S fertilizer were 0, 25, 50 and 75 g ha⁻¹. The variables observed consisted of selected soil chemical properties, available N, P, K, and S, and uptake, growth and yield of shallots. The results showed that the nitrogen slow release fertilizer applications increased soil available N and S, N uptake, the number of tubers, the weight of fresh shallot bulbs but decreased the soil available P. The applications of S increased soil electrical conductivity and available N and S but decreased the soil pH, available soil P, S and N uptake, and number of bulbs. The applications of S at the highest rate (75 kg ha⁻¹) decreased the bulbs fresh and dry weight. The combination of 200 kg ha⁻¹ NZEO-SR and 75 kg ha⁻¹ S gave the best results in available soil N. The applications NZEO-SR and S generated negative interaction on the soil available P.

Keywords—slow release nitrogen fertilizer, zeolite, sulfur, shallot

I. INTRODUCTION

Red onion or shallot (*Allium cepa L.*) is a very popular and somewhat pricey vegetable in Indonesia as it is a spicy needed for almost every cuisine. It is estimated that shallot consumption has increased by 10 % for the last four years [1]. The main essential nutrients that are mostly required by shallots are N (nitrogen) and P (phosphor) for the vegetative growth and S (sulfur) for flavor and taste development.

NZEO-SR is a zeolite-based, slow-release N fertilizer made through impregnation and adsorption of urea fertilizer into zeolite nano-sized pores and negatively charged surfaces [2]. Zeolites are naturally occurring crystalline hydrated aluminosilicate minerals having three dimensional crystal structure with very high cation exchange capacity and surface area [3]. The negatively charged surface of zeolites is counterbalanced by cations of alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium). Due to these characteristics, zeolites have been widely used in many industrial areas such as for cation exchanger [4][5], waste water treatments [6][7] and a reaction catalyst[8]. In the field of agriculture, zeolites have been used to reduce gaseous N losses either in water logged or non water logged soils[9][10][11], as a slow release fertilizer [12][13][14][15]. Zeolites have also been reported to improve phosphorus uptake by plants [16].

Sulphur (S) plays a significant role in the nutrition of onion plants. However, S is rarely included in the plant fertilization resulting in low S availability in some soils. The applications of Sulphur in onion have been reported to increase the bulb production and enhanced the bulb quality particularly pungency and flavors [17][18][19].

This experiment was designed to evaluate the effects of NZEO-SR slow-release fertilizer in combination with S applications on N, P, K and S dynamics and growth and yields of red onion in an Inceptisol.

II. MATERIALS AND METHOD

A. Materials

The slow-released fertilizer NZEO-SR was obtained through the method described by Kharisun et al. (2017). 100-mesh ground natural zeolites were activated hydrothermally at 100°C using 2.5 N NaOH solution for 12 hours. The excess of NaOH was then removed by leaching processes. The activated zeolites were mixed with urea fertilizer, 100-mesh size montmorillonite (as an adhesive) and rice husk ash by adding water amounting to 30 % w/w. The proportions of zeolite, urea-N, montmorillonite, and rice husk ash were 10, 1, 0.5, 0.5, respectively. The mixtures were then granulated to the size of 2.0-2.5 mm.
B. Methods

The experiment was carried out in a greenhouse and laid out in the Completely Randomized Block Design (RCBD) with 2 factor i.e. NZEO-SR fertilizer and Sulphur. Each factor consisted of 4 rates with 3 replications generating 48 experimental units. The details of the treatments are depicted in Table I.

| TABLE I. EXPERIMENTAL FACTORS AND RATES |
|------------------------------------------|
| Factor               | Code  | Rates (kg ha⁻¹) |
| NZEO-SR  | N0 (control)  | 0               |
|                | N1     | 100              |
|                | N2     | 200              |
|                | N3     | 300              |
| Sulphur     | S0 (control)  | 0               |
|                | S1     | 25               |
|                | S2     | 50               |
|                | S3     | 75               |

The soil was air-dried and sieved to the granule size of 2 mm. Each polybag received an amount of oven-dry 10 kg-equivalent of soil. The fertilizers were applied once, just before planting. The variables observed included soil available N, P, K and S, plant uptake of N, P, K and S, the growth and the yield of red onion, and selected soil chemical properties. The laboratory analysis was undertaken in the Soil Science Laboratory of The Faculty of Agriculture, Jenderal Soedirman University, Indonesia.

III. RESULTS AND DISCUSSION

The analysis of variance showed that the applications of slow-release NZEO-SR and elemental Sulfur gave significant effects on most observed variables. Both factors independently affected the soil available N, P, and S, uptake of N and P, and bulb fresh weight (Table I). The applications of Sulphur also gave significant effects on soil pH and electrical conductivity (EC). There were interactive effects between NZEO-SR and S on the soil available N and S.

| TABLE II. ANALYSIS OF VARIANCE OF TREATMENTS |
|----------------------------------------------|
| No   | Variable | Treatment | N | S | N x S |
|------|----------|-----------|---|---|-------|
| 1.   | Avail-N  |           | * | * |       |
| 2.   | Avail-P  |           |   | * |       |
| 3.   | Avail-S  |           | * | * |       |
| 4.   | Avail-K  |           |   |   |       |
| 5.   | N uptake |           | * |   |       |
| 6.   | P uptake |           |   |   |       |
| 7.   | S uptake |           | * |   |       |
| 8.   | Bulb fresh weight | * |   |   |
| 9.   | Bulb dry weight | * |   |   |
| 10.  | Bulb diameter |       |   |   | |
| 11.  | Soil pH  |           |   |   |       |
| 12.  | Soil EC  |           |   |   |       |

Notes: * = significant at P < 0.05. Avail-N = Soil available N; Avail-P = Soil available P; Avail-S = Soil available S; Avail-K = Soil available K.

Table II. also shows that the applications of slow-release fertilizer and S did not give significant effects on the availability of K in the soil. In NZEO-SR fertilizer, the negatively charged zeolite surfaces are saturated with NH₄⁺ ions (Kharisun et al., 2017). These cations are gradually released to the soil solution in exchange of other cations already present in the soil like K⁺. This mechanism explains why K availability in the soil was not affected by the application of the slow N-release fertilizer.

As can be seen from Table 2, soil available N increased with the higher rates of NZEO-SR applications particularly when S applied at the highest rate. This phenomenon could be attributed to two mechanisms. At the higher rates of NZEO-SR applications, more NH₄⁺ adsorbed in the zeolite fertilizer was gradually released to the soil through the cation exchange mechanism resulting in more N being available to the plant. The second mechanism is that the applications of S markedly lowered the soil pH (Table 3). The low pH conditions might have inhibited the gaseous N loss through ammonia volatilization leading to more N available to the plants. A study reported that ammonia emissions could be reduced by 15 percent with the applications of urea and S [20]. The soil acidification process as the results of H₂SO₄ formation resulted in more favorable conditions that could inhibit the conversions of NH₄⁺ to NH₃ gas [9][10].

| TABLE III. SOIL AVAILABLE N AND P AS AFFECTED BY INTERACTIONS BETWEEN SLOW-RELEASE FERTILIZER NZEO-SR AND SULFUR |
|---------------------------------------------------------------|
| Variable | NZEO-SR | S0 | S1 | S2 | S3 |
|----------|---------|----|----|----|----|
| Avail-N  | N0      | 34.03A | 29.78B | 66.44A | 68.36A |
|          | N1      | 27.54B | 29.89C | 83.14B | 108.43A |
|          | N2      | 45.75B | 51.72B | 59.02B | 116.72A |
|          | N3      | 25.79B | 46.76B | 45.74B | 101.25A |
| Avail-P  | N0      | 11.22A | 5.20B  | 4.76B  | 6.33B  |
|          | N1      | 6.84A  | 0.38B  | 1.92B  | 4.80A  |
|          | N2      | 7.76A  | 6.92AB | 3.58C  | 4.30BC |
|          | N3      | 3.98B  | 1.98B  | 1.17B  | 7.62A  |

Notes: Numbers followed by same small letters in the same column and variable and numbers followed by capital letter in the same row do not significantly different according to DMRT at P < 0.05. Avail-N = Soil available N; Avail-P = Soil available P.

Table III. shows that in the control plot, where there was no S applied, the applications of NZEO-SR decreased the plant-available P in the soil. The highest reduction in the available P was observed in the application of NZEO-SR at the highest rate (300 kg. ha⁻¹). The applications of NZEO-SR increased the availability of soil N, thus more N could be taken up by the plants and made the red onion plants grow well. This condition would result in more P nutrient being taken up by the plants which in turn lead to the reductions of the plan-available P in the soil. The similar results were also observed with the applications of S in the plots received no N fertilizer (Table 2). The reductions of the available P were mainly due to the decline in the soil pH as a result of the addition of elemental S. In low pH conditions, Al becomes more active and can be toxic to the plants. This Al form is also able to react with plant-available forms of P like H₃PO₄ to produce a non-soluble substance which is not available to the plants [21].
As depicted in Table 3, the applications of elemental S markedly decreased the soil pH from a pH of 5.8 in the control to 3.64 in the application of S at 300 kg ha⁻¹. The soil pH was negatively correlated with the rates of elemental S following a linear relationship (Figure 1). The great reductions were mainly due to the more elemental S that could undergo oxidation reactions mediated by soil microorganisms to form $\text{SO}_4^{2-}$ ions [22]. There are various organisms capable of mediating the oxidation reactions. But most studies have been focused on sulfur-oxidizing bacteria in the family of *Thiobacillaceae* especially in the terrestrial environments [21][23].

The consistent results were observed with the applications of S on the nitrogen uptake by the plants. Table 3 demonstrated that the applications of S at the rate of 75 kg ha⁻¹ reduced the N uptake by more than 50%. This might be attributable to the aluminum toxicity and lower microbial activity responsible for the transformation of N in the soil.

![Graph showing the relationship between soil pH and S rates](image)

**Fig. 1. Relationships between soil pH and rates of Sulfur applications**

The application of slow-release N fertilizer NZEO-SR was not able to increase the N uptake by the red shallots (Table 3). It was expected that more N that was gradually released from the fertilizer to the soil could be taken up by the plants [24][25]. This inconsistency might have been attributed the fact that the rates of NZEO-SR were too low. The highest rate of NZEO-SR is 300 kg ha⁻¹ which is equivalent to only 30 kg urea ha⁻¹ or 13.5 kg N ha⁻¹.

As indicated by Table 3, there seems to be a contradiction between the S availability and the S uptake with the applications of elemental S. The applications of S consistently increased the plant-available S in the soil with the higher S applied. However, this increased availability of S did not improve the plant uptake of S. This might be attributed to the lower pH conditions which were not favorable for the S uptake. When the soil pH declines to 5 or less, aluminum (Al) is more soluble and may become toxic. In low pH Al³⁺ is released to the soil. This ionic form is readily taken up by the roots and causes Al toxicity as it inhibits cell elongation and blocks the mechanisms of cell division resulting in stunted roots and poor root hair development [26]. The root growth retardation also leads to other ions and water absorption by the plants [27].

The increase in $\text{SO}_4^{2-}$ as a result of the elemental S applications was also indicated by the increase in the soil electrical conductivity (EC) (Figure 2). Electrical conductivity basically measures the concentrations of ions either cations or anions in a solution.

![Graph showing the relationship between EC and S rates](image)

**Fig. 2. Soil Electrical Conductivity (EC) at different rates of S applications**

As depicted in Figure 2, the EC values were linearly correlated with the rates of S applications. This is because the applied S will undergo oxidation to form sulfate ions mediated by various sulfur-oxidizing microbes living in the soils. The application of S as low as 25 kg ha⁻¹ increased the EC value by 336% while the application of S at the highest rate (75 kg ha⁻¹) increased very sharpily the EC values from 320 to 2817 µS/cm. This EC value is considered to be above the critical value of most plants. An experiment conducted...
by [28] showed that during the germination stage, onion plants were tolerant to the EC values up to 9.5 mS/cm. However, the onion plants were very sensitive to the EC when the seedlings were already transplanted. The plants were adversely affected by the EC values as low as 1.2 mS/m. The onion plant sensitivity to high EC values explains why the S uptake by red onion plants in the present experiment was reduced at the highest rate of S application (Table 3). As can be seen from Table 4, the S applications up to the rate of 50 kg/ha increased the bulb fresh weight and dry weight and thereafter the bulb weight decreased as the rate was increased to 75 kg/ha.

TABLE V. RED ONION GROWTH AND YIELD PARAMETERS AS EFFECTED BY THE APPLICATIONS OF NZEO-SR FERTILIZER AND S.

| Factor         | NB   | BFW (g/clump) | BDW (g/clump) | ABD (cm) |
|----------------|------|---------------|---------------|----------|
| NZEO-SR        |      |               |               |          |
| N0             | 8.25 ab | 27.35 ab     | 23.42 a       | 13.84 a  |
| N1             | 8.66 ab | 23.39 b       | 21.68 a       | 14.90 a  |
| N2             | 7.83 b  | 27.85 a       | 24.66 a       | 16.45 a  |
| N3             | 9.33 a  | 24.24 ab      | 21.12 a       | 17.15 a  |
| Sulfur         |      |               |               |          |
| S0             | 9.41 a  | 28.80 a       | 25.29 a       | 16.57 a  |
| S1             | 7.58 c  | 22.55 b       | 19.40 b       | 15.66 a  |
| S2             | 9.0 ab  | 28.36 a       | 25.92 a       | 15.81 a  |
| S3             | 8.08 bc | 23.12 b       | 20.27 b       | 14.29 a  |

Notes: Numbers followed by same small letters in the same column and factor are not significantly different according to DMRT at P < 0.05. NB=Number of Bulbs; BFW=Bulb Fresh Weight; BDW=Bulb Dry Weight; ABD=Average Bulb Diameter.

IV. CONCLUSION

Based on the results of the experiment, some conclusions can be drawn:

1. The applications of slow-release fertilizer NZEO-SR and elemental Si affected the availability of N, P and S, growth and yield of red onions, did not affect availability of soil K.

2. The results showed that the nitrogen slow release fertilizer applications increased soil available N and S, N uptake, the number of tubers, the weight of fresh shallot bulbs but decreased the soil available P.

3. The applications of S increased soil electrical conductivity and available N and S but decreased the soil pH, available soil P, S and N uptake, and number of bulbs.

4. The combination of 200 kg/ha NZEO-SR and 75 kg/ha S gave the best results in available soil N.

5. The applications NZEO-SR and S generated negative interaction on the soil available P.

REFERENCES

[1] The Ministry of Agriculture. 2018. Performance Report of Year. 2017. The Directorate General of Horticulture, The Agriculture Ministry, Jakarta.

[2] Khartoum, M. Rif an, M.N. Budiono, and R. Kuniiwan. 2017. Development and Testing of Zeolite-Based Slow Release Fertilizer NZEO-SR in Water and Soil Media. SAINS TANAH – Journal of Soil Science and Agroclimatology, 14 (2): 72-82.

[3] Ming, D.W. and F.A. Mumpton. 1993. Natural Zeolites: Occurrence, Properties, Applications. International Committee of Natural Zeolite. Brockton, NY.

[4] Pansini, M. 1996. Natural zeolites as cation exchangers for environmental protection. Mineralium Deposita. 31(6):563-575

[5] Chandra, W.P., B. Lenora, W. Budhijanto, and H. Hinode. 2017. Sorption and Ion Exchange Behaviour of Natural Zeolite Packing. Makara J. Technol. (21):33-36.

[6] Wang, S. and Y., Peng. 2009.. Natural zeolites as effective adsorbents in water and water treatment. Chemical Engineering Journal. 156(1): 11–24

[7] Gadepalle, V.P., S.K. Ouki, R. van Herwijnen, dan T. Hutchings. 2007. Immobilization of heavy metals in soil using natural and waste materials for vegetation establishment on contaminated soils. Soil & Sediment Contamination, Vol. 16: 233-251

[8] Marakatti, V.S., A.B. Halgeri, and G.V. Shambag. 2014. Metal ion-exchanged zeolites as solid acid catalysts for the green synthesis of nopol from Prins reaction”. Catal. Sci. Technol. 4 (11): 4065–4074

[9] Ahmed, O.H., C.H.B. Yap dan A.M.N. Muhamad. 2010. Minimizing ammonia loss from urea through mixing with zeolite and acid sulphate soil. International Journal of the Physical Sciences, Vol. 5(14): 2198-2202.

[10] Palanivel, P., O.H. Ahmed, K. Susilawati1 and N.M.A.Majid. 2015. Mitigating Ammonia Loss in Waterlogged Condition using Zeolite. Int. J. Agric. Biol. 17(1) : 149-155.

[11] Latifah, O., O.H. Ahmed and A.M.N. Muhamad, 2011. Reducing ammonia loss from urea and improving soil exchangeable ammonium and available nitrate in non-water logged soils through mixing zeolite and sago (Metroxyylon sago) waste tree. Int. J. Phy. Sci. (6): 866–870

[12] Bansiwal, A.K., S. Rayalu, N.K. Labhasetwar, A.A. Jawarkaa, and S. Devotta. 2006. Surfactant-modified zeolite as a slow release fertilizer for phosphorus. J. Agric. Food Chem. (54)13: 4773–4779.

[13] Ji, X.H., S.X. Zheng, Y.H. Lu, dan Y.L. Liao. 2007. Study of dynamics food water nitrogen and regulation of its run off loss in paddy field based two cropping rice with urea and controlled release nitrogen fertilizer application. Agricultural Science in China 6(2):189-199

[14] Li, Z., Y. Zhang, and Y. Li. 2013. Zeolite as slow release fertilizer on spinach yields and quality in a greenhouse test. Journal of Plant Nutrition. 36:1496–1505

[15] Rabai, K.A., O.H. Ahmed, dan S. Kasim. 2013. Use of formulated N, phosphorus, and potassium compound fertilizer using clinoptilolite zeolite in maize (Zea mays L.) cultivation. Emirates Journal of Food and Agriculture, Vol. 25(9): 713-722.

[16] Moharani S. dan M. Jalali. 2015. Use of modified clays for removal of phosphorus from aqueous solutions. Environmental Monitoring and Assessment, Vol. 187(10): 1-11.

[17] Nasreen, S., Imamul-Haq, S. M. and Hossain, M. A. 2003. Sulphur effects on growth and yield of onion. Asian J. Plant Sciences. 2: 897-902

[18] Rains, S. K., Jaggi, R. C., Chohan-Ahba and Dar, M. A. 2012. Direct, residual and direct + residual effects of sulphur in onion-maize cropping sequence. Communications in Soil Science and Plant Analysis 43: 1861-1866.

[19] Rains, S. K., R. C. Jaggi, Chohan-Ahba, D. Ram, C. Subhash, MA. Malik, J.A. Wani, and M. Dar. 2017. Effects of sulphur on onion (Allium cepa L.) in presence and absence of farmyard manure in onion - maize (Zea mays) sequence. The Bioscan. 12(3): 1763-1767, 2017

[20] Soaad, A.A., M.E. Saleh, K.A. El-Tarabily, M. Sofian-Azirun, dan M.M. Rahman. 2011. Effect of elemental sulfur application on ammonia volatilization from surface applied urea fertilizer to calcareous sandy soils. Australian Journal of Crop Sciences, Vol. 5(5): 611-619.

[21] Tisdale, S.L., W.L. Nelson, and J.D. Beaton. 1985. Soil Fertility And Fertilizers (3rd Edition). Collier Macmillan International, New York.

[22] Van Straten, P. 2007. Agrogeology ; The Use of Rocks for Crops. Van Straten, P. 2007. Agrogeology ; The Use of Rocks for Crops. Department of Land Resource Science. University of Guelph. Canada.

[23] Yang, Zhi, K. Stoven, S. Haneklaus, B.R.Singh, E.Schmug, 2010. Elemental Sulfur Oxidation by Thiobacillus spp. and Aerobic Heterotrophic Sulfur-Oxidizing Bacteria. Pedosphere 20 (1): 71 – 79.
[24] Rahman, M.M., A.A. Soaud, F.H. Al Darwish, dan M. Sofian-Azirun. 2011. Responses of sulfur, nitrogen and irrigation water on Zea mays growth and nutrients uptake. Australian Journal of Crop Science, Vol. 5(3): 350-360.

[25] Salvagiotti, F., J.M. Castellarin, D.J. Miralles, H.M. Pedrol. 2009. Sulfur fertilization improves nitrogen use efficiency in wheat by increasing nitrogen uptake. Field Crops Research, 113(2): 170-177.

[26] Sivaguru, M. and W.J. Horst. 1998. The distal part of the transition zone is the most aluminum-sensitive apical root zone of maize. Plant Physiol. 116:155–163

[27] Panda, S.K. F. Baluska, 2 and H. Matsumoto. 2009. Aluminum stress signaling in plants. Plant Signal Behav. 20: 592–597

[28] Sta-Baba, R. M. Hachicha, M. Mansou, H. Nahdi, and M.B. Kheder. 2010. Response of Onion to Salinity. The African Journal of Plant Science and Biotechnology. 4(2):7 – 12.