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Competitive adsorption of phosphate with sulfate, humic acid, and fulvic acid by allophane in different parent materials in Central Java

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Abstract

Andisol is a soil that has andic properties and develops from volcanic parent materials, especially ash. Andic soil properties are formed due to weathering of tephra or other parent materials that contain volcanic glass in large quantities. The main components of soil-forming Andisol are amorphous (short-range-order) minerals, such as allophane, imogolite, ferrihydrite, and Al/Fe-humus complexes. The existence of short-range-order minerals causes Andisol to have high P-tapping ability, but efforts to lower the amount of P plunged with organic and inorganic an-ons have not been widely studied. This study aimed to compare the ability of humic acid, fulvic acid, and sulfate in suppressing P adsorption by amorphous minerals from the Andisol of Mount Dieng, Merbabu, and Sumbing. The highest calculation of % ferrihydrite was found at the location of Mount Merbabu with a value of 3.05%, while the % allophane + imogolite was determined by the content of Sio in the ground. The calculation results showed that the highest was found at the location of Mount Sumbing with a value of 7.17%. Based on TEM analysis, Mount Sumbing has allophane diameter of 2.24 – 5.93 nm and the imogolite length of 24 – 187 nm.

INTRODUCTION

Java island has fertile soil, as there are 45 dynamic volcanoes. There are many active volcanoes located in relatively short distance so that most of Java island is covered by volcanic material (Sukarman and Dariah, 2014). Andisol is anterior and composed mainly of volcanic material of ash measuring <2 mm measurement (Buol et al., 2011; Soil Survey Staff, 2014). The tephra rotting or other stem material with countless volcanic mugs formed natural inland. It has the main component of amorphous minerals, such as allophane, imogolite, ferrihydrite and complex Al/Fe-humus (Hanudin et al., 2014; Sadao Shoji et al., 1993).

Andisols material distinguished by SiO_2 containing of: (1) riolit (70 – 100% SiO_2), (2) dasit (62 – 70% SiO_2), (3) andesite (58 – 62% SiO_2), (4) andesite basaltic (53,5 – 58% SiO_2), and (5) basalt (45 – 53,5% SiO_2) (Shoji et al., 1975). According to Sukarman and Dariah (2014), licious rocks, andesite, and basaltic andesite are the basic compounds that make up Indonesian Andisol soils. The volcanic tufa regions of Central Java, including Dieng, Merbabu and Sumbing mountains range, have various sources, climates, and land use, producing a specific soil characteristic. The Dieng and Sumbing mountains have 58 to 62% SiO_2 main andesite substance, while Merbabu has 53.5 to 58% SiO_2 basaltic andesite (Badan Geologi, 2014).

Physical and chemical properties of soil, including clay, organic matter, Al and Fe oxide content, and pH affect the process of phosphate adsorption in the soil (Xiao et al., 2017) as well as in andisols, which have low

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phosphate due to the dominance by short range orders and Al and Fe oxide (Hanudin et al., 2014). Organic matter can increase P in the soil, and organic matter is an important factor influencing the adsorption and desorption of P in the soil (Wang and Liang, 2014). The aim of this study was to compare the characteristics of phosphate adsorption from minerals amorf derived from Mount Dieng, Merbabu dan Sumbing treated by humic acid, fulvic acid and sulfate.

MATERIALS AND METHODS

The amorf mineral samples were extracted from Mount Dieng, Sumbing and Merbabu in Central Java Province of Indonesia. Soil samples were collected from the horizon C and immediately placed in polyethylene bags and tied tightly. Air-dried soil samples passing through a 2.0 mm sieve were measured prior to analysis, and the results were presented on an air-dried soil basis. Detailed description of the research location is presented on Figure 1 and described in Table 1.

Based on Schmidt and Ferguson classification, the climate conditions around Mount Dieng, Merbabu and Sumbing are categorized into B type of wet areas, with high intensity of rainy season (September – May) and dry season (June – August). The annual rainfall is between 2,000 – 4,300 mm per year, with 2,015 mm annum lowest rainfall and the highest one of 4,340 mm per year. Q score is between 14.3 – 33.3 (BMKG, 2021).

Preparation, analysis and soil fractionation

The sample of dry air was sifted with 0.5 and 2 mm-sieves. The analysis of soil characteristic includes, soil reactions of pH-H_2O (1:5), pH-KCl (1:5) and 1:50

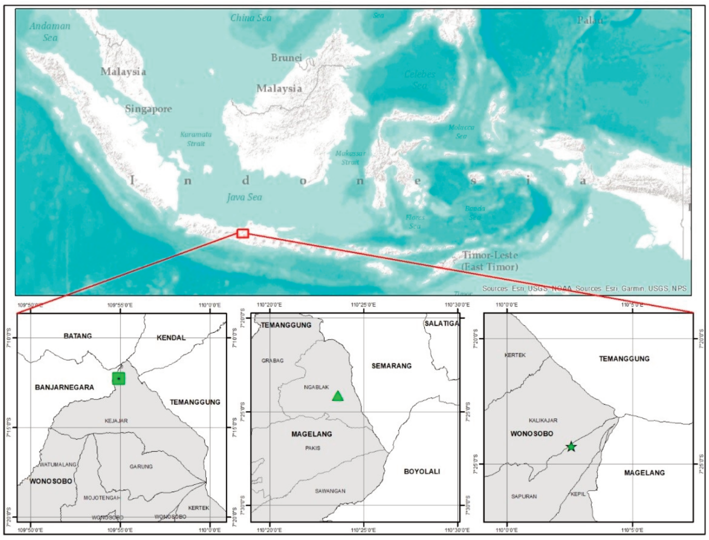

Figure 1. Studied areas of (a) Mt. Dieng, (b) Mt. Merbabu and (c) Mt. Sumbing in Central Java, Indonesia

Table 1. Research area description

Description	Location		
	Mt. Dieng	Mt. Merbabu	Mt. Sumbing
Coordinate	7°12’17.299” N 109°54’49.716” E	7°24’9.974” S 110°23’37.842” E	7°24’17.652” S 110°2’33.972” E
Main Subtance	Andesit intermediet	Andesit intermediet	Basaltik andesitik
Topography	Hilly >25%	Hilly >20%	Montanous >60%
Altitude (mdpl)	2.105	1.392	1.409
Research Plot	Monoculture farming	Monoculture farming	Forest
Vegetation	Potato, Cabbage, Carica	Red Pepper, Corn,	Pine, Ferns, Shrubs
Rainfall based on Schmidt and Ferguson	B Type, category wet area (tropical rain forest) Q = 17,87%	B Type, category wet area (tropical rain forest) Q = 18,47%	B Type, category wet area (tropical rain forest) Q = 20,81%

to 1M pH-NaF (1:50), organic C using Walkey-Black methods, cation exchange capacity (CEC), Ca-dd, Mg-dd, K-dd, Na-dd, base saturation (BS), and phosphate fractionation.

Clay fractionation was performed using a pipet method to separate fractions of sand, dust, and clay. Aquadest (distilled water) and H_2O_2 30% (technical) for removing the soil organic material were heated with a hot plate. Aquadest and HCl or NaOH were then added to lower the pH to 4 or increase the pH of the soil to 10 so that the soil was completely dispersed and placed on an ultrasonic device (20 kHz) to obtain a transparent fraction by separating sand and artificial dust (Yuliani et al., 2017). The Ultrasonic soil was the put into the sedimentation tube, added with 1000 ml aquadest and preserved for 24 hours. The next day, it was filled to a depth of 5 cm, added with more 1000 ml aquadest, waited for three hours and then hauled back to 5 cm continually until it got more clay. To obtain a dry clay fraction, the colloid was heated in oven at a temperature of 40°C.

Adsorption experiment

The adsorption experiment used NaH_2PO_4 for 0.6 g clay. Humic acid (AH), fulvat acid (AF) and sulfate (SO_4^{2-}) of 100 mg.L^{-1} by 50 ml were also used as competitors. The mixture of clay and each of block were spin out out for 16 hours, then filtered using the whatman 42. The clay blocks with AH, AF, and SO_4^{2-} were added 0–10 mM P using NaH_2PO_4 and NaCl 0.1 M (5 ml amount) as background solution and set in pH 6 by adding NaOH or HCL.

The soil blocks were balanced, and the pH was measured after completion for 20 hours. The solution was centrifuged and distilled by whatman's 42 paper sieve to separate supernatant and clay. The unlisted P was calculated by subtracting the added P with the remaining P. The effect of the administration of AH, AF and sulfate was enhanced by the clay of three locations and analyzed by Langmuir and Freundlich equations.

Langmuir and Freundlich

Common isotherm equations, the Langmuir and Freundlich, are used to calibrate phosphate adsorption (Barrow, 1978)

Langmuir's equation,

$$x = \frac{(K_L x_m c)}{(1+K_L c)} \quad \text{..(1)}$$

Redrafted becomes the linear equation

$$\frac{c}{x} = \frac{1}{(K_L x_m)} + \frac{1}{x_m} c \quad \text{......................................(2)}$$

where:
c = p concentration in equilibrium solution (mg p ml^{-1}),
x = amount of p absorbed (mg p g^{-1} soil),
x_m = maximum drag (mg g^{-1} land), and
K_L = coefficient associated with energy bond.

Freundlich equations are usually written:

$$x = K_F c^b \text{.. (3)}$$

transformed into a log to be a simple linear equation:

$$\log x = \log K_F + b \log c \text{ .... (4)}$$

c = P concentrate in equilibrium solution (g P mL^{-1}),
x = amount of P absorbed (mg P g^{-1}),
K_F and b = constant, by KF surface adsorpsi and b cennected to energy adsorption (Barrow, 1978).

RESULTS AND DISCUSSION

Psycho-chemical properties

Table 2 present the data of soil physical and chemical properties at the research site. The soil physical properties observed include texture analysis (the percentage of sand, dust, and clay), bulk density, particles density and porosity estimation. The result of texture analysis at Mt. Sumbing showed that percentage of the clay was the highest (20%). A high percentage of clay in Mt. Sumbing is estimated due to the more developed area than the other two locations. This development can be estimated from the higher intensity of rainfall on Mount Sumbing with a value of Q = 20.81% based on the classification of Schmidt and Ferguson compared to the other two locations. The increasing rainfall in a location will enhance the development of soil texture, and the more developed texture is marked by a higher value of clay. The Indonesian Andisol texture greatly varies from sandy soil to sandy loam, depending on the type and size of volcanic ash particles that are spewed at both eruptions and weathering (Sukarman and Dariah, 2014).

Bulk density and particle density type are presented in Table 2. The bulk density on Mt. Sumbing showed

Table 2. Physicochemical properties

Parameters	Mt. Dieng	Mt. Merbabu	Mt. Sumbing
Bulk density ($g.cm^{-3}$)	0.85	0.84	0.89
Particle density ($g.cm^{-3}$)	1.46	1.82	1.47
Porosity (%)	41.68	53.76	39.25
Textures	Sandy loam	Sandy loam	Loam
Sand (%)	54.00	59.00	55.00
Dust (%)	36.00	31.00	24.00
Clay (%)	10.00	10.00	20.00
pH H_2O	6.14	6.97	6.30
pH KCl	4.88	5.37	5.11
pH NaF	10.74	11.34	11.57
C-Organic ($mg.kg^{-1}$)	200.00	4000.00	4800.00
KPK cmol(+)kg^{-1}	15.01	18.60	16.33
K-dd	0.64	0.11	0.22
Na-dd	0.84	0.63	0.64
Ca-dd	8.62	9.71	3.62
Mg-dd	1.05	0.62	0.12
Base saturation	74.21	59.55	28.18

the highest value of 0.89 $g.cm^{-3}$. The possibility is because the loam percentage is 20% than the other two mountains. Meanwhile, the highest particles density (1.82 $g.cm^{-3}$) was found on Mt. Merbabu. Particle density is used to calculate porosity, and Mt. Merbabu had the highest porosity at over 50%, presumably due to its highest percentage of sand compared to the other locations. According to Agus et al. (2006), bulk density of Andisols between 0.6 to 0.9 $g.mm^{-3}$ is included low category in comparison to other mineral lands, and the bulk density mineral soil in this study ranges 0.8–1.4 $g.cm^{-3}$.

The results of soil chemical analysis are presented in Table 2. The soil acidic reaction value (pH) criteria was based on the Eviati and Sulaeman (2009). The lowest soil reaction in water (pH H_2O) was on Mt. Dieng (6.14) at the slightly acidic criteria, the feasibility of which was related to the monoculture intensive agricultural land use system, thus allowing high inorganic fertilizers to penetrate into the soil at the site. Generally, Andisols are acidic, in the pH range (H_2O) between 4.8–6.0 (Dahlgren et al., 2004). The three locations have a value > 10,00 of acidity using sodium fluoride (pH NaF), which is exchange complex dominated by amorphous minerals as one of the characteristic (Soil Survey Staff, 2014). The amorphous minerals Andisol (allophane, imogolite and ferrihydrite) contain a lot of OH monodentate, thus pH NaF is used to reduce OH monodentate in the following reactions:

$$\equiv Al/Fe\text{-}OH + NaF \text{ --------> } \equiv Al/Fe\text{-}F + Na^+ + OH^-$$

Mount Dieng has a total organic carbon content of 200 $mg.kg^{-1}$. the lowest organic carbon content at the site is possibly due to monoculture farming, with yields of only a small amount of organic matter through the absorption of vegetation litter. Meanwhile, total organic carbon content in Mount Merbabu and Sumbing is included in a poor criterion of 4,800 $mg.kg^{-1}$, due to their site use as shrub and forest, respectively.

The cation exchange capacity at the three sites ranged from low to moderate, classified as moderate in Mt. Dieng (15.01 cm(+) kg^1) and Sumbing (16.33 cm(+) kg^1). The cation exchange capacity of Mount Sumbing meets the medium criteria with CEC of 16.33 cmol(+) kg^1, while Mount Sumbing has the lowest based saturation of 28.18%, with a total Ca, Na, K and Mg of only 4.60. This means that more acidic cations are prevalent in the Mt. Sumbing area, which can reduce soil fertility in the area.

Inorganic phosphate fraction

The results of the analysis of phosphorus (P) content in the soil at all three research locations are presented in Table 3. Phosphorus fraction analysis includes available P, Al-P, Fe-P, and Ca-P. Mount Merbabu (6,10 mg.L^{-1}) showed the highest available P compared to other research locations. Available phosphorus is phosphorus that is ready to be utilized by plants, usually in the form of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. The highest P absorption by Al and Fe was found in the location of Mt. Dieng (Al-P 342,90 mg.L^{-1} and Fe-P 313,10 mg.L^{-1}). The results can be assumed that the phosphorus values of Al and Fe decreased a lot at the Mount Dieng. The availability of phosphorus is low, one of which is due to the slow diffusion of phosphorus and high phosphorus fixation in the soil, making it one of the unique characters of phosphorus in the soil and one of the reasons why phosphate can be a limiting factor for plant growth (Asomaning, 2020). Fractionation analysis of phosphorus in all fractions, in which the lowest value was found on Mount Sumbing, is an indication that the P adsorption value is the highest compared to other locations. Available phosphorus and labile phosphorus are in the soil solution. Phosphorus easily moves from a solid phase to a solution. Phosphate adsorption by active soil surfaces, such as allophane, imogolite and ferrihydrite, can convert available phosphorus into unavailable phosphorus in the soil (Gonzalez-Rodriguez and Fernandez-Marcos, 2018).

Selective dissolution and XRF analysis

The results of selective dissolution analysis are presented to Table 4. The highest Feo element on Mt. Merbabu is 1.79%. Feo is associated with a percentage of ferrihydrite in clay fractions. The highest Alo was found on Mt. Sumbing (2.80 %), while the lowest one was found on the Mt. Dieng (at 1.32%). Alo and Feo content is also used in determining andic properties. Pyrophosphate extracts are used to determine the shape of Fe, Al, Si elements that are associated with organic material (Fep, Alp, Sip). Based on the analysis using pyrophosphate extract, the highest Fep content was 0.08%, found on the Mt. Dieng, while the highest Alp was 0.04%, found on Mt. Sumbing, which suggests that few elements are bonded with organic matter, according to low and moderate analysis of the same organic material. Dithionite extract is used to determine the crystalline properties of fe and al oxide (Fed and Ald). The highest level of Fed analysis on Mt. Merbabu was 7.19%. Low results of analysis for elements of Fed and Ald showed that the elements were in the form of crystals or low crystallization.

Amorphous material calculations are presented in Table 4. The Alp/Alo comparison of the three locations is almost the same in the three locations, ranging from 0.01–0.02. The Alp/Alo value comparison is one of the markers of allophanic andisols or non-allophanic andisols. As the Alp/Alo ratio increases, it is likely that the allophane+ imogolite are lower. According to Nanzyo et al. (1993), the Alp/Alo value comparison is often used to distinguish between types of allophanic and non-allophanic andisol, in which the allophanic Alp/Alo value ranges 0.1–0.4, while the value range for non-allophanic is 0.8–1.0. Thus, it could be concluded that in all three research locations, allophanic had an Alo/Alp value of no more than 0.4%.

Table 3. Phosphate fractionations levels of Mount Dieng, Merbabu and Sumbing

Location	P-Available	Al-P	Fe-P	Ca-P
	(mg.L^{-1})			
Mt. Dieng	2.70	342.90	313.10	35.90
Mt. Merbabu	6.10	324.90	239.80	31.00
Mt. Sumbing	1.70	164.70	54.00	24.70

Table 4. Selective dissolution and short range order minerals in the clay fraction on Mt. Dieng, Merbabu and Sumbing

Location	Feo	Alo	Sio	Fep	Alp	Sip	Fed	Ald	Alp/Alo	Alo+ 1/2Feo	% feri	% Alo+Imo
Mt. Dieng	1.73	1.32	0.37	0.08	0.03	0.02	2.05	0.19	0.02	2.19	2.95	2.60
Mt. Merbabu	1.79	2.01	0.52	0.06	0.03	0.02	7.19	0.35	0.01	2.90	3.05	3.71
Mt. Sumbing	1.02	2.80	1.01	0.03	0.04	0.02	2.84	0.33	0.01	3.31	1.73	7.17

Calculation of Alo +1/2 Feo was used to determine if the soil at the research site had andic properties. According to the Soil Survey Staff (2014), soil with andic properties have minimum Alo + ½ Feo of 2.0%. Based on the results presented in Table 4, the three locations had Alo + ½ Feo value > 2.0%. The largest Alo+½ Feo was found on Mt. Sumbing (3.31%), and the lowest one was found on Mt. Dieng (2.19%). According to Parfitt and Wilson (1985), percentage of ferrihydrites can be suspected by using a formula % Feo × 1.7. The highest percentage of ferrihydrite at the location of the specimen taken was 3.05% on Mount Merbabu, followed by Mount Dieng (2.95%) and Mount Sumbing (1.73%). The surface area of ferrihydrite is highly reactive and has a high ion adsorption capacity. The surface area of ferrihydrite is an important characteristic because ferrihydrite particles have a charge (Hirmstra et al., 2019)

The percentage of allophane+imogolite was estimated based on Nanzyo et al. (1993). It was calculated based on the formula of 7.1 × Sio. The highest percentage of the % allophane + imogolite was found on Mt. Sumbing (7.17%), and the lowest one was found on Mt. Merbabu (2.60%). The percentage of allophane + imogolite score is inversely proportional to the Alp/Alo value, the smaller the humus complex formation, the higher the allophane formation. The formation of % allophane + imogolite requires a low concentration of organic matter and pH, resulting in the presence of Al and Si.

Based on the analysis using XRF of SiO_2, Al_2O_3 and Fe_2O_3 (Table 5), the highest SiO_2 value was found on Mt. Dieng (14.00%), the highest Al_2O_3 value was on Mt. Sumbing, and the highest Fe_2O_3 value was found on Mt. Sumbing (5.23%). Meanwhile, the value of the Si/Al ratio in Mt. Dieng has the highest Si/Al ratio, which is 2.77%. Higher Al content per unit mass causes higher Al-OH and Al-OH_2 groups, low Si/Al ratio causes higher phosphate adsorption compared to allophane that has higher Si/Al ratio, because an aluminol, Al-OH or $AlOH_2$, is responsible for the adsorption of phosphates and organic anions in the soil (Jara et al., 2006).

Phosphate adsorption isotherm

Figure 2 suggests phosphate adsorption isotherm in allophane of the Dieng, Merbabu and Sumbing mountains at pH 6. The higher the phosphorous concentration given, the greater the phosphate mineral allophane. Figure 2 shows that the amount of P is covered by loam fractions from Sumbing > Merbabu

Table 5. Analysis XRF on Mt. Dieng, Merbabu and Sumbing

Components	Mt. Dieng	Mt. Merbabu	Mt. Sumbing
		%	
Al_2O_3	8.92	8.37	9.47
Al	2.36	2.21	2.51
SiO_2	14.00	11.90	12.29
Si	6.54	5.56	5.74
Si/Al	2.77	2.51	2.29
Fe_2O_3	4.09	5.23	4.49

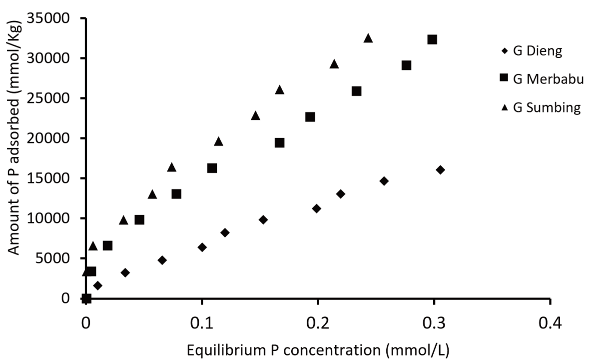

Figure 2. Isotherm adsorption of P by allophane on Mt. Dieng, Merbabu and Sumbing

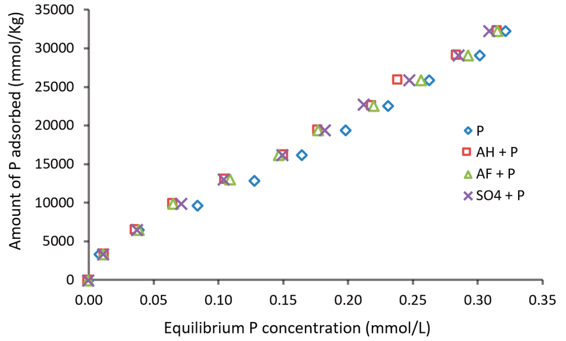

Figure 3. Impact of AH, AF and SO_4 to Isotherm adsorption of phosphate by allophane on Mt. Dieng

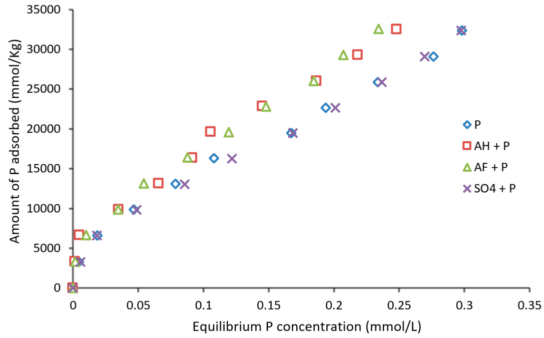

Figure 4. Impact of AH, AF and SO_4 on Isotherm adsorption of phosphate by allophane on Mt. Merbabu

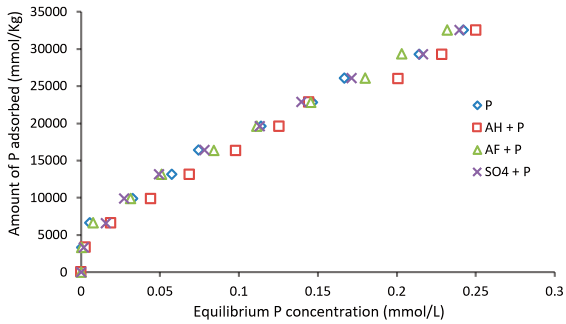

Figure 5. Impact of AH, AF dan SO_4 on Isotherm adsorption of phosphate by allophane on Mt. Sumbing

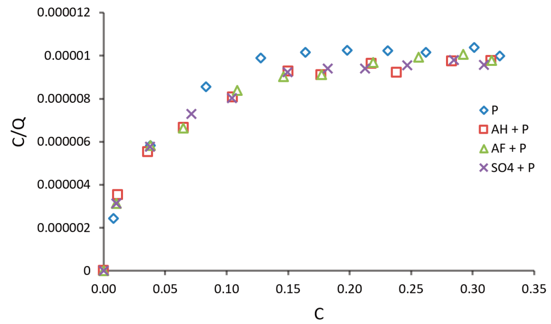

Figure 6. Langmuir between treatments on Mt. Dieng

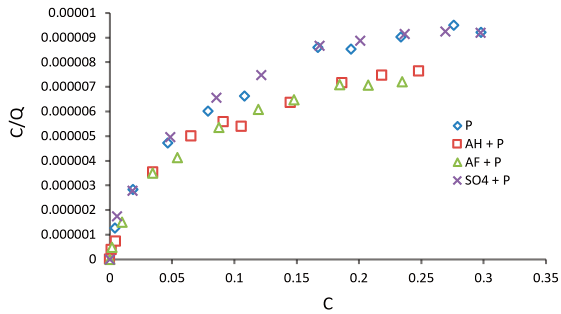

Figure 7. Langmuir between treatments on Mt. Merbabu

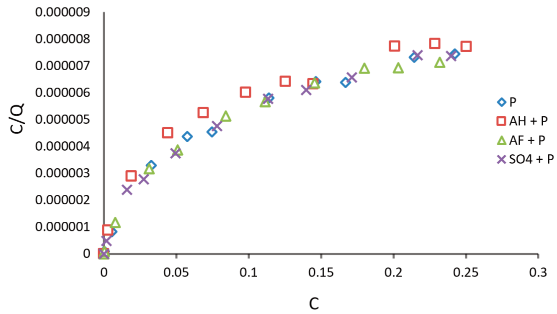

Figure 8. Langmuir between treatments on Mt. Sumbing

> Dieng. The adsorption isotherms on Mt. Sumbing has the highest values due to the high content of Al-OH and Al-OH_2 and the lower Si/Al values compared to Mt. Dieng and Merbabu. In addition to the high content of Al-OH and Al-OH_2, the highest adsorption on Mount Sumbing due to the amorphous substance, such as % Allophane + Imogolite, reached the highest at 7.17%. (Table 5).

Figures 3, 4 and 5 present the graph of adsorption isotherm blocked by humic acid (AH), fulvic acid (AF), and sulfuric (SO_4) on Mount Dieng, Merbabu and Sumbing. The three research sites have an almost similar graph pattern, in which the adsorption isotherm will increase with the addition of NaH_2PO_4 in each sample. The addition of AF and SO_4 reduced the level of P adsorption on Mount Merbabu. This indicates that there is a stretching of the line between treatments, so there may be a significant difference between treatments on Mount Merbabu. Allophane, imogolite, and Al-humus complexes have the most role in phosphate adsorption in Andisols (Takahashi and Dahlgren, 2016).

The analysis result of P adsorption isotherms on Mount Dieng and Sumbing showed no difference between AH, AF and SO_4 treatments. This is indicated by the presence of lines between treatments that are close to each other. According to Jara et al. (2006), phosphate is a very strong termite on the variable charge. However, humic and fulvic acids and inorganic ligands (including SO_4) compete with PO_4 on adsorption sites. The adsorption of PO_4 in Andisols is slightly affected by the presence of SO_4.

Characteristics of P adsorption by Langmuir and Freundlich equation

The isotherm of Langmuir equation is used to estimate the maximum adsorption value and P binding energy of the Andisol loam fraction. Graphs of Langmuir equations are presented in Figures 6, 7, and 8, and Table 6 presents maximum adsorption and binding energies. Figures 6, 7 and 8 show all treatments almost parallel to the equilibrium phosphate concentration of 0.23–0.32 mm. P adsorption in allophane is influenced by the Si/Al ratio, in which the lower the Si/Al ratio, the higher the P adsorption along with the decrease in pH (Ariefandra et al., 2020). Sulfate adsorbed on the mineral's outer surface is displaced by phosphate, and it is more difficult to be displaced by sulphate because phosphate adsorption occurs within the mineral (Pigna and Violante, 2003).

The most common mathematical model used to calculate adsorption is the Langmuir and Freundlich equation. The parameters of this equation have no mechanistic significance but still have practical use in comparing P retention in different soils (Shafqat and Pierzynski, 2014), similar to k value of Langmuir (adsorption capacity) and n (adsorption afinity). Table 6 presents coefficient value determinations (R^2) to allophane treatment (genuine) blocked by AH, AF and SO_4. R^2 on Mount Dieng (0.96–0.99), Merbabu (0.99–0.99), and Sumbing (0.94–0.98) are included in very satisfactory category. The Freundlich equation is shown in the description of P loam adsorption at three mountainous sites. The n and k values for Mount Dieng were 1.45–62 and 0.13–0.14, while those for Mount Merbabu were 1.80 to 2.46 and 0.09 to 0.12. The higher the affinity value (n), the lower the capacity, and vice versa.

All treatments serving B points on Mount Sumbing and Merbabu showed the same results, namely 3.333. Meanwhile, on Mount Dieng, the lowest point was 3.333 (without treatment), and the highest was 5,000 (AH, AF, and SO_4 treatments). Maximum adsorption (k) on Mount Merbabu is 7.5 for unblocked treatments and 5 for the addition of AH, AF and SO_4. The maximum adsorption value on Mount Merbabu with the addition of AF and SO_4 was 15 and 30. Meanwhile, the maximum adsorption value on Mount Merbabu without block and AF addition was 30, and the value was 15 for AH and SO_4 addition.

A higher k value indicates an increase in adsorption capacity, one of which is Al-OH and Al-OH_2 from allophane, because the samples from Mount Sumbing have lower Si/Al rate than those from Mount Dieng and Merbabu. The aluminol groups including AL-OH or AL-OH are responsible for the adsorption of phosphate and inorganic anions in soil and loam minerals. According to Hiradate and Uchida (2004), the amount of P adsorption increases by removing organic substance from Andisols, which indicates the presence of organic substance occupying P adsorption resistance. However,

Table 6. Parameters of Langmuir and Freundlich equations for phasing before and after the treatment of the 3 mountain locations

Location	Treatment	Langmuir				Freundlich			
		b	k	R^2	R	b	k	R^2	R
Mt. Dieng	Asli	33333	7.5	0.66	0.81	1.62	0.13	0.96	0.98
	AH + P	50000	5	0.71	0.84	1.45	0.14	0.99	0.99
	AF + P	50000	5	0.72	0.85	1.50	0.14	0.99	0.99
	SO_4 + P	50000	5	0.69	0.83	1.49	0.14	0.99	0.99
Mt. Merbabu	Asli	33333	15	0.85	0.92	1.90	0.11	0.99	0.99
	AH + P	33333	30	0.85	0.92	2.46	0.09	0.96	0.98
	AF + P	33333	15	0.86	0.93	2.21	0.10	0.98	0.99
	SO_4 + P	33333	10	0.83	0.91	1.80	0.12	0.99	0.99
Mt. Sumbing	Asli	33333	30	0.87	0.93	2.94	0.07	0.95	0.97
	AH + P	33333	15	0.82	0.91	1.93	0.29	0.97	0.98
	AF + P	33333	30	0.87	0.93	2.89	0.21	0.94	0.97
	SO_4 + P	33333	15	0.88	0.94	2.24	0.09	0.98	0.99

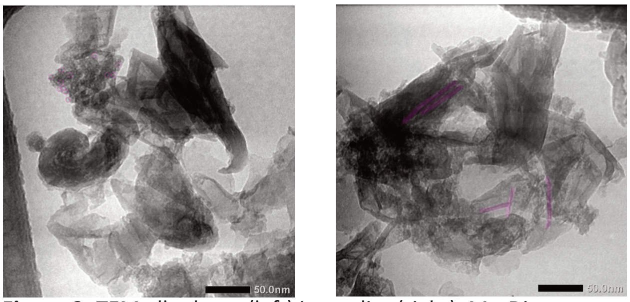

Figure 9. TEM allophane (left) imogolite (right), Mt. Dieng

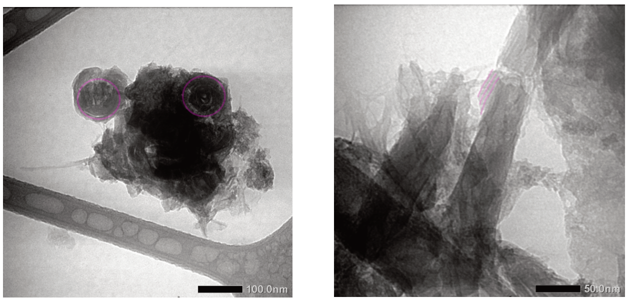

Figure 10. TEM allophane (left) imogolite (right), Mt. Merbabu

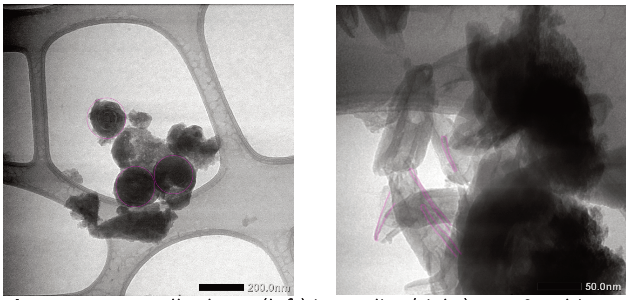

Figure 11. TEM allophane (left) imogolite (right), Mt. Sumbing

Table 7. Diameter of allophane and imogolite length

Location	Diameter	Length
	nm	
Mt. Dieng	0.50 – 4.50	14 – 110
Mt. Merbabu	1.12 – 5.93	12 – 143
Mt. Sumbing	2.24 – 5.93	24 – 187

the addition of AH, AF and SO_4 was not able to reduce P adsorption at 3 locations, it is possible that the acids present are not quite intense to withstand and reduce the ability of allophane loam of P adsorption (Hanudin et al., 2014). Phosphate availability can be increased efficiently by adding organic matter, and the addition of organic matter can reduce the power of P adsorption (Yang et al., 2019).

Allophane and imogolite characteristics in TEM analysis

The analysis of clay morphology using TEM is presented in Figures 9–11. The TEM has shown a variety of clay morphology in the three research sites. The result of clay analysis at three research sites revealed the presence of thin ring-shaped particles and fibrous tubes. The ring-shaped particle is allophane mineral, which was described by Dahlgren et al. (1993) as a hollow sphere (hallow sphere/nano ball) with many highly reactive holes, diameter of 5 nm (50 Å), and a wall thickness of 0.7–10.

Whereas a thin fiber tube may form an imogolite, it is a nanotube aluminum silicate with 10 Å diameter inside and 20 Å diameter outside. Having a tube shape causes the ability to bind distinct anions between the tip and the center of the body stem. Imogolite is usually found together with allophane in Andisol (Hanudin et al., 2014).

The results of TEM analysis on the three research sites are presented in Table 7. The allophane diameter on Mount Dieng, Merbabu, and Sumbing was 0.5–4.0, 51.12–5.93, and 2.24–593 nm, respectively. Meanwhile, the imogolite length on Mount Dieng, Merbabu, and Sumbing was was 140–110, 12–143, and 24–187 nm, consecutively. The allophane diameter is approximately 3.5 nm with 0.7 nm thickness (Wada et al., 1979), and imogolite length may reach 1000 nm (Yuliani et al., 2017).

CONCLUSIONS

The allophane on Mount Dieng, Merbabu, and Sumbing's have the highest Phosphate adsorption, as of humic acid, fulvic acid and SO_4 applied to decrease Phosphate adsorption could not have significant effect. The Phosphate adsorption in allophane is affected by Si/Al, % ferrihydrite and % allophane+imogolite ration. The low Si/Al ratio thus elevated the % ferrihydrite and %allophane + imogolite, resulting in higher phosphate adsorption. The addition of humic acid, fulvic acid, and sulphate could not compete with PO_4 at the adsorption site, and could not resist the adsorption of phosphate in the allophane loam site when 100 mg.L^{-1} doses of humic acid, fulvic acid and sulfuric acid were provided. The adsorption of phosphate is in the inner-sphere complex, while the anion displaces the inlet of the outer-sphere complex. Moun. Dieng has clay forms, an allophane diameter of 0.5–4.5 nm and an imogolite length of 14–110 nm. In Mount Merbabu, the allophane has a diameter of 1.12–5.93 nm and imogolite length of 12–143 nm, while Mount Sumbing has an allophane diameter of 2.24 to 5.93.

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