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The Characteristic and Activation of Mixed Andisol Soil/Bayat Clays/Rice Husk Ash as Adsorbent of Heavy Metal Chromium (Cr)

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Abstract. Chromium (Cr) concentration in water can be reduced by adsorption. This study aimed to determine the effect of Andisol soil composition/Bayat clay/ husk ash, activation temperature and contact time of the adsorption capacity of Cr in the model solution; the optimum adsorption conditions and the effectiveness of ceramic filters and purifiers to reduce contaminant of Cr in the water. The mixture of Andisol soil, Bayat clay, and husk ash is used as adsorbent of metal ion of Cr(III) using batch method. The identification and characterisation of adsorbent was done with NaF test, infrared spectroscopy (FTIR), X-ray diffraction (XRD). Cr metal concentrations were analyzed by atomic absorption spectroscopy. Sorption isotherms determined by Freundlich equation and Langmuir. The optimum conditions of sorption were achieved at 150ºC activation temperature, contact time of 30 minutes and a composition Andisol soil / Bayat clay / husk ash by comparison 80/10/10. The results show a ceramic filter effectively reduces total dissolved solids (TDS) and Chromium in the water with the percentage decrease respectively by 75.91% and 9.44%.

1. Introduction

The increasing of industry gives negative impact in the form of an increase in terms of number and type of waste generated. Pollutants that enter the water (groundwater or surface water) can affect the parameters of aquatic environment. Heavy metals is one of the pollutants because of toxic and it is not degraded in the nature [1]. The adsorption method is very effective for reducing pollutants [2].

Andisol soil is soil that occurs from the weathering of volcanic rocks, which both of rock that has been frozen, or from volcanic ash. The soil is composed of andesite is Andisol soil, while allophane an aluminosilicate contained in Andisol soil. Allophane adsorbent has good characteristics, such as porosity, high absorption and cation exchange. Using the natural allophane of mountains in Java Island (Papandayan, Arjuna and Wilis) for adsorbting heavy metals (Cr, Fe, Cd, Cu, Pb and Mn) with batch method [3].

Bayat Clay has been choosen as adsorbent because its existence many found in District Bayat, Klaten Regency, Central Java, Indonesia and is currently only used by mostly Bayat community for pottery production. Clay is an aggregate of minerals that form of land consisting mainly of hydrous aluminum silicates, has active sites on the surface, it is hard and stiff when it is dry, stable at high temperatures and is plastically when it is crushed and moistened [4].

Rice husk many found as agricultural waste in Indonesia. During this time the rice husks are usually only used as a fuel or even just burned away. By making it as adsorbent, it is expected to add value to the waste. Some researchers have been using rice husk ash in processing cooking oil and it gives great results.

Based on numerous studies by using Andisol soil, natural clay and rice husk ash, so this study conducted the development adsorbent of a mixture Andisol soil, Bayat clay and rice husk ash to increase the effectiveness of the entrapment of the chromium (Cr) heavy metal and its development as a ceramic filter and pipe purifiers to reduce the content of heavy metals chromium (Cr) in groundwater.

The purpose of this study was to determine the effect of Andisol soil composition: Bayat clay: husk ash, activation temperature and contact time on the sorption of chromium (Cr) heavy metal ions in a model solution, determine the optimum conditions adsorbent of mixture Andisol soil: Bayat clay: husk ash as adsorbent chromium (Cr) heavy metal in a model solution, examine the effectiveness of ceramic filters and purifiers pipe in reducing chromium (Cr) heavy metal ion content in water.

2. Experimental

2.1. Adsorbent Preparation

2.1.1. Rice Husk Ash

Rice husks that had been washed with water for 3-4 times dried, then has been ashed at temperatures of 300ºC for 2 hours. Rice husk ash obtained is then stored in sealed bottles for later use.

2.1.2. Clay

The clay used in this study came from Bayat, Klaten, Central of Java Province, Indonesia. The clay obtained is cleaned of impurities and dried with aerated in the open air to make it dry, then crushed clay until it is smooth. Clay then sieved with a 150 mesh sieve. The powder that passed 150 mesh was soaked in distilled water and filtered, then dried at 105º C for 4 hours [5].

2.1.3. Andisol Soil

Andisol soil used in this study came from the Cemoro Kandang, Lawu, Central Java, Indonesia. Andisol soil obtained cleaned of impurities, washed with water and dried with aerated in the open air to dry, then Andisol soil is crushed until smooth. Furthermore, Andisol soil has sieved with a 150 mesh. The powder that passed 150 mesh was soaked in distilled water and filtered, then dried at 105ºC for 4 hours [5].

2.2. Adsorbent Identification and Characterization

The identification of the adsorbent was done by testing the pH of Sodium Fluoride (NaF), XRD, FTIR.

2.3. Adsorbent Activation

Adsorbent activation is done chemically and physically. Chemical activation is only done for Andisol soil, as many as 50 grams of ground Andisol NaOH is added to 250 mL with a concentration of 3 M. Then the mixture was stirred at a temperature of 70ºC with a stirring for 5 hours, then cooled. Once the mixture is cool then filtered and washed with distilled water until the pH is neutral. After that, the Andisol soil were dried in an oven for 4 hours or until dried at a temperature of 105ºC [5].
Later on, a composition variation of adsorbent was made among Andisol soil, Bayat clay, and rice husk ash, such as 100/0/0, 80/10/10, 60/20/20, 40/40/20, 20/40/40, 20/20/60, 10/80/10, 10/10/80, 0/0/100 dan 0/100/0.Each composition of the mixture of rice husk ash and Andisol soil then performed physical activation at temperature variations of 100, 150 and 200ºC for 3 hours. The adsorbent used

for the performance test for optimum conditions to the adsorption of metal ions of chromium (Cr^{3+}) in solution models.

2.4. Adsorbent Performance Test

2.4.1. Sorption of Ion Cr (III) in Solution Model
Metal ion adsorption process of chromium was conducted by immersion (batch), namely by as much as 0.05 gram of adsorbent mixture put in a 100 mL glass beaker containing 15 mL solution of Cr (III) 8 ppm. Then it stirred at a constant speed (150 rpm) at room temperature for 30, 60 and 90 minutes. Then filtered with Whatman No. 40 and the filtrate was measured by Atomic Absorption Spectroscopy (AAS) to determine the metal ion concentration of Cr (III) which is not adsorbed by adsorbent. Furthermore, the results of an adsorbent against metal ion Cr (III) (mg / g) to determine the contact time, which has a maximum power adsorb. Ion Cr (III) adsorbed is calculated from the concentration of Cr (III) initially reduced by concentration after sorption process. Then graphed concentration of chromium (Cr^{3+}) adsorbed with time variation. Ion Cr (III) analysis using atomic absorption spectroscopy.

2.4.2. Determination type of sorption isotherm
The best adsorbent that has been obtained then carried sorption variation adsorbed ion concentration to determine the type of isotherm. A total of 0.05 grams of adsorbent put in a 100 mL glass beaker and added to each 15 ml of Cr (III) with various concentrations of 2, 4, 6, and 8 ppm and then stirred at the optimum time. The sorption results filtered with Whatman No. 40, then the filtrate obtained, was measured by AAS. The results are then analyzed to determine the type of Langmuir or Freundlich isotherm.

2.5. Ceramic Filter Manufacture and Purifier Pipe

2.5.1. Ceramic Filter.
The process of making ceramic filter made by craftsmen of pottery in Bayat, Klaten, Central Java, Indonesia to adjust the composition of raw materials and the desire of researchers with dry mixing between Andisol, clay and rice husk ash adsorbent by comparison based on optimum conditions. The material mix gypsum cylindrical mold with a diameter of 4 cm inside, the outside diameter of 5 cm, thickness of 0.5 cm and a length of 20 cm.

2.5.2. Purifier Pipe
Water purifiers pipe use Poly Vinyl Chloride (PVC) pipe with diameter ½ inch (1.25 cm), 20 cm long with a mixture contained Andisol, clay and rice husk ash is spherical diameter of 1.2 cm and a variation of the addition of deodorizing shell charcoal.

3. Result and Discussion

3.1. Adsorbent Identification

3.1.1. NaF Test
The allophane existence of minerals in the soil can be identified by test NaF. The NaF test is done, by measuring the pH of 1 gram of soil in 50 ml of NaF 1 solution for 2 minutes. Soil pH value greater than 9.4

3.1.2. FTIR Analysis

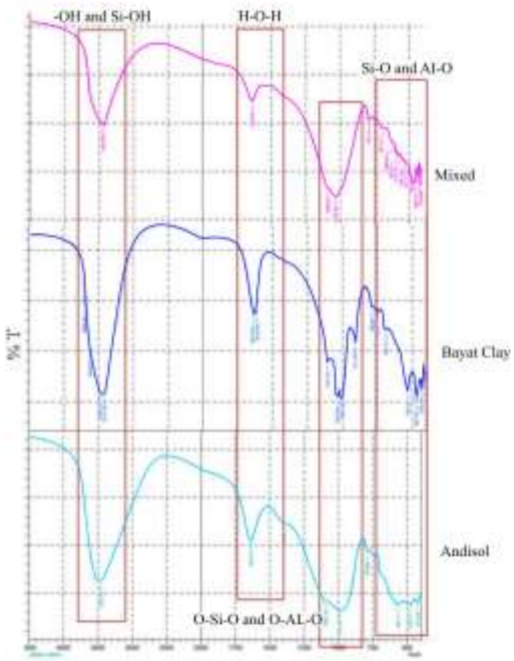

Figure 1. Sample Spectrum of andisol soil, bayat clay and mixed

As shown in Figure 1, the spectra for all natural samples are similar one to another, and they are typical for allophane.

Table 1. Comparison between the spectra of samples

Functional Groups	Allophane Uptake (Cm^{-1})		
	Allophane/ Andisol	Bayat Clay	Mixed
Vibration –OH (Al-OH/Si-OH)	3455	3444	3437
Vibration AlOh/SiOH	1108;973	912.33	960.55
The Existence of Si-O bond	579;485	428	432

3.1.3. XRD Analysis

XRD for the samples were recorded and shown in Figure 2. They are similar each other.

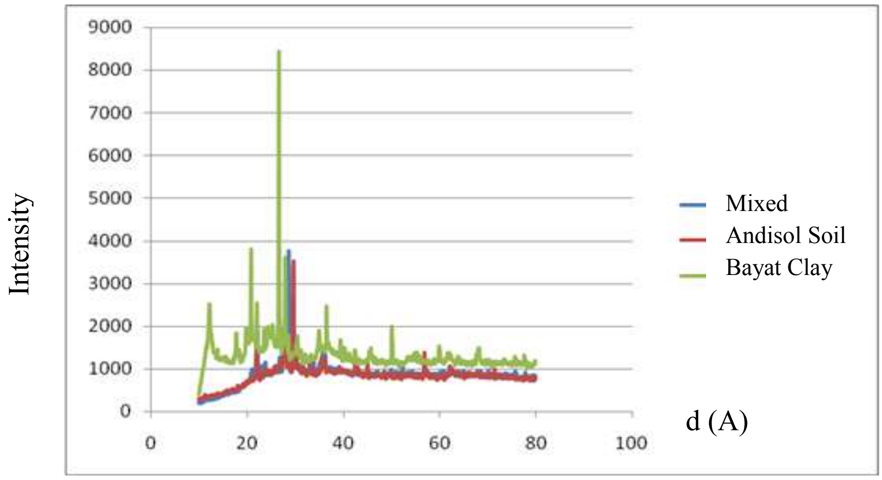

Figure 2. Difraktogram Sample of andisol soil, bayat clay and mixed

The details of particular d-spacings are confirmed with JCPDS for allophane as shown in table 2.

Table 2. typical d-spacings data of three samples compared to JCPDS

JCPDS (38-0444)	d-Spacing (Å) of allophane				
	3.300	2.250	1.860	1.400	1.230
Andisol Soil	3.305	2.249	1.861	1.400	1.230
Bayat Clay	3.305	2.249	1.861	1.400	1.230
Mixed	3.305	2.249	1.861	1.400	1.230

3.2. Adsorbent Activation

Activation of Andisol soil, Bayat clay and rice husk has done to improve the chemical and physical character as adsorbent. The chemical activation has done by soaking Andisol soil in 3 M NaOH for 5 hours. Activation using a strong base 3 M NaOH for 5 hours refers to the research that has been done [6], which resulted in an increase in specific surface area on the adsorbent of Andisol activated by 1.62% and amounted to 90.87% total acidity. As for clay and rice husk ash is not performed chemical activation. Physical activation performed on a mixture adsorbent of Andisol soil, Bayat clay and rice husk ash with their weight ratio 100/0/0, 80/10/10, 60/20/20, 40/40/20, 20/40/40, 20/20/60, 10/80/10, 10/10/80, 0/0/100 and 0/100/0.

Table 3. Data of Surface Area

No	Sample	Surface area (m^2/g)
1	Andisol	66,42
2	Bayat Clay	34,53
3	Rice husk ash	15,18
4	Mixture	35.85

Source: Primary Data

Table 4. Data of Acidity

No	Sample	Acidity (mmol/g)
1	Andisol	6,75
2	Bayat Clay	3,27
3	Rice husk ash	4,02

Source: Primary Data

3.3. Adsorbent Performance Test

Andisol soil absorbent, Bayat clay and rice husk ash, have a high affinity for metal ions. All three have active groups Si-OH and -OH, whereas Andisol soil and clay Also has an active Al-OH groups, so that all three has the electronegative surface charge. The exchange of cations in the process of metal sorption of chromium (Cr) in solution [6]. Sorption ability of silicate minerals derived from the number of negative charge on the structure of silicate minerals. The negative charge is neutralized by adsorption adsorbed positively charged ions, such as heavy metal cations. Based on the data from sorption that the three absorbent namely Andisol soil, Bayat clay and rice husk ash. All three have the ability to adsorb metal ions with different adsorption capacity[7].

Adsorbent with composition of 100% ground Andisol (100/0/0) has a sorption capacity greater than 100% clay dsorbent (0/100/0) and rice husk ash adsorbent 100% (0/0/100). Adsorbed amount of metal ions decreases with increasing percentage clay adsorbent and rice husk ash in the composition of the adsorbent mixture. This shows that the presence of clay and rice husk ash in the adsorbent mix less support adsorbent ability to adsorb the metal ion Cr (III). Reduced ability Andisol sorption of a mixture of soil, clay and rice husk ash can be explained based on the data of surface area and the number of acidity of each adsorbent.

Heating the mixture of clay and Andisol adsorbent also intended to free water molecules, both the water bound physically or chemically bound in the form of hydrated.

In this study conducted temperature variations of 100, 150 and 200°C. Through the third activation on these temperature variations, it would be known to influence the temperature difference in the ability to absorb metal chromium.

The sorption capacity of the soil mixture adsorbent of Andisol, clay and rice husk ash increased with the length of contact time. When its adsorption has reached the maximum, and the adsorption capacity to be reduced with increasing contact time. At a temperature of 100 and 150 ° C of all adsorbent compositions increased adsorption capacity with increasing contact time of 30 to 60 minutes and sorption capacity decreased when the contact time of 90 minutes. Based on data from sorption capacity results prove that the contact time influence in the process of sorption.

The research showed the best condition sorption of metal ions Cr (III) is an adsorbent with composition of Andisol soil, clay and rice husk ash (80/10/10), the activation temperature of 150^o C and a contact time of 30 minutes. It is also expected to provide an overview adsorbent effectiveness Andisol soil mixture, clay and rice husk ash treatment if carried metal ion adsorption. Furthermore, the final stage of this research is the manufacture of water purification using raw material mixture of adsorbent.

3.4. Determination type sorption isotherm

Freundlich isotherm explains that the adsorption occurs on more than one surface (multilayer) and adsorbent have heterogeneous surfaces with a binding energy of different [8]. Cr (III) ion adsorption by adsorbent mixture of clay and Andisol occur fisisorption. Sorption type is suitable for sorption mechanisms that require regeneration process because the substance adsorbed only weakly bound to the surface of adsorbent.

3.5. Filter Performance Pottery Test and Pipes Purifier

3.5.1. Ceramic Filter

Ceramic filter performance test were conducted by well water drained from the tank through a PVC pipe to the water purification. Water is passed three housing containing a ceramic filter, activated carbon granules, carbon block, then the head housing contains osmosis membranes and the last pass of activated carbon powder. The water treatment outcomes, was collected and measured Total Dissolve Solids (TDS), pH, conductivity, turbidity, salinity and metal ion of Cr (III).

4. Conclusion

The composition of Andisol soil, Bayat clay and rice husk ash, activation temperature and contact time affect the adsorption capacity of Cr (III) metal ions in solution models with optimum conditions of Andisol soil composition, Bayat clay and rice husk ash (80/10/10), the activation temperature of 150 $^{\circ}$C and contact time of 30 minutes. Absorbent of Andisol soil mixture, Bayat clay and rice husk ash in optimum conditions effective to reduce the content of Cr (III) metal ions in solution models with an efficiency of 97, 56%. The measurement results show a ceramic filter effectively reduced Total Dissolved Solids (TDS) and Chromium in the water with the percentage decrease respectively by 75.91% and 9.44%. While the pipe purifiers can reduce total dissolved solids (TDS) from 260 to 249 ppm and Chromium from 0.064 to 0.052 ppm.

References

[1] Zhao, G., Wu, X., Tan, X., dan Wang, X 2011 *The Open Colloid Science Journal* **4** 19-31.
[2] Manohar, D.M., Noeline, B.F., and Anirudhan, T.S. 2006 *Applied Clay Science* **31** pp.194-206
[3] Pranoto, Suranto, Sugiyarto, K. H. and Ashadi 2013 *Journal of Environment and Earth Science* **3(5)** ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
[4] Sulastri, S. dan Kristianingrum, S. 2007 *Prosiding Seminar Nasional Kimia dan Pendidikan Kimia* ISBN: 978-979-98063-1-4.
[5] Sulistyarini, Ari 2012 Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Sebelas Maret
[6] Widjonarko, D. W., Pranoto dan Christina, Y 2003 *Journal Alchemy* **2(2)** September 2003
[7] Diantariani, N. P. 2010 Jurnal Kimia **4(1)** Januari hlm. 91-100 Universitas Udayana Bukit Jimbaran ISSN 1907-9850
[8] Alemayehu, D. D., Sing, S. J., and Tessema, D. A. 2012 *Universal Journal of Environmental Research and Technology* **2(5)** pp 411-420