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Volcanic Soils: Their Characteristics, Management Practices, and Potential Sollution for Water Pollution

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Abstract

Volcanic soils are formed from materials originating from volcanic eruptions, and with various pedogenic processes occurring, volcanic soils have unique physical, chemical, and biological characteristics. This paper aims to review the characteristics of volcanic soils, constraints, management practices, and their potential as adsorbents for contaminants. The paper was based on secondary information using a systematic review. The studies carried out include identifying manuscripts, analyzing report data, critically assessing the topic, and combining the results of relevant published manuscripts. The issues raised include data on volcanic soils, management practices, water pollution, and using volcanic soils as an environmentally friendly adsorbent. Colloidal compounds in the clay fraction of volcanic soils generally contain active Al and Fe compounds, allophane, imogolite, ferrihydrite, or Al/Fe-humus complex, and together with opaline silica. The volcanic soil material produces a pool of Al and Fe solid phases with high reactivity, which contributes to the unique physicochemical properties of Andisol. The main problem chemically is the high adsorption of phosphate and nitrate ions which causes the fertilization process to be inefficient. The main problem affects the adsorption of phosphate and nitrate on agricultural lands, so fertilization becomes inefficient. However, the high reactivity of volcanic soils can be used as a basic pollutant adsorbent. This is quite a promising opportunity, given the wide distribution of volcanic soils, so this resource is a very prospective candidate as an adsorbent material in water purification.

Keywords: Volcanic soils, Allophane, Imogolite, Adsorbent

1. Introduction

Indonesia is a region that has interesting geological conditions. Indonesia was formed by the collision of large tectonic plates and was located at the confluence of three world plates: the Eurasian, Pacific, and Australian. These plates move and collide with each other, resulting in the formation of volcanoes and volcanic trails in Indonesia. The existence of fire lanes in the territory of Indonesia causes several regions of Indonesia to have mountainous and hilly landforms with gentle to steep slopes. The nature and behavior of the volcano affect the natural conditions and living things around it. The nature of the volcanic material causes differences in land, soil, water, and topography characteristics.

Volcanic soils are essentially fertile, especially those with low to high base saturation. With physical characteristics such as aeration and high porosity, it is easy for plants to penetrate the soil, and the nutrients in the form of alkaline cations are sufficiently available for plants. Although volcanic soil is not the largest land area in Indonesia, it has unique characteristics and is suitable for most upland agricultural cultivation plants, and is inhabited by many residents. Volcanic soil often experiences material renewal every time because it is located in an active volcanic mountain path.

Many volcanic soils are cultivated for large-scale plantation crops and some for the production of seasonal crops in Indonesia. Volcanic soils spread across agricultural cultivation areas, limited production forests, protected forests, national parks, wildlife reserve forests, and convertible forests [26]. Most of the volcanic soil in agricultural cultivation areas has been used for plantations, food crop farming, horticultural crop farming and also rice fields. Volcanic soil has the potential for seasonal and annual crops. Besides that, it can also be used for secondary crops and rice or protected forests. However, several soil types that develop from volcanic parent material, such as andisols, have a significant problem with high ion adsorption. The high reactivity in the clay fraction of volcanic soils also causes high uptake of ions, especially phosphate and nitrate, which makes fertilization activities less effective.

The phenomenon of ion adsorption reactions on soil clay particles occurs when chemical compounds, either in the form of ions or molecules, interact with the surface of soil particles. When these chemical compounds are near the surface of the soil particles, the surface charge of the particles can attract and hold the chemical compounds. Soil adsorption reactions involve interactions between chemical compounds and the surface of soil particles. These chemical compounds become adsorbed on soil particles and are no longer freely available in the environment. Adsorption is a process in which particles in the soil absorb and store chemical compounds from the surrounding environment, such as nutrients, heavy metals, and pesticides. Soil adsorption can affect the availability of nutrients to plants, but these soil particles can minimize the negative impact of chemical pollutants on the environment. Based on this, soils with high ion adsorption reactivity can be used as contaminant adsorbents in waters.

In water and waste treatment, adsorbents are often used as an alternative that is more environmentally friendly and economical than other treatment technologies such as chemicals or oxidation processes. However, using adsorbents can also affect the effectiveness of water and waste treatment processes depending on the type of adsorbent used and the environmental conditions in which the treatment process is carried out.

Colloidal compounds in the clay fraction generally contain active Al and Fe, allophane, imogolite, ferrihydrite, or Al/Fe-humus complex together with opaline silica. The volcanic parent material produces a pool of Al and Fe solid phases with high reactivity, which contributes to the unique physicochemical properties of Andisols [20]. The high reactivity in the clay fraction of volcanic soils also causes high uptake of ions, especially phosphate and nitrate, which makes fertilization activities less effective. On the other hand, the characteristics of reactive soil minerals also have the potential to be used as a contaminant adsorbent. This paper aims to review the characteristics of volcanic soils, constraints, management practices, and their potential as adsorbents for contaminants. The high reactivity of these soils is an essential characteristic in various aspects of agriculture and the environment, especially in wastewater management. This paper aims to review the characteristics of volcanic soils, constraints, management practices, and their potential as contaminant adsorbents.

2. Material and Methods

This paper is based on secondary information using a systematic review. The studies carried out include identifying manuscripts, analyzing report data, critically assessing the topic, and combining the results of relevant published manuscripts. The issues raised include data on volcanic soils, management practices, water pollution, and using volcanic soils as environmentally friendly adsorbents. The data is presented in table form and as a comparison to describe important points in the discussion of volcanic soils. This paper was prepared using peer-reviewed publications related explicitly to the Characteristics of Volcanic soils. On the other hand, the preparation of this paper uses the literature published in the article to enrich the discussion on issues concerning the subject being assessed for which publication date is not considered as a criterion.

3. Results and Discussion

3.1 Characteristic of Volcanic Soil

Volcanic soil is one of the most fertile and productive soils compared to other soils. This soil is formed from weathered material from volcanic eruptions, which is fertile and contains high nutrients. Volcanic soil types can be found around the slopes of volcanoes. This soil comes from a volcanic eruption that erupts and releases three types of materials, the form of solid, liquid, and gas. The solid material that comes out is volcanic ash, sand, and dust, while the liquid material is lava. Dust and sand on volcanic soil will cover the soil surface and then experience rejuvenation. The dust covering the soil layer will decay over time, mixed with the soil, and then the formation (genesis) of new soil begins. The phenomenon of the Pacific Ring of Fire can show how much energy works and influences the nature around it, including the occurrence of volcanoes resulting in land formation. The term volcanic soil is used to refer to soil formed from pyroclastic material, which is material that comes out of a volcanic crater during an eruption. Pyroclastic materials contain much volcanic glass, both those that are still loose or have not been removed, such as volcanic ash and tephra, or those that have undergone transportation, such as lava deposits and volcanic alluvium. Most volcanic soils have a unique material content that is inherited from the parent material. In its classification, volcanic soil is better known as Andisol.

Volcanic soil or andosol has a black or dark brown color, crumb structure, high organic matter content, and is slippery (smeary). Andosols are found in non-solid volcanic materials at an altitude of 750 to 3,000 m above sea level (masl). Andosol is soil type with a mollic A horizon, an umbric that may be found above the cambic B horizon, or the okhric A horizon and has no other diagnostic horizon (unless covered by 50 cm or more of new material). In depths of up to 35 cm or more having one or both of; (a) the bulk density (at 1/3 bar of water content) of the fine-earth fraction (less than 2 mm), is less than 0.85 g cm-3 and the exchange complex is predominantly amorphous material, (b) 60% or more is vitric volcanic ash, ash or other vitric proclastic materials in the dust, sand, and gravel fractions [4]. Andosol found in Indonesia has thick mollic or melanic horizons (more than 50 cm). In the classification of Soil Taxonomy (Soil Survey Staff 2014), this trait is commonly referred to as the Pachic trait, which can be used to differentiate sub-group categories, for example, Pachic Melanudands. Volcanic soils or Andosols have parent material in the form of volcanic ash or tuff, which is rich in volcanic glass and easily weathered minerals. Results of weathering from the parent material of volcanic tuff will form a nanoclay fraction containing aluminosilicate mineral allophane-nanoballs with a diameter of 3.5-5 nm and imogolite nanotubes with a diameter of 1-3 nm with a pH-dependent charge [25].

Volcanic glass is an amorphous (non-crystalline) material that comes from remnants of magma that have undergone imperfect crystallization. The volcanic glass content in the soil reflects the degree of weathering and mineral reserves contained in the soil. The further the level of weathering, the less available volcanic glass is because it has weathered into crystalline minerals or secondary minerals. Volcanic activity can provide different ash deposits. Volcanic deposits are in the form of phreatomagmatic and magmatic with strict alternation [9]. The dark characterizes phreatomagmatic deposits to light gray form volcanic ash, laminated to thin layered structures, hollow (vesicles), containing accretionary lapilli. Magmatic deposits are composed of alternating layers of scoria and volcanic ash.

3.1.1. Chemistry of Volcanic Soils

Soils formed from volcanic materials have chemical, physical and biological properties that are unique and have a positive value on soil fertility, thereby supporting optimal plant growth. Volcanic soils have chemical properties that can reflect the influence of the parent material and the degree of weathering. The role of these chemical properties is very large in determining whether the soil is fertile or not. The most prominent elements in regulating the chemical reactions of volcanic soils are active organic matter, aluminium (Al), iron (Fe), and silica (Si). The main forms of active Al and Fe are allophane, imogolite, and ferrihydrite. Volcanic soils or Andosols in Indonesia have the highest Al content compared to Fe and Si [25]. This can be seen from the nature of the andosol soil parent material, which develops from acidic parent material (liparit), which has the highest Al content. In contrast, soil that has a low Al content develops from alkaline parent material (Basalt). Andosols soil has a high retention of phosphate, and andosol soil derived from the parent material liparit has a high P retention.

In Indonesia, volcanic soils or andosols have a fairly wide pH range, namely between 3.4 to 6.7, with an average of 5.4. The range of pH 4.5 to 5.5 and 5.5 to 6.5 indicate that amorphous clay minerals dominate the andosol soil. The volcanic soil in West Java has acidic, and this is because the parent material of the soils in Java Island from the east to the heaviest changes from alkaline to acid type. Volcanic soils, which are classified as acidic, limit macronutrient content, especially phosphate, because it is bound by soil minerals. The phosphorus content in the soil is relatively stable, so losses due to leaching relatively never occur. Phosphorus is very reactive, binding with Al and Fe and forming complex compounds so that the amount of phosphorus available is limited [16]. The low available P can be caused by the clay mineral content of the soil, namely allophane minerals. The presence of allophane in the soil is inversely proportional to the availability of nutrients, especially phosphorus and nitrogen.

CEC of volcanic soil varies from 6.5-52.0 cmol (+) kg^{-1} or varies from very low to very high with an average value of 23.8 cmol (+)kg^{-1}. CEC of volcanic soils has a positive correlation with soil C-organic content. The higher the C-organic content, the higher the soil CEC. Volcanic soils have a high level of fertility except for phosphate retention. However, low C-organic content may indicate a decrease in the fertility of volcanic soils [25]. Soil from volcanic ash is classified as fertile, so it is suitable for agricultural land. According to the Agricultural Research and Development Agency, volcanic soils that are located on land with flat to wavy and undulating terrain can be used for seasonal agriculture (food and vegetables), which has a slope of less than 15%, covering an area of 1,166,452 ha or 21 .62%. Whereas for land with slopes of more than 15 to 45%, plantation crops such as tea, coffee, quinine, and cinnamon are suitable for agricultural cultivation.

3.1.2. Physical Properties of Volcanic Soils

Volcanic soils have unique physical properties which are associated with high allophane minerals. Allophane is one of the materials that contribute to the low bulk density of volcanic soils by developing porous soil structures. This mineral has many holes that allow the entry and exit of water molecules. Most of the volcanic soil textures are moderate and vary from clay loam to sandy loam [4]. Besides having a high organic matter content, low bulk density, high water holding capacity, and high total porosity, volcanic soils are also loose in nature with less plastic consistency and are not sticky. Volcanic soil, when wet, is oily (greasy) and polished (smeary). In addition, volcanic soil also has irreversible dry properties.

In general, volcanic soils have low bulk density, moderate to low availability of water for plants, high melting limit, low plasticity index, difficulty to disperse, and irreversible changes that occur. Another important physical property of volcanic soil is its macro and microstructure [28]. The macrostructure is usually found in the A horizon, characterized by a typical granular structure formed from mountain granulation. This structure is different from the usual granular structure because the structural unit is very resistant to the destructive power of rainwater. The results of volcanic eruptions in volcanic soil areas emit volcanic ash. Volcanic dust contains alkaline cations, which can increase the pH and macronutrients (N, P, K, Mg, Ca, S) in the topsoil, which first experiences washing and weathering with volcanic ash.

3.1.3. Biological Characteristic of Volcanic Soils

In the soil, there are various types of organisms. Some of the organisms in the soil are useful, some are annoying, but some are not useful and do not bother either. Volcanic soil has a hollow element; this structure will provide space for roots to grow and develop properly. Volcanic soil has macro and microfauna populations, including earthworms and soil microorganisms such as protozoa and nematodes. Earthworms play a role in fertilizing and loosening the soil, mixing the soil, and improving soil air conditioning so that water infiltration becomes better and more accessible for roots to penetrate. In a soil ecosystem, various microbes live, survive, and compete to obtain space, oxygen, water, nutrients, and other necessities of life, both symbiotic and non-symbiotic, giving rise to various forms of interactions between microbes [25]. The population of microbes is one of the important parameters which can predictions land productivity because microorganisms are the primary breaker to determine differences in soil biological properties, which are approached by measuring soil respiration, total bacterial population, and total fungal population. Soil biological properties are different for each type of soil and land use.

3.2 Allophane and Imogolite on Volcanic Soil

Minerals are the main constituents of soil and play an important role in determining soil's chemical and physical properties. Minerals are an important indicator of weathering, so the presence or absence of a type of mineral in the soil can be used as an indicator of the process of soil formation. Organic matter content, soil depth (horizon), and soil pH can influence minerals that form other than the parent material. Soil minerals are divided into primary minerals called sand fraction minerals and secondary or clay fraction minerals. Secondary minerals or clay minerals have a fine size (<2 μm). Clay minerals are secondary minerals that have a role in soil fertility (Simamora et al., 2015). The characteristics and amount of clay minerals influence the soil's chemical characteristics, such as cation exchange capacity (CEC), the amount of nutrient fixation, and others. The structure and type of clay minerals can determine their properties and affect soil characteristics. Identification of mineralogical properties is essential in agriculture because it is related to the fertility potential of the soil [15].

Colloidal compounds in the volcanic clay fraction generally contain active Al and Fe in allophane, imogolite, and ferrihydrite, or Al/Fe-humus complex together with opaline silica. The volcanic parent material produces a pool of Al and Fe solid phases with high reactivity, which contributes to the unique physicochemical properties of Andisols [20]. Allophane and imogolite are found together as the main components of the clay fraction from pyroclastic materials such as volcanic tuff and pumice [1]. Both are also sometimes found in soils that develop from other parent materials, for example, basalt to basaltic saprolite. Allophane and imogolite are the largest components of the B horizon in podzolic soils worldwide. Both allophane and imogolite are clay formed in the same environment and have the same chemical structure but have different morphologies. The chemical structure of allophane and imogolite is presented in Figure 1.

Allophane is the most reactive clay mineral because it has a large surface area and many active functional groups. Allophane has a very high specific surface area and is relatively dominated by micropores when compared to aluminosilicates such as montmorillonite. Allophane is a group of crystalline alumino hydrous silicate minerals with various chemical compositions. Allophane consists of plane hollow, spherical irregular particles with an area diameter of about 35 to 50 Å and a wall thickness of 0.7 to 10 Å. Allophane does not have a specific chemical composition and displays various concentrations of AL and Si, namely the atomic ratio Al: Si = 1:1

to 2:1 [19]. Al: Si atomic ratios of less than 1:1 and greater than 2:1 can occur in nature but have not been isolated and characterized. Allophane which contains a lot of Al (Al: Si = 2:1), is a type of allophane that is often found in volcanic soils. Allophane which is rarely found in volcanic soils, is in the hick moisture regime, namely allophane Si (Al: Si = 1:1). Allophane minerals have properties such as cation and anion exchange, adsorption of organic and inorganic compounds, and acidity derived from the functional groups of silanol (Si-OH) and alumuniol (Al-OH and $AlOH_2$; -OH and $-OH_2$ single coordinates which are influenced by organic acids or other ingredients [27].

Allophane minerals in volcanic soils come from the weathering of volcanic ash, especially volcanic glass, in humid conditions. Then, good drainage conditions will form imogolite through the desilication process from allophane. The continuous washing process will form minerals like halloysite, kaolinite, and gibbsite. Allophane and imogolite minerals will interact with organic materials, like humic acid and fulvic acid, resulting in a complex form. Humic acid has a negative charge, therefore, its functional group is able to interact with allophane which has a positive charge from organo-aluminosilicate, which can bind a negative charge [19]. Humic acid absorbed by allophane can be identified by calculating the C solution (Walkley-Black method) in equilibrium. The difference between the amount of humate given and the amount of C (humic indicator) in equilibrium is the amount of C or the amount of humic acid absorbed by allophane.

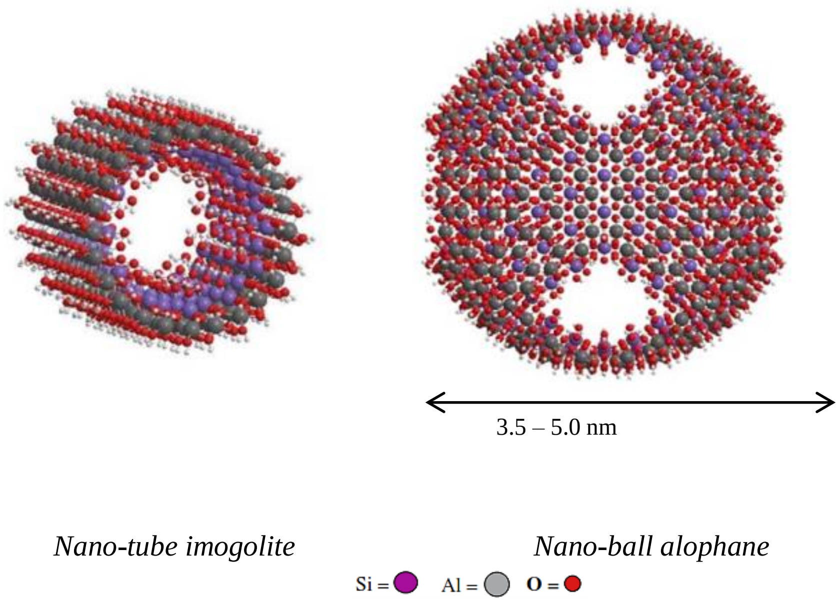

Figure 1. Chemical strucuter of *nanotube imogolite* and *nanoball alophane*.

Allophane and imogolite both have a high surface area, which is 700-1500 m^2g^{-1}, with pH-dependent charge characteristics, and the opening of the (OH)-Al-(OH_2) group on the perforation wall causes a high affinity to bind water, metals, organic molecules and other soil minerals [29]; [17]. Allophane is naturally an aluminosilicate hydrate mineral with a Si/Al molar ratio varying from 0.5–1.0, and its particle units are hollow spheres with an outer diameter of 3.5–5 nm and a wall thickness of 0.7–1.0 nm [10]; [29]. The outer layer of allophane consists of gibbsite-like sheets with Si-tetrahedral interiors and having open pores in the wall structure with a diameter of about 0.3 nm [1]. X-ray observations showed that allophane is close to amorphous, but an electron microscope showed that allophane has a structure with a chemical composition of (1-2)SiO_2•Al_2O_3•(2-3)H_2O. Some researchers refer to it as "nanocrystalline" [11],[15].

Allophane has a very high specific surface area, and micropores relatively dominate it compared to aluminosilicates such as montmorillonite. The specific surface area of allophane observed using the ethylene glycol monoethyl ether (EGME) method ranged from 700–900 m2.g-1 [5]. The validation results showed that the total surface area of allophane was 1.114 m^2.g-1 with an inner layer thickness of 0.7 nm [1]. The chemical structure of allophane nano-balls in nature has a diameter of ± 4.25 nm. The presence of allophane which is very abundant in nature, is very prospective and cheaper to use as an adsorbent to remediate phosphate-polluted waters compared to synthetic adsorbents such as fluorolith [32].

In contrast with allophane, imogolite has a tubular nanostructure with 1.0 nm inner diameter. Then, the outer diameter has 2.0 nm. Imogolite is a short and long-range order mineral. The electron diffraction pattern confirmed that imogolite is a uni-dimensional crystal. Imogolite is referred to as a paracrystalline mineral, meaning that crystallization only occurs in one direction. The surface area of the imogolite was determined using the ethylene glycol method of 1,000 $m^2.g^{-1}$ [5]. The tube structure of the imogolite is several nanometers long and consists of $Al_2(OH)_3$•SiO_3OH with a Si/Al ratio of 0.5. The basic structure of imogolite is mostly of gibbsite layers that connected from the sides by orthosilicic acid via oxygen and three Al atoms [1]. The critical properties of imogolite are the high surface area and anion adsorption capacity due to the gibbsite sheets on the outer layer.

The clay minerals, like allophane, imogolite, ferrihydrite, and the Al/Fe-humus complex. They are of great concern to researchers because they give andic properties to Andisols. However, most clay minerals develop from non-volcanic materials such as gibbsite, kaolinite, vermiculite, smectite, and Crystalline Fe-oxides hematite and goethite cristobalite are also found in Andosol [30]. Allophane, imogolite, and ferrihydrite are formed by the combination of Al, Si, or Fe, which is released from volcanic glass or other minerals (mainly feldspar or various mafic minerals) by rapid dissolution and hydrolysis by carbonic acid (H_2CO_3) typically under slightly acidic and humid conditions [29] [30].

3.3 Management Issues and Practices in Volcanic Soils

Landforms from the process of volcanic eruptions have different products which affect a landform's formation. This landform is dominantly formed because processes influence it from volcanism's endogenous (inner) energy. Different landforms make the use of volcanic soil different. Volcanic soil farming systems are diverse, ranging from food to plantation crops. The management of plantation commodities on volcanic soils is generally carried out professionally with significant investments and is market-oriented. Steep slopes are not a severe problem because the management has paid attention to environmental sustainability. Vegetable cultivation activities on volcanic land on sloping slopes are carried out intensively [3]. However, they need to pay attention to soil and water conservation aspects. Land with this topography is prone to soil and environmental damage. Intensive cultivation activities also cause high erosion.

Most upland vegetable cultivators still need to properly apply soil and water conservation techniques. That is partly because applying conservation techniques is complicated, requires a long time, and requires many workers. Without soil and water conservation on volcanic land, the area will often experience erosion and landslides. Vegetable farmers generally make bunds in the direction of the slope, and this makes the soil easier to erode because the water flow is concentrated at specific points so that the damage is more serious. High erosion can increase sediment concentration in surface runoff, which can enter water bodies such as rivers, reservoirs, and irrigation canals, resulting in extensive sedimentation.

This sedimentation results in the siltation of water bodies and the more fertile water hyacinth plants, making it difficult to control their growth. In addition, the elements needed by plants, such as nitrogen, C-organic, phosphate, potassium, etc., will be lost and carried away by surface runoff. Several things can reduce the quality of land, namely farming that is not more profitable, decreased land productivity, pest and disease explosions, and loss of community ability to build social capital so they cannot control environmental damage. Most of the volcanic soil in agricultural cultivation areas has been used for plantations, including tea, Arabica coffee, quinine, apples, oranges, and cinnamon, as well as forestry plants such as *Eucalyptus urophylla*, *Casuarina* sp., Dryland food crop farming (upland rice, and crops), horticultural crops (vegetables and fruits), and rice fields.

The volcanic soil that occupies the mountainous area is a productive agricultural area, especially horticultural crops, both vegetables, and seasonal and annual fruit plants. One of the production centers of vegetables and fruits. Arabica coffee is one of the most widely planted plantation commodities in highland volcanic soils. This commodity is an important export commodity and a source of foreign exchange for the country. Arabica coffee production potential in Indonesia can reach 1.5 tons/ha/year, although its productivity is still low at around 0.77 tons/ha/year. Many other plantation crops are cultivated in the volcanic mountains of tea plants. Indonesia is the seventh largest tea producer in the world, after China and India, which are in first and second place. Provinces that produce the most tea and have the largest planted area in Indonesia are West Java, Central Java, West Sumatra, and North Sumatra [2].

Volcanic activity can have a positive or negative impact on the surrounding population. This activity can harm the surrounding community because volcanic ash and flowing land can carry materials several kilometers away. Besides that, volcanic eruptions emit thick dust that can cover thousands of plants. As is the case with the eruption of Mount Semeru in 2021 and 2022. This can result in losses in food production. Apart from harming several aspects, volcanic ash contains nutrients that plants can utilize so that it can improve soil fertility in the long term. The sulfur content in eruption ash can provide additional nutrients for plants so that nutrients are not yet available or have low availability for plants and do not contribute significantly to the supply of plant nutrients.

Volcanic eruption activity is a very dynamic phenomenon that does not always stay at one point. One of the volcanic eruptions occurred on Mount Guntur in 1960. This activity produced various forms of volcanic land, especially lava flows (lava flow). This flow flows from its origin and southeast to form other formations, such as a crater on the summit and pyroclastic plains on the lower slopes. This volcanic mountain activity can produce lava plains obtained from fluvo-volcanic processes, which originate from fluvial processes mainly pyroclastic materials, such as ash, sand, gravel, and chunks of rock that are carried away by water currents during rains [9].

3.4 Volcanic Soil as Adsorbens

Need for clean water is necessary for humans. Humans need clean water for daily needs, industrial needs, city sanitation, etc. The need for clean water quality must be an essential concern because water has been polluted by various kinds of waste from various human activities. That causes the water quality to decrease, as well as the quantity. Due to industrial, household, and agricultural wastewater pollution, water crises have also occurred in almost all of Java Island and parts of Sumatra, especially in big cities. In addition to the decline in water quality due to pollution, the water crisis also occurs from a lack of water availability and erosion due to upstream logging and changes in land use upstream and downstream.

In addition, water pollution can be caused by various things and have different characteristics, such as 1. Increased nutrient content can lead to eutrophication. 2. Organic waste, such as sewage water, causes an increase in the demand for oxygen in the receiving water, which leads to reduced oxygen and can severely impact the entire ecosystem. 3. Industry discharges various pollutants into its wastewater, such as heavy metals, organic toxins, oil, nutrients, and solids. The wastewater has a thermal effect, especially that power plants release, which can also reduce oxygen in the water.

One alternative that is used to overcome water pollution is the use of adsorbent materials. Unfortunately, although the adsorbents effectively absorb contaminants, the materials used are still synthetic. In addition, in terms of price, synthetic adsorbents are still relatively expensive. An alternative that can be used is material from volcanic soils. The unique characteristics of volcanic soils, mainly due to the reactivity of the clay minerals and the high adsorption of anions and cations, these soils have the potential as natural adsorbent materials.

Volcanic soil originating from the volcanic tuff of Mount Salak-Indonesia has been extracted in the form of nano-clay material, then applied to phosphate waste on a laboratory scale [23]. The results of the study by Sudadi et al 2019, volcanic tuff (nano-clay) extraction had a significant effect on phosphate adsorption with an equilibration time of 48 hours with a maximum adsorption capacity of 117.54 mg/g (Table 1). The reason for the variation in the size of the nano clay component between Nc_3 and Nc_4 is attributed to variances in the level of crystallization. The Nc_4 layer is closer to the parent material layer than Nc_3, which serves as the base material for Nc_3. This makes *Nc4* less weathered and crystallized than *Nc3*, resulting in a lower degree of weathering and crystallization for the mineral fraction of Nc_4 than Nc_3. When the degree of weathering and crystallization is higher, the resulting nano clay fraction is smaller. This, in turn, leads to a higher specific surface area and reactivity. Conversely, the bond energy required for kn3 to adsorb phosphate is lower than *Nc4*. Hence the maximum phosphate adsorption or absorption of phosphate *Nc3* is higher than *Nc4*.

Table 1.
Adsorption maximum and bond energy of nano-clay extracted from volcanic tuff

	Adsorption maxima (mg/g) on Equilibration time (hour)			Bonding Energy (L/g) on Equilibration time (hour)		
	12	24	48	12	24	48
Nc3	76.48*a**	92.10*ab*	117.54*c*	0.34*l*	0.28*j*	0.26*jk*
Nc4	50.17*e*	59.52*fg*	71.99*h*	0.37*q*	0.32*p*	0.27*o*

*The maximum entrapment value and bond energy followed by the same letter in the same line shows no significant difference at the 5% t-test level [23].

Furthermore, Elhadi (2000) extracted nanoscale allophane minerals from the volcanic soil clay fraction (<0.2 µm) in Tottori and Kumamoto - Japan, using a 28 kHz ultrasonic technique. Allophane with a low Al/Si ratio. The volcanic material in the form of volcanic ash can also be used as an adsorbent for Methylene blue with an adsorption capacity of up to 6.9 mg/g [18].

Table 2.
Some experiments on volcanic materials as adsorbents

Type of Adsorbate	Information
Phosphate [12]	Allophane nano-balls were extracted and used to study the characteristics of phosphate adsorption. The amount of adsorbed phosphate increases with increasing concentration of phosphate in equilibrium. The increase is steep at lower equilibrium phosphate concentrations, then the curve gradually P becomes nearly plateau at higher equilibrium phosphate concentrations.
Molybdate [6]	Allophane samples were separated from inner part of pumice grains collected from different places in Japan. The strong interaction between molybdate anion and positively charged allophane was concluded as electrostatic one followedby ligand exchange reaction between Mo and aluminol groups. At higher Mo concentrations, more than 0.2 mM, shape of the isotherms were linear indicating further polymerization reaction on

	the allophane surfaces, and partial destructionof allophane structure was observed as Si and Al release with the adsorption.
Copper [7]	Allophane nano-balls were extracted from several volcanic ash sources and used for copper adsorption experiments and to study the charge characteristics of allophanes.
Zinc [8]	Allophane nano-balls were extracted from several sources of volcanic ash and used for Zinc adsorption experiments and to study the charge characteristics of allophane.
Fluoride [13]	Allophane was used for fluorite adsorption experiments and compared with synthetic adsorbents.
Arsenate [21]	Allophane nano-balls were extracted from volcanic materials and used to study the mechanism of arsenic adsorption.
Methylene Blue [18]	Volcanic ash soil materials with modifications were used to adsorb methylene blue and were compared to pure volcanic ash materials.
Nitrate [24]	Volcanic tuff originating from Mount Salak, extracted as the nano-clay material, is then used to adsorb nitrate in palm oil mill effluent.

From the results of some of the studies carried out in various places (table 2), it has been proven that volcanic soils can be used as a base for natural adsorbent materials. This is inseparable from the presence of nano-scale materials, namely allophane and imogolite. The adsorption mechanism of contaminants such as arsenate is similar to that of phosphate adsorption. The results of research on arsenate, in which lab-scale experiments using the Langmuir isothermal equation model, found that there are sites one and site two on allophane minerals, where site II has a higher arsenate adsorption capacity compared to site 1, but the bond energy from sit 1 is significantly higher than site II [21]. This can be explained by the presence of aluminol groups Al-OH and Al-OH_2, which are responsible for the adsorption process. Allophane is known to form aggregates with many unit particles, creating outer and inner surfaces on and in the aggregates [31]. Arsenate reacts with the aluminol group in the aggregate (site I) because this site has greater adsorption energy, then after saturation of site I arsenate reacts with the aluminol group on the outer surface of the allophane (site II).

4. CONCLUSION

Volcanic soil has unique physical, chemical and biological characteristics. It is an essential natural resource to be managed sustainably. Physically related constraints such as landforms can be overcome by a farming model with the principles of soil and water conservation. The unique characteristics of volcanic soils are characterized by the presence of allophane and imogolite minerals. These characteristics are related to the pH-dependent charge and the high reactivity to ions in the soil. The main problem in terms of utilizing volcanic soil for farming is the high adsorption of phosphate and nitrate ions which causes the fertilization process to be inefficient. Fertilization inefficiencies are overcome by balancing the use of organic fertilizers and the addition of beneficial microbes. However, the very high reactivity of volcanic soils can be used as a more environmentally friendly pollutant adsorbent. This is a quite promising opportunity, considering that the distribution of volcanic soils in Indonesia is quite wide so this resource is a very prospective candidate as an adsorbent material in water purification. Future prospects are not only its use as an adsorbent but as a recycled material for wastes containing macronutrients such as nitrate and phosphate so that they can be reused as recycled fertilizer or seed coatings. Thus the use of volcanic soil is not only a resource to be explored but is also sustainable in agriculture and the environment.

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