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The effect of humic substances and potassium-solubilizing bacteria on the release of nutrients from pyroclastic materials of Mount Merapi, Indonesia

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Abstract

Indonesia, which is in the Ring of Fire, has many active volcanoes, including Mount Merapi, whose eruptions produce pyroclastic material rich in essential minerals. Pyroclastic material comes out when a volcano erupts and contains various minerals containing nutrients which are easily weathered minerals. Although this material has the potential to be a source of nutrients for plants and is included in the category of easily weathered minerals, the process of leaching nutrients from minerals takes a long time to make them available to plants. This study aims to determine the effect of humic substances and potassium-solubilizing bacteria on releasing nutrients from pyroclastic materials from Mount Merapi using humic substances and potassium-solubilizing bacteria. The study was conducted by taking pyroclastic samples from Mount Merapi and carrying out a percolation process with variations in grain size (passing 2 mm and 0.05 mm sieves), pyroclastic doses (0, 9.375, 18.75, 37.5, 75, and 150 g/washing tubes), and the addition of humic substances and potassium-solubilizing bacteria. The results showed that the finer the size of the pyroclastic grains, the faster the release of nutrients, especially calcium (Ca), potassium (K), and sodium (Na). The combination of humic substances and potassium-solubilizing bacteria increases the release of nutrients from pyroclastic materials, making them more available to plants. The best dose is to provide 75 g of pyroclastic material, both fine and coarse-sized pyroclastic. This study offers an alternative in soil management by increasing the effectiveness of nutrient leaching from volcanic materials.

1. Introduction

Indonesia is located within the Ring of Fire (Ring of Fire) Pacific, where this zone is the center of energy sources for earthquakes and where most of the world's volcanoes grow. Merapi is one of 129 active volcanoes in Indonesia and is included in the row of volcanoes in Java with the main threat of danger being the flow of hot clouds (pyroclastic flow). Mount Merapi is an active volcano in Indonesia and is one of the most active and youngest volcanoes in Java with the main threat being the flow of hot clouds (pyroclastic flow). The volcano is located on the southern slopes under the administration of Sleman Regency, Special Region of Yogyakarta, and the rest is in the Central Java Province, namely Magelang Regency on the west side, Boyolali Regency on the north and east sides, and Klaten Regency on the southeast side. Mount Merapi has a strato volcano type with andesite-basaltic magma content. This mountain has a height of 2,978 m, a diameter of 28 km, an area of 300–400 km^2 and a volume of 150 km^3. Merapi eruptions often occur with an average cycle of between 2–5 years (Pusat Vulkanologi dan Mitigasi Bencana Geologi, 2006). This mountain is known for its type of activity that emits semi-continuous thick lava eruptions that form dome peaks, interrupted by periodic dome collapses caused by very powerful hot clouds. Mount Merapi has erupted more than 80 times since the 10th-century (Ratdomopurbo and Poupinet, 2000).

The chemical weathering process of rocks and minerals has an important role in agriculture, especially as a source of macro and micronutrients in the soil. Factors such as climate and continuous land management/utilization can cause a decrease in nutrient levels in the soil, even deficiencies due to the leaching process. Soil formed from the weathering of rocks and nutrient-rich minerals can turn into nutrient-poor and acidic soil. Adding organic matter is one way to reduce the level of nutrient leaching in the soil. In addition, soil nutrient deficiencies can be overcome by adding chemical fertilizers. However, the demand for fertilizer continues to increase along with the soaring price of fertilizer on the market. Not only is the price high but there is also a shortage of fertilizer supplies. To overcome this problem, it is necessary to develop new fertilizer materials and increase the effectiveness of existing fertilizer materials. One alternative fertilizer material that requires increased effectiveness is fertilizer from rock flour. Although rock flour contains high concentrations of macro and micronutrients, nutrient leaching from rocks is slow, making it unsuitable for short-term crops. Therefore, innovation to increase nutrient leaching from igneous rocks is very necessary.

The main obstacle in leaching nutrients from minerals in rocks is the weathering process which takes a relatively long time. Brady (1990) stated that many factors affect the rate of mineral weathering, including climate, vegetation, and the physical-chemical properties of minerals. Particle size, hardness, and degree of cementation are three physical properties that can affect weathering. Minerals with fine particle sizes are more resistant to physical weathering but are more susceptible to chemical weathering than large-sized minerals. Hardness and degree of cementation affect chemical weathering. In addition, the chemical properties and structure of minerals also affect the weathering process. According to (Wilson, 2004; Uroz et al. 2009), in general, mineral weathering is influenced by composition, expansion coefficient, presence of cleavage or fracture, crystal structure, and hardness and specific surface area of the mineral. Environmental factors such as pH, oxidation/reduction conditions, hydration, hydrolysis, carbonation, and other factors also greatly influence the weathering process.

According to Fiantis et al. (2009), the main mineral composition of pyroclastic deposits produced by Mount Merapi consists of crystalline and non-crystalline minerals. Non-crystalline minerals are mainly volcanic glass (53–60%), while crystalline minerals include plagioclase (labradorite, andesine, bytownite, and anorthite) and lithic fragments. In addition, there are two types of pyroxene minerals (hypersthene and augite), amphibole, opaque minerals, and a little apatite. The labradorite content is greater than anorthite, bytownite, and andesine, which indicates that the calcium (Ca) and sodium (Na) content is higher than potassium (K).

The weathering of volcanic ash begins with the washing away of relatively soluble compounds by rainwater such as H^+, SiO^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+. Sesquioxide compounds accumulate, while Al and silicic acid form secondary minerals (Samuels et al. 2020). Based on Fiantis et al. (2010), water-soluble organic materials and inorganic acids in the washing process can accelerate the weathering of primary minerals contained in volcanic materials. However, this study was conducted through simulation of volcanic material washing experiments with various types of organic acids such as citric acid, oxalic acid, nitric acid, and sulfuric acid with a concentration of 0.02 M, which does not fully reflect natural conditions. Therefore, research is needed that can provide information on the nutrient-washing process using natural materials that can accelerate nutrient washing from volcanic ash.

Andisol soils are formed from volcanic parent material. They have a fairly high level of fertility, which is due to the addition of material originating from volcanoes, where the eruption results are materials dominated by easily weathered minerals so that they contribute greatly to enriching the essential elements needed by plants. However, even though these minerals are included in the category of easily weathered, it still takes a relatively long time in the process to release their nutrients. So that in the process of weathering these minerals requires external intervention that has a role in helping to accelerate the process of nutrient leaching, so that it can be immediately utilized by plants.

Based on this, the acceleration of mineral weathering in rocks is needed by adding materials that can create conditions and environments that reduce mineral stability so that nutrients can be immediately utilized by plants. One way is to use organic compounds in the form of humic substances and also potassium-solubilizing bacteria. Several experts have put forward the role of organic compounds in accelerating primary mineral weathering through the chelation process that helps leaching of nutrients. Tan (1993) explained that various organic compounds produced in the biosphere can act as mineral solvents. Various organic acids, including humic acid, have been known to play an important role in the dissolution and mobility of elements from minerals in rocks. In addition, Huang and Schnitzer (1997) stated that the effectiveness of organic acids in dissolving minerals depends on several factors, including the concentration and chemical reactivity of the organic acids. The involvement of humic substances enables the formation of complexes with metal ions, which can increase the solubility of minerals in the soil. This process helps release nutrients bound within the mineral structure, making them more available to plants. Humic substances contain functional groups that can interact with metal ions in minerals, forming complexes that enhance the dissolution of these minerals (Ismangil and Eko Hanudin, 2005).

Potassium-solubilizing bacteria in this study were used with the aim of facilitating the process of dissolving potassium from pyroclastic materials. Potassium solubilizing bacteria (PSB) are microorganisms capable of dissolving potassium from insoluble minerals, such as feldspar and mica, into a form that can be absorbed by plants. According to Ribeiro et al. 2020, potassium-solubilizing bacteria produce organic acids that can dissolve silicate minerals, thereby releasing potassium ions into the soil solution. These acids lower the local pH and form complexes with metal ions, which accelerates mineral weathering. In addition, they can produce organic acids that dissolve silicate minerals containing potassium, further releasing potassium into the soil.

Thus, the combination of humic substances and PSB can increase the efficiency of mineral weathering, as humic substances provide energy sources and an environment that supports the growth of PSB, while PSB enhances the availability of nutrients through mineral weathering. The use of humic substances and PSB in soil management can accelerate the process of mineral or rock weathering, increase nutrient availability, and support sustainable plant growth. Ultimately, research on nutrient release from pyroclastic materials through the utilization of humic substances and potassium solubilizing bacteria, in the long term, contributes both directly and indirectly to agricultural efficiency by reducing the need for chemical fertilizers, through increased availability and uptake of plant nutrients. This improves soil health and supports agricultural sustainability. The integrated use of humic substances and PSB can become an important part of a modern agricultural strategy that is more environmentally friendly, efficient, and productive.

The purpose of this study was to determine the nutrients released from pyroclastic materials with different sizes and different doses; to determine the effect of humic materials and potassium-solubilizing bacteria on the release of nutrients from pyroclastic materials; and to determine the amount of nutrients released from pyroclastic materials during the 5-month washing process.

2. Materials and methods

2.1. Time and Place

This research was conducted from November 2023 to June 2024. Pyroclastic materials were taken from Mount Merapi, Yogyakarta, Indonesia, with sampling points at 7°32.5' S and 110°26.5' E. The soil sample was taken from Mamunyu Village, Mamuju District, Mamuju Regency, West Sulawesi, with the point of collection being how many at 2°42'51.98" LS and 118°57'35.78 East. Incubation and percolation treatment to observe the solubility level of nutrients from pyroclastic materials were carried out at the Laboratory of the Department of Soil Science and Land Resources, Faculty of Agriculture, IPB University. Analysis of mineral elements usingX-Ray Fluorescence(XRF) was conducted at Mineral and Coal Technology (TekMira – Bandung), and analysis of the mineral types of the pyroclastic sand fraction was conducted at the Laboratory of the Department of Soil Science and Land Resources, Faculty of Agriculture, IPB University.

2.2. Research Procedures and Stages

2.2.1. Analysis of sand fraction minerals

Analysis of the mineral composition of the sand fraction aims to determine the amount of easily weathered mineral content in pyroclastic materials as a carrier of plant nutrient reserves. This analysis uses a polarization microscope. Analysis of the sand fraction minerals is carried out in two stages, namely separation of sand fractions and identification of mineral types.

Sand Fraction Separation: The fundamental principle of sand fraction separation is to remove the cementing materials that bind the sand grains, allowing for the separation of sand, silt, and clay particles. After the mineral grains are thoroughly washed, the sand fraction is isolated using a sieve with a mesh size between 1 mm and 0.05 mm. Primary mineral analyses typically conducted include heavy fraction and total fraction analyses. For heavy fraction analysis, the sand is first separated into heavy and light fractions. Heavy fraction sand minerals are those that sink in a bromoform solution with a specific gravity of 2.87. For total fraction analysis, the sieved sand can be directly examined without further separation.

Identification of Sand Minerals: For sand mineral identification, the process requires a 2.5 cm x 5 cm glass slide, nitrobenzene liquid, and a polarizing microscope. Sand grains are evenly spread across the glass slide, and nitrobenzene is added and stirred until no sand particles float. The slide is then placed under the microscope for observation. A "line counting" method is used, where only the sand grains that fall on a horizontal line within the microscope's field of view are counted. For routine analysis, up to 100 sand grains are counted to ensure accurate identification.

2.2.2. Nutrient leaching analysis

The stages conducted during the nutrient-leaching experiment are as follows:

1. Soil sampling involves collecting the topsoil (0–30 cm depth). After collection, the soil is air-dried, crushed, and sieved using a 2 mm sieve to ensure uniform grain size.
2. Pyroclastic sand sampling is done by taking samples from a 0–10 cm depth. The sand is then air-dried and sieved into two grain sizes: coarse (passing through a 2 mm sieve) and fine (passing through a 0.5 mm sieve).
3. The processed soil and sand samples are placed into percolation tubes (Fig. 1) according to the predetermined treatment plan. Each sample weighs 1.5 kg, and the percolation tubes used have a diameter of 8.5 cm and a height of 27 cm.
4. The percolation device shown in (Fig. 1) is a simple, self-designed tool used to perform the nutrient leaching process, as there is no standardized method or tool for this process.
5. To ensure consistent density, the soil and sand, at field capacity, are compacted by tapping each sample 100 times.
6. Pyroclastic material is applied in varying dosages: (control, 12.5, 25, 50, 100, and 200 tons) per hectare, equivalent to (0, 9.375 g, 18.75 g, 37.5 g, 75 g, and 150 g) per sample, respectively according to (Table 1).

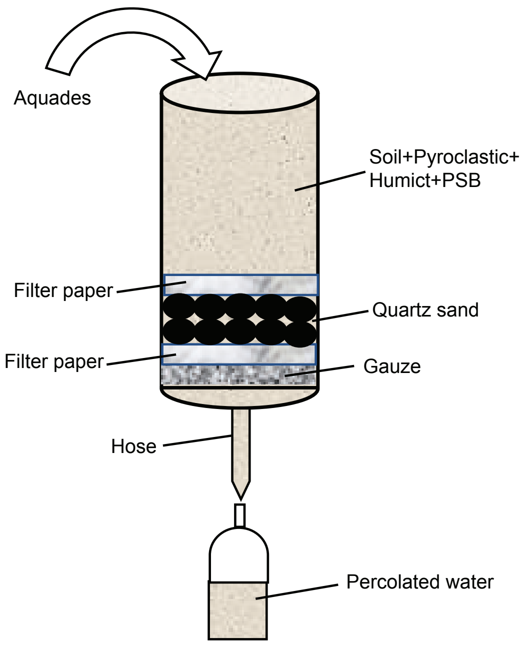

Fig. 1. Illustration of percolation apparatus (leaching of nutrients)

Table 1
Percolation treatment (nutrient leaching) of pyroclastics material

Code Treatment	Fine Pyroclastic (Passing 0.05 mm sieve)	Coarse Pyroclastic (Passes 2 mm sieve)
M0	Soil	Soil
M1	Pyroclastic 1500 g	Pyroclastic 1500 g
M2	Soil + pyroclastic 9.375 g	Soil + pyroclastic 9.375 g
M3	Soil + pyroclastic 18.75 g	Soil + pyroclastic 18.75 g
M4	Soil + pyroclastic 37.5 g	Soil + pyroclastic 37.5 g
M5	Soil + pyroclastic 75 g	Soil + pyroclastic 75 g
M6	Soil + pyroclastic 150 g	Soil + pyroclastic 150 g
M7	Soil + pyroclastic 75 g + humic substances	Soil + pyroclastic 75 g + humic substances
M8	Soil + pyroclastic 75 g + PSB	Soil + pyroclastic 75 g + PSB
M9	Soil + pyroclastic 75 g + humic substances + PSB	Soil + pyroclastic 75 g + humic substances + PSB

7. The reference dosage of humic substances is based on 80 L/ha with a 36% humic content, adjusted for 20% humic content, resulting in 0.108 g per 1.5 kg of soil sample.
8. The potassium solubilizing bacteria used was *Bacillus mucilaginosus*, obtained from the Soil Biology Laboratory collection of Jember University, with isolate code PSB 05, at a rate of 1.2 mL per sample. This dose was chosen because it was the optimal dose based on the results of the (Mutmainnah, 2018) research.
9. Then, add humic substances and potassium-solubilizing bacteria.
10. The number of treatments for fine pyroclastics is 10, and for coarse pyroclastics, it is also 10, making a total of 20 treatments. Each treatment was repeated 3 times, resulting in 120 experimental samples.
11. After adding the humic substances and bacteria, the samples are incubated for 15 days. During the incubation, distilled water is applied daily to simulate nutrient leaching, with each sample receiving 124 mL per day, reflecting the average annual rainfall of 2000 mm in Mamuju 2021. The calculation for the amount of aquadest needed is as follows:

Cross-sectional area of percolation tube (r=8.5)

L = πr^2
= $22/7 \times (8.5)^2$ cm
= 226.865 cm^2

Water requirement calculation

Rainfall = 2000 mm/Year
= 5.48 mm/day
= 0.548 cm/day

Water requirements =
= Rainfall x L
= 0.548 cm x 226.865 cm^2
= 124.32 cm^3
= 0.124 dm^3
= 0.124 L
= 124 mL/day

12. After 30 days of leaching, the percolate was collected to measure how many nutrients were released from the pyroclastic material.
13. Since the study was conducted over 5 months, there were 5 percolate water collections.
14. The harvested percolate water was then measured for pH using a pH meter, and leached elements such as Ca, Mg, Fe, Mn, Cu, and Zn were measured using an Atomic Absorption Spectrophotometer (Shimadzu model AA6300). K and Na were measured using a Flame Photometer (Cole-Parmer Dual-Channel model EW-02655-10), while Si was measured using a Spectrophotometer (Shimadzu UV-1280, model A120653) (Jackson, 1969; Nelson and Sommers, 1982; Eviati et al. 2023).
15. Data from nutrient measurements were analyzed by simply averaging the results of 3 replicates for each treatment.

3. Results and interpretation

3.1. Sand fraction minerals

The results of the analysis of sand fraction minerals show that the most dominant minerals found are plagioclase minerals at 52% and volcanic glass at 23%, the rest are augite, magnetite, amphibole, and hyperstein minerals (Table 2). According to Aini et al., (2016) Pyroclastic material released by the 2006 eruption was different from the 2010 eruption. The results of the 2006 eruption were dominated by volcanic glass (60%) and labradorite (34%) mineral types. While in 2010 it was dominated by Plagioclase (57%) and Pyroxene (37%), the rest were Opaque mineral types (6%).

Based on the types of minerals that have been identified, it can be seen that augite, amphibole and hypersteine are sources of Ca and Mg, plagioclase is a source of Na, volcanic glass is a source of K and other easily weathered elements, magnetite is a source of Fe, while Si is found in almost every type of mineral.

Table 2
Results of observations of sand fraction minerals using a polarizing microscope

No.	Minerals	Chemical Formulas	Percentage (%)
1	Augite	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)	9
2	Amphibole	$(Ca,Na,K)_{2,3}(Mg,Fe,Al)_5(OH)_2[(Si,Al)_4O_{11}]_2$	5
3	Hypersthene	$MgFe^{2+}$Si2O6	4
4	Plagioclase	$NaAlSi_3O_8 – CaAl_2Si_2O_8$	52
5	Magnetite	Fe_3O_4	7
6	Volcanic Glass	–	23
		Total minerals	100

Source: Primary Data, 2024

3.2. Nutrient leaching (percolation)

3.2.1. The effect of pyroclastic size and dose on nutrient release

In the M1 treatment with 1500 g pyroclastic (Table 1), the amount of nutrients leached was 122.78 mg (Fig. 2). This shows that in pure pyroclastic with a mass of 1500 g, there was a relatively lower nutrient leaching compared to several other treatments. This may be due to the nature of the pyroclastic itself which has a greater capacity to absorb water and nutrients due to the denser consistency of the material without any soil mixture. In treatment M2, the amount of nutrients leached increased to 175.32 mg. Treatment M3 with a pyroclastic dose of 18.75 g showed that the amount of nutrients leached increased again to 204.04 mg. In treatment M4 (pyroclastic dose 37.5 g), the amount of nutrients leached decreased to 150.84 mg. Although the pyroclastic dose was greater than M2, the amount of nutrients leached was lower than M3. This shows that at a certain dose, increasing the amount of pyroclastic dose is not always linear to the increase in nutrient leaching. However, in the M5 treatment with a pyroclastic dose of 75 g, the amount of nutrients leached reached its peak, which was 209.07 mg, which was the highest amount of nutrients leached from all treatments. In contrast to the subsequent higher dose increase, namely the dose (150 g), the amount of nutrients leached decreased to 180.85 mg. This shows that after a certain point, the addition of pyroclastic no longer significantly increases nutrient leaching, and may even decrease.

Based on Fig. 3, nutrient leaching increases with the addition of coarse pyroclastic dose until it reaches its peak at dose M5 (75 g), then decreases at higher doses (M6). Coarse pyroclastic tends to produce less nutrient leaching compared to fine pyroclastic at the same dose. This is likely due to differences in the size and porosity of pyroclastic which affect the movement of water and nutrients. The effectiveness of nutrient leaching appears to be influenced by the interaction between soil and pyroclastic, where the combination of both at the optimal dose can accelerate nutrient release.

In treatment M1 (pyroclastic alone with a dose of 1500 g), the amount of nutrients leached was 96.43 mg, the lowest value compared to other treatments. This indicates that coarse pyroclastic

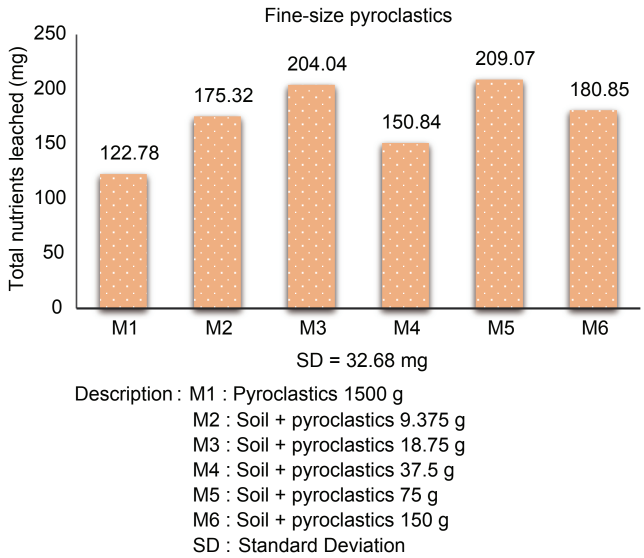

Fig. 2. Total nutrient leaching over 5 months on fine-sized pyroclastics with various doses after being averaged over three replicates

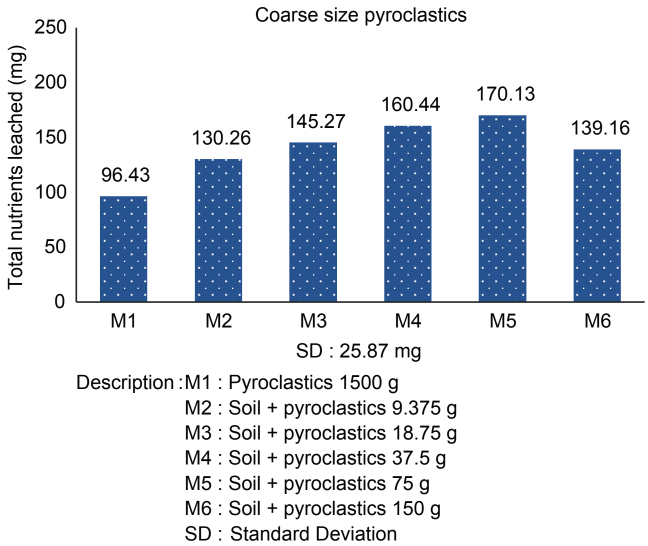

Fig. 3. Total nutrient leaching over 5 months on coarse-size pyroclastics with various doses after being averaged over three replicates

in large doses without soil tends to release less nutrients than treatments with smaller doses involving interaction with soil. In treatment M2 with a dose of 9.375 g, the amount of nutrients leached increased to 130.26 mg. Mixing coarse pyroclastic in low doses with soil increased nutrient leaching compared to M1. This indicates that the combination of soil with coarse pyroclastic affects the dynamics of nutrient leaching. In treatment M3 with a dose of 18.75 g, the amount of nutrients leached increased to 145.27 mg. Although a higher dose of coarse pyroclastic in the soil mixture increased nutrient release, the rate of increase was not very significant compared to M2. In the M4 treatment (dose 37.5 g), the amount of leached nutrients increased to 160.44 mg. At a higher coarse pyroclastic dose, M5 (75 g), the amount of leached nutrients reached 170.13 mg, which was the highest value in Fig. 3. This significant increase indicates that this dose can be considered the optimum dose for coarse pyroclastic. However, in the M6 treatment with the highest coarse pyroclastic dose (150 g), the amount of leached nutrients actually decreased to 139.16 mg. This trend is similar to that seen in fine pyroclastic, where after a certain dose, the addition of more pyroclastic no longer increased nutrient leaching, and even decreased it.

The particle size of rocks or minerals affects the weathering rate because it is related to the reactive surface area, which increases with decreasing particle size. Several studies have reported that decreasing particle size increases solubility, for example, in alkali feldspar, gneiss (Wang et al. 2000), basalt (Gillman et al. 2002), trachyte, diorite, and basalt (Ahmad, 2011), volcanic ash (Simare, 2012), and alkaline volcanic rocks (Basak et al. 2018, Basak, 2019). Convergent weathering rates have been reported for some felsic rocks, with higher initial weathering rates for particles finer than 60 μm compared to particle sizes ranging from 60 to 140 and 250–350 μm, while all rates became similar after 6 weeks. This is also in accordance with the results of research conducted by (Simare, 2012) which show that the smaller the grain size, the greater the nutrients released. According to Brady (1990), fine-grained minerals are more resistant to physical weathering, but more sensitive to chemical weathering than coarse-grained minerals.

3.2.2. The effect of adding humic substances and potassium-solubilizing bacteria on nutrient release

Based on Fig. 4, in the M0 treatment, the amount of leached nutrients was recorded at 130.02 mg. As a control, this treatment shows the level of nutrient leaching in the soil without the addition of pyroclastic, humic substances, or potassium-solubilizing bacteria (PSB). In the M7 treatment, the amount of leached nutrients increased drastically to 209.07 mg. The addition of 75 g of fine pyroclastic in the soil mixture caused a significant increase in nutrient leaching compared to the control (M0). In the M8 treatment, with the addition of humic substances, the amount of leached nutrients decreased slightly to 186.74 mg. Furthermore, in the M9 treatment, which involved the addition of potassium-solubilizing bacteria, the amount of leached nutrients reached 207.00 mg, almost equivalent to M7. In the M10 treatment, which involved the addition of humic substances and potassium-solubilizing bacteria simultaneously, the amount of leached nutrients reached 222.60 mg, which was the highest value of all treatments. The combination of humic substances and PSB appears to have a significant synergistic effect in increasing nutrient leaching. This combined effect provides the most maximum nutrient leaching results compared to other treatments, indicating that the interaction between humic substances and PSB is very effective in increasing nutrient release from the soil.

In the control treatment (M0) Fig. 4, which is soil without the addition of pyroclastic, humic substances, or potassium-solubilizing bacteria (PSB), the amount of nutrients leached was 130.02 mg. In treatment M5, with the addition of 75 g of coarse pyroclastic, the amount of nutrients leached increased significantly to 209.07 mg. The increase in soil porosity due to the addition of pyroclastic allows better water movement, thus encouraging increased nutrient leaching. In treatment M7, with the addition of humic substances, the amount of nutrients leached decreased to 186.74 mg, slightly lower than M5. Meanwhile, in the M8 treatment, with the addition of potassium-solubilizing bacteria, the amount of leached nutrients increased again to 207.00 mg, approaching the results obtained in M5. The addition of PSB helped dissolve potassium nutrients, although the leaching results were not higher than pyroclastic without PSB (M7). In the M9 treatment, with a combination of humic substances and PSB, the amount of leached nutrients reached 222.60 mg, the highest among all treatments. The combination of coarse pyroclastic, humic substances, and PSB showed a strong synergistic effect in increasing nutrient leaching, resulting in much higher leaching than other treatments.

Treatment M0 (pure soil) Fig. 5 showed the lowest nutrient 130.02 mg, leaching the release of nutrients from the soil was very limited. In treatment M5 (soil with pyroclastic), there was a significant increase in nutrient leaching (170.13 mg), indicating that coarse pyroclastic was effective in increasing the mobility and release of nutrients from the soil. In M7 (soil with pyroclastic and humic substances), nutrient leaching continues

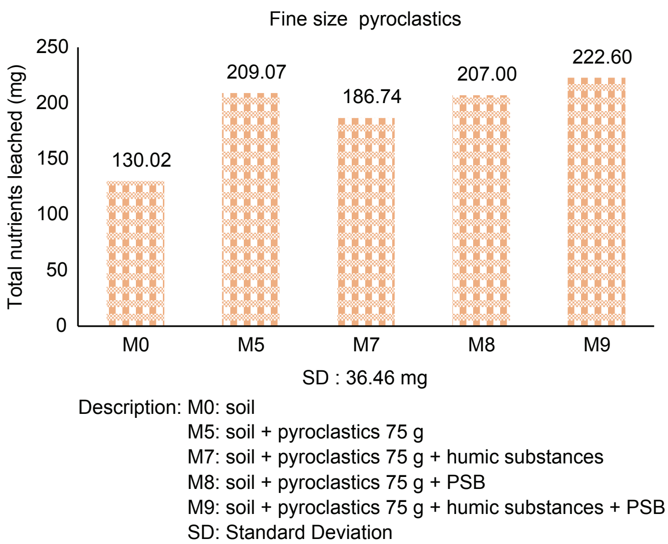

Fig. 4. Total nutrient leaching over 5 months on fine-size pyroclastics with added humic substances and potassium-dissolving bacteria after being averaged over three replicates

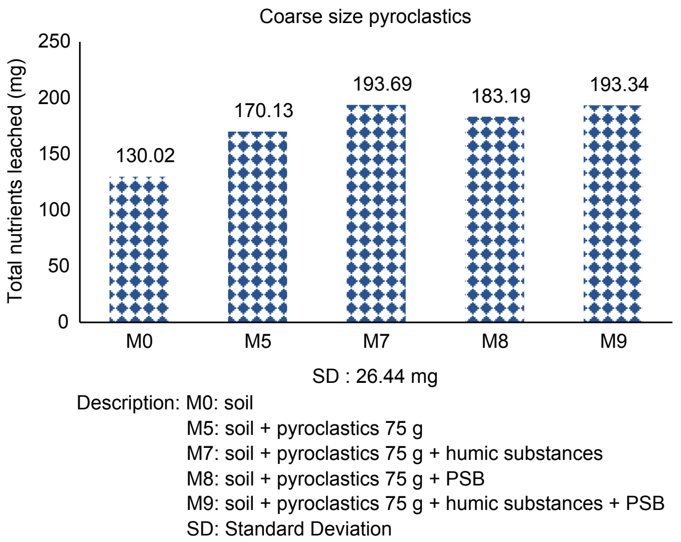

Fig. 5. Total nutrient leaching over 5 months on coarse-sized pyroclastics with the addition of humic substances and potassium-solubilizing bacteria after being averaged over three replicates

to experience an increase (193.69 mg). In treatment M8 (soil with pyroclastic and potassium-solubilizing bacteria), nutrient leaching slightly decreased (183.19 mg), although the difference was not too far from M5. However, in treatment M9 (soil with pyroclastic, humic substances, and PSB), nutrient leaching reached the highest value (193.34 mg), indicating that the combination of humic substances and PSB works synergistically.

Tables 3 and 4 below display the calculated data, obtained by averaging 3 replicates for each treatment. The treatments are grouped into categories such as the pyroclastic group, humic substances group, PSB group, and pyroclastic + humic substances + PSB group, to illustrate the full effect of the addition of humic substances and PSB on the solubility of nutrients from fine and coarse pyroclastic materials.

The average nutrient leaching from fine-sized pyroclastic material in various treatment groups is as presented in Table 3. Calcium (Ca) experienced a significant increase with the addition of humic substances and bacteria potassium solubilizer. Treatment without additional humic substances or potassium solubilizing bacteria only produced 112.69 mg, but with the addition of humic substances, the calcium value increased to 134.81 mg, and with the addition of PSB to 141.44 mg. The combination of humic substances and potassium solubilizing bacteria produced the highest value, which was 147.62 mg. The increase in magnesium nutrient leaching was not very significant compared to calcium. The addition of humic substances slightly increased magnesium leaching from 7.24 mg to 7.98 mg. The addition of PSB produced a slightly lower value than the combination of humic substances alone, but still higher than the treatment without the addition of humic substances or potassium solubilizing bacteria. Potassium showed a fairly significant increase with the addition of humic substances and PSB. The control treatment (combination of soil + pyroclastic) alone produced 17.71 mg of potassium, but with the addition of humic substances it became 24.08 mg, and with potassium solubilizing bacteria it became 24.38 mg. The combination of the two

Table 3
Average nutrients released in the fine pyroclastic treatment group, after averaging three replicates of each treatment

Treatment Combination	Calcium	Magnesium	Potassium	Sodium	Iron	Manganese	Silica
	(mg kg^{-1})						
Soil+ pyroclastics	112.69	7.24	17.71	12.52	0.07	0.29	17.05
Soil + pyroclastics + humic substances	134.81	7.98	24.08	12.69	0.13	0.85	14.56
Soil + pyroclastics +PSB	141.44	7.68	24.38	13.43	0.15	0.49	13.40
Soil + pyroclastics + humic substances +PSB	147.62	7.64	27.48	17.00	0.17	0.52	15.19

Source: Primary Data After Processing, 2024

Table 4
Average nutrients released in the coarse pyroclastics treatment group, after averaging three replicates of each treatment

Treatment Combination	Calcium	Magnesium	Potassium	Sodium	Iron	Manganese	Silica
	(mg kg^{-1})						
Soil+ pyroclastics	96.86	6.95	10.24	8.97	0.21	0.26	15.32
Soil + pyroclastics + humic substances	124.27	8.12	17.42	10.25	0.20	0.81	15.91
Soil + pyroclastics +PSB	127.03	7.40	16.94	11.31	0.21	0.72	15.75
Soil + pyroclastics + humic substances +PSB	134.80	7.20	19.39	15.04	0.20	0.29	15.44

Source: Primary Data After Processing, 2024 produced the highest potassium leaching of 27.48 mg. This shows that both materials (humic substances and PSB) are very effective in increasing potassium leaching. Sodium also increased, especially when potassium-solubilizing bacteria were added, and a combination of humic substances and potassium-solubilizing bacteria were added. The control treatment with a combination (soil + pyroclastic only) only produced 12.52 mg, but with potassium-solubilizing bacteria, it increased to 13.43 mg, and the combination of humic substances and potassium-solubilizing bacteria produced the highest sodium leaching of 17.00 mg. The increase in iron leaching was quite significant when humic substances were added. In the control treatment, iron leaching was only 0.07 mg, but with the addition of humic substances, it became 0.13 mg, and with the addition of potassium-solubilizing bacteria, it became 0.15 mg. The combination of the two materials (humic substances and potassium-solubilizing bacteria) produced the highest leaching of 0.17 mg. Manganese showed a significant increase with the addition of humic substances, from 0.29 mg to 0.85 mg. The addition of potassium-solubilizing bacteria also increased manganese leaching, but was not as effective as humic substances, producing 0.49 mg. The combination (humic substances + potassium solubilizing bacteria) only slightly increased manganese leaching to 0.52 mg. Unlike other elements, silica experienced a slight decrease with the addition of humic. The control treatment showed the highest leaching value of 17.05 mg, while the treatment with the addition of humic substances and potassium-solubilizing bacteria showed a slight decrease to 14.56 mg and 13.40 mg. The combination of both resulted in a slight increase compared to potassium-solubilizing bacteria alone, which was 15.19 mg.

Calcium increased significantly with the addition of humic (Table 4). Treatment with a combination of soil and pyroclastic only released 96.86 mg of calcium, but with the addition of humic substances, the value increased to 124.27 mg. The addition of potassium-solubilizing bacteria increased calcium leaching to 127.03 mg. The combination (humic substances and PSB) produced the highest leaching of 134.80 mg. Magnesium nutrient leaching showed a slight increase with the addition of humic substances, from 6.95 mg to 8.12 mg. The addition of potassium-solubilizing bacteria resulted in lower magnesium leaching than humic substances, which was 7.40 mg. Meanwhile, the treatment with a combination of humic substances and potassium-solubilizing bacteria actually resulted in a decrease in magnesium leaching, reaching 7.20 mg. Control treatment (soil + pyroclastic) only produces 10.24 mg of potassium, but with the addition of humic substances it increases drastically to 17.42 mg, and with potassium-solubilizing bacteria to 16.94 mg. The combination of the two materials (soil + pyroclastic + humic substances + potassium-solubilizing bacteria) produced the highest leaching, which was 19.39 mg. Sodium leaching increased with the addition of humic substances, especially in the combination of humic substances and potassium-solubilizing bacteria. Without humic substances , the sodium released was 8.97 mg. The addition of humic substances slightly increased leaching to 10.25 mg, and with potassium-solubilizing bacteria to 11.31 mg. The combination of humic substances and potassium-solubilizing bacteria produced the largest increase, reaching 15.04 mg.

Iron did not show significant changes with the addition of humic substances or potassium-solubilizing bacteria. The iron leaching values ranged from 0.20 to 0.21 mg in all treatments. This may be due to the nature of iron in coarse pyroclastic soils which is not greatly affected by the addition of organic matter. Manganese increased significantly with the addition of humic substances, from 0.26 mg to 0.81 mg. The addition of potassium-solubilizing bacteria resulted in an increase, but lower than humic substances, which was 0.72 mg. The combination of humic substances and potassium-solubilizing bacteria actually resulted in much lower manganese leaching, which was 0.29 mg, approaching the basic leaching value. Silica did not experience significant changes with the addition of humic substances or potassium- solubilizing bacteria. The leaching values ranged from 15.32 mg to 15.91 mg. The differences between the treatments of humic substances, potassium-solubilizing bacteria, and the combination of both were not too large, indicating that silica leaching from coarse pyroclastic was not greatly affected by humic substances or PSB.

The addition of humic substances gives a quite different response, especially in the solubility of Ca which increases in both fine and coarse pyroclastics. While for other elements, such as Mg, K, Na, Fe, Mn, and Si tend to have stable solubility. This can happen because humic substances is a complex organic compound containing carboxylate (-COOH) and phenolate (-OH) groups which are acidic. These groups play a role in the chemical weathering process of minerals through the chelation process. Humic substances is able to bind metal ions (Fe, Al, Mg, and Ca) contained in minerals through this process, thereby accelerating the leaching of nutrients from these minerals. In addition, humic substances can also exchange H^+ ions which it has with cations (such as K^+, Mg^{2+}, and Ca^{2+}) that are adsorbed on the mineral surface. This causes the ions to become more available to plants.

Varadachari et al. (1997), organic acids derived from the activity of microorganisms and the decomposition of organic matter in the soil play a central role in the process of dissolving cations from silicate minerals. Citric acid, oxalic acid, and malic acid. These acids have the ability to bind metal ions in minerals through chelating and acidification mechanisms, which accelerate mineral weathering. H ions+derived from organic acids replace cations bound in the mineral structure, which then causes the leaching of these cations into the soil solution. Organic acids bind the released cations by forming stable complexes, thus preventing back reactions that can trigger re-precipitation of these cations into insoluble mineral forms. Organic acids have a significant effect on the degree of solubilization of cation leaching from several minerals, such as feldspar and mica. The results of the experiment showed that cation leaching is highly dependent on the type of organic acid and its concentration, as well as the chemical nature of the weathered minerals. This is also in line with the findings expressed by Canellas et al. (2009) that, humic substances have the ability to bind and dissolve nutrients from minerals that are difficult to dissolve, such as phosphorus, iron, and potassium. The author discusses that humic substances act as chelating agents that can mobilize nutrients and make them more available to plants. This helps plants obtain essential nutrients in less fertile soil conditions or when mineral content is strongly bound to soil particles.

This is in line with the results presented by Basak et al. (2010), that the use of potassium-solubilizing bacteria can increase potassium leaching from mica waste. These bacteria work by producing organic acids that dissolve silicate minerals and release the potassium contained in them. This study found that soil treated with mica waste that had been modified with potassium-solubilizing bacteria had a higher potassium content than soil that was not treated similarly. This study also concluded that mica waste that had been modified with potassium-solubilizing bacteria has great potential as an alternative source of potassium in agriculture. With the use of these bacteria, potassium trapped in mica minerals can be released and utilized by plants as a source of nutrients. This not only provides a more economical solution for farmers, but also provides a more environmentally friendly alternative compared to the use of synthetic fertilizers. Sheng et al. (2006) also explained from the results of his research that natural strains *Bacillus edaphicus* and its mutants are able to dissolve potassium from biotite and feldspar minerals. These bacteria produce organic acids such as citric acid and malic acid which function to break down the mineral structure and release the potassium contained therein, so that it becomes available and can be used by plants. Fiantis et al. (2010) results showed that the leaching of K from volcanic material in the presence of organic acids was seen to be greater in citric acid than in oxalic acid, both in the form of tricarboxylic and dicarboxylic acids, respectively. In addition, water isleaching agentwhich is weak in releasing K from Mount Talang volcanic material.

4. Discussion

In general, nutrient leaching from all treatments starting from M0 – M24, both in coarse pyroclastic and fine pyroclastic, both with only pyroclastic or with the addition of humic substances, potassium-solubilizing bacteria, or a combination of humic substances and potassium-solubilizing bacteria, the most released nutrient is Ca as shown in (Table 3). Based on Table 3, the average Ca^{2+} released in the treatment (soil + pyroclastic) was 96.86 mg, after adding humic substances it increased to 112.06 mg, there was a slight increase after being combined with potassium-solubilizing bacteria, to 114.12 mg, and after being combined simultaneously between humic substances and potassium-solubilizing bacteria to 123.12 mg. Based on the results of the total chemical analysis using X-Ray Fluorescence XRF) of pyroclastic material shows that the CaO element content is 8.49%, which is a cation with a relatively high content after SiO_2 and Al_2O_3. Other elements that then have a high average solubility after Ca are Si>K>Na>Mg>Mn and the least is Fe. Si is the element that is most contained in pyroclastic materials, namely 53.34%, then Al, Na, Mg, which sources come from augite, amphibole, hyperstein, and plagioclase minerals, while the source of Fe comes from magnetite minerals. This shows that the volcanic soil in Central Java Island has high mineral reserves as a provider of Ca, Mg, and Fe elements. These minerals are a supply of plant nutrients and greatly enrich the fertility of volcanic soil. The presence of potassium and magnesium minerals in these primary minerals shows that volcanic soil in Java Island has high fertility both potentially and actually. However, besides these minerals contributing to nutrient supply, minerals that are more easily weathered and contribute greatly to nutrient leaching are amorphous minerals (volcanic glass).

Volcanic glass is an amorphous (non-crystalline) material derived from the remains of magma that has undergone imperfect crystallization. Volcanic glass is a mineral that makes up volcanic rocks (Afany and Partoyo, 2001). The content of volcanic glass in the soil reflects the level of weathering and mineral reserves contained in the soil. The weathering of amorphous minerals, such as volcanic glass and opal, is an important process in soil formation and providing nutrients for plants. Amorphous minerals tend to be more reactive to water and acids than crystalline minerals. Chemical reactions, such as hydration, hydrolysis, and dissolution, cause amorphous minerals such as obsidian or volcanic glass to weather quickly. Water that enters the amorphous mineral structure causes microscopic cracks and releases important ions such as silica (Si), calcium (Ca), magnesium (Mg), and potassium (K) into the soil. In addition, the addition of humic substances and PSB further increases the level of weathering of amorphous minerals. So that with the total solubility of cations as found in (table 3), it is clear that there is an influence of humic substances and PSB in an effort to accelerate the weathering process that occurs. Soil microorganisms, especially mineral-solubilizing microbes, release organic acids that can break down chemical bonds in amorphous minerals. According to Sukarman and Dariah (2014), one of the primary minerals that has unique properties and greatly affects the properties of volcanic soil is volcanic glass. According to study Shoji et al. (1993) the more advanced the level of weathering, the less volcanic glass is available, because it has weathered into crystalline minerals or into secondary minerals (clay-sized).

5. Conclusions

Based on the results and discussion, it can be concluded that:

Pyroclastic material is a potential source of nutrients for plants, as evidenced by this study, which shows that a 5-month percolation process releases a promising amount of nutrients.

1. The combination of humic substances and potassium-solubilizing bacteria increases the release of nutrients from pyroclastic materials, making them more available to plants.
2. The best dose is to provide 75 g of pyroclastic material, both fine and coarse-sized pyroclastic.

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Author Contributions

Kurniati – Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing). **Suwardi** – Conceptualization, Data curation, Investigation, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. **Budi Mulyanto** – Investigation, Supervision, Validation, Writing – original draft, Writing – review & editing. **Budi Nugroho** – Supervision, Validation, Writing – original draft, Writing – review & editing. **Welly Herman** – Writing – original draft, Writing – review & editing.

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