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Changes of Soil Chemistry Characteristics of Tephra Mount Anak Krakatau-Indonesia, Through Leaching Experiment

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ABSTRACT

Studying the weathering process in pristine volcanic materials is crucial as this process will determine further soil characteristics. Mount Anak Krakatau is reported as one of the fastest-growing volcanoes. This volcano erupted powerfully in December 2018, ejecting tons of volcanic materials. These materials are considered pristine and unweathered tephra. Hence, a leaching experiment can be one of the crucial methods to predict further soil characteristics formed as climatic factors. Tephra sampling was conducted on 13 Augustus 2019 or eight months after the massive eruption of Mount Anak Krakatau in December 2018. Tephra samples were leached by deionized water (H_2O), oxalic acid ($H_2C_2O_4$) 0.02 M, and citric acid ($C_6H_8O_7$) 0.02 M (solvents) for 90 days. pH of tephra increased approximately from (3.95– 4.99) to (5.12–8.11). Organic-C rose about 0.2 to 1 point higher than organic-C of tephra before the leaching experiment. The increasing value of organic-C was predicted to increase CEC (Cation Exchange Capacity) (2.13–5.36 $cmol_c$ kg^{-1}). After the leaching experiment, the tephra's surface was weathered clearly as an impact of solvents and the growing of algae.

Keywords: Entisols, Indonesia, leaching experiment, Mount Anak Krakatau, tephra, the weathering process

INTRODUCTION

Volcanic soils investigation in Indonesia has been conducted by many soil scientists (Supriyo et al., 1992; Van Ranst et al., 2004, 2008; Fiantis et al., 2010, 2011, 2016; Utami et al., 2019; Anda and Dahlgren, 2020; Setiawati et al., 2020; Fiantis et al., 2021). Most of these studies were conducted in developed volcanic soils and focused on the relationship between the physico-chemistry of soil characteristics (bulk density, base saturation, and P-retention) with the mineralogy composition. However, research conducted in very young volcanic soil needs to be improved, particularly in Mount Anak Krakatau, due to the isolated location and the massive volcanic activities. Recent studies exploring the soil and tephra of Mount Anak Krakatau were reported by Fiantis et al., (2019), Setiawati et al., (2020), and Fiantis et al., (2021).

Research on very young volcanic soils is crucial as it demonstrates the soil formation process through the changes in soil chemical properties during the weathering process. After Mount Anak Krakatau 2018's eruption, the first study about the change in soil chemical properties was done by Fiantis et al., (2021). This research reported that the pH value of Mount Anak Krakatau samples collected at 63 days and 82 days after the eruption was 5.9 (std.dev.0.6), the CEC of the materials was very low but variable (3.11 ± 2.3 $cmol_c kg^{-1}$) and the cations easily leached in order were (Mg>Ca>K>Na) as extracted successively with H_2O and CH_3COONH_4. While climate plays a crucial role in weathering process, research focusing on changes in soil chemistry characteristics of tephra Mount Anak Krakatau through a continuous leaching experiment design is needed. Furthermore, this research explored the changes in soil chemistry characteristics of tephra Mount Anak Krakatau through a leaching experiment in a given period. When tephra samples were taken, Mount Anak Krakatau was still in its first weathering stage. Hence, leaching experiment data, including the changes of tephra characteristics after the leaching period, can be valuable information to predict the characteristics of the soils in the future as a function of climate and weathering process.

The leaching experiment provides primary data explaining how soil develops its unique characteristics. Interaction of tephra after deposition with H_2O or other acids is one of the critical geochemical processes (Fiantis et al., 2010). This process releases several essential nutrients required for plant growth and indicates the chemical weathering process. Climatic factors, particularly precipitation, and temperature, dramatically influence soil properties by affecting types and rates of physical, chemical, and biological weathering processes (Dahlgren et al., 1997). Indeed, the weathering process study is the first step to determining soil formation and the changes in soil properties.

Weathering parent materials by water and organic acid is the crucial cycle in soil formation. These interactions are the essential geochemistry in the stage of parent materials weathering and releasing essential nutrients needed for plant growth and the environment (Fiantis et al., 2010). Organic acid found in soil solutions and groundwater plays a vital role in weathering primary minerals, where chelation is implicated as a weathering mechanism (Sohalscha et al., 1967). Chemical weathering of soil minerals is a sustaining and dynamic geochemical process enhancing the supply of base cations determining the long-term availability of plant nutrients and the chemical status of the soil (Duan et al., 2002). Therefore, this paper reports the changes in soil chemistry characteristics of tephra Mount Anak Krakatau as a function of the chemical weathering process through a leaching experiment.

MATERIALS AND METHODS

Geological Setting

Krakatau volcanic complex lies in the Sunda Strait (Indonesia) between Java and Sumatra islands. It belongs to the volcanic arc related to the subduction of the Indo-Australian plate beneath the South-East Asian plate (Deplus et al., 1994). Krakatau Mountain (Rakata, Danan, and Perbuatan) erupted violently for the first time on August 25–27th, 1883 (after being dormant for ± 200 years). This massive eruption remains half of Rakata Island and is recorded as one of the two deadliest volcanic events in historical times after the great Tambora eruption in 1815 (Verbeek, 1884; Francis and Oppenheimer, 2004). Mount Anak Krakatau is an active cone that built up in the caldera of Krakatau volcano after the 1883 cataclysmic eruption that appeared for the first time on sea level in 1930 (Zen, 1970; Ninkovich, 1979; Yokohama, 1987; Deplus et al., 1994; Bani et al., 2015).

Anak Krakatau is considered one of the fastest-growing volcanoes on Earth (Hoffmann-Rothe et al., 2006). This volcano ejects a more comprehensive compositional range of materials than other volcanoes in the Sunda Arch subduction system (Harjono et al. 1989). Furthermore, before of December 2018' eruption, the volcano had been vegetated by several pioneer plants such as *Barringtonia asiatica*, *Terminalia catappa*, *Casuarina*, and *Ipomoea pescaprae* and already had about 340 m a.s.l height. However, the eruption of December 2018 has completely changed the morphology of the volcano, including reducing the volcano's height (±130 m a.s.l) and sweeping all the vegetated areas.

Fieldwork and Sample Collection

Tephra sampling was conducted on 13 Augustus 2019 (eight months after the eruption of December 2018). As the condition of the field study was hazardous, with many loose materials and the probability of the volcano experiencing unpredictable eruption, tephra samples were collected quickly. It took approximately five to six hours in the field to take the tephra sample, where the leading teams of the survey were divided into four teams. Four tephra sampling sites were selected along the northern slope of Mount Anak Krakatau using topo sequence soil survey methods with four intervals of elevations (Figure 1). Each location was symbolized by P (profile of tephra): (1) (P.I (± 10 m a.s.l); P.II (± 25 m a.s.l); PIII (± 40 m a.s.l); PIV (± 47 m a.s.l). Tephra samples were collected in every depth (layer) of site observation. There were four depths in P.I; five in P.II; six in P.III; and four in P.IV (Figure 1). The color of tephra was assessed on field moist soil using a soil Munsell color chart (Table 1). Undisturbed soil samples for bulk density analysis were done only at the first depth.

Design of Leaching Experiment

Tephra samples were leached by deionized water (H_2O), oxalic acid ($H_2C_2O_4$) 0.02 M, and citric acid ($C_6H_8O_7$) 0.02 M (solvents). Deionized water was used to represent rainfall in weathering process, while $H_2C_2O_4$ and $C_6H_8O_7$ were used to represent the effect of organic acid produced by metabolic-organism during the weathering process.

The leaching experiment was arranged for 90 days through a design imitating the weathering

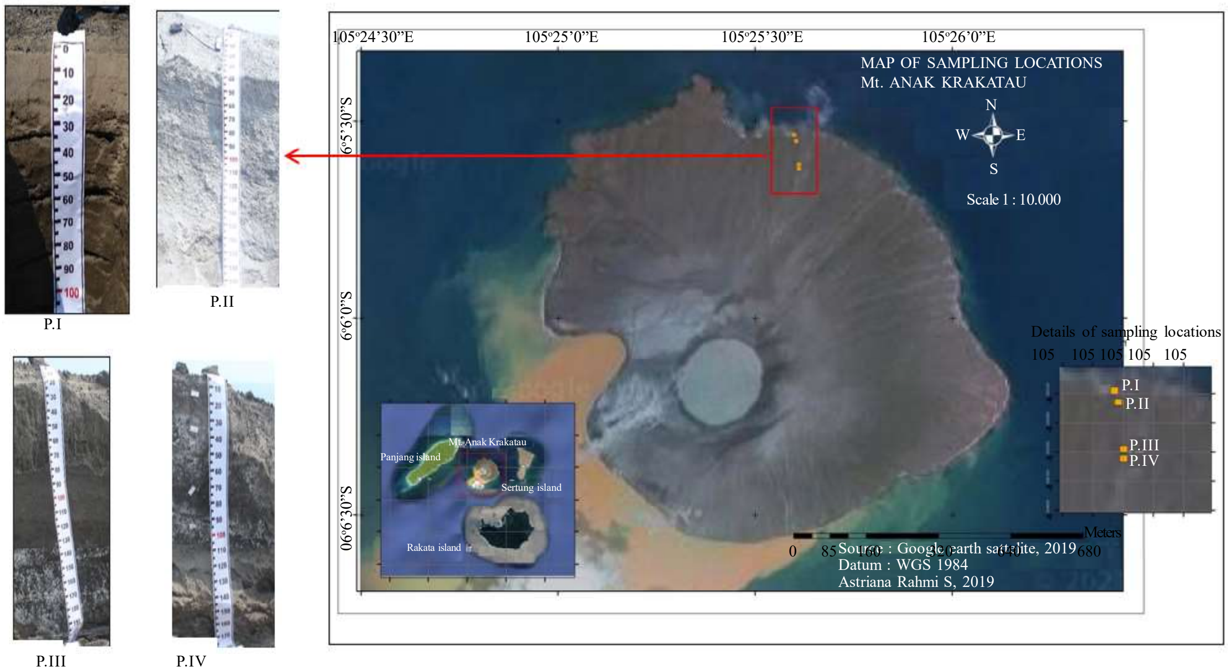

Figure 1. Sampling locations and the tephra profiles.

process in nature (Figure 2). Transparent PVP pipes with 3 inches of diameter were used as leaching columns. 250 g of tephra sample (in each depth) was placed into the columns and arranged systematically according to its order in nature. Infusion hoses were used to arrange the speed and volume of the leachate. The leaching experiment started at 9.00 AM to 3.00 PM, and the accommodated extract solution was collected and transferred to other bottles. The environment

Table 1. Description of sampling location and samples' color of tephra Mount Anak Krakatau.

Tephra profile	Geographic location	Depth (cm)	Elevation (m a.s.l)	Tephra color	Description
I	06°05'33"S and 105°25'36,2"E	0-35	10	5Y 3/2	dark grey
		35-60		5Y 2.5/2	black
		60-88		5Y 2.5/2	black
		88-100		5Y 2.5/2	black
II	06°05'32,1"S and 105°25'35,9"E	0-56	25	7.5Y 5/1	grey
		56-85		2.5Y 5/1	grey
		85-106		2.5Y 3/1	very dark grey
		106-143		2.5Y 4/1	dark grey
		143- 170		2.5Y 4/1	dark grey
III	06°05'36,6"S dan 105°25'36,6"E	0-50	40	2.5Y 5/1	grey
		50-67		2.5Y 5/1	grey
		67-103		2.5Y 5/1	grey
		103-125		2.5Y 2.5/1	black
		125-139		5Y 2.5/1	black
		139-200		5Y 2.5/1	black
IV	06°05'37,3"S dan 105°25'36,6"E	0-23	47	5Y 6/1	grey
		23-47		5Y 5/1	grey
		47-87		5Y 3/1	vey dark grey
		87-100		5Y 2.5/1	black

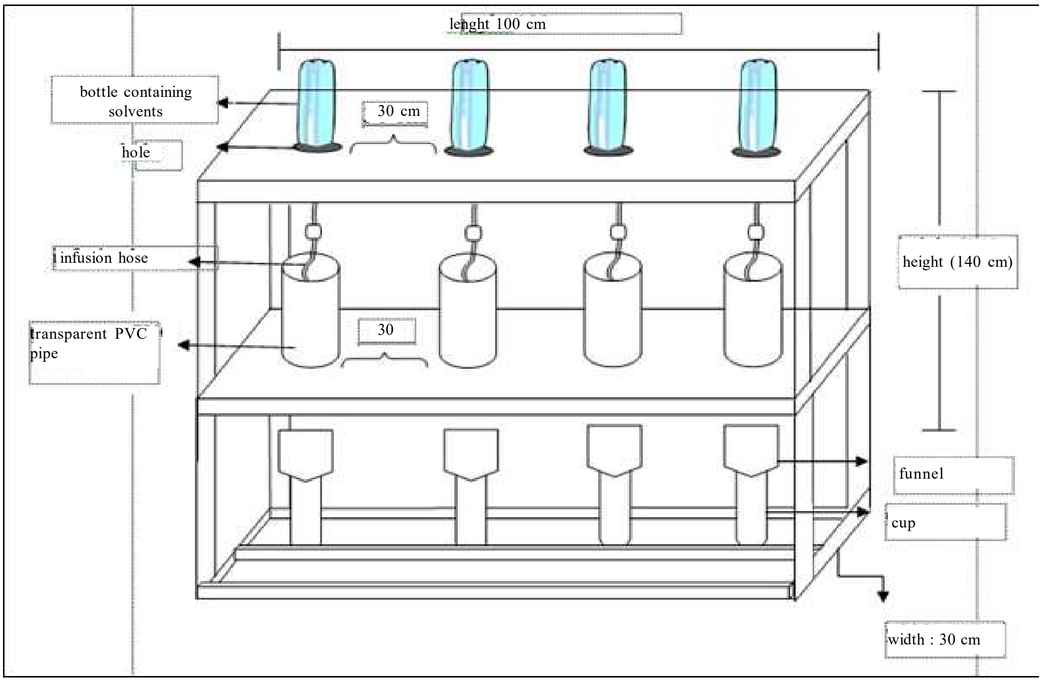

Figure 2. Leaching experiment design.

temperature was set at room temperature (± 25 ºC). Afterward, the volume of the leachate was measured before being transferred to another bottle for element measurement. Ca and Mg elements were measured by Atomic Absorption Spectrophotometry (AAS), while K and Na elements were measured using a flame photometer.

Sample preparation and analytical techniques Physical and chemical analysis

Samples were collected in each depth of the tephra profile. The samples were immediately packed in a polyethylene bag that was tightly closed. All samples were air-dried, sieved to pass a 2-mm (without crusting the particles), and applied methods recommended for volcanic soils (Mizota and van Reeuwijk, 1989). Some parts of the samples were kept for water content analysis as a correction factor. All soil analyses were done with three times repetitions.

The sieve and pipette method determined nine fractions of particle size distribution analysis (Sudjadi et al., 1971). Bulk density was determined on an oven-dry weight basis (gravimetric). The pH of tephra was measured by electrode potentiometric using a 1:2.5 ratio (soil: solution) in H_2O (pH H_2O) and KCl I N (pH KCl) (Tan, 2005). CEC was determined by leaching 1 M CH_3COONH_4 pH 7.0. Exchangeable base cations (Ca, Mg, K, and Na) were removed by leaching with 1 M of ammonium acetate solution (pH 7.0), then leachate analysis using AAS for Ca and Mg and flame photometer for K and Na. Phosphate retention (P-retention) was determined by the method of Blakemore et al. (1981). The potential of K_2O, Na_2O, CaO, and MgO was measured by extraction of HCl 25% and measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). Organic-C content was determined by Walkey and Black wet combustion method (Allison, 1965).

The content of pyrophosphate-extractable Al and Fe (Alp and Fep) and oxalate-extractable Al and Fe (Alo and Feo) were measured by ICP-OES. The content of ferrihydrite was determined using the expression: % ferrihydrite = 1.7 " Feo (Childs, 1985). Cations (K, Na, Ca, Mg, and Fe) from the leachate were measured by AAS. SEM-EDX analysis used ZEISS/EVO MA 10 instrument. Samples were prepared by adhering the tephra grain (≤ 2 mm) samples onto an Al sample holder with double-sided tape and coated with gold.

RESULTS AND DISCUSSION

Particle size distribution and chemical properties of tephra Anak Krakatau volcano before leaching experiment.

Particle size distribution and bulk density of tephra Mount Anak Krakatau

Particle size distribution is an essential soil parameter, influencing numerous soil properties (Zimmermann & Horn 2020), such as CEC, base saturation, and soil surface charge. Soil particle-size distribution was similar among the four sampling sites, dominated by a fine sand fraction (0.25 - 0.1 mm) (Table 2)—the percentage of fine sand fraction in P.I was 26.21 - 32 %; PII (11.49 - 25.97 %); PIII (16.46 - 24.20 %); and PIV (17.98 - 21.97 %). The coarse sand fraction (1 - 0.5 mm) had the lowest percentage compared to other fractions. The increase in depth is followed by an increase in coarse sand fraction: P.I (16.55 - 23.33 %); PII (21.21 -

Table 2. Particle size distribution and bulk density of Mount Anak Krakatau's tephra after December 2018 eruption

Profile number	Depth (cm)	Particle size (%)									BV	
		2 - 1 mm	1 - 0.5 mm	0.5 - 0.25 Mm	0.25-0.1 mm	0.1 - 0.05 mm	50-20 µm	20-10 µm	10 - 2 µm	2 - 0 µm	Depth (cm)	g cm^{-3}
P. I	0-35	11.50	22.59	19.27	27.71	15.37	2.33	0.45	0.47	0.31	0-20	1.58
	35-65	5.08	17.70	20.30	32.93	20.66	2.23	0.42	0.36	0.30		
	65-88	4.95	16.55	19.57	32.26	23.30	2.18	0.43	0.40	0.37	21-40	1.50
	88-100	11.06	23.33	20.02	26.21	16.03	2.24	0.41	0.40	0.30		
P.II	0-56	17.55	24.45	16.80	18.96	18.04	2.85	0.51	0.47	0.37	0-20	1.61
	56-85	14.51	25.46	16.48	22.29	17.50	2.54	0.45	0.43	0.35		
	85-106	10.78	21.21	18.20	25.97	20.48	2.33	0.39	0.36	0.28	21-40	1.54
	106-143	30.46	30.41	12.44	11.49	11.72	2.38	0.43	0.39	0.28		
	143-170	19.48	29.82	17.16	16.93	12.97	2.51	0.44	0.40	0.28		
P.III	0-50	11.77	22.10	16.59	25.10	15.61	7.76	0.42	0.38	0.28	0-20	1.55
	50-67	16.46	28.56	17.63	19.56	14.28	2.41	0.42	0.39	0.29		
	67-103	10.24	27.26	20.33	24.20	14.40	2.42	0.46	0.39	0.29	21-40	1.50
	103-125	9.66	24.50	19.84	24.09	18.30	2.46	0.43	0.40	0.30		
	125-139	19.29	27.48	15.85	17.52	16.15	2.43	0.47	0.43	0.39		
	139-200	21.70	30.12	14.92	16.46	13.31	2.27	0.45	0.42	0.36		
P.IV	0-23	14.86	26.16	18.46	21.97	15.44	1.99	0.40	0.37	0.35	0-20	1.53
	23-47	16.37	26.71	16.90	21.01	16.05	1.88	0.38	0.37	0.33		
	47-87	22.54	27.92	14.88	17.98	13.39	2.12	0.43	0.39	0.35	21-40	1.43
	87-100	18.87	26.75	16.38	19.53	14.96	2.30	0.46	0.41	0.35		

(1) 2 – 1 mm: sand-fraction, (2) 1 – 0.5 mm : coarse sand (cS), (3) 0.5 – 0.25: medium sand (mS), (4) 0.25 – 0.1 mm: fine sand (fS), (5) 0.1 – 0.05 mm: very fine sand (vfS), (6) 50 – 20 µm: coarse silt (cSi), (7) 20 – 10 µm: medium silt (mSi), (8) 10 – 2 µm:fine silt (fSi) (9) 2 - 0 µm: clay (C).

30.41 %); PIII (22.10 - 30.12 %); PIV (26.16 - 27.92 %). On the other hand, the percentage of sand fraction (very coarse sand fraction) (2 - 1 mm) was low compared to that of other sand fractions. The percentage of sand-fraction fluctuated: PI (4.95 - 11.50 %); PII (10.78 - 30.46%); PIII (9.66 - 21.70%); and PIV (14.86 - 22.54 %).

As a sand fraction dominated particles sizes distribution, the weathering process of Mount Anak Krakatau is categorized in the new stage of the weathering process, where this process probably will be fast and easily weathered due to the domination of fine fraction (0.25 – 0.1 mm). Particle size distribution has a tight relationship with the rate of soil formation and could provide pedogenetic evidence (Villas et al. 2022).

The value of bulk density (D_b) was categorized as high (1.43 - 1.61 g cm^{-3}) (Table 2). The dominance of particles more than 2 mm in size (gravel) affected the high value of bulk density. In addition, as the tephra was still at the first stage of weathering, these materials were predicted to lack secondary minerals in amorphous form and organic-C, contributing to low porosity and high bulk density value. The abundance of amorphous and poorly crystalline materials and organic matter that contribute to highly stable and very well-structured soils under natural conditions contributes to the low value of bulk density (Anda & Dahlgren 2020).

Chemistry characteristic of Tephra Anak Krakatau volcano before and after the leaching experiment

General soil chemistry characteristics related to pedogenesis processes

Soil pH

In general, the pH H_2O and KCl value increased through the increasing depth in each profile—the pH H_2O at P.I was about 4.18 – 4.84; PII (4.54 - 4.98); PIII (4.55 - 4.99); PIV (4.47 - 4.53) (Table 3). The pH of KCl in PI was 3.95 - 4.03; P2 (3.98 - 4.36); P3 (4.16 - 4.72); P4 (3.92 - 4.49). There was

Table 3. General chemistry characteristics of Mount Anak Krakatau's tephra before the leaching experiment.

Profil Number	Depth (cm)	pH			CEC	Amonium asetat extract				BS
						Exc-dd	Exc-dd	Exc -dd	Exc-Mg	
		H_2O	KCl	Δ pH	$cmol_c$ Kg^{-1}	$cmol_c$ Kg^{-1}				%
P.I	0-35	4.53	3.95	- 0.58	0.25	0.00047	0.013	0.22	0.008	96.74
	35-65	4.18	4.03	- 0.15	0.26	0.00045	0.015	0.24	0.009	103.82
	65-88	4.49	3.99	- 0.50	0.27	0.00027	0.016	0.26	0.008	108.40
	88-100	4.84	3.99	- 0.85	0.29	0.00045	0.014	0.25	0.010	95.62
P.II	0-56	4.67	3.98	- 0.69	0.33	0.00037	0.008	0.35	0.009	111.86
	56-85	4.54	3.96	- 0.58	0.35	0.00047	0.009	0.38	0.008	114.68
	85-106	4.73	4.13	- 0.60	0.38	0.00024	0.012	0.40	0.005	110.43
	106-143	4.74	4.02	- 0.72	0.27	0.00019	0.013	0.46	0.004	177.58
	143-170	4.98	4.36	- 0.62	0.46	0.00024	0.013	0.47	0.008	105.95
P.III	0-50	4.83	4.16	-0.67	0.42	0.00042	0.013	0.48	0.009	120.26
	50-67	4.80	4.34	-0.46	0.63	0.00034	0.016	0.37	0.011	62.97
	67-103	4.92	4.42	-0.50	0.56	0.00029	0.014	0.38	0.008	71.22
	103-125	4.55	4.34	-0.21	0.69	0.00024	0.013	0.39	0.009	59.11
	125-139	4.99	4.36	-0.63	0.65	0.00024	0.012	0.42	0.010	67.07
	139-200	4.95	4.72	-0.23	0.61	0.00045	0.014	0.42	0.011	71.85
P.IV	0-23	4.49	3.92	-0.57	0.56	0.00037	0.014	0.29	0.006	55.43
	23-47	4.47	3.95	-0.52	0.57	0.00032	0.012	0.35	0.009	65.35
	47-87	4.53	4.49	-0.04	0.63	0.00050	0.011	0.49	0.008	80.33
	87-100	4.52	4.31	-0.21	0.70	0.0048	0.013	0.49	0.010	73.63

Note: CEC = Cation Exchange Capacity; Exc = exchangeable cations; BS = Base saturation a similar pattern between the value of pH H_2O with the percentage of clay fraction (0 - 2 µm). The pH H_2O value of Mount Anak Krakatau tephra was low compared to that of other volcanic soils or volcanic ashes in Indonesia. Fiantis (2019) reported that the pH of the volcanic ash of Mount Talang in west Sumatra was approximately 5 to 6. Anda and Dahlgren (2020) reported that the pH H_2O of volcanic soils southeast of Mount Tangkuban Perahu was 4.4 to 6.1, and the pH KCl was 4.2 to 5.6. Utami et al., (2019) reported that the pH of H_2O from soils affected by quaternary volcanic ash along a climatic gradient on Java Island was about 4.7 - 6.2, and the pH of KCl was 5.0 - 6.0. The low pH of Mount Anak Krakatau was probably caused by the volcanic material containing more sulfur and acid. Moreover, soil in the first stage of weathering is affected by the amount of reduced cations base.

Interestingly, the increase in soil pH after the leaching experiment period was significant (Table 4). The pH value of H_2O and KCl after the leaching experiment in each extraction was higher than the pH of H_2O and KCl before the leaching experiment. However, the pH value in each layer fairly fluctuated and was near neutral. The pH of H_2O extracted by H_2O was approximately: 4.47 to 7.79, with $H_2C_2O_4$ (6.35 to 8.34) and $C_6H_8O_7$ (6.10 to 7.67). Meanwhile, the pH of KCl extracted by H_2O was about 5.12 to 7.67, with $H_2C_2O_4$ (6.55 to 8.11) and $C_6H_8O_7$ (5.29 to 6.53). Overall, the amount of pH KCl was lower than pH H_2O. It indicated that the soil of Mount Anak Krakatau had a negative (-) charge after the leaching experiment.

The higher pH value after the leaching experiment was estimated to be caused by continuous leaching (90 days). Several cations and hydroxide (OH^-) have been released from the tephra complex to the surface during the leaching period. In this stage, base cations were accumulated on the surface of the tephra particle while the tephra particle started disintegrating due to the weathering process. As a result, this condition was assumed to contribute to elevating the pH after 90 days of the leaching experiment.

In addition, during the leaching period, organic acid from $H_2C_2O_4$ and $C_6H_8O_7$ had been chelating the Fe and Al as a ligand or complex reaction. Thus, Fe and Al become tightly bound and not contributing H^+ to the solution. It can be proved that the tephra pH after leaching by $H_2C_2O_4$ and $C_6H_8O_7$ was higher than the tephra leached by water due to the strength of organic acid to hold the Fe and Al. pH played a core role in the organo mineral stabilization (Niu et al., 2023)

CEC (Cation Exchange Capacity) and organic carbon

The amount of clay fraction in soil highly affects CEC content as it is related to physicochemical properties (Shoji et al., 1994). As the Anak Krakatau volcanos' tephra was dominated by a sand fraction, the CEC of tephra was very low (0.25 – 0.70 cmol kg^{-1}) (Table 3). However, Fiantis et al., 2021 reported that the amount of CEC of volcanic ash was 3.38 cmol kg^{-1} with Std.dev 2.96.

Before weathering process, tephra had a low amount of CEC due to the lack of clay particles and the domination of sand-size particles that were chemically inactive. Furthermore, the amount of CEC increases along with the increasing weathering rate affected by the presence of clay as a weathering product. Clay fraction is crucial as an inorganic-soil-colloid (Iturri and Buschiazzo, 2014). Indeed, Particles with smaller diameters have a higher surface area to mass ratio than larger particles. Before the eruption of December 2018, materials from these volcanoes had been weathered, particularly in low altitudes. Therefore, these weathered materials contributed to low CEC, approximately 0.41 - 2.03 cmol kg-1 (Setiawati et al., 2020).

In addition, the distribution of CEC in the tephra profile was influenced by the distribution of clay (2 - 0 µm) and organic carbon. Clay fraction and C organic carbon are crucial for CEC as soil colloids. As the vegetation was destroyed during the eruption, the percentage of carbon organic of tephra Mount Anak Krakatau was very low, ± 0.08 to 0.32 % (Table 3). Generally, the total of CEC/CEC_t was predominantly associated with SOM (Soil Organic Carbon), with only a minor contribution from clay minerals, as suggested by a small intercept of the linear relationship between the total of organic carbon (C_t) and the total of CEC (Gruba & Mulder, 2015).

The percentage of organic carbon after the leaching experiment increased significantly to 0.44 - 0.88 % in tephra leached by water, 0.74 - 1.05 % in tephra leached by $H_2C_2O_4$, and 0.74 - 1.10 % in tephra leached by $C_6H_8O_7$ (Table 4). It is assumed that organic-C increased more than 100 times respectively, in each solvent. During the leaching period, the microorganism (algae) that lived at the tephra surface was starting to photosynthesis and created a living cycle (Figure 7, 8, 9). Microorganisms secrete a wide range of organic compounds into the environment. However, it is widely believed that the increase of organic-C after the leaching experiment was due to the ability of

Table 4. Chemistry characteristics of Mount Anak Krakatau's tephra after leaching experiment.

Profil Number	Depth (cm)	pH H_2O			pH KCl			Δ pH			C-Organik (%)			CEC (cmol/kg)			P-Retensi (%)		
		H_2O	Oxalic	Citric	H_2O	Oxalic	Citric	H_2O	Oxalic	Citric	H_2O	Oxalic	Citric	H_2O	Oxalic	Citric	H_2O	Oxalic	Citric
	0-35	7.56	7.98	7.18	7.05	7.75	6.14	-0.51	-0.23	-1.04	0.74	0.89	0.90	3.08	3.01	3.35	85.89	87.03	86.86
	35-60	7.08	8.20	7.02	7.00	8.03	6.05	-0.08	-0.17	-0.97	0.60	0.75	1.04	3.26	3.24	3.13	83.15	85.89	86.59
P.I	60-88	7.79	7.56	7.67	7.35	7.76	6.53	-0.44	0.2	-1.14	0.59	0.74	0.84	3.22	2.29	3.57	83.49	84.73	88.38
	88-100	7.35	6.89	7.54	6.89	7.02	6.46	-0.46	0.13	-1.08	0.59	0.75	0.89	3.28	3.08	2.87	82.52	85.75	88.10
	0-56	7.40	8.34	6.78	7.68	8.11	6.00	0.28	-0.23	-0.78	0.88	0.95	0.89	3.54	3.51	2.47	83.53	84.40	86.90
P.II	56-85	7.16	8.12	6.32	7.07	7.89	5.88	-0.09	-0.23	-0.44	0.51	0.84	0.88	2.33	3.33	3.26	82.99	84.36	87.03
	85-106	4.99	7.66	6.21	5.36	7.26	5.88	0.37	-0.4	-0.33	0.69	0.74	0.89	3.20	3.20	2.35	82.92	85.47	86.90
	106-143	4.77	6.35	6.20	5.65	6.55	5.60	0.88	0.2	-0.6	0.75	0.75	0.85	3.26	3.26	3.19	84.2	85.01	86.63
	143-170	6.91	7.59	6.32	6.70	6.59	5.29	-0.21	-1	-1.03	0.59	0.75	0.80	3.00	4.00	2.93	84.18	88.15	87.16
	0-50	6.05	7.99	6.45	5.69	7.37	5.64	-0.36	-0.62	-0.81	0.44	0.60	0.83	2.67	2.67	3.42	84.11	86.27	85.43
P.III	50-67	5.44	7.76	6.76	5.12	7.24	5.69	-0.32	-0.52	-1.07	0.45	0.79	0.74	2.49	2.49	3.48	87.89	86.02	86.29
	67-103	5.83	6.90	6.46	5.36	6.80	5.80	-0.47	-0.1	-0.66	0.80	0.98	0.89	2.13	2.13	3.72	89.24	84.44	87.60
	103-125	5.21	7.10	6.10	5.39	6.99	5.68	0.18	-0.11	-0.42	0.75	0.65	0.81	2.21	2.21	5.36	83.61	83.37	85.11
	125-139	5.20	7.69	6.58	5.51	7.25	5.90	0.31	-0.44	-0.68	0.74	0.83	0.84	3.59	2.59	3.74	85.39	86.90	85.91
	139-200	6.74	8.30	6.84	6.63	7.96	6.42	-0.11	-0.34	-0.42	0.74	0.74	0.83	2.81	2.81	2.96	83.77	86.95	85.91
P.IV	0-23	5.57	8.34	6.45	6.03	8.02	5.73	0.46	-0.32	-0.72	0.80	1.05	1.10	2.27	2.27	2.94	86.12	83.83	89.09
	23-47	6.46	7.80	7.08	6.22	7.33	6.00	-0.24	-0.47	-1.08	0.75	1.04	0.89	3.71	2.71	3.84	84.24	85.26	85.96
	47-87	5.36	7.12	7.12	6.19	7.00	6.21	0.83	-0.12	-0.91	0.65	0.74	0.95	3.13	3.13	5.02	83.61	86.42	88.88
	87-100	6.39	7.00	7.20	6.09	6.89	6.35	-0.3	-0.11	-0.85	0.69	0.60	0.84	3.31	4.31	4.42	84.31	85.66	87.20

tephra (during the weathering process) to capture C from the atmosphere. Minasny et al., (2021) reported that there are two mechanisms of carbon capture: (1) through weathering and (2) through the accumulation of organic matter.

A Higher amount of organic-C after the leaching experiment contributes significantly to increasing the CE period was tephra leached by $C_6H_8O_7$ (2.35 to 5.36 $cmol_c\ kg^{-1}$), followed by $H_2C_2O_4$ (2.13 to 4.31 $cmol_c\ kg^{-1}$) and water (2.18 to 3.54 $cmol_c\ kg^{-1}$) (Table 4). Humus contains many acid groups and is an essential source of variable charge (Zhang & Zhao, 1997). These negative charges originate mainly from carboxyl groups (C-O-OH). There is a strong correlation between organic-C with the total CEC (Gruba & Mulder 2015).

Total of exchange cations and base saturation

Exchangeable cations were considerably low: exchangeable K (0.00019 - 0.048 $cmol_c\ kg^{-1}$); exchangeable Na (0.008 - 0.016 $cmol_c\ kg^{-1}$); exchangeable Ca (0.22 - 0.49 $cmol_c\ kg^{-1}$); and

Table 5. Chemistry characteristics of Mount Anak Krakatau's tephra related to soil andic properties.

Profil Number	Depth (cm)	P-Retensi	HCl 25 % extract				Ammonium acid extract			Ferrihydrite	Sodium yrophosfat extract	
			K_2O	Na_2O	CaO	MgO	%Alo	%Feo	Alo + ½ Feo	(1.7 *Feox%)	%Alp	%Fep
		(%)		(%)					(%)		(%)	
P.I	0-35	84.06	0.018	0.087	0.33	0.59	0.272	0.747	0.646	1.270	0.063	0.095
	35-60	83.71	0.008	0.086	0.32	0.7	0.164	0.850	0.589	1.445	0.247	0.171
	60-88	90.79	0.012	0.083	0.35	0.53	0.243	0.742	0.614	1.261	0.169	0.076
	88-100	88.54	0.018	0.11	0.38	0.7	0.207	0.864	0.639	1.469	0.151	0.074
P.II	0-56	85.63	0.013	0.122	0.53	0.54	0.253	0.844	0.675	1.435	0.136	0.101
	56-85	84.87	0.015	0.101	0.52	0.58	0.227	0.741	0.598	1.260	0.114	0.096
	85-106	84.86	0.017	0.102	0.46	0.62	0.210	0.740	0.580	1.258	0.099	0.073
	106-143	86.87	0.059	0.151	0.46	0.47	0.206	1.041	0.727	1.770	0.138	0.086
	143-170	87.17	0.04	0.234	0.65	0.55	0.010	0.039	0.030	0.066	0.155	0.072
P.III	0-50	84.99	0.021	0.214	0.55	0.61	0.247	0.992	0.743	1.686	0.130	0.097
	50-67	83.32	0.031	0.255	0.42	0.62	0.213	0.988	0.707	1.680	0.163	0.090
	67-103	84.48	0.022	0.328	0.48	0.59	0.194	0.893	0.641	1.518	0.120	0.077
	103-125	89.29	0.03	0.743	0.43	0.7	0.204	0.915	0.662	1.556	0.118	0.066
	125-139	84.91	0.049	0.676	0.51	0.48	0.201	0.809	0.606	1.375	0.178	0.069
	139-200	85.08	0.066	0.872	0.50	0.61	0.167	0.823	0.579	1.399	0.081	0.056
P.IV	0-23	85.76	0.021	0.104	0.45	0.71	0.207	1.068	0.741	1.816	0.168	0.081
	23-47	86.07	0.021	0.154	0.57	0.71	0.251	1.172	0.837	1.992	0.084	0.069
	47-87	87.23	0.03	0.215	0.45	0.57	0.219	0.970	0.704	1.649	0.166	0.100
	87-100	85.75	0.03	0.181	0.51	0.64	0.276	1.156	0.854	1.965	0.087	0.056

exchangeable Mg (0.004 - 0.011 $cmol_c\ kg^{-1}$) (Table 3). The order of exchangeable cation was Ca>Mg>Na>K. The low value of exchangeable was presumably caused by the material of tephra dominated by sand fraction. Sand fraction released elements slower than other finest fractions. Rapid dissolution of ultrafine particles and high-energy sites may also contribute to the rapid consumption of H^+ through silicate hydrolysis (Dahlgren et al. 1999).

In contrast, the percentage of base saturation of tephra was considerably high (55.43 - 177.58%) as the total of exchangeable cations was higher than the amount of CEC content. The in-weathered rich parent material caused the high value of base saturation. Similarly, Anda and Dahlgren (2020) reported that the percentage of base saturation of andisols in the southeast slope of Mount Tangkuban Perahu, west Java, under horticultural crops was 163 - 312 %.

Soil chemistry of tephra Mount Anak Krakatau related to the volcanic soils properties

The amount of K_2O extracted by HCl 25 % was 0.008 - 0.03 %; Na_2O (0.083 - 0.872%); CaO (0.33 - 0.65%); and MgO (0.47 - 0.71%). The order of release was MgO>CaO>Na_2O>K_2O (Table 5). The low amount of Al and Fe extracted by ammonium oxalate indicated that the tephra of Mount Anak Krakatau had a meager reactive form of Al and Fe in the solid phase. The percentage of Alo and Feo was 0.164 to 0.276 % and 0.039 - 1.172 %, respectively. The higher percentage of Feo than Alo content indicates that non-crystalline Fe is predominant in these volcanic deposits. Alo + 0.5 Feo was 0.030 - 0.854%, which was not qualified for soil andic properties (Alo + 0.5 Feo is ≥ 2 %).

In addition, ferrihydrite content was considerably low: 0.066 - 1.965 %. These results indicated that short-range order minerals (allophane or immogolite) can be negligible as these volcanic materials were still pristine and vitric state dominated by volcanic glass and primary crystalline minerals. Subsequently, these minerals will be transformed into secondary minerals in the future, such as allophane, imogolite, and ferrihydrite (Fiantis et al. 2021). The percentage of P retention has fairly fluctuated among the tephra profile and depth: P.I (83.71 to 90.79 %); P.II (84.86 to 87.17 %); P.III (83.32 to 89.29); P.IV

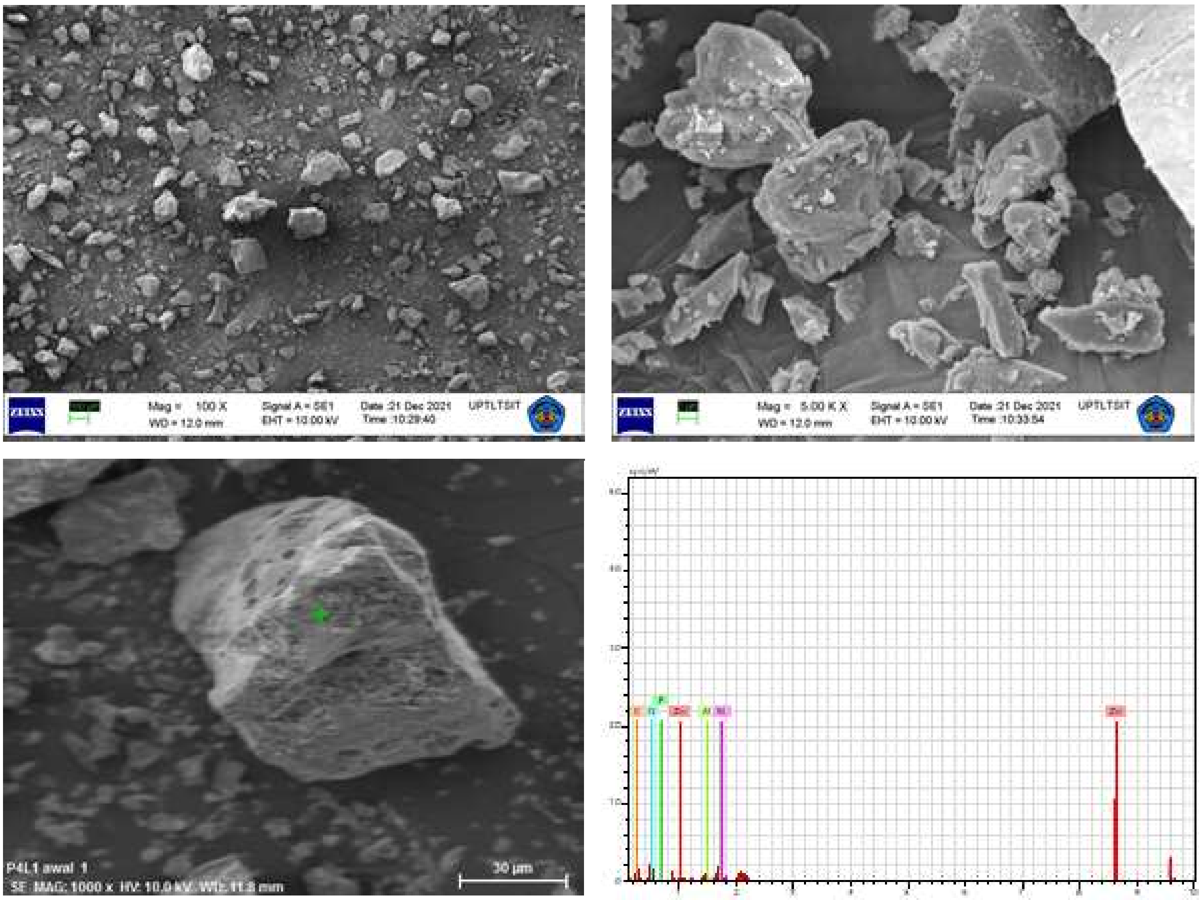

Figure 3. Scanning electron microscope (SEM-EDX) images of tephra before the leaching experiment showing the absence of biological activities in the tephra surface.

(85.75 to 87.23 %) (Tabel 4). These percentages were similar to the P retention of Mount Anak Krakatau before December 2018 eruption: 82.10% up to 84.74% (Setiawati et al. 2020). Furthermore, there were no significant differences in P retention value among the solvents after the leaching experiment (approximately $\geq$ 80 %). However, it can be noticed that the percentage of retention leached by water was low compared to tephra leached by $H_2C_2O_4$ and $C_6H_8O_7$ (it was about 2 points lower).

Tephra surface texture (SEM-EDX Analysis)

The tephra's surface texture can detect weathering's impact through the leaching experiment. Samples were selected representing the condition of volatile tephra (tephra before the leaching experiment) and after the leaching experiment. Before the leaching experiment (Figure 3), the surface of the tephra was undamaged and unconsolidated. As expected, the surface texture of the tephra after the leaching period was completely different from the surface of the tephra before the leaching experiment.

There were three pieces of evidence of weathering process occurring that can be mentioned: (1) the surface of tephra after the leaching experiment seems broken clearly (Figure 4, 5, 6); (2) there is a significant amount of algae can be found as weathered tephra provides harboring dynamic microbial colonies supported by light-dependent carbon fixation by algae; (3) the algae has been aggregating the finer particle from the weathering product become a single aggregate (it was found at tephra leached by $C_6H_8O_7$, Figure 6). As $H_2C_2O_4$ and $C_6H_8O_7$ are energy sources for microorganisms (algae), it is presumed that the number of algae in tephra leached by $C_6H_8O_7$ was greater than algae in tephra leached by $H_2C_2O_4$ than by water. These results were assumed as part of the biochemical weathering process. Biomechanical weathering integrates the effects of living organisms on physical changes in soils, regolith, and bedrock (Yatsu 1988; Pawlik et al. 2020).

CONCLUSIONS

Several characteristics of the tephra Mount Anak Krakatau increased significantly after the

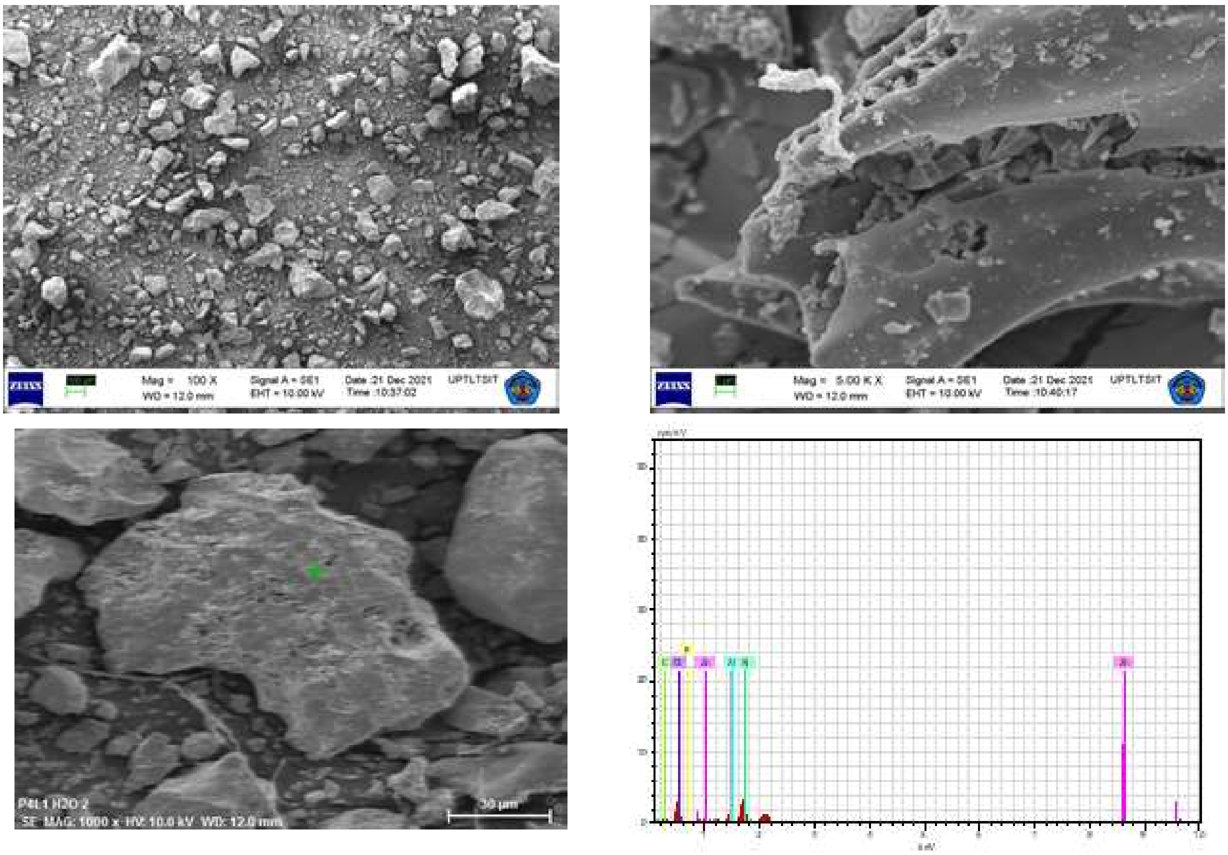

Figure 4. Scanning electron microscope (SEM-EDX) images of tephra leached by water showing algae colonies in the tephra surface.

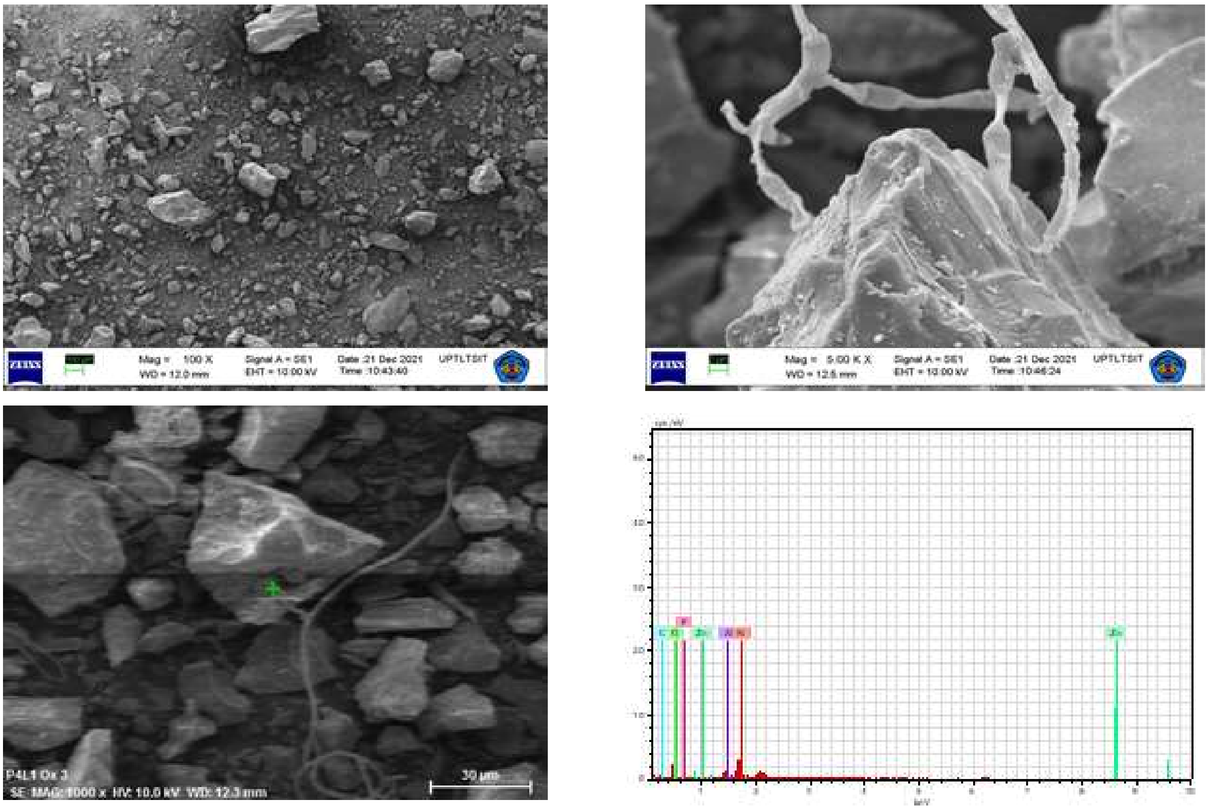

Figure 5. Scanning electron microscope (SEM-EDX) images of tephra leached by oxalic acid showing algae colonies in tephra surface.

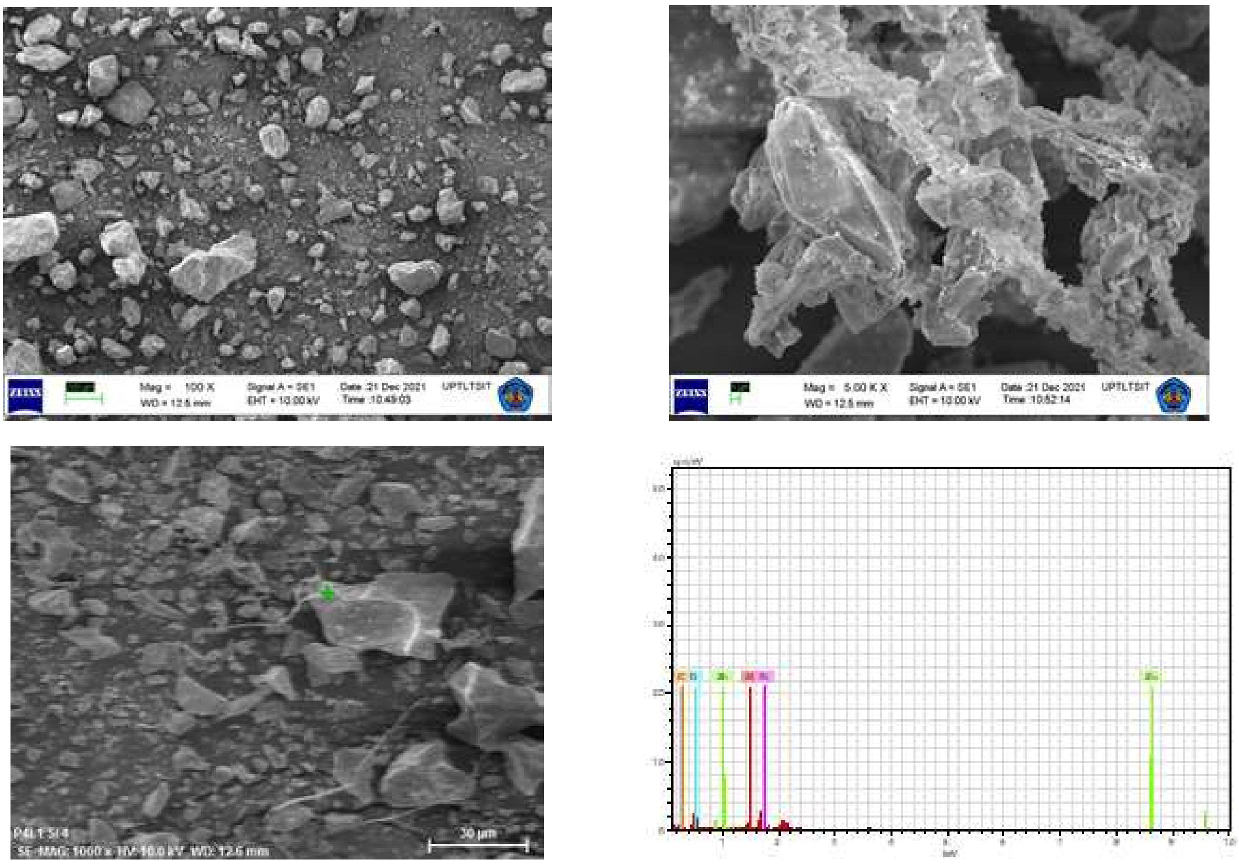

Figure 6. Scanning electron microscope (SEM-EDX) images of tephra leached by citric acid showing algae colonies in tephra surface.

leaching experiment as an impact of the weathering process. The pH of tephra increased from ± 3.95 – 4.99 to 5.12 to 8.11. The Organic carbon rose about 0.2 to 1 point higher than the organic-C of tephra before the leaching experiment. The increasing value of organic carbon is predicted to increase the CEC of tephra as well. $C_6H_8O_7$ and $H_2C_2O_4$ were two solvents releasing elements rapidly. In addition, after the leaching experiment, there was evidence that the weathering process has been destroying and aggregating the finer articles of tephra.

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