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## Synthesis of Low-Cost Adsorbent Based on Fly Ash for Heavy Metal Reduction of Cu and Cr In Textile Industrial Liquid Waste

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### Abstract

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Heavy metal copper (Cu (II)), Chromium (Cr (IV)) is a heavy metal that dominates textile industrial wastewater. Too large concentrations of Cu (II) in water can cause poisoning which has side effects of liver damage and gastrointestinal disorders. Cr metal in the body will cause interference with DNA synthesis and increase mutagen changes that can cause tumors. The use of fly ash as a Low Cost Adsorbent is an alternative. The research method used is a physical activation process with carbonization at high temperatures (300°C, 400°C and 500°C) in the furnace to be continued with chemical activation using concentrated acids (H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH) or base (KOH) in fly ash. Morphological analysis and the synthesized adsorbent function groups were performed using Scanning Electron Microscopes (SEM) and FTIR. Based on the adsorption capacity test, the ability of fly ash to adsorb Cu metal waste was 0.9962 mg/g and for Cr metal was 0.4760 mg/g. The temperature increase on the physical activation of fly ash (300 OC, 4000C, 5000C) causes an increase in the adsorption capacity of the synthesized fly ash. The best adsorbent for Cu metal is A5K with an adsorption capacity of 0.9994 mg/g under optimal conditions. The best adsorbent for Cr metal is A5S with an adsorption capacity of 0.9325 mg/g under optimal conditions. ©2018 JNSMR UIN Walisongo. All rights reserved.

**Keywords:** *Low Cost Adsorbent, Fly Ash, Cu, Cr*

### 1. Introduction

Progress of the Indonesian textile industry can not only be seen from the technology but also from the amount of production which has increased from year to year. Indonesian textile

exports to several developed countries such as the United States, Thailand, Japan and Canada contributed to a significant increase in foreign exchange. The progress of the Indonesian textile industry in addition to having a positive impact on development, on the other hand, also has a

negative impact on the environment. Textile production processes generally include desizing (starch removal), scouring (wax removal), bleaching, mercerizing (the process of producing a shiny color), dyeing (the process of giving color to fabrics with pigment ink), printing (process giving color to the fabric), finishing (the process of softening the fabric using formaldehyde) (Babu 2007; Wang 2011). Several processes in the textile industry produce liquid waste which is harmful to the environment.

Most of the liquid waste generated from the textile industry consists of dyes, metal ions, suspended solids and relatively low levels of COD and BOD (Sundar, 2007). Heavy metals in textile wastewater come from dyes in the dyeing and printing processes. Some of the heavy metals commonly contained in textile industrial wastewater are copper (Cu (II)), chromium (Cr (III) & Cr (VI)), zinc (Zn (II)), lead (Pb (II)), cadmium. (Cd (II)), cobalt (Co (II)) and nickel (Ni (II)). The heavy metal copper (Cu (II)) and chromium (Cr (IV)) are heavy metals that dominate the textile industry wastewater. Both metals have a very bad impact on human health and the environment because they are very toxic (Lakherwal, 2014). Concentrations of Cu (II) that are too large in water can cause poisoning which has side effects of liver damage and gastrointestinal disorders. Heavy metal Cr (VI) is a toxic metal. Cr metal in the body will cause interference with DNA synthesis and increase mutagen changes that can cause tumors.

To protect the water system from the negative impact of heavy metals, many efforts have been made. Precipitation method is a classic method that is widely used to reduce heavy metals in textile industrial waste. Precipitation method is very effective to use when heavy metals are in high concentrations. If the heavy metals in the wastewater are low, the most effective method is adsorption. Adsorption of heavy metals using adsorbents is a simple and inexpensive method (Kurniawan et al., 2006).

The use of adsorbents in the adsorption process of heavy metals in liquid waste has long been known. This process is actually still quite suitable to be developed in Indonesia. Only one of the things that makes this process not widely

used by many industries is the high price of the price of the adsorbent used. The adsorbent commonly used is activated carbon produced from the coal carbonization process, but its synthesis costs a lot. The production of activated carbon using materials that are easy to find and inexpensive has also begun to be developed, including using coconut shells, biomass materials, rice straw, egg shells, mangosteen peels, etc. (Gopalakrishnan 2011; Renge 2012). The limited availability of these basic materials both in quantity and continuity is a separate obstacle in the development of adsorbents.

The development of adsorbents using materials with inexpensive prices, good quantity and continuity and the process that can be carried out by the industry itself will certainly be interesting to develop. One of the materials that meet these criteria is fly ash. Fly ash is ash from coal combustion with fine grains carried by the flow of combustion gases and is a hazardous waste if inhaled. According to the technical report of PT PLN (Persero) (2009), in Indonesia the production of fly ash from power plants continues to increase, the production of fly ash and bottom ash from PLTU has reached 2 million tonnes in 2006, and increased to nearly 3.3 million tonnes in 2009. If fly ash is left idle and untreated it will have an impact on the environment and humans, because fly ash is one of the B3 (Hazardous and toxic substances) wastes. This material is very fine, light and contains high silica, making it a serious problem for the environment. Free silica dust contamination contained in fly ash, in the form of SiO<sub>2</sub>, which is inhaled into the lungs causing acute respiratory problems. Solutions so that fly ash waste does not have a negative impact and has high use value needs to be managed and utilized properly and wisely. One of the efforts that can be done is to increase the use of fly ash as an adsorbent of hazardous metals in textile waste.

Fly ash is a porous fine material, and contains silica, alumina and carbon in it, making fly ash potential as an adsorbent. Fly ash can remove organic contaminants because it contains high carbon, has a large surface area, and contains Al, Fe, Ca, Mg, and Si (Kolemen 2013). Components such as K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, CaO and

SiO<sub>2</sub> which are usually involved in the formation of zeolite and are present in it make fly ash potential as an adsorbent. Fly ash can be increased its use value by using it as an adsorbent for industrial wastewater treatment.

Making adsorbent from fly ash does not require high costs (low cost adsorbent). The use of fly ash as a Low-cost Adsorbent is an alternative application of the 3R principle (Reuse, Reduce, and Recycle) in handling B3 (Hazardous and toxic substances) waste in the form of fly ash. Low – cost adsorbent from fly ash waste is environmentally friendly because it can use the waste material of PLTU Tanjung Jati and the process of making the adsorbent does not consume too much energy. The technology for making low cost adsorbents from fly ash is a way to reduce hazardous metal waste Cu, Cr in textile industry wastewater which pollutes the environment. The description above encourages the need to conduct research "Synthesis of low-cost adsorbent based on fly Ash for the reduction of heavy metals Cu and Cr in textile industry wastewater".

## **2. Experiments Procedure**

### *Adsorbent Synthesis*

Manufacture of adsorbents is carried out in two stages, namely carbonation (physical activation) and chemical activation. The adsorbent used is low cost adsorbent made from fly ash. The carbonation stage (physical activation) of fly ash is carried out to increase the porosity and surface area of the adsorbent. Carbonation (physical activation) is carried out by heating fly ash at temperatures of 400°C, 500°C and 600°C for 1 hour. In this study, variations in carbonation temperature were carried out to obtain an adsorbent with optimal ability.

Chemical activation is carried out in order to increase the porosity and increase the selectivity of the adsorbent. In this research, the variation of the activator was carried out at the time of chemical activation. Two types of activators used in this study are KOH, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH. Chemical activation is carried out by mixing fly ash with an activator (KOH, H<sub>2</sub>SO<sub>4</sub> and

CH<sub>3</sub>COOH) with a mass ratio of fly ash: activator = 1: 1,2.

### *Characterization*

Analysis of the Adsorbent crystal structure was carried out using X-ray diffraction techniques (XRD, Philips brand X'Pert MPD) with Cu Kradiation ( $\lambda = 1.5405 \text{ \AA}$ ) at 40 kV and 30 mA,  $2\theta$  5–50o with a scan speed of 0.02. o / second. To detect functional groups and the active side of the adsorbent using Fourier Transform Infrared Spectroscopy (FTIR, Bruker) at a wavelength of 400–4000cm<sup>-1</sup> with a spectrum separation of 2 cm<sup>-1</sup>, at a temperature of 20 oC with the KBr pellet method.

The adsorbent surface morphological analysis was determined using a Scanning Electron Microscope SEM (FEIQuanta 200, FEI, USA). Analysis of the surface area (The Brunauer-Emmett-Teller (BET) surface area), the total volume and the distribution of the adsorbent pore size were determined by the nitrogen adsorption method.

### *Adsorption Capacity*

A solution consisting of chromium and copper were dissolved in distilled water with a concentration of 1000 ppm each. The concentration of metal ions absorbed was determined using an Atomic Absorption Spectrophotometer (AAS). All samples were analyzed by triplet for a more accurate and quantitative concentration of the waste solution.

Synthesis wastewater was prepared by preparing Cu and Cr mother liquor. The main solution of Cr was prepared by weighing 5.657 grams of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> carefully and then dissolving it in distilled water up to 1 liter so that the main solution content was 1000 ppm. Mains solution of Cu was prepared by weighing as much as 3.927 grams of CuSO<sub>4</sub>. 5H<sub>2</sub>O, carefully weighed, then dissolved in distilled water up to 1 liter so that the main solution content is 1000 ppm. The mother liquor is then diluted according to the concentration required to test the adsorption capacity of the adsorbent as a result of the synthesis.

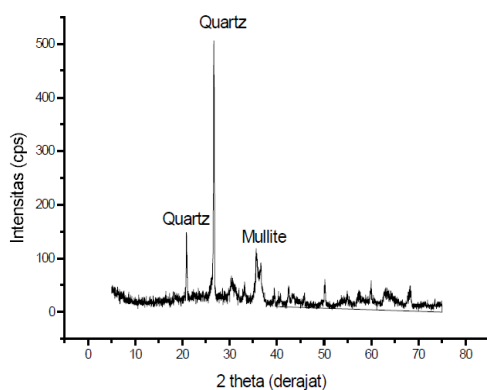
The adsorption process is carried out to reduce heavy metals found in textile industrial wastewater. In this study, a heavy metal concentration of 50 ppm was used. Adsorption was carried out on 20 ml of artificial waste with a variation of the contact time for 1 hour. Analysis of heavy metal concentrations (Cr and Cu) was carried out using AAS.

### 3. Results and Discussion

The results of the chemical composition analysis of fly ash PLTU Tanjung Jati Jepara were carried out at the Chemical Laboratory of State University of Malang. The XRF method (Table 4.1) states that fly ash contains heterogeneous components with the main component (the major amount), namely the weight of SiO<sub>2</sub>: 22.40%, the weight of Al<sub>2</sub>O<sub>3</sub>: 9.224% the weight of CaO: 11.21%, the weight of Fe<sub>2</sub>O<sub>3</sub>: 45.77. , TiO<sub>2</sub>: 2.18%, K<sub>2</sub>O: 4.07 and other minerals 4.07%

The composition of fly ash is very unique depending on the type of coal, the source of coal, and the treatment of fly ash itself (Hsu et al., 2008; Stellaci et al., 2009; Nascimento et al., 2009; Al-Zboon et al., 2011).

The results of the phase analysis of the fly ash mineral at PLTU Tanjung Jati Jepara using X-ray diffraction with a wavelength of 1.54060 Å wavelength using radiation from a Cu targeted tube, a voltage of 40.0 kV, a current of 30.0 mA and the observation area between 3,000-90.00 degrees (Figure 1). The results of the analysis stated that most of the fly ash contained an amorphous aluminosilicate phase with the main content of Quartz and Mullite minerals.

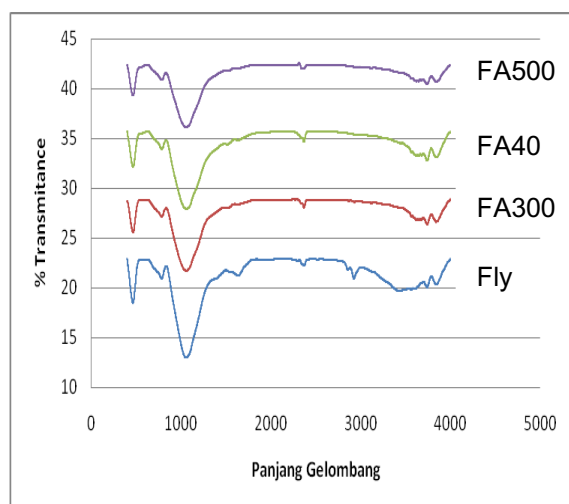


**Figure 1.** Ash Fly Ash Diffractogram of Tanjung Jati Jepara

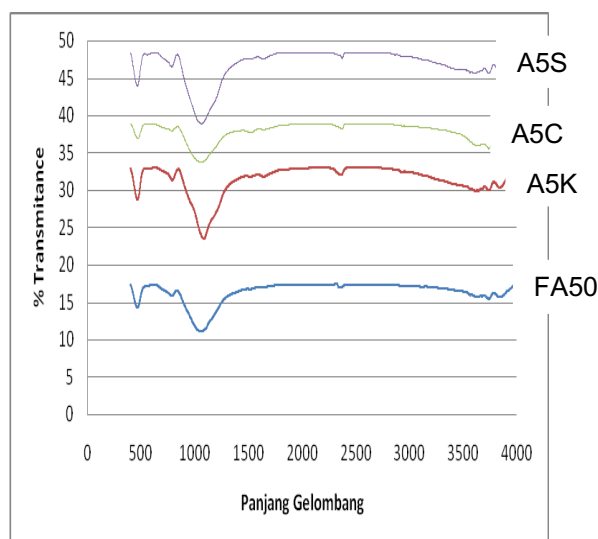
Identification is done by matching the X-ray diffraction pattern with diffraction according to the JCPDS standard (Joint Committee of Powder Diffraction Standard). The main mineral (Q) Quartz (SiO<sub>2</sub>) is shown by the sharp diffraction peaks in the main mineral (Q) Quartz (SiO<sub>2</sub>) shown by the sharp diffraction peaks at  $2\theta = 20.94; 26.64; 50.38; 54.95$  and  $60.02$ . Mullite (3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>) phase at  $2\theta = 33.31$  and  $42.94$ , these sharp peaks show a crystalline phase that is not reactive, while the amorphous phase is indicated by the presence of a wide hump at  $2\theta$  between 20 to 37.

The XRD analysis results show that the most dominant mineral is amorphous structure and the crystalline phase is quartz (SiO<sub>2</sub>). Minerals needed in the adsorption process are minerals that contain silicate elements. In addition, there are several minerals that can influence the adsorption process, both helping and inhibiting the adsorption process. Minerals that can help in the adsorption process are minerals that contain elements of Fe (such as hematite and maghemite) and Mg (periclase). Meanwhile, minerals that inhibit the adsorption process are anorthite and anhydrite because they contain Ca element.

FTIR analysis was applied to estimate the presence of functional groups on the surface of the synthesized adsorbent. The FTIR spectra of the synthesized adsorbent are shown in Figure 2. The spectra of the fly ash before activation show that the absorption band at the wave number  $3407.98\text{ cm}^{-1}$  is the stretching vibration of the -OH group, the wave number  $1400.80\text{ cm}^{-1}$  is the bending vibration of the -OH group from the absorbed H<sub>2</sub>O molecule, The wide wave number  $1029.92\text{ cm}^{-1}$  with sharp intensity shows the Si-O-Si asymmetric range vibration which indicates the presence of a Si-O or Al-O group in the structure related to the Si-OH group. The peak width shows the number of Si-OH groups so that the crystallinity in the fly ash structure decreases. The absorption at  $775.33\text{ cm}^{-1}$  showed a symmetrical vibration range of Si-O-Si followed by a Si-O bending mode at  $455.17\text{ cm}^{-1}$ , indicating the presence of a pore structure in fly ash.



**Figure 2.** FTIR Spectra of Fly Ash, FA300, FA400 and FA 500



**Figure 3.** FTIR spectra of FA 500, A5K, A5C and A5S

Based on Figure 2, it can be seen that physical activation causes the loss of absorption band of the wave number  $2906.53\text{ cm}^{-1}$  this is due to the impurity in the fly ash pore is lost so that the fly ash pore is getting cleaner. The emergence of new absorption bands at wave numbers  $792.69\text{ cm}^{-1}$ ,  $777.26\text{ cm}^{-1}$  and  $1093.56\text{ cm}^{-1}$  is a vibration of the O-Si-O asymmetrical range. The shift also occurs in the wave number  $455.17\text{ cm}^{-1}$  shifted to  $459.03\text{ cm}^{-1}$  accompanied

by a decrease in intensity, this indicates that the Si-O bond is weak.

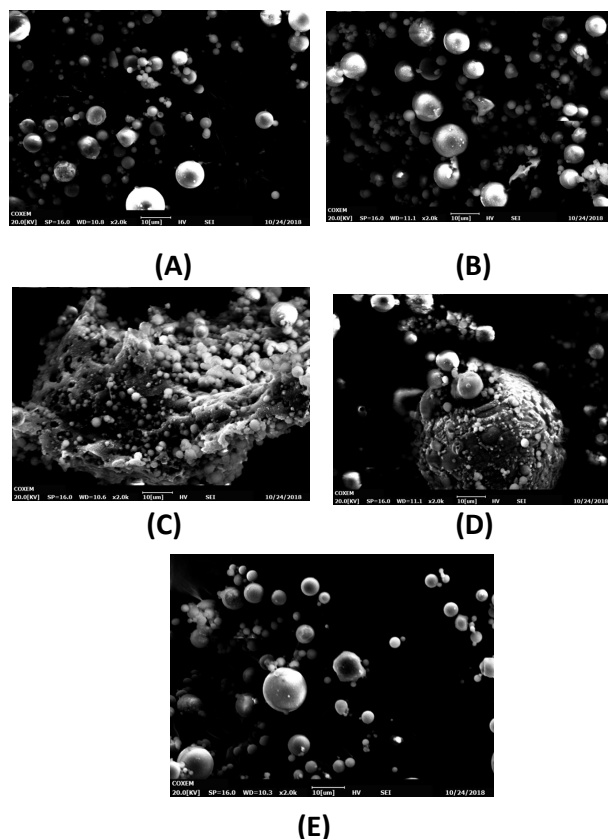
Based on figure 3 it is known that after the FA500 adsorbent was activated using  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$  and  $\text{KOH}$  activators showed that the absorption band at wave number  $3407.98\text{ cm}^{-1}$  shifted to  $3442.70\text{ cm}^{-1}$  accompanied by a decrease in intensity. The shift also occurs at wave number  $1400.80\text{ cm}^{-1}$  to  $1633.59\text{ cm}^{-1}$  indicating weak -OH group interactions. This indicates that the addition of activator or activation chemically damages the -OH group structure due to the release of water molecules that are physically bound in fly ash. The emergence of new absorption bands at wave numbers  $792.69\text{ cm}^{-1}$ ,  $777.26\text{ cm}^{-1}$  and  $1093.56\text{ cm}^{-1}$  is a vibration of the O-Si-O asymmetrical range. The shift also occurs in the wave number  $455.17\text{ cm}^{-1}$ , shifting  $459.03\text{ cm}^{-1}$  accompanied by a decrease in intensity, this indicates that the Si-O bond is weak.

This phenomenon proves that the concentration of  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$  and  $\text{KOH}$  activators can weaken the interaction of the Si-O group with impurities so that the impurities that are in the fly ash pore are lost so that the fly ash pore is cleaner. Figure 3 shows the absorption band at wave number  $1643.67\text{ cm}^{-1}$ - $1641.81\text{ cm}^{-1}$  showing the OH bending vibration of the silano (Si-OH) group where in synthetic zeolites appears at the wave number  $1635.64\text{ cm}^{-1}$ . The small and sharp absorption bands on synthetic zeolites are found in wave numbers  $748.38\text{ cm}^{-1}$  and  $671.23\text{ cm}^{-1}$  indicating external and internal vibrations of the TO symmetrical range, where the sharp bands indicate a high enough crystallinity.

SEM analysis was performed on the resulting adsorbent. The purpose of SEM analysis is to determine the morphology and physical properties of the adsorbent surface. SEM analysis was not performed on all synthesized adsorbents. This analysis was only carried out for a few adsorbents, namely Fly Ash, FA500, A5K, A5S and A5C. SEM analysis results can be seen in Figure 4.

SEM results for fly ash without treatment can be seen in Figure 4. (A). It can be seen that fly ash has a caterpillar shape with a relatively smooth surface and has few pores. In the SEM

analysis results with a magnification of 2000 times. It can be seen that fly ash contains alumina, silica, and iron oxide which have the potential for zeolite synthesis. Alumina, silica and iron oxides can act as good coagulants to reduce pollutants in waste (Shah et al., 2013). The solution will bind to the silanol (Si-O) group from the silica and the OH group from Al and Fe (Shakhpure et al., 2005).



**Figure 4.** SEM analysis results (A) *Fly Ash* without 2000x magnification treatment, (B) FA500 2000x magnification treatment, (C) A5K, (D) A5s and ( E) A5C

SEM results for 500°C carbonized fly ash can be seen in Figure 4. (B). It can be seen that the surface of the fly ash is still relatively smooth and there are no cracks. Pores began to appear on the fly ash surface and the resulting pore size was relatively small. This is due to the release of a number of volatile compounds (such as Mg) on the fly ash surface when heating, so that the Si content on the fly ash surface increases (Wang and Wu, 2006).

SEM results for 500°C carbonized fly ash with KOH activator can be seen in Figure 4 (C). It can be seen that the fly ash surface becomes rough and there are cracks on the fly ash surface. The pores that are formed are getting bigger and bigger, which indicates an increase in surface area when carbonization is carried out (Kutchko and Kim, 2006). The resulting pores have an irregular size and shape. This indicates an increase in surface area due to activation by KOH. KOH will destroy the fly ash walls and form pores in the adsorbent.

SEM results for 500°C carbonized fly ash with H<sub>2</sub>SO<sub>4</sub> activation can be seen in Figure 4. (D). It can be seen that fly ash has an irregular shape with a relatively smooth surface. The pores formed are getting bigger and bigger, which indicates an increase in surface area due to activation by H<sub>2</sub>SO<sub>4</sub>. This pore formation occurs because the corrosive H<sub>2</sub>SO<sub>4</sub> will destroy the inside of the fly ash and increase the volume of the micropores, and reduce the particle size distribution (Bada and Potgieter-Vermaak, 2008).

SEM results for 500°C carbonization fly ash with CH<sub>3</sub>COOH activation can be seen in Figure 4. (E) .. It can be seen that the surface of the fly ash is still relatively smooth and there are no cracks. Pores appear on the surface of fly ash and the resulting pore size is relatively small compared to untreated fly ash.

Based on the effect of carbonization, it can be seen in the SEM results for the adsorbent without activation that carbonization can increase the porosity and surface area of the adsorbent. Adsorbent with carbonization temperature has greater surface area and porosity than adsorbent without carbonation (Kutchko and Kim, 2006).

Based on the effect of activation, it can be seen from the SEM results that activation (both with KOH, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH) can cause a significant increase in the porosity and surface area of the adsorbent compared to carbonization alone, so that the adsorption power is better.

The performance test of the synthesized adsorbent to determine the adsorption capacity of Cu metal was carried out through the adsorption process on 20 ml of artificial waste



with a Cu<sup>2+</sup> concentration of 50 ppm. The amount of adsorbent used was 1 gram, with a contact time of 1 hour at room temperature. In the adsorption process, stirring is carried out at a speed of 60 rpm so that the adsorbent is more evenly distributed and the entire surface of the adsorbent can come into contact with the solution. Then the solution is filtered using Whatman paper no.42. The filtrate was analyzed using an atomic absorption spectrophotometer using AAS (Atomic absorption spectroscopy). The value of adsorption capacity and the percentage of adsorbent adsorbent results of synthesis on Cu metal is presented in Table 2.

**Table 2.** The value of adsorption capacity and the percentage of adsorbent reduction from synthesis of Cu (II) metal

Adsorbent	Suhu Aktivasi Fisika (°C)	Aktivator	Konsentrasi Cu (II) setelah adsorpsi (ppm)	Kapasitas Adsorpsi (mg/g)	% Adsorpsi
Fly Ash			0.189	0.9962	99.62
Fly ash	300		0.180	0.9964	99.64
Fly ash	400		0.178	0.9964	99.64
Fly ash	500		0.209	0.9958	99.58
A3K	300	KOH	0.234	0.9953	99.53
A3S	300	H <sub>2</sub> SO <sub>4</sub>	25.290	0.4942	49.42
A3C	300	CH <sub>3</sub> COOH	23.490	0.5302	53.02
A4K	400	KOH	0.242	0.995	99.52
A4S	400	H <sub>2</sub> SO <sub>4</sub>	31.070	0.3786	37.86
A4C	400	CH <sub>3</sub> COOH	23.620	0.5276	52.76
A5K	500	KOH	0.031	0.9994	99.94
A5S	500	H <sub>2</sub> SO <sub>4</sub>	28.560	0.4288	42.88
A5C	500	CH <sub>3</sub> COOH	25.740	0.4852	48.52

Based on Table 2, it can be seen that physical activation of fly ash can increase the adsorption capacity, and the reduction percentage of Cu. Fly ash has the ability to adsorb Cu (II) heavy metal with an adsorption capacity of 0.9962 mg/g and a reduction of 99.62% of Cu (II) metal. Physical activation in this study with variations in carbonation temperature, which is 300°C, 400°C and 500°C.

The performance test of the adsorbent against Cu ions can be seen in table 2. In this study, with physical activation temperatures of 300°C, 400°C and 500°C, the optimum

adsorption capacity was obtained at 400°C. The adsorption capacity value of the adsorbent as a result of synthesis increased with increasing physical activation temperature then decreased at 500°C of physical activation temperature. This is in accordance with the results of research conducted by (Olafadehan, 2012). It was found that the higher the carbonization temperature, a number of compounds contained in the particles can be destroyed and form more pores, so that their adsorption ability increases.

The adsorbent produced from physical activation is then chemically activated using KOH, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH activators. Earlier in table 3, it can be seen that the adsorbent that has the greatest adsorption capacity of Cu is A5K adsorbent with an adsorption capacity of 0.9994 mg / g with an adsorption percentage of 99.94%. Adsorbent with KOH activator has a better adsorption capacity than adsorbent activated with H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH at all temperatures (physical activation). These results are consistent with research conducted by Kehinde et al., 2009 which states that Cu (II) metal ions can be better adsorbed on adsorbents with activation by alkalis (NaOH) than acid (HCl).

On activation with KOH, the OH<sup>-</sup> ion content on the adsorbent surface increases. Cu (II) metal which is present in the form of cations has a great attraction to OH<sup>-</sup> ions and can be well adsorbed. similar. Adsorbent with activation of KOH has a greater adsorption power against Cu ions than adsorbent with activation of H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH. On activation with H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH, the content of H<sup>+</sup> ions on the adsorbent surface increases. The Cu ion which has a positive charge will repel each other with the H<sup>+</sup> ion, making it difficult to adsorb.

The performance test of the synthesized adsorbent to determine the adsorption capacity of the Cr metal adsorption was carried out through the adsorption process on 20 ml of artificial waste with a Cu<sup>2+</sup> concentration of 50 ppm. The amount of adsorbent used was 1 gram, with a contact time of 1 hour at room temperature. In the adsorption process, stirring is carried out at a speed of 60 rpm so that the adsorbent is more evenly distributed and the entire surface of the adsorbent can come into contact with the solution.

**Table 3.** The value of adsorption capacity and the percentage of adsorbent reduction resulting from synthesis of Cr (VI) metal

Adsorbent	Suhu Aktivasi Fisika	Aktivator	Konsentrasi Cr (VI) setelah adsorpsi (ppm)	Kapasitas Adsorpsi (mg/g)	% Asorpsi
Fly Ash			26.2	0.4760	47.60
Fly ash	300		23.26	0.5348	53.48
Fly ash	400		24.99	0.5002	50.02
Fly ash	500		20.42	0.5916	59.16
A3K	300	KOH	30.51	0.3898	38.98
A3S	300	H <sub>2</sub> SO <sub>4</sub>	26.57	0.4686	46.86
A3C	300	CH <sub>3</sub> COOH	29.68	0.4064	40.64
A4K	400	KOH	30.53	0.3894	38.94
A4S	400	H <sub>2</sub> SO <sub>4</sub>	24.73	0.5054	50.54
A4C	400	CH <sub>3</sub> COOH	28.62	0.4276	42.76
A5K	500	KOH	26.6	0.4680	46.80
A5S	500	H <sub>2</sub> SO <sub>4</sub>	3.376	0.9325	93.25
A5C	500	CH <sub>3</sub> COOH	26.25	0.4750	47.50

Based on Table 3, it can be seen that physical activation of fly ash can increase the adsorption capacity and the percentage of reduction in Cr (VI) metal. Fly ash has the ability to adsorb heavy metal Cr (VI) with an adsorption capacity of 0.4760 mg / g and with a reduction of Cr (VI) metal of 47.60%. Physical activation in this study with variations in carbonation temperature, namely 300°C, 400°C and 500°C.

Testing the adsorbent performance against Cr (VI) ions can be seen in table 3. In this study, with physical activation temperatures of 300°C, 400°C and 500°C, the optimum adsorption capacity was obtained at 500°C. The value of the adsorbent adsorption capacity of the synthesized adsorbent increased with increasing physical activation temperature. This is in accordance with the results of research conducted by (Olafadehan, 2012) which states that the higher the carbonization temperature, a number of compounds contained in the particles can be destroyed and form more pores, so that their adsorption capacity increases.

The adsorbent produced from physical activation is then chemically activated using KOH, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH activators. Earlier in Table 3, it can be seen that the adsorbent that has the greatest adsorption capacity of Cr (VI) is A5S adsorbent with an adsorption capacity of 0.9325 mg / g with an adsorption percentage of

93.25%. Adsorbent with H<sub>2</sub>SO<sub>4</sub> activator has a better adsorption capacity than adsorbent activated with CH<sub>3</sub>COOH and KOH at all temperatures (physical activation).

On activation with base (KOH), the OH<sup>-</sup> ion content on the adsorbent surface increases. The metal Cr (VI), which is present in the anion form, has resistance to OH<sup>-</sup> ions so that it is difficult to be adsorbed. The same thing was found by previous researchers (Olayinka et al., 2009) that Cr (VI) metal can be better adsorbed on adsorbents with activation by acid (HCl) than alkaline (NaOH). On activation with H<sub>2</sub>SO<sub>4</sub>, the content of H<sup>+</sup> ions on the adsorbent surface increases. Cr (VI) metal which is present in the anion form has a large electrostatic attraction to H<sup>+</sup> ions and can be well adsorbed.

#### 4. Conclusion

Analysis of the chemical content of PLTU Tanjung Jati Jepara fly ash shows that this material contains silica and alumina with the potential to be used as a Cu and Cr heavy metal adsorbent. Based on the adsorption capacity test, the ability of fly ash to adsorb Cu metal waste was 0.9962 mg/g and for Cr metal was 0.4760 mg/g. The temperature increase on physical activation of fly ash (300°C, 400°C, 500°C) causes an increase in the adsorption capacity of fly ash as a result of the synthesis, and the optimal temperature for Cu metal is 400°C and for Cr metal is 500°C.

The best adsorbent for Cu metal is A5K with an adsorption capacity of 0.9994 mg/g under optimal conditions, namely 60 minutes reaction time, 1 g adsorbent mass, reaction pH 6 and an initial concentration of Cu waste of 50 ppm. The best adsorbent for Cr metal is A5S with an adsorption capacity of 0.9325 mg / g under optimal conditions, namely reaction time of 60 minutes, adsorbent mass of 1 g, reaction pH of 4 and initial concentration of Cu waste of 50 ppm.

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