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Javanese Volcanic Allophane Adsorbent as Heavy Metal Adsorber to Improve the Quality of Drinking Water in Surakarta

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Abstract

The present study is concern with the identification, characterization and activation of natural allophane as an adsorbent of heavy metal ions Cr, Fe, Cd, Cu, Pb and Mn. The purposes of this study were to identify and characterize the natural allophane of Javanese volcanoes (Papandayan, Arjuna and Wilis), and to determine the optimum conditions of adsorption and adsorption isotherms that happened. The identification of natural allophane was performed by using NaF, pH, FTIR, and XRD. The characterization of the acidity of allophane was analyzed by using ammonia adsorption. The activation was done in the NaOH solution of 1 N and 3 N, and in the soaking time of 1, 3, and 5 hours. The adsorption was done according to *batch* method with the variations of contact time of 30, 60, 90 and 120 minutes. The adsorption isotherms performed by using the variations of the amount of adsorbate. Atomic Absorption Spectroscopy (AAS) was used in the analysis to determine the concentration of heavy metal ions in solution. The results show that the analysis of NaF, pH, FTIR and XRD indicate the presence of allophane in the volcanic samples. The optimum conditions of activation and adsorption of the metal ions of Cr and Cd are in the activation of NaOH 3N for 3 hours within 120 minutes contact time, those of metal ions of Fe are in the activation of NaOH 3N for 1 hour within 30 minutes contact time, those of the metal ions of Pb and Mn are in the activation of NaOH 3N for 5 hours within 90 minutes contact time, and those of metal ions of Cu are in the activation of NaOH 3N for 5 hours within 60 minutes contact time. The adsorption isotherms performed to all kinds of metals follow Freundlich equation which suggests that physical interactions occur. Thus, an activation with NaOH can increase the acidity of allophane causing to improve adsorption capacity to the metals by about 50-100%..

Keywords: allophane, heavy metals, adsorption

1. Introduction

One type of pollutants that requires a lot of attention in environmental management is that of heavy metals. The disposal of waste contaminated by heavy metals into water sources (ground water or surface water) becomes a major problem of pollution because of its toxic and nonbiodegradable characteristics. The types of heavy metals that are considered as having a high level of toxicity are Hg, Cd, Cu, Ag, Ni, Pb, As, Cr, Sn, Zn and Mn (Suprihatin and Indrasti, 2010).

Some of the most significant techniques to remove heavy metals in liquid wastes are: chemical precipitation, filtration, ion exchange resin, and a membrane system. The main thing to think of with these technologies is that not all metals can be removed, the reagents are high and they require much energy and high operating costs (Esmaili, et al., 2003). Lately, adsorption has become an alternative method for dissolving metal ions from liquid wastes. It is also used to minimize costs, and thus, as a kind of extensive research using a low-cost adsorbent types of soil (Potgeiter, et al., 2005).

Allophane was found to be very good for adsorption of some heavy metals (e.g. Clark & McBride, 1984; Denaix et al, 1999, Abd-Elfatah & Wada, 1981). Iyoda et al (2011) reported the adsorption of heavy metals (Cu, Cd, Pb, and V) by natural and synthetic allophanes. An Al-rich allophane has also been synthesized, and a portion of the organic matter was extracted from the clay fraction, and their reactivities towards Cu2+ orZ n2+ were studied by potentiometry (Latrill et al, 2003). The synthetic allophane was usually prepared due to Wada et al (1979).

Allophane may be defined as an amorphous clay mineral and a promising material which is naturally available in volcanic soils. The single unit of allophane consists of a hollow spherule with a diameter of ~5 nm, and possess perforations in the wall with a (HO)Al(OH2) structure and diameter of ~0.3 nm (Iyoda et al, 2011). Thus, it should be widely available in the wild, as is located in the flat to mountainous areas with an altitude of 0-3000 m above sea level and is formed under the influence of wet tropical climate such as Indonesia.

The activators H2SO4 and NaOH have been applied to determine the effect on the allophane's surface width and acidity (Widjanarko, et al, 2003). When they are compared, the activation with NaOH produces a wider specific surface area than that with H2SO4.

In this research, the identification, characterization, and activation of natural allophane with NaOH were applied. It was then used as an adsorbent in the removal of heavy metals in water.

2. Materials and Methods

2.1 Materials and Tools

The main materials used in this study were allophane taken from volcanic mountains in Java (Papandayan, Arjuna and Wilis), distilled water, NaOH, NaF, pH stick, HNO3, ammonia, Whatman filter paper 42, and the model of solution of metals Fe, Mn , Cr, Cd, Cu, Pb 1000 ppm.

The particular tools used were furnace, 200 mesh sieve, a set of Atomic Absorption Spectroscopy (AAS) Brand Shimadzu Type AA-6650 F, a set of X-Ray Diffraction (XRD) Brand Shimadzu Type 600, a set of Fourier Transform Infra Red (FT-IR) Brand Shimadzu Type FT-IR-8201 PC, TOA pH meter, and desiccator.

2.2 Preparation of Activated Allophane, Physical Characterization and Measurements

The natural allophane was aerated and then crushed. The powder obtained was sieved, which was then soaked in distilled water, filtered, and dried at a temperature of 105 0C for about 4 hours. The final product of dried allophane powder was then identified and characterized by NaF, FT-IR, and XRD.

After activation process with 1 N and 3 N of NaOH within the time variations of 1, 3 and 5 hours, the activated allophane, was finally used to adsorb the heavy metals, Fe, Mn Cr, Cd, Cu, and Pb, to determine the adsorption isotherms, as well as to characterize the acidity. The natural allophane, without activation, was also used to absorb the metals for comparison.

3. Result and Discussion

An initial test of the presence of allophane on the andisol ground was done by means of NaF-pH test. The NaF test results for each of the mountains are shown in Table 1. The pH of all samples being greater than 9.4 should fonfirm that it is due to the presence of allophane (Munir, 1996).

Table 1. pH NaF of samples

Sample	pH NaF
Mount Papandayan	11,08
Mount Arjuna	12,20
Mount Wilis	11,73

3.1 Infrared of allophane sample:

3.1.1 Analysis of FTIR

As shown in Fig. 1a, the IR spectra for all natural samples are similar one to another, and they are typical for allophane as compared to the IR spectrum of allophane recorded by Devnita, et al. (2005) and shown in Fig. 1b. The details of analysis are recorded in Table 2.

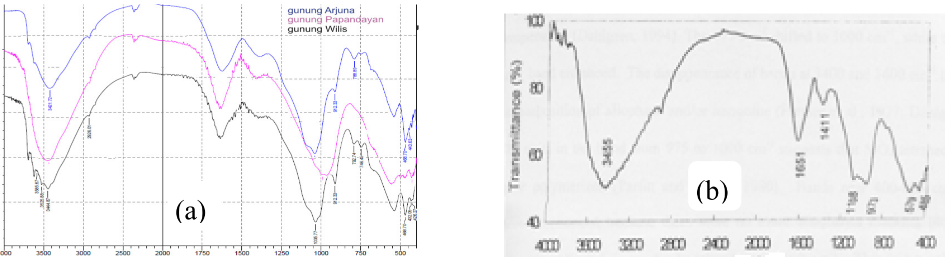

Figure 1. a. FTIR spectra of natural samples; b. FTIR spectrum of allophane (Devnita, et al., 2005)

Table 2. The comparison between the spectra of samples and the analysis by Devnita, et al. (2005)

Functional groups	**Allophane uptake (cm^{-1})**			
	Devnita (2005)	**Papandayan**	**Arjuna**	**Wilis**
Vibration –OH (Al-OH/Si-OH)	3455	3437	3421,72	3444,87
Vibration AlOH/SiOH	1108; 973	960,55; 991,41	912,33;1039,63	912,33;1035,77
The existence of Si-O bond	579; 485	428,2	443,63; 468,7	426,27;432,05

3.1.2 XRD of Natural Allophane

X-Ry powder diffraction for the three samples were recorded, and as shown in Fig. 2 they are similar each others. The details of particular *d-spacings* are confirmed with JCPDS for allophane as shown in Table 3.

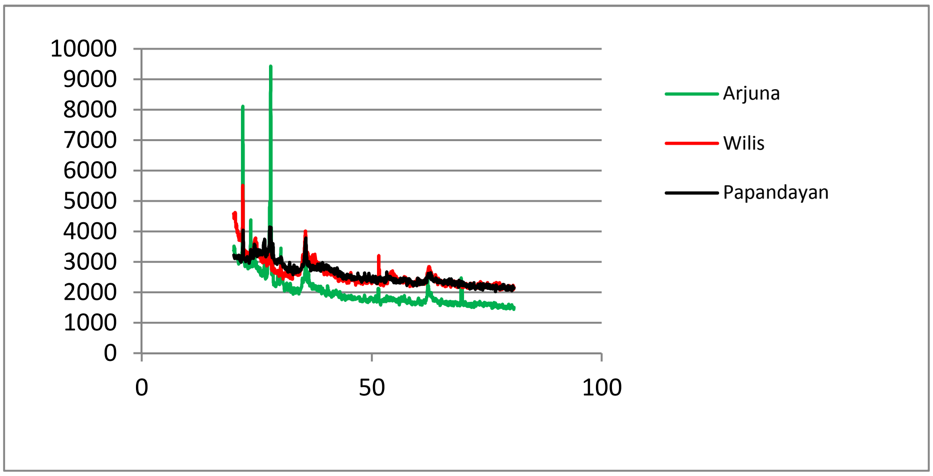

Figure 2. XRD spectra of Samples

Table 3. Typical *d-spacings* data of the three samples compared to that of JCPDS

JCPDS (38-0449)	**d-*spacing*(Å)**				
	3,300	2,250	1,860	1,400	1,230
Papandayan	3,305	2,249	1,861	1,400	1,230
Wilis	3,305	2,249	1,861	1,400	1,230
Arjuna	3,305	2,249	1,861	1,400	1,230

3.2 Adsorption of the Activated Allophane

The natural (without activation) and the activated allophanes were then applied to adsorption of the solutions containing metal ions of Fe, Cr, Cu, Cd, Pb, and Mn within 30, 60, 90, and 120 minutes contact time of adsorption. The number of the heavy metals adsorbed was analyzed by AAS. The results were collected in Table 4 (for Cr and Fe), Table 5 (for Pb and Mn), and Table 6 (for Cd and Cu).

Table 4. The percentage of metal ions uptake of Cr and Fe

Sample	Metal	Treatment	The percentage of absorption (%)			
			30'	60'	90'	120'
Mount Papandayan	Chromium	Without activation	0	0.8	0	0
		1N 1hour	51.8	55.8	63.5	60.9
		1N 3 hours	51.7	65.0	70.2	71.4
		1N 5 hours	70.0	74.1	80.1	76.0
		3N 1 hour	76.7	89.8	88.0	86.8
		3N 3 hours	82.9	95.7	97.6	**97.8**
		3N 5 hours	64.2	75.8	65.1	93.2
	Iron	Without activation	96.3	94.7	94.0	86.4
		1N 1 hour	97.5	96.9	95.8	95.3
		1N 3 hours	98.1	96.8	93.9	88.9
		1N 5 hours	97.9	95.8	95.4	95.2
		3N 1 hour	**99.9**	98.7	94.5	93.2
		3N 3 hours	99.7	96.8	96.3	95.9
		3N 5 hours	97.2	95.9	95.8	86.8

The adsorption performed on the initial concentration of 1 ppm and 5 ppm of metals Cr and Fe respectively produced the adsorbents weighing 0.25 g and 0.5 g respectively. Table 4 shows that the optimum condition for metal adsorption of Cr-ions is on the activation with NaOH (3N) for 3 hours within 120 minutes contact time, while that of Fe-ions is on the activation of NaOH (3N) for 1 hour within 30 minutes contact time. The percentages of the maximum adsorptions of Cr and Fe metals to the activated allophane are 97% and 99.9% respectively. While for the iron adsorption there is not so significant allophane increased from 96.3 (without activation) to about 100% (for the activated), it is significantly to be the case for Cr, being increased about 97% (for the activated) from none (without activation).

Table 5. The percentage of metal ions uptake of Pb and Mn

Sample	Metal	Treatment	The percentage of absorption (%)			
			30'	60'	90'	120'
Mount Wilis	Lead	Without activation	13.1	12.0	15.9	14.9
		1N 1hour	8.34	8.94	10.1	9.03
		1N 3 hours	8.74	8.79	10.6	9.30
		1N 5 hours	9.93	10.3	12.7	10.9
		3N 1 hour	12.9	14.8	15.6	14.1
		3N 3 hours	16.1	18.3	22.8	20.3
		3N 5 hours	41.6	44.8	**46.9**	39.9
	Manganese	Without activation	42.9	12.2	9.21	16.9
		1N 1 hour	12.9	25.6	7.36	33.9
		1N 3 hours	41.2	29.3	26.8	11.7
		1N 5 hours	50.2	38.6	34.6	24.6
		3N 1 hour	50.5	48.5	49.7	43.1
		3N 3 hours	79.5	77.2	74.2	71.8
		3N 5 hours	82.8	86.8	**88.8**	79.7

The adsorption performed on the initial concentrations of 40 ppm and 3 ppm of metals Pb and Mn respectively produced the adsorbents weighing 0.25 g and 0.5 g respectively. Table 5 shows that the optimum condition for metal adsorption of Pb and Mn is on the activation with NaOH (3 N) for 5 hours within 90 minutes contact time. The percentages of the maximum adsorption of Pb and Mn metals to the activated allophane were found to be about 46.9% and 88.8% respectively. Thus, there is an increasing adsorption of Pb for about nearly three times from 15.9% (without activation) to 46.9% (for the activated). The increasing adsorption of Mn was also observed in more significance; it is about nine times from only 9.21% (without activation) to 88.8% (for the activated).

Table 6. The percentage of metal ions uptake of Cd and Cu

Sample	**Metal**	**Treatment**	**The percentage of absorption (%)**			
			30'	**60'**	**90'**	**120'**
Mount Arjuna	Cadmium	Without activation	5.27	5.47	5.74	5.21
		1N 1hour	90.8	97.3	94.4	88.73
		1N 3 hours	98.3	97.2	91.0	91.68
		1N 5 hours	64.0	93.4	97.8	92.31
		3N 1 hour	64.0	96.5	97.8	92.31
		3N 3 hours	93.9	97.9	97.2	**98.8**
		3N 5 hours	90.2	97.4	96.8	95.20
	Copper	Without activation	31.8	30.6	34.2	31.62
		1N 1 hour	73.9	60.7	72.8	64.82
		1N 3 hours	69.8	53.0	76.6	68.41
		1N 5 hours	66.2	53.8	76.6	76.75
		3N 1 hour	67.6	62.7	68.7	66.22
		3N 3 hours	74.6	68.1	78.5	69.54
		3N 5 hours	70.6	**87.4**	86.3	85.48

The adsorption performed on the initial concentrations of 2 ppm of Cd and 4 ppm of Cu produced the adsorbents weighing 0.5 g. Table 6 shows that the optimum condition of adsorption of Cd were is on the activation of NaOH (3 N) for 3 hours within 120 minutes contact time , while that of Cu is on the activation of NaOH (3N) for 5 hours within 60 minutes contact time. The percentages of the maximum adsorption of Cd and Cu metals to the activated allophane were found to be about 98.8% and 87.4% respectively. Thus, there is an huge increasing adsorption of Cd for more than sixteen times from 5.21% (without activation) to 98.8% (for the activated). The increasing adsorption of Cu was also observed in a slightly lesser significance; it is nearly three times from only 30.6% (without activation) to 87.4% (for the activated).

It is not surprising that the difference in optimum adsorption conditions for each sample is affected by the difference in ability of the adsorbent to adsorb the adsorbate and by the difference in characteristics of the adsorbate to be absorbed.

3.3 Determination of the Type of Adsorption Isotherms

The determination of adsorption isotherms aims to know the types of adsorption to occur. The type of adsorption is performed only for the activated allophane at the optimum conditions. Linear regression test is performed by using Langmuir and Freundlich equations (Slejko: 1985; Helfferich: 1962), and the results are shown in Fig. 3 - Fig. 8.

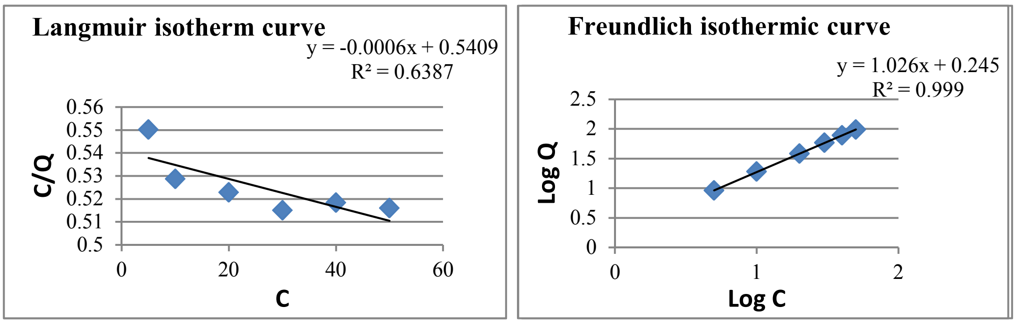

Figure 3. The isothermic curves of adsorption of Fe within contact time of 30 minutes by allophane of Mount Papandayan activated with NaOH (3 N) in 1 hours

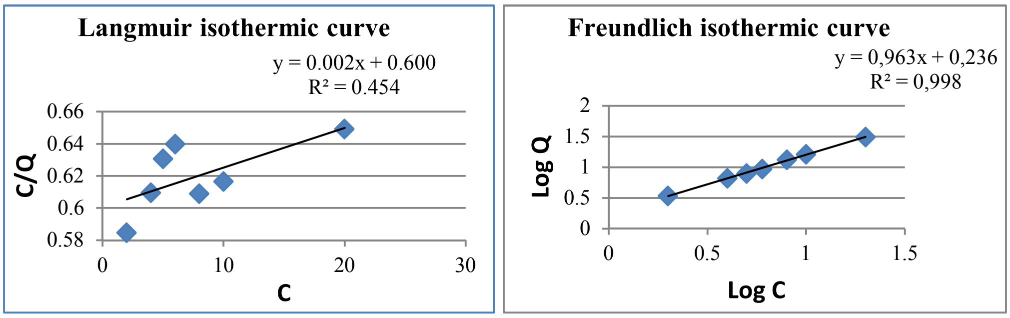

Figure 4. The isothermic curves of adsorption of Cr within contact time of 120 minutes by allophane of Mount Papandayan activated with NaOH (3 N) in 3 hours

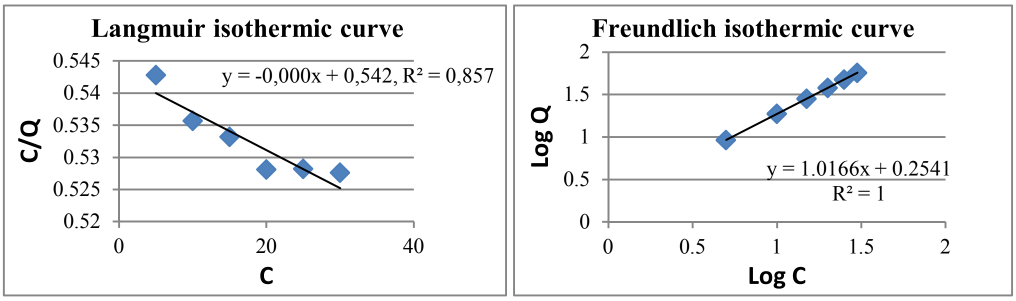

Figure 5. The isothermic curves of adsorption of Mn within contact time of 90 minutes by allophane of Mount Wilis activated with NaOH (3 N) in 5 hours

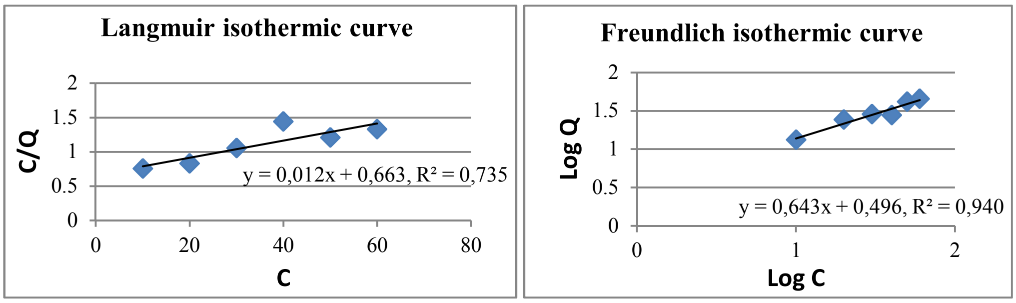

Figure 6. The isothermic curves of adsorption of Pb within contact time of 90 minutes by allophane of Mount Wilis activated with NaOH (3 N) in 5 hours

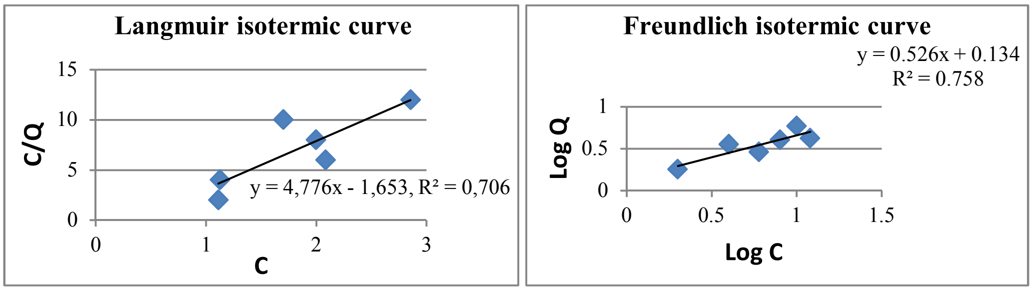

Figure 7. The isothermic curves of adsorption of Cd within contact time of 120 minutes by allophane of Mount Arjuna activated with NaOH (3 N) in 3 hours

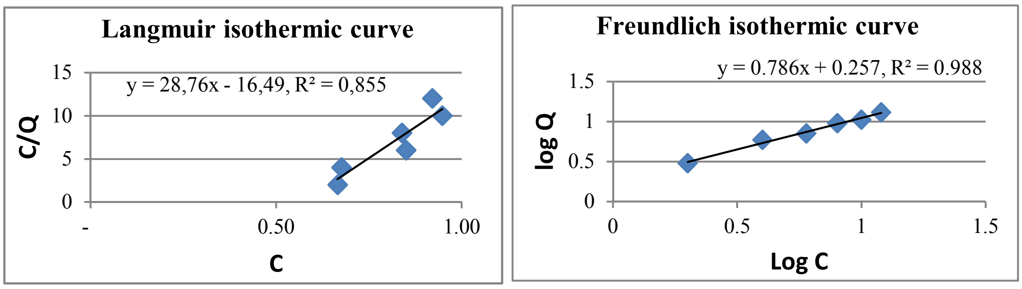

Figure 8. The isothermic curves of adsorption of Cu within contact time of 60 minutes by allophane of Mount Arjuna activated with NaOH (3 N) in 5 hours

Langmuir isotherm fits for the adsorption of a single adsorbate onto a series of equivalent sites on the surface of the solid. It may indicate that the adsorption process occurs “chemically” in which each group of active adsorbents will only absorb one adsorbate species (metal ion), so it is limited only to the formation of a single layer (Slejko: 1985; Helfferich: 1962). This is a specific adsorption. On the other hand, the Freundlich isotherm is the most important multisite adsorption isotherm for rough surfaces of the (allophane) solid (Futomo, *et. al*:1996). It may describe that the the adsorption occurs physically. Metal ions will only stick to the surface of allophane and is not chemically tightly bonded so that they will be easily separated.

Figures 3 to 8 exhibit significantly that the data of adsorption of the metal ions by the allophanes follows readily Freundlich isotherm equation as indicated by the values of R^2 fitting to the linearity of the lines. Thi is in line with the adsorption by natural as well as synthetic allophanes reported by Iyoda *et al* (2011). Therefore, it might be interpreted that the interaction that occurs in the adsorption is likely only physically in nature.

3.4 Acidity Characterization

The measurements of acidity was performed with alkaline ammonia adsorption method, and again, this is only to the activated allophane at the optimum conditions and the non-activated for comparison. The results of acidity measurement are recorded as shown in Table 6.

Table 6. The Acidity of Volcanic Allophanes

Sample	Treatment	Acidity (mmol/g)
Mount Papandayan	Without activation	1,7045 ± 0,0856
	3N 1Hours	2,2355 ± 0,1670
	3N 3 Hours	2,8240 ± 0,1660
Mount Wilis	Without activation	2,8823± 0,2495
	3N 5 Hours	6,4117±0,0832
Mount Arjuna	Without activation	1,2941 ± 0,0832
	3N 3 Hours	1,3529 ± 0,0832
	3N 5 Hours	1,5882 ± 0,0831

From the data in Table 6, it suggests that the acidity of the activated allophanes be greater than that of the non-activated natural allophanes. This is likely due to the fact that the activation process can get rid of the impurities attached to the allophanes and then the acid sites become visible.

4. Conclusion

A series of volcanic soils of Mountain Papandayan, Mountain Wilis, and Mountain Arjuna were found to contain natural allophanes with difference in acidity and in capacity for adsorbing the metal ions. Activation with NaOH solution of 3N (within 1- 5 hours) to the allopanes resulted in the optimum and significant increase of adsorbing the metal ions in a various contact time of 30 to 120 minutes. It was found that the allophane of Papandayan was to be typical for adsorbing the metal ions of Cr and Fe, while allophane of Wilis was for the metal ions of Pb and Mn, and that of Arjuna was for the metal ions of Cd and Cu. The type of adsorption isotherm follows readily Freundlich equation, suggesting typically for the rough surfaces of the allophanes and likely physical adsorption. Thus, the potential of allophanes in the adsorption of heavy metal ions (Cr, Fe, Pb, Mn, Cd, and Cu) which pose a serious threat to the environment and human health shall be investigated soon with an eye on an economic and viable water treatment technology, and the result should be reported immedaiately.

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