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A comprehensive review of rock dust for soil remineralization in sustainable agriculture and preliminary assessment of nutrient values in micronized porous basalt rock from Nghe An province, Viet Nam

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Abstract. This review delves into the utilization of rock powder as a mineral-derived fertilizer to support soil remineralization in the context of sustainable agriculture. Soil remineralization has emerged as a key strategy for ensuring long-term soil fertility and reducing the dependency on synthetic fertilizers. This review critically assesses the methodological approaches applied in various studies, taking into account factors such as local rock mineralogy, soil conditions, crop types, and nutrient uptake by plants. The review covers a range of methods, including nutrient value analysis, assessment of nutrient release rates, crop cultivation experiments in both laboratory and field settings, and the resulting implications for soil remineralization. Additionally, we present findings from a preliminary study focusing on the nutrient content of basalt rock from Nghe An Province, Viet Nam. This experimental investigation is centered on the assessment of nutrient values in a specific porous basalt material, which has been processed into micro-nanometer particles using a high-energy ball mill, thereby enhancing nutrient release efficiency. The study employs a range of analytical techniques, including XRD, XRF, SEM/EDS, and ICP-MS, to quantify macro- and micro-nutrient compositions. While the basalt rock samples may exhibit limitations in providing macronutrients (such as K) compared to commercial azomite rock, they offer distinct advantages in furnishing secondary macronutrients (like Ca). This comprehensive analysis provides insights into the potential use of micronized basalt rock for soil remineralization.

Keywords: soil remineralization, stonemeal, mineral derived fertilizer, basalt rock, sustainable agriculture.

Classification numbers: 2.9.2, 2.10.2, 2.10.3.

1. INTRODUCTION

According to Tilman et al.'s research [1], global cereal production has doubled in the last 40 years, thanks to increased fertilizer use, improved technology, and new crop strains. Between 1960 and 1995, nitrogen fertilizer use grew sevenfold, and phosphorus use increased 3.5 times. Both are projected to triple by 2050 unless fertilizer efficiency improves. Synthetic fertilizers have been crucial for expanding food production and preventing the conversion of natural ecosystems into farmland. They are now essential for boosting overall biomass output in agriculture. Looking to 2050, with a 50 % larger global population and double the grain demand, increasing agricultural output remains vital for global stability, equity, and food security.

1.1. Nutrients demand and challenge of soil depletion in agriculture

Table 1. Sixteen plant essential nutrients and their form, source, mode of uptake [3].

Nutrient family	Nutrient	Percentage of plant	Form taken up by plants (ion)	Mode of uptake	Major function in plants
Primary	Carbon	45	Carbon dioxide (CO_2), bicarbonate (HCO_3^-)	Open somates	Plant structures
	Oxygen	45	Water (H_2O)	Mass flows	Respiration, energy production, plant structure
	Hydrogen	6.0	Water (H_2O)	Mass flow	pH regulation, water retention, synthesis of carbohydrates
	Nitrogen	1.75	Nitrate (NO_3^-), ammonium (NH_4^+)	Mass flow	Protein/amino acids, chlorophyll, cell formation
	Phosphorus	0.25	Dihydrogen phosphate ($H_2PO_4^-$, HPO_4^{2-}), phosphate (PO_4^{3-})	Root interception	Cell formation, protein syntheses, fat and carbohydrate metabolism
	Potassium	1.5	Potassium ion (K^+)	Mass flow	Water regulation, enzyme activity
Secondary	Calcium	0.50	Calcium ion (Ca^{2+})	Mass flow	Root permeability, enzyme acitivity
	Magnesium	0.20	Magnesium ion (Mg^{2+})	Mass flow	Chlorophyll, fat formation and metabolism
	Sulfur	0.03	Sulfate (SO_4^{2-})	Mass flow	Protein, amino acid, vitamin and oil formation
Micro	Chlorine	0.01	Chloride (Cl^-)	Root interception	Chlorophyll formation, enzyme activity, cellular development
	Iron	0.01	Iron ion (Fe^{3+}, Fe^{2+})	Root interception	Enzyme development and activity
	Zinc	0.002	Zinc ion (Zn^{2+})	Root interception	Enzyme activity
	Maganese	0.005	Mângnese ion (Mn^{2+})	Root interception	Enzyme activity and pigmentation
	Boron	0.0001	Boric acid (H_3BO_7), borate (BO_3^{3-}), tetraborate (B_4O_7)	Root interception	Enzyme activity
	Copper	0.0001	Copper ion (Cu^{2+})	Mass flow	Enzyme activity
	Molybdenum	0.00001	Molybdenum ions ($HMoO^{4-}$, MoO_4^{2-})	Mass flow	Enzyme activity and nitrogen fxation in legumes

Different crops have distinct nutrient demands that can vary significantly. To achieve optimal growth and productivity, it is essential to carefully manage the specific fertilizer used for each crop, following the principle of the Four Rs: right rate, right nutrient, right time, and right place (terminology promoted by the International Plant Nutrition Institute) [2]. In general, nutrients can be categorized into macronutrients, secondary macronutrients and micronutrients based on the quantities required by plants. Macronutrients, such as nitrogen (N), phosphorus (P), and potassium (K), are critical for crops growth and development. Additionally, crops require secondary macronutrients like calcium (Ca), magnesium (Mg), and sulfur (S), as well as micronutrients including iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), and molybdenum (Mo). Plants require macronutrients in larger quantities compared to micronutrients, which are necessary in trace amounts. Both types of nutrients are crucial in carrying out vital physiological processes [3].

In pratice, crops absorb nutrients in different chemical forms. For example, they take up nitrogen as nitrate (NO_3^-) and ammonium (NH_4^+), phosphorus as phosphate ($H_2PO_4^-$ and HPO_4^{2}), and potassium as potassium ions (K^+). Other nutrients are absorbed in various forms, including oxides, sulfates, and chelates. The chemical forms in which nutrients exist in the soil influence their availability to plants and their uptake efficiency. Table 1 provides relevant information about nutrients and their chemical forms taken by plants [4].

Nutrient deficiencies in crops can have severe consequences on their growth and productivity. Insufficient levels of specific nutrients can lead to stunted growth, reduced yields, poor-quality product, and increased vulnerability to pests and diseases [4]. For example, nitrogen deficiency can cause chlorosis and reduced photosynthesis, while phosphorus deficiency can result in poor root development and delayed flowering. Identifying and addressing nutrient deficiencies is crucial for maintaining rice crop health and maximizing agricultural productivity.

Synthetic fertilizers have offered a convenient and effective way to nourish crops, leading to substantial yield increases. Yet, their excessive application, coupled with erosion and unsustainable farming methods, has negatively impacted soil health and nutrient levels. This has caused imbalances, soil degradation, and environmental pollution. To promote sustainable agriculture, it's imperative to rectify nutrient deficiencies in farmland soils and alleviate the adverse consequences associated with synthetic fertilizers [1].

1.2. Soil remineralization and its mechanism of providing nutrients in sustainable agriculture

Conventional farming practices are characterized by continuous cultivation without adequate nutrient replenishment. These methods heavily rely on synthetic fertilizers that primarily supply macronutrients such as nitrogen, phosphorus, and potassium, neglecting the importance of other essential minerals and trace elements (micronutrients). Consequently, this approach leads to the depletion of natural nutrient reservoirs in agricultural soils over time, resulting in diminished crop yields and unsustainable agricultural practices. The concept of mass food production through intensive soil manipulation, extensive use of industrial inputs, irrigation, and mechanization, known as the Green Revolution, emerged as a response to the global crisis in food production, population growth, and concerns about food availability [5]. However, the widespread use of chemical fertilizers has disrupted the balance of the agricultural sector, creating dependencies on imported raw materials and exacerbating the challenges posed by low fertility soils, which are predominantly acidic and prone to nutrient deficiencies, particularly phosphorus and potassium [6].

Recognizing the significance of addressing nutrient depletion, the technique of soil remineralization or stonemeal has emerged as a promising approach in sustainable agriculture. This practice involves the incorporation of rocks and minerals into the soil, with liming being a popular example [7]. Soil remineralization serves as an alternative to reduce reliance on synthetic fertilizers, aiming to rejuvenate impoverished soils and maintain balanced fertility, while also conserving natural resources and promoting sustainable productivity [8]. Interestingly, during the same period when Justus von Liebig, a German chemist, discovered NPK and ushered in the era of chemical fertilizers in 1890, Hensel proposed in his book "Bread from Stone" in 1894 that powdered rocks could achieve similar effects without compromising the environment and at a lower cost [9]. However, this practice gained limited recognition among farmers at that time. It was only with the book's reissue in 1997, capitalizing on concerns about nutritional quality and food safety, that its significance garnered attention. The utilization of rocks as a source of plant nutrients, soil reclamation, and revitalization presents an alternative technology for reducing the reliance on chemical fertilizers, particularly those in highly soluble forms such as NPK formulations [10]. Studies indicate potential cost savings of up to 50 % in production expenses by reducing the use of chemical fertilizers [11]. Additionally, using rock powder in agriculture offers advantages in terms of cost-effectiveness, waste transformation into valuable products, and expansion of market opportunities for mineral fertilizer.

Rock powder or rock dust, an inexpensive material produced in a decentralized manner, is highly recommended for soil remineralization [12]. It plays a crucial role in achieving nutrient balance in the soil by providing essential minerals and trace elements. Various rock minerals, such as basalt, granite, limestone, and volcanic rock dust, are commonly utilized to replenish these vital nutrients. Basalt, an igneous rock, is abundant in minerals like calcium, magnesium, and iron, as well as trace elements such as manganese and zinc. Granite, another frequently used rock for remineralization, contains potassium, phosphorus, and silica. Limestone, primarily composed of calcium carbonate, helps elevate soil pH and supplies calcium for plant growth. Volcanic rock dust, derived from ancient volcanic ash, carries minerals and trace elements accumulated over millions of years of volcanic activity. Each type of rock mineral offers unique advantages to the soil and plants. Volcanic rock, for instance, consists mainly of SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, Na_2O, K_2O, and CaO [13].

The process of soil remineralization involves the gradual breakdown of rock minerals, which releases essential nutrients into the soil over time. This breakdown occurs through various mechanisms, including mineral weathering, cation exchange, and microbial activity. Mineral weathering is a natural process where rock minerals react with water, oxygen, and organic acids, gradually releasing different elements in forms that plants can easily absorb. As these minerals weather, positively charged ions (cations) such as Ca^{2+}, K^+, and Mg^{2+} are released into the soil and can exchange with other cations present on soil particles. Microbial activity plays a crucial role in soil remineralization as well. Beneficial soil microorganisms, including bacteria and fungi, interact with rock minerals, aiding in their breakdown and the subsequent release of nutrients. These microorganisms produce organic acids and enzymes that facilitate the weathering process, thereby enhancing nutrient availability. This entire process ensures improved nutrient availability and enables plant roots to acquire the necessary nutrients effectively.

The effects of these mechanisms can persist for several consecutive years, thanks to the gradual release of nutrients. The presence of rock powder as a nutrient source for plants promotes an increase in the cation exchange capacity of the soil, primarily due to the formation of new clay minerals during the process of mineral alteration [14]. The release of nutrients from the crystal lattice of rocks occurs through the action of organic acids produced by plants and microorganisms in the soil [15]. It is important to highlight that soil remineralization using rock powder is influenced by its mineral characteristics and interaction with the surrounding environment, as this ultimately contributes to improving soil fertility conditions [11].

One example illustrating the positive effects of applying high concentrations of basaltic rock to low-fertility soil was described by Melamed *et al*. [16]. Such a study demonstrated a significant increase in pH and cation exchange capacity after twelve months of incubation, with more pronounced effects observed with smaller particle sizes and longer contact times between the material and soil. Gillman *et al.* [17] investigated the behavior of soils from seven Queensland sites incubated with different concentrations of basalt particles (0.1, 5.25, and 50 t/ha) and observed significant increases in pH, cation exchange capacity, and alkali cation levels.

In 1998, Escosteguy and Klant concluded that ground rocks have a low release of nutrients and cannot be used as the primary source of plant nutrients. However, they found that small doses tested increased potassium, calcium, magnesium, and pH. It is important to note that using rock dust is a soil fertilization practice that yields results in the medium and long term, and its effects are more durable than chemical fertilization, which is necessary for all crops [18].

Blum et al.,[19] also reported that nutrient release rates from rock particles are very slow. The effectiveness of rock particles as a nutrient source for the soil is questioned due to their low solubility, requiring large quantities for positive responses [20]. The dissolution of rock particles is a slow and complex process influenced by factors such as the chemical mineralogical composition, particle size, pH, biological activity of the soil, and weather exposure.

1.3. Benefits, challenges in previous research and application of rock dust for soil remineralization

Considered an alternative method for soil fertilization, the practice of soil remineralization improves the physico-chemical characteristics of the soil and mitigates the negative environmental impacts associated with high-cost synthetic fertilizers, which can be detrimental to small-scale agriculture. Crops can reach their maximum productivity by providing ample essential nutrients, resulting in higher yields of high-quality fruits, vegetables, grains, and other agricultural products. Furthermore, remineralized soil enhances the flavor and nutritional value of produce. The balanced supply of minerals and trace elements enriches fruits, vegetables, and herbs' taste, aroma, and sensory qualities. Research suggests that remineralization can also enhance the nutritional content of crops, ensuring they are abundant in vitamins, minerals, and beneficial phytochemicals, thus promoting human health and well-being [21]. Incorporating rock powder into the soil enhances water-holding capacity, reducing runoff and improving water retention, which is particularly advantageous in arid or drought-prone regions. Moreover, soil remineralization fosters overall soil health and resilience by supporting beneficial soil microorganisms in nutrient cycling and decomposition of organic matter. This contributes to long-term soil fertility, ensuring a balanced nutrient profile in remineralized soil, ultimately leading to increased crop yields.

Experiments and research on the utilization of powdered rocks have been conducted globally, including notable contributions by James Hutton in the eighteenth century [22]. Hutton, widely recognized as the pioneer of geological sciences, applied loam and similar rocks to enhance soil fertility on his Scottish farm. The potential of rock-derived nutrients was further emphasized by Lacroix [23], who highlighted the significance of incorporating various rocks for agricultural purposes. Graham suggested the use of plagioclase as a calcium source based on experimental data [24], while Keller advocated for the utilization of numerous rock types as sources of potassium, calcium, and trace elements, promoting the practice of stonemeal [25]. D'hotman de Vulliers recommended the application of powdered basalt rock in Congo for rejuvenating depleted soils, demonstrating significant increases in cane sugar production through field experiments [26]. Evans observed substantial dry matter production improvements with oats cultivated in pots using basaltic rock powder at different rates. Il'chenko and Guimarães highlighted the potential of Cedro do Abaeté, Serra da Mata da Corda, and Poços de Caldas rocks in Brazil [27]. Fraya conducted surveys on phonolites, which showed high levels of K_2O alteration, as potential rock powder fertilizers [28]. Kavaleridze reported that predominant basaltic rocks in southern Brazil are rich in silica, calcium, magnesium, and potassium, recommending their conversion into powder for stonemeal application [29]. Motta and Feiden found that applying 40 t/ha of basalt powder effectively raised the available phosphorus level, serving as corrective fertilization for the soil [30]. Kiehl noted positive results with basalt rock dust as a soil amendment, making it a favorable alternative for farmers, recommending the application of 50-100 t of basalt powder per hectare in poor soils to enhance fertility [31].

When considering large-scale applications, the Remineralize the Earth (RTE) program emerges as a notable and commendable initiative in the field of soil remineralization using rock dust. RTE has successfully implemented numerous projects worldwide, focusing on harnessing the potential of rock dust, such as basalt and granite to enhance soil fertility and increase agricultural productivity [32]. Through strategic application of rock dust, these projects have yielded remarkable results, including significant improvements in soil fertility, notable increases in crop yields, and enrichment of harvested produce with essential nutrients. The achievements of the RTE program serve as a compelling testament to the effectiveness of soil remineralization through rock dust. Through their dedicated efforts, the RTE initiative has not only advanced soil remineralization techniques but also raised awareness about the crucial role of soil health and the significance of rock dust in promoting sustainable agriculture. Indigenous farming communities worldwide have long recognized the benefits of incorporating rock minerals, such as volcanic rock dust, into their agricultural practices. These traditional approaches have contributed to sustainable food production, enhanced soil fertility, and increased resilience in challenging environmental conditions. By harnessing the natural mineral properties of rock dust, indigenous farmers have revitalized crucial nutrients in the soil and enhanced its quality. This has allowed them to grow crops resilient to drought, pests, and diseases, showcasing their resourcefulness and ingenuity [33]. Furthermore, organic farms in the United States and Europe have successfully embraced soil remineralization as an integral part of their agricultural practices. These farms have reported significant enhancements in soil health, nutrient availability, and crop yields by integrating rock minerals into their soil. Incorporating rock minerals promotes a balanced nutrient profile, improves soil structure, and supports the activity of beneficial microorganisms. Consequently, organic farms implementing soil remineralization experience improved soil fertility, increasing crop productivity and overall sustainability [34].

While soil remineralization using rock minerals provides numerous benefits, it is important to acknowledge the challenges and limitations associated with this practice. One major challenge is the cost of obtaining and applying rock mineral amendments. High-quality rock minerals can be expensive, especially for large-scale treatment of land. Transportation and application costs can further add to the overall expenses. Another challenge is the necessity for long-term application and monitoring. Soil remineralization is not a one-time solution but an ongoing process that requires regular application and monitoring to maintain optimal nutrient levels in the soil. The rate of mineral breakdown and nutrient release varies depending on factors like soil type, climate, and microbial activity. Regular soil testing and analysis are crucial to ensure balanced mineral ratios and sufficient nutrient levels for plant growth and productivity. Achieving a proper balance of mineral ratios is essential for optimal plant growth. While rock minerals contain a wide range of essential minerals, considering the ratios in which these minerals are present is important. Imbalances in mineral ratios can negatively impact on plant health and potentially lead to nutrient deficiencies or toxicities [34].

1.4. Micronized volcanic rock as a potential mineral derived fertilizer

In recent years, micronized volcanic rock has become as a valuable mineral-derived fertilizer for soil remineralization [21]. Micronization technology involves finely grinding natural rock into micron-sized particles, typically ranging from a few micrometers to tens of micrometers (Figure 1). Specialized equipment such as ball mills or jet mills are utilized in this process to achieve the desired particle size. Compared to natural rock dust, micronization significantly increases the surface area of the volcanic rock, facilitating greater contact between the soil and mineral particles. This expanded surface area plays a crucial role in improving the effectiveness of volcanic rock as a fertilizer by enhancing nutrient release and availability to plants. The micronized particles establish closer contact with the soil, enabling the minerals to weather and release essential nutrients over an extended period gradually. This slow-release characteristic ensures a sustained nutrient supply to plants, reducing the risk of nutrient leaching and optimizing nutrient uptake efficiency. Additionally, micronization aids in the breakdown of complex mineral structures within the volcanic rock, making the nutrients more accessible to plant roots [35]. Consequently, using of micronized volcanic rock as a fertilizer promotes robust plant growth, increased crop yields, and soil fertility.

(A) (B) (C)

Figure 1. Commercial azomite rock of Azomite Mineral Products, Inc – USA (adapted from website [35]) : (A) Azomite Micronized D_{90} < 74 µm, (B) Azomite Field Grade 74µm < D_{90} < 3 mm, (C) Azomite Granulated D_{90} > 3 mm.

Micronized volcanic rock has positively impacted soil health and crop yield, leading to increased research efforts dedicated to this subject in recent years. Various approaches can be employed to apply micronized rock to the soil, depending on the specific needs and characteristics of the agricultural system [36]. One method involves directly applying micronized rock to the soil surface, which can be incorporated into the topsoil through mechanical means such as tilling or harrowing. This ensures physical contact between the minerals and the soil, facilitating gradual breakdown and nutrient release. Another approach is to mix rock minerals with compost or organic matter before applying them to the soil. This method promotes nutrient integration and enhances the organic matter content of the soil, thereby improving its structure, moisture retention, and nutrient-holding capacity. In some instances, micronized rocks can also be applied as foliar sprays directly onto the leaves of plants. This method allows for the direct absorption of minerals by the foliage, supplementing the plants' nutrient uptake and supporting their overall health. Determining the optimal application rates and timing of rock minerals depends on soil composition, crop type, nutrient requirements, and local climatic conditions. Conducting soil tests to assess nutrient deficiencies and determine the appropriate application rates is crucial.

Investigating powdered rock as a potential fertilizer, considering nutrient content, release, economic viability, and market potential, remains a global research necessity. Therefore, this study aims to characterize the micronized porous basalt rock sourced from Nghe-An province, Vietnam, with regard to the reference of commercial azomite rock. We carried out different materials analysis and test to assess the nutrient release properties of this basalt rock and its potential to contribute macro- and micro-nutrients for enhancing soil fertility. Furthermore, this research aims to pave the way for future studies on utilizing such micronized basalt rock as a substitute for chemical fertilizers.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Vocanic rocks and chemicals

The porous basalt rock (Figure 2-A) is currently used in the building materials industry, serving as mineral additives and lightweight aggregates. It is characterized by a gray-brown color, interconnected porous structure, and an approximately 10 - 50 cm diameter. This type of basalt is formed through the rapid cooling of volcanic basalt lava with air infiltration. It possesses a high water absorption capacity and tends to break easily upon slight impact. In Nghe An province, the distribution of pumice basalt is concentrated in Nghia Dan district, with estimated reserves ranging from 70 to 100 million tons.

(A)

(B)

Figure 2. (A) Porous basalt rock from Nghe-An province; (B) High energy ball mill developed by Sai Gon Nanomat Co., Ltd .

To prepare the micronized basalt material, it undergoes a preliminary crushing process to reduce its size to 0.1 - 1 cm after being washed with tap water. Subsequently, the material is ground in a high-energy ball mill machine at Saigon Nanomaterials Co., Ltd. The grinding process takes approximately 45 minutes and utilizes stainless steel balls designed for ultra-fine grinding of powdered materials. Such an industrial-scale ball mill machine (Figure 2-B) consists of four steel containers and is employed for this purpose. The resulting mixture after grinding forms a colloidal suspension containing a small quantity of organic dispersant (polycarboxylate ether-PCE), allowing the suspension to flow easily and be extracted from the container using a diaphragm pump. Commercial azomite micronized (D_{90} < 74 µm), sourced from Azomite

Mineral Products, Inc – USA, was used without further purification. The experiment involved grinding this micronized azomite in the high-energy ball mill machine, similar to the process used for basalt rock. Overall, the porous basalt rock exhibits characteristics similar to commercial azomite rock, being soft and easily grindable.

Distilled water (pH = 7.8) was used in the dissolution method of micronized rock in water. Citric acid ($C_6H_8O_7$, 99.9 %) procured from Xilong was utilized at analytical grade without additional purification in the leaching test.

2.2. Experimental methods

Various analytical techniques were employed to characterize the ground basalt rock materials. The stability across different batches of colloidal samples was checked using Brunauer–Emmett–Teller (BET, Quantachrome NOVA 2200E) surface area analysis. The particle size and elemental composition were determined through Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) using the Hitachi S-4800 FE-SEM. X-ray diffraction (XRD, EMPYREAN - PANalytical) was used to identify the mineral composition, and X-ray fluorescence spectrometers (XRF, ARLADVANT'X - ThermoScientific) determined the percentage of oxides in fine powder samples. The ICP-MS method (Inductively Coupled Plasma – Mass Spectrometry) was used to quantify the elemental composition in the raw materials and extracted solution samples. These analytical methods provided comprehensive insights into the properties, composition, and stability of the basalt rock materials.

The water dissolution method of micronized rock was adhered to the guidelines outlined in EN 12457-2:2002. The leaching test by using acidic solutions are meant to reproduce the soil environment during the assimilation of nutrients by plant roots as highlighted in study of Ramos et al.,[15]. Various factors, including temperature, extraction solution type, solid/solution ratio, number of extractions, stirring speed, particle size, and pH, influence the nutrient release process in the extraction solution. Notably, pH plays a significant role, often characterizing the acidic environment near the roots of secretory plants, facilitating nutrient dissolution. The experiment of nutrient leaching employed a 2 % wt citric acid solution as the extraction medium, with continuous pH monitoring (pH = 2.2). The solid/distilled water dissolution ratio remained fixed at 1 g/100 ml, and Erlen flasks were shaken for 30 minutes (with acid solution) or 1440 minutes (with distilled water) to promote the dissolution process (Figure 3-A). Subsequently, the extracted solution samples underwent vacuum filtration (Figure 3-B) and were stored stably for 4 hours before quantitative analysis of K, Ca, and Al elements using the ICP-MS method.

(A) (B)

Figure 3. (A) Solubility of micronized basalt rock in acidic solution after 30 minutes of shaking time, (B) Solution under vacuum filter for ICP-MS analysis.

3. RESULTS AND DISCUSSIONS

3.1. Results of analysis of micronized basalt rock

The specific surface area measurement of the ground basalt suspension sample yielded a value of 41.11 m^2/g, with a high confidence level. This indicates a significantly larger specific surface area than the ground limestone sample mentioned in our previous publication (16 m^2/g) [37]. The average particle size equivalent is estimated to be in the micro-nanometer range, which aligns with expectations considering the softer and more easily crushable nature of porous basalt rock.

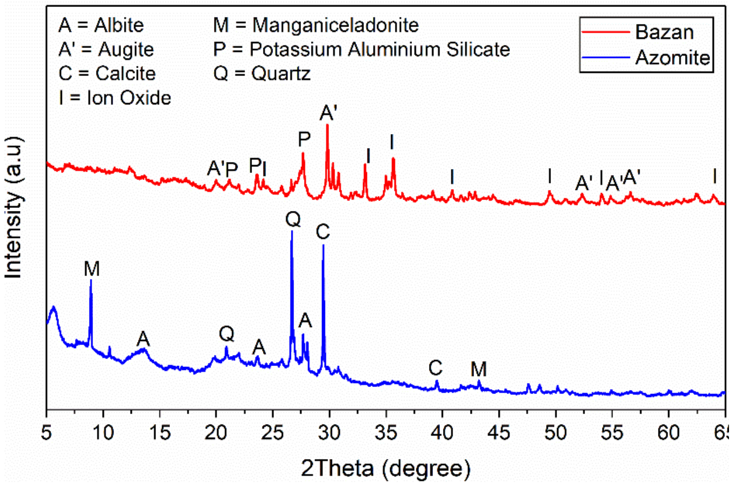

Figure 4. XRD spectrum of basalt rock from Nghe An province and commercial azomite rock.

Figure 4 reveals the primary mineral components of the porous basalt rock sample as Augite, Potassium Aluminum Silicate (mica), and Iron oxides. Mica, belonging to the alkaline feldspar group, exhibits low resistance to weathering processes, making it prone to dissolving nutrients into the environment. Augite, a mineral from the Pyroxenes group, exhibits limited stability in the environment and can release Mg, Fe, Ca, and facilitate the formation of new minerals. In contrast, the Azomite rock sample consists of Quartz, Albite, Manganiceladonite, Calcite, and Manganiceladonite. Albite, similar to mica mineral, belongs to the feldspar group. Quartz and calcite are commonly known for their calcium and silicon components contribution.

Table 2. Result of oxides composition (wt.%) by XRF analysis.

	Oxides (%wt)													
Rock samples	SiO_2	Al_2O_3	K_2O	CaO	Fe_2O_3	Na_2O	MgO	TiO_2	BaO	MnO	P_2O_5	SrO	ZrO_2	Cl
Commercial azomite	70.00	13.20	7.12	4.29	2.10	1.52	1.01	0.30	0.15	0.11	0.41	0.83	0.55	0.20
Bazalt	40.70	21.00	3.25	8.04	16.70	1.39	2.80	3.78	0.27	0.25	1.14	0.21	0.11	0.05

Referring to Table 2, the main oxide compositions of the two volcanic rocks include SiO_2, Al_2O_3, K_2O, CaO, Fe_2O_3, Na_2O, and MgO. Basalt exhibits a lower SiO_2 content (40.70 %) compared to the reference of Azomite (70.00 %). This difference can be attributed to the mineral composition of Azomite rock, which contains Quartz (SiO_2) and Albite ($NaAlSi_3O_8$), while the basalt used in the study contains mica (alkaline feldspar). Basalt rock demonstrates higher contents of CaO (8.04 % vs. 4.29 % by weight) and Fe_2O_3 (16.07 % vs. 2.10 % by weight), as well as MgO (2.80 % vs. 1.01 % by weight), compared to the reference of Azomite rock. Notably, the potassium oxide content in Azomite rock is significantly higher than in basalt rock (7.12 % vs. 3.25 % by weight).

Table 3. Result of elemental compositions by ICP-MS analysis.

	Elemental compositions (by ppm)									
	Ag	Al	As	B	Ba	Be	Bi	Cd	Co	Cr
Commercial azomite	0.43	15863.78	2.00	225.61	259.72	0.49	21.76	-	1.51	186..29
Bazalt	1.20	27377.89	1.73	216.24	333.18	0.70	0.76	-	12.77	184.74

Cs	Cu	Ga	Ge	In	K	Li	Mg	Mn	Mo	Na	Pb
1.88	3.93	35.95	0.16	0.01	9981.48	10.16	2798.01	321.58	6.23	2633.43	8.19
0.16	13.20	55.64	0.41	0.03	2806.49	2.72	16149.49	590.09	1.34	1542.46	2.39

Rb	Se	Si	Sr	Ti	Tl	U	V	Zn	Ca (%wt)	Fe (%wt)
42.02	-	557.52	53.67	333.53	0.17	0.75	7.68	25.65	0.57	8.60
8.58	-	543.44	161.39	4482.65	0.05	0.41	55.91	39.67	1.64	1.98

Table 3 reveals key distinctions between azomite and basalt rock. Azomite has three times more potassium (K) than basalt. Basalt contains higher secondary elements, calcium (Ca) and magnesium (Mg), than azomite. While the ICP-MS analysis indicates higher iron (Fe) content in azomite, the XRF and XRD results imply a significant presence of iron oxide traces in basalt rock. We will revisit this point later in the discussion. Basalt rock also has more copper (Cu) and manganese (Mn) than azomite. Both samples contain potentially harmful aluminum (Al), with basalt containing a significantly higher amount. This high Al content in basalt rock can limit its use in plant applications.

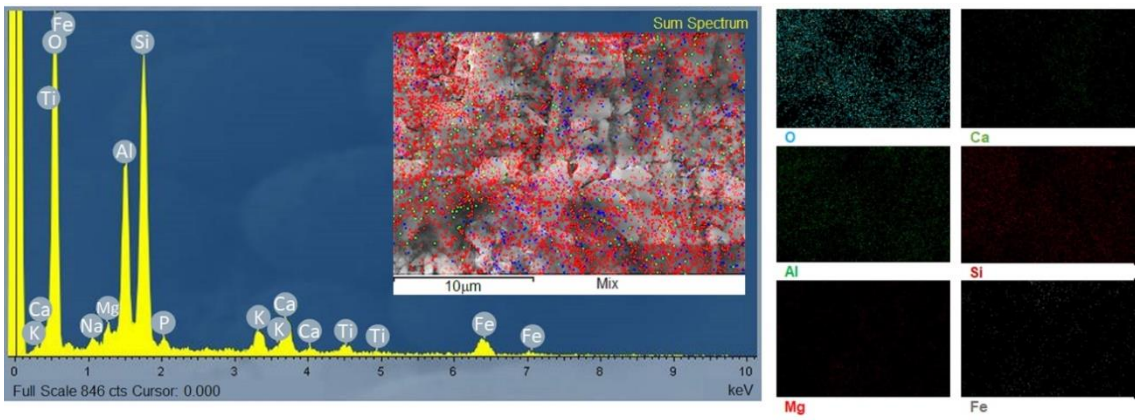

Figure 5. SEM/EDS spectrum of basalt rock from Nghe An province and chemical elements distribution.

Table 4. Elemental composition (wt.%) estimated by SEM/EDS analysis.

	Chemical elements (wt.%)									
Rock samples	O	Na	Mg	Al	Si	P	K	Ca	Ti	Fe
Commercial azomite	52.54	0.96	0.55	6.04	31.80	-	4.94	2.25	-	0.92
Bazalt	53.42	1.26	1.25	10.14	17.29	0.73	2.15	2.71	2.87	8.18

The SEM image reveals a good distribution map of different elements on the cutting surface of the basalt rock sample (Figure 5). Mass percentages of elements in the basalt rock sample are presented in Table 4, estimated through SEM/EDSs spectra. Among these, O has the highest mass percentage (53.24 %), followed by Si (17.29 %), Al (10.14 %), Fe (8.18 %), Ti (2.87 %), Ca (2.71 %), K (2.15 %), Na (1.26 %), Mg (1.25 %), and P (0.73 %). Compared to the azomite rock sample, the basalt sample shows higher levels of Al, Mg, Ca, and Fe, alongside lower levels of K and Si, aligning with XRF analysis results. While there are discrepancies in elemental contents reported by ICP-MS, including Na, Si, Ca, and Fe especially, a careful analysis of XRD and XRF spectra reveals a higher iron oxide content in basalt compared to azomite. Furthermore, Azomite's producer indicates relatively low levels of iron oxide and iron content by ICP-OES [38]. The variations in compared values stem from the fact that SEM/EDS estimated values were derived from the detection spectrum on the surface image. Consequently, based on the comparison of main elements like K, Si, Ca, Mg, and Fe, the porous basalt sample exhibits higher concentrations of secondary and micronutrient elements, whereas the azomite sample has a greater macronutrient composition. However, it's crucial to take into account the solubility of these elements, as it directly influences their capacity to supply nutrients to plants.

3.2. Results of nutrient leaching in the extracted solution

The dissolution test results in distilled water (pH = 7.8) reveal that commercial azomite rock exhibits higher solubility than basalt rock for elements K and Ca. Conversely, basalt rock demonstrates higher solubility for element Al. However, considering the total element content in the sample, the concentrations of dissolved K, Ca, and Al in the distilled water solution over 24 hours are very low for both rocks samples. Thus, despite the fine grinding, the release of nutrients can be considered slow. In the acid solution dissolution test (pH = 2.2), a lower pH of the extraction solution leads to higher nutrient content dissolved in the extract within the same timeframe. The acidic solutions enhance the conversion capacity of nutritional elements in volcanic rock as it becomes more susceptible to weathering. This finding aligns with the conclusive analysis conducted by Plata et al. [39].

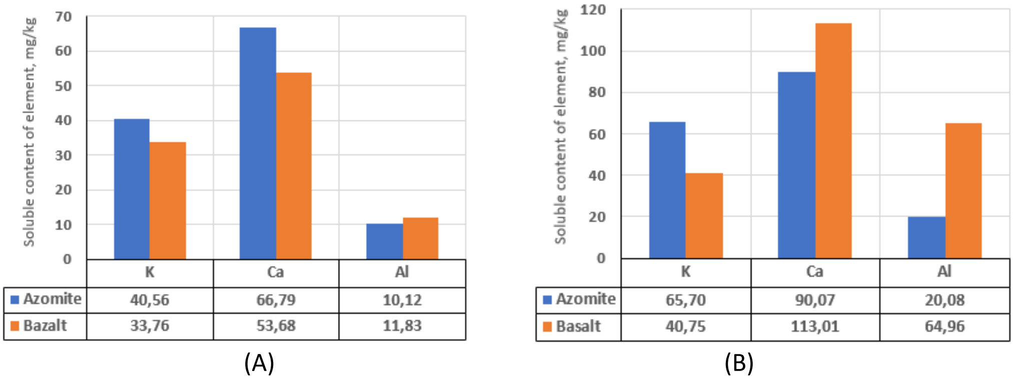

Figure 6. (A) Solubility content of K, Ca, Al elements in distilled water, (B) Solubility content of K, Ca, Al elements in acidic solution.

The dissolution results under identical conditions revealed the notable differences between the two rock samples. Commercial azomite rock exhibited superior solubility for the element K compared to basalt rock, mainly due to its significantly higher K content, three times that of basalt rock. Conversely, basalt rock showed higher dissolution results for the elements Ca and Al in the extraction solutions compared to commercial azomite rock. These findings align with the elemental composition analysis, confirming that basalt contains higher amounts of Ca and Al elements than commercial azomite rock (Figure 6). Consequently, the solution analysis results can be deemed reliable and consistent with the elemental composition of the two rock samples.

It is worth noting that the element K belongs to the group of primary macronutrients and exhibits high solubility. Meanwhile, Ca is also classified as a secondary macronutrient, and Al is considered harmful to plants. Therefore, when evaluating the ability of the rock samples to provide nutrients, commercial azomite rock stands out for its higher concentration of the macronutrient K compared to basalt rock. Conversely, basalt rock provides substantial amounts of the secondary macronutrient element Ca and even the harmful element Al, surpassing commercial azomite rock samples. This characteristic of basalt rock can be perceived as both advantageous and limiting when considering its use as a fertilizer for plants.

4. CONCLUSIONS AND FUTURE WORKS

In conclusion, this article encompasses a comprehensive literature review and experimental investigation on using volcanic rock powder as a sustainable alternative fertilizer for soil remineralization in agriculture. From this study, several key findings and recommendations emerge, warranting further attention and future research:

- Recognizing the critical role of primary and secondary macronutrients and micronutrients in crop nutrition is essential for selecting appropriate fertilizers and quantities to prevent soil depletion. Volcanic rock dust, with its rich nutrient composition, has historically proven effective in maintaining soil fertility and enhancing crop yields. Despite challenges in reducing chemical fertilizer usage, the global interest in rock powder as an alternative is growing. Scientists and practitioners are exploring its potential, aligning with sustainable agricultural practices and the demand for high-quality agricultural products. Utilizing rock powder-derived materials and fertilizers not only enhances food security but also reduces reliance on imported chemical fertilizers, supported by advancements in technology for producing functional fertilizers from this resource.

- Basalt rock has emerged as a popular research subject for mineral fertilizer applications. Utilizing high-energy ball mill equipment developed by Saigon Nanomaterials Co., Ltd., we have successfully processed porous basalt rock (from Nghe-An province) into micro-nanometer particles, enhancing nutrient release efficiency. The results of compositional analysis and elemental content in extraction solution reveal that both basalt and commercial azomite rock contain minerals belonging to the alkaline feldspar group, with key oxide components including SiO_2, Al_2O_3, K_2O, CaO, Fe_2O_3, Na_2O and MgO. Although finely ground, both rocks exhibit a limited ability to dissolve nutrients in distilled water. However, in an acidic solution (pH=2.2), the commercial azomite rock sample demonstrates higher dissolution of potassium (K) elements, while the basalt sample exhibits higher dissolution of calcium (Ca) and aluminum (Al) elements. Consequently, basalt samples may have limitations in providing macronutrients (K), but offer advantages in supplying secondary macronutrients (Ca) compared to commercial azomite rock.

- Based on the preliminary findings discussed earlier, additional research is warranted to comprehensively assess the influence of finely ground particle size on the solubility of other essential secondary macronutrients and micronutrient components, such as magnesium (Mg), iron (Fe), and copper (Cu). Furthermore, experimental studies should be conducted to examine the growth response of plants when fertilized with micronized basalt rock, progressively scaling up the experiments in both laboratory and field settings. These investigations will yield valuable insights into the effectiveness and potential advantages of employing micronized basalt rock as an alternative fertilizer.

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