Synthesis and Characterization of Allophane-Like as Chromium (Cr) Ion Adsorbent

Pranoto¹, C Purnawan, A N Husnina
Research Group of Analytical and Environmental Chemistry, Faculty of Mathematics and Natural Sciences
Universitas Sebelas Maret, Ir. Sutami street No. 36 A, Surakarta, Central Java, 57125, Indonesia.

E-mail: pakpranoto@gmail.com

Abstract. The synthesis and characterization of allophane-like as chrom (Cr) ion adsorbent has been studied. The objectives of this study is to determine the characteristics of allophane-like and determine ratio of Al/Si, chromium solution pH, and contact time to get the best decreasing metal ion chrom (Cr) adsorption condition. The study was conducted with the ratio of Al/Si ratios 0.5; 0.75; 1.0; 1.25 and 1.5 from Tetraethyl Orthosilicate (TEOS) solution and Aluminium Nitrate Nonahydrate [Al(NO₃)₃.9H₂O] in pH 3-4. The result of synthetic was characterized on functional groups and cristallinity. Experiment of adsorption ability using variation of Cr solution pH 3-7, contact time 30, 60, 90 and 120 minutes with batch method. The results by FTIR shows that functional groups -OH, the asymmetry groups O-Si-O or O-Al-O, relatively weak absorption which stronger then the presence of OH and bending vibration Si-O or Al-O on allophane-like. The best conditions of chromium metal adsorption with adsorbent allophane-like was obtained at pH 5, contact time 90 minutes, and the ratio Al/Si 1.5. Types of adsorption in this study follows Freundlich and Langmuir isotherm.

1. Introduction

Allophane is one of the reactive soil minerals because it has a very large surface area and many active functional groups [2]. The allophane surface has properties such as cations and anions exchange, the uptake of organic and inorganic compounds, and the acidity source from silanol (Si-OH) and aluminol (Al-OH) functional groups [11,15], so it can be utilized as an adsorbent. However, the presence of natural allophane as an adsorbent is considered less effective and optimum in adsorbing compounds such as heavy metals. The formation of natural allophane derived from the volcanoes also takes a long time. In addition, natural allophane will change with geographic location differences [9,14]. Uncontrolled and continuous use of natural allophane can damage the environment. Therefore it is necessary to use a new alternative by making allophane synthetic or allophane-like materials.

Allophane-like synthesis can be prepared in a Tetraethyl Orthosilicate (TeOS) and aluminium nitrate nonahydrate solution with an Al / Si ratio of 0.5; 1; 1.5 and 2 [10]. According to Peelletier et al. (2005), the surface area of allophane-like is greater than natural allophane so it can also be utilized as heavy metal adsorbent [12]. One of the heavy metals that often pollute the environment is chromium

¹ pakpranoto@gmail.com
Chromium (Cr) is a heavy metal that is harmful to health and the environment. If chrome is used excessively, chrome will result in acute poisoning. Other impacts such as lung cancer [8], kidney failure, anemia, skin allergies, asthma and stomach cancer may also be mutagenic and carcinogenic [5].

There have been many developed methods to reduce Cr heavy metals ion in the environment, one of them using adsorption. Adsorption becomes the preferred method because the process is relatively simple [6]. Factors affecting the adsorption process of heavy metals are the pH of the solution, contact time, initial concentration of solution, temperature, and adsorption method [7]. Based on the description above, then conducted research on the characterization of Allophane-like as adsorbent of chromium metal ion (Cr).

2. Experimental
2.1. Synthesis Allophane-like
100, 66.67, 50, 40 and 30 mL of Tetraethyl Orthosilicate (TeOS) solution were mixed into 50 mL Aluminum Nitric Nonahydrate (Al(NO₃)₃·9H₂O) solution at room temperature to obtain an Al/Si ratio of 0.5; 0.75; 1; 1.25 and 1.5. Furthermore, 150 ml of 0.1 N NaOH added to the mixture for 3 hours. NaOH was added to solution using ratio of OH/Al by 3. The obtained mixture measured the pH of the solution and made the pH of the solution to acid (pH 3-4), then precipitated for a night until the mixture became gel. Then, the gel dried with a temperature 95 °C for 7 days. The solid is then heated in a furnace at 400 °C for 3 hours. The allophane-like obtained were characterized by FTIR, XRD, SEM, Specific Surface Area and Acidity.

2.2. Determination of Cr ion in Aqueous Solution
0.01 g of allophane-like added to flask. Then, 10 mL Cr artificial solution was added using pH variation 3, 4, 5, 6 and 7. The mixture was shake with contact time variation 30, 60, 90 and 120 minute. The obtained mixture was filtered and ion Cr was determinated using AAS for determination of Cr ion in Aqueous Solution.

2.3. Determination of Isotherm Adsorption
0.01 g of allophane-like added to flask and 10 mL Cr artificial solution was added with concentration 2, 4, 6, and 10 ppm. Then mixture was shake with constant temperature. The obtained mixture was filtered and analysed using AAS for determining Cr ion in solution. Then AAS analysis result was used to determine isotherm adsorption.

3. Result and Discussion
3.1. Synthesis and Characterization of Allophane-Like
Allophane-like was made using Tetraetil Ortosilikat (TeOS) solution as Si group source and Aluminium Nitrat Nonahidrat [Al(NO₃)₃·9H₂O] solution as alumina group source. Allophane-like using volume ratio Al/Si 0.5; 0.75; 1; 1.25 and 1.5. Obtained allophane-like was characterized using Sufare Area Analysis.

3.2. Surface Area and Acidity Analysis
Surface area is important factor in adsorption process because the greater surface area then the greater adsorption capacity. Acidity analysis was used ammonia adsorption using gravimetry methods. Specific surface area and acidity characterization was showed in table 1.
Table 1. Surface Area and Acidity Characterization

| Adsorbent        | Surface Area (m²/g) | Acidity (mmol/gram) |
|------------------|---------------------|---------------------|
| Natural Allophane | 85.529              | 1.725               |
| [4]              |                     |                     |
| Allophane-Like   | 201.558             | 2.728               |

Table 1. was showed that allophane-like surface area was greater than natural allophane surface area. According SAA analysis, obtained allophane-like pore volume 0.2395 cc/g with pore diameter 4.6 nm. Acidity value of allophane-like is greater then natural allophane. It show that active site of allophane-like is much more than natural allophane so cation exchange in allophane-like more occur.

3.3. Adsorption effectivity of Allophane-like against Cr ion

The ratio of Al / Si ratio can influence the adsorption capacity, whereas the higher the Al/Si ratio of the adsorption capacity will rise to the maximum. The diagram of the adsorption capacity at each ratio can be seen in Figure 6. The higher Al/Si ratio, the adsorption capacity will increase, but at the Al/Si ratio of 1.25 adsorption capacity was decreases, it happen because of the amount of Si contained. From synthesis result, the higher ratio Al/Si content of Al content in Allophane-like is increasing, so that more active sites could increase the surface area. The largest ratio of Al/Si is 1.5 with adsorption capacity of 0.61 mg/g.

The pH value and contact time greatly affect the adsorption process. The increase pH can cause the adsorption process to increase but will decrease again if it passes through the optimum point reached. At low pH (<5) protonation will occur resulting in the formation of H₃O⁺. This will cause competition between Cr₃⁺ and H₂O⁺ to bind to the adsorbent negative sites so that Cr ion absorption will be impaired. At an alkaline pH or pH above 5 the number of protons H⁺ is small resulting in the possibility of metal binding by a relatively large adsorbent, so that metal ions can form hydroxide precipitates and result in decreased adsorption ability [1]. The adsorption capacity diagram based on the effect of pH can be seen in Figure 2 and the largest adsorption capacity is at pH 5 of 0.87 mg/g.
The contact time is the time it takes for the adsorbent to adsorb metal ions. The longer contact time between the adsorbent and Cr solution, the adsorption capacity will increase until the optimum condition. However, prolonged contact time causes the adsorption condition to become saturated and the bond between the adsorbent and the adsorbate will be released. From the data obtained has happened adsorption equilibrium between the concentration of Cr ion adsorbed by the Cr ion concentration remaining in solution at the contact time of 90 minutes, while the contact time of 120 minutes in general adsorption ability Allophane-like decline. It can be caused by the surface of the adsorbent has reached a saturation point so that Cr ion could desorbed or escape back into the solution, whereby the release of metal ions of Cr that has been tied to the adsorbent active group. The largest adsorption capacity of Cr metal occurs at a contact time of 90 minutes with an adsorption capacity of 0.71 mg/g. The diagram of adsorption capacity based on pH variation can be seen in Figure 3.

**Figure 2.** Adsorption Capacity of Allophane-like based on pH variation

The optimum composition of Al/Si ratio is 1.5, then analysed using FTIR for determining possibility of Cr metal ion adsorbed to functional group of allophane-like. FTIR result was showed in Figure 4.

**Figure 3.** Adsorption Capacity Diagram of Allophane-like based on contact time
According in figure 4 showed that there is a change of spectra where in the absorption -OH stretching occur the shift of the wavelength from 3463 cm\(^{-1}\) to 3437 cm\(^{-1}\). This is thought to be due to the formation of a hydrogen bond between the adsorbent and Cr metal ion resulting in a decrease in the binding energy of the -OH group on Si-OH or Al-OH \([12,13]\). The decrease of the wavelength in the hydroxyl group is also due to the bonding that occurs between the Cr metal with oxygen in the hydroxyl group thereby causing the bond length to increase and the -OH binding energy becomes weak.

3.4. Isotherm Adsorption

Isotherm adsorption is used to determine adsorption process happen on chemically or physically process. Langmuir isotherm curve obtained showed in figure 5.

![FTIR Spectra of Allophane-like with Al/Si ratio 1.5 before (a) and after (b) adsorption](image)

**Figure 4.** FTIR Spectra of Allophane-like with Al/Si ratio 1.5 before (a) and after (b) adsorption

In figure 5 obtained value \(R^2 = 0.9905\). Langmuir isotherms indicate that the adsorption process occurs chemically that the active site of the adsorbent will interact with Cr metal ions in the solution by forming a coordinate covalent bond with the heavy metal ion group in the solution by forming a compound. The adsorption capacity of allophane-like according to Langmuir isotherm is 0.914 mg/g. The determination of the Freundlich isotherm shown in Figure 6.
In Figure 6 obtained value $R^2 = 0.9932$. Isotherm Freundlich is an isotherm that describes the process of adsorption physically. Physical adsorption occurs when the intermolecular force is greater than the attraction between molecules. Interaction occurs when heavy metals ion entering the pores of the allophane-like without forming bonds or interacting with weak binding energies through van der waals bonds. This weak pull force causes the adsorbate to move from one part of the surface to the other surface of the adsorbent. The allophane-like adsorption capacity according to freundlich isotherm is 0.353 mg/g. Allophane-like isotherm adsorption data will be shown in Table 2.

**Table 2. Isotherm adsorption for Allophane-like ratio Al/Si 1,5**

| Isotherm Langmuir | Isotherm Freundlich |
|-------------------|---------------------|
| $Q_{max}$ (mg/g)  | 0.914               |
| $b$ (L/g)         | 0.494               |
| $r$               | 0.991               |
| $K_f$ (mg/g)      | 0.353               |
| $n$               | 2.897               |
| $r$               | 0.993               |

Based on table 2, $R^2$ value Freundlich isotherms equation higher than the $R^2$ value of the Langmuir equation even though they are close to 1 with a difference that is not significantly different. It can be concluded that this study follows Freundlich isotherms and Langmuir isotherms or adsorption processes occur physically and chemically.

**4. Conclusion**

Based on the result, Surface area of Allophane-like 201.558 m$^2$/g and more large than natural allophane. The acidity of Allophane-like is 2.728 mmol/g. The best absorption condition of Allophane-like to chromium (Cr) metal ion occurs in variation of Al/Si ratio 1.5 buffer solution pH 5, contact time 90 minutes. The type of adsorption isotherms follow the isotherms Langmuir with $Q_{max}$ 0.914 mg/g and Freundlich with $K_f$ 0.353 mg/g.

**Reference**

[1] Cordero B, Loidero P, Herrero R, and Vicente 2004 *J. Environ. Chem.* 11 180-187
[2] Devnita R, Yuniarti H 2005 *Fakultas Pertanian UNPAD*
[3] Eliopoulos M E, Antivachi D, Vasilatos C, dan Megremi I 2012 *Geoscience Frontiers* 3 523-539
[4] Husna M N 2012 *Skripsi* Kimia FMIPA UNS Surakarta.
[5] Kaszycki P, Gabrys H, Appenroth K J, Jaglarz A, Sedziwy S, Walczak T, and Koloczek H 2005 *Plant Cell. Environ.* 29 260-268
[6] Khasanah E N 2009 *Oseana* 34 1-7
[7] Mc Cabe 1999 *Operasi Teknik Kimia Jilid 2* (Jakarta : Erlangga)
[8] Palar, H. (2008). *Pencemaran dan Toksikologi Logam Berat*. PT Rineka Cipta. 133-144, Jakarta.
[9] Parfitt, R.L., 1990, *Proceedings of the Six International Soil Classification Workshop. Chile and Equador* 9 – 20 January 1984.
[10] Pelletier, E.M., Bogenez, S., Pelletier, M., Razafitianamaharavo, A., Ghanbaja, J., Lartiges, B., and Michot,L., 2005, *Colloids and Surfaces*, 255, pp 1-10.
[11] Sukmawati., 2011, *Media Litbang Sulteng IV*, 2, pp 118-124.
[12] Iyoda, F., Hayashi, S., Arakawa, S., John, B., Okamoto, M., Hayashi, H., Yuan, G. 2012 *Applied Clay Science* 56 pp 77-83
[13] Opiso, E., Sato, T., Yoneda, T., 2009 *Journal of Hazardous Materials* 170(1) pp 79-86
[14] Pranoto, Suranto, Sugiyarto K. H., Ashadi 2013 *Journal of Environmental and Earth Science* 3(5) pp 48-56
[15] Reinert L., Ohashi F., Kehal M., Bantignies J-L., Goze-Bac C., Duclaux L. 2011 *Applied Clay Science* 54(3-4) pp 274-280