Nano Silica application for inducing rice resistance and the possibility for Ytterbium Rare Earth Elements green mining

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Abstract. There is a growing interest and recognition of Silicon (Si) in plants to increase growth, productivity, and plant resistance. This research examines the role of Nano Silica to increase yield and resistance. This study set out to assess the effect of hydrophilic fumed Nano Silica application with the frequency of 1×, 2×, 3×, and 4× applications respectively with three replications using RCBD as well as SEM-EDX and XRF analysis. Nano Silica frequencies showed a distinctive decrease of damage intensity at the 3× and 4× applications. The rice husk increases of metal-like surface appearance as more Nano Silica frequency was applied. It is proposed that Nano Si induced plant resistance through the modification of surface layer and stronger plant tolerance against environmental stress. The most unexpected observation to emerge was the Ytterbium (Yb) concentration known as a Rare Earth Elements at the 3× and 4× Nano Si applications. This indicates that Nano Silica application provides insights and opportunities to Nano Si application on Rice for the purpose of acquiring Ytterbium from farmland. Nano Silica can play an important role as a new method in addressing the Ytterbium green mining.

1. Introduction
Silicon (Si) has been recognized in recent decades for its positive impacts on plants and has a variety of functions in plant physiology with the main role concentrated on the cell wall activity due its acts as a physical barrier. Silicon on the plant's cell wall could increases photosynthetic activity as well as strength, resistance, and tolerance to biotic and abiotic stresses [1,2]. Silicon in a form of exogenous silicon nanoparticles could increase growth, yield, induce pest/pathogen resistance, and higher availability of plant nutrients [3,4].

The use of nano-agricultural products becoming increasingly feasible with experimental results which show great potential to reduce the impact of traditional agrochemicals on the environment, while significantly increasing crop yields and crop quality [5]. Nano Silica is an amorphous synthesized silica powder with diameters between 10–100 nm. Foliar Nano Silica sprays tend to decrease biotic stress and stimulate increase in growth and yield [6]. The application of Nano Silica was also proven to affect the increase of plant height and number of rice tillers [7], number of leaves, leaf area index, leaf area duration, total dry matter, crop growth rate, grain yield and straw yield [8]. This research aims to experimentally investigate the Nano Silica capability to increase rice yield and decrease abiotic stress especially pest intensity. The result may be able to support evidence of the Nano Silica capability to enhance plant growth and yield as well as supporting the sustainable agriculture.
2. Materials and methods

The experiment conducted from May to August 2019 at Probolinggo, located on 7°47'17.2"S 113°30'41.1"E with altitude of 86 meter above sea level. The rice used in this experiment was Cibera variety as the favorite variety among local farmers. The rice was planted using 25 days germinated rice seed. An AEROSIL® 200 hydrophilic fumed Nano Silica with specific surface area of 200 m².g⁻¹, containing 99.8% laboratory grade SiO₂, were applied with the concentration of 25 ppm. The fertilizers used in the agricultural practices were: 120 kg of Urea, 50 kg of SP36 and 50 kg of KCl.

The plant growth observation includes the pest intensity percentage (absolute) and yield as dry weight (g.plant⁻¹). The pest intensity observation performed from 60 DAP at the intervals of 7 days, which were conducted after each Nano Silica application (1st observation: 60 DAP), 2nd observation: 67 DAP, 3rd observation: 74 DAP, and 4th observation: 81 DAP. Pest intensity percentage rate to measure damages that occurs permanently to rice plant, was calculated as stated in equation (1):

\[ \text{Pest Intensity} = \frac{(n-N)}{N} \]  \hspace{1cm} (1)

n = number of samples of plants that caused absolute damaged; and
N = number of plant samples observed.

The Nano Silica application treatments were the frequency of one time, two times, three times, and four times of Nano Silica respectively. Statistical analysis of variance using Randomized Complete Block Design were applied to the obtained data and continued by Least Square Design of 5%.

As further analysis, a Scanning Electron Microscope Energy-Dispersive X-ray spectroscopy analysis were conducted to analyze the rice grain surface morphologically. The SEM Phenom device was used to examine physical structures and the morphology of sample material with magnification of up to 1,000 times. The X-Ray Fluorescence spectrometer analysis using PANalytical MiniPal 4 Energy-dispersive X-ray fluorescence was also being carried out to analyze the concentration of each nutrient available in the rice grain.

3. Results and discussion

To support the result findings, the supporting data of local research condition of soil analysis and environment such as precipitation/ rainfall, solar energy and temperature also served. The soil analysis served in Table 1 show that the soil was dominated by Clay (50%) and high level of Cation Exchange Capacity (with CEC of 38.53 Cmol kg⁻¹), the clay texture was more dominant compared to the 12% of Sand and 38% of Silt particle content respectively. The pH was in the neutral range of 5.6 – 6.6 with a tendency to acid. Most essential nutrients availability (nitrogen, phosphorus, potassium, sodium, calcium, magnesium, and organic carbon) as well as C/N ratio were showing very low in quantity.

| Table 1. The soil analysis result |
|----------------------------------|
| pH 1:1  | C Org | N total | C/N | P Olsen | K | Na | Ca | Mg | CEC | Sand | Silt | Clay |
|-------|-------|--------|-----|--------|----|----|----|----|-----|------|------|------|
| H₂O KCl \text{1N}   | \text{ mg kg}⁻¹ | \text{ NH₄OAC1N pH} 7 | \text{ \% \%} | 6.6 | 5.6 | 0.97 | 0.11 | 8 | 10.69 | 0.20 | 0.30 | 15.03 | 1.74 | 38.53 | 12 | 38 | 50 |

The data served on Figure 1 showing the Precipitation (%) and Rainfall (mm), while Figure 2 for Solar Energy (kWh) and Average Temperature (°C), where the precipitation probability and average rainfall throughout the field experiment tend to be in alignment of showing decrease supply as the rice grow. The solar energy otherwise showing slight increase overtime, while the temperature tends to be colder. The overall soil and environment condition supports good rice cultivation stage during the experiment.
3.1. Analysis of variance on rice plant
The ANOVA result for the pest intensity at different nano silica application on rice plant (Figure 3) showed that especially on 74 DAP, the N₃ and N₄ (3 and 4 times nano silica applications) could significantly decrease rice plants damages intensity (12.77 and 14.9 % respectively) compared to N₁ and N₂ (17.43 and 17.9 % respectively). While the results on the first, second and fourth pest intensity observation were not statistically significant (at 60, 67, and 81 DAP respectively).

According to the Directorate of Food Crop, the score scale for the damaged plants of all crops in the experiments shows in the range of moderate damages if the pest intensity value 25–50% at the end of observation. In this experiment, most damages were caused by Rice blast as the main threat to rice plant
production loss. Indonesia mainly counting on rice production as main staple food to cover for most of its citizens, and currently still in the struggle to achieve national food security. In most low-income countries, blast represents is a clear threat to food security [9]. The calculated yield loss potential from rice blast is up to 3.65 ton ha$^{-1}$, which is equivalent to 61% the Ciherang rice variety average yield [10].

Blast entry to plant by forming a melanin-pigmented dome-shaped appressorium [9]. According to the field experiment result, it is proposed that with the application of Nano silica could decrease the blast entry to plant surface. Nano silica can be turned smart by crafting a surface coating [11], as nano silica particles could accumulates on the surface of the rice cells [12] and could be used to control pest [13].

The rice plant dry weight of the $N_1$ (1× Nano Si application), $N_2$ (2× Nano Si applications), $N_3$ (3× Nano Si applications), and $N_4$ (4× Nano Si applications) were 41.72, 57.52, 58.23, and 39.17 gram respectively, with the highest result acquired by $N_3$ and followed by $N_2$, as shown in Figure 4.

3.2. Scanning Electron Microscope Energy-Dispersive X-ray spectroscopy analysis

The Scanning Electron Microscope Energy-Dispersive X-ray spectroscopy analysis result show that the more nano Si applied, the surface of rice husk becoming more resemble to the metallic appearance to silicone, which was tend to be shinier outlook, especially in the three times ($N_3$), and four times ($N_4$) applications respectively. The explanation of this phenomena is possibly caused by most Silicone compounds were made from silicon metal [14] and nano Si as highly hydrophilic compound has potential for surface appearance modification [15]. Silica nanoparticles hold a special position among the various types of functional nanoparticles, due to their unique structural and functional properties. Si has the ability to control the morphology, particle size, uniformity, and dispersity; furthermore, Si have been shown to be safe for biological application [16].

![Figure 5](image_url)

**Figure 5.** The Scanning Electron Microscope Energy-Dispersive X-ray spectroscopy analysis of rice grain outer layer with the frequency of one time ($N_1$), two times ($N_2$), three times ($N_3$), and four times ($N_4$) respectively with 1000x magnifications.

The result image on the frequency treatment of one time ($N_1$) and two times ($N_2$) nano Si also showed more traces of dirt-like substance or pathogen attaching/ covering on the rice husk surface than the three times ($N_3$) and four times ($N_4$) nano Si applications (Figure 5). This showed that nano Si also can play
effective roles to act as pesticides in plants [17]. Si with its physicomechanical barrier capacity could be deposited on the walls of epidermis and plants' vascular tissues [18].

3.3. The X-Ray Fluorescence spectrometer analysis

The X-Ray Fluorescence spectrometer analysis showing the availability of some nutrient such as: silicone, phosphorus, potassium, calcium, manganese, iron, nickel, copper, zinc, europium, and rhenium, where in all treatment with relatively narrow differences in quantity (Figure 6). The highest element concentration in Ciherang rice grain was silicon, with content was ranging from 71.40 to 77.90 %; the phosphorus content was ranging from 2.40 to 3.70 %; the potassium content was ranging from 11.10 to 19.90 %; the calcium content was ranging from 3.79 to 5.60 %; the manganese content was ranging from 0.15 to 0.62 %; the iron content was ranging from 0.22 to 0.56 %; the nickel content was ranging from 0.10 to 0.43 %; the copper content was ranging from 0.08 to 0.31 %; the zinc content was ranging from 0.06 to 0.25 %; the europium content was ranging from 0.40 to 0.50 %; and the rhenium content was ranging from 0.30 to 0.40 %. The Si foliar sprays was proven to reduce infections of rice blast incidence, but did not increase Si absorption or its accumulation by the plant [19].

With the result of the Ytterbium (Yb) the element content was ranging from to 0.00 to 0.43 %, but the availability of 0.3% and 0.43% of Yb only exist on the N3 and N4 treatment, showed a very interesting fact and becomes an unexpected finding. The rice grain peak concentration spectrum of nutrient element content, showing the Yb spectra at 20kV only available in N3 and N4 treatment which ranged from 7.2 to 9.6 keV with higher accumulation at 8.4 keV (Figure 7). Yb is one of Rare Earth Element that widely used in high technologies such as computer, telecommunication, nuclear, outer space sophisticated instruments [20], wind turbines, batteries, catalysts, electric cars [21], medical devices, military defense systems, and are especially indispensable in emerging clean energy [22].

The experiment findings was in alignment with the statement that there were relations between Si and Yb can contribute beneficially to support plant growth and yield [23]. The research of Yb direct effect for plant are still limited, but other rare earth elements of lanthanum (La) and cerium (Ce) were already been used to enhance plant growth, the mixture had been used on a large-scale in China as foliar sprays or seed treatment of agricultural and horticultural crop species [24]. In the material science, the usage of both Si and Yb latest example are the environmental barrier coating system of a pore-free ytterbium monosilicate (Yb5Si3O7) and ytterbium disilicate (Yb2Si2O7) to protect SiC structures from high temperatures in vapor-rich exposure [25].

![Figure 6](image)

**Figure 6.** Components Concentration in Rice Grain (%) with nano silica treatments with the frequency of: one time (N1), two times (N2), three times (N3), and four times (N4) respectively.
Figure 7. The X-Ray Fluorescence spectrometer showing the concentration spectrum of each nutrient component inside the rice grain with nano silica treatments with the frequency of one time (N₁), two times (N₂), three times (N₃), and four times (N₄) respectively.

4. Conclusion
Silicon increased the yield and decreased pest intensity with optimal performance at three times of foliar nano silicon applications, due to the ability to stronger mechanical defense and surface morphological appearance. On the SEM analysis of 3× and 4× nano Si applications, showing the rice husk surface of becoming more metallic-like, and the unpredicted existence of Ytterbium. It is proposed to be a relation between Si application and Yb content in plant, which also play favorable role for rice plant growth and productivity. It is recommended to conduct further research on nano Si application for Yb green mining (Phyto-mining), by using rice or other Si accumulator plants to acquire rare earth element from soil, to support clean energy and sustainable environment.

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