

# Modification of Volcanic Ash of Kelud (2014) as Selective Adsorbent Material for Zn(II) and Cr(VI) Metal Ions

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**Abstract.** This research aims to prepare an adsorbent from Kelud volcanic ash for better adsorption efficiency of Zn(II) and Cr(VI) than Kieselgel60GEMerck. Adsorbent synthesis has been carried out by dissolving 6 grams of volcanic ash, activated at 700 °C for 4 hours and washed with HCl 0.1 M into 200 mL of sodium hydroxide 3 M with stirring and heating at 100 °C for 1 hour. Then, sodium silicate filtrate was neutralized using hydrochloric acid. The mixture was allowed to stand for 24 hours then filtered and washed with aqua DM, then dried and crushed. The procedure was repeated for nitric acid with a contact time of 24 hours. The products were then characterized using FTIR subsequently determined acidity, moisture content, and tested for its adsorption of the Zn(II) and Cr(VI) ions, by using AAS. The results showed that the type of acid that produced highest rendement is AK-HCl-3M i.e. 25.50%, acidity of the synthesized adsorbent silica gel all have similarities with Kiesel gel 60G E' Merck i.e. 6.302mmol/g and the water content of the silica gel adsorbent synthesized similar to Kiesel gel 60G E' Merck i.e. adsorbent AK- HCl-3 M. The character of the functional groups of silica gel synthesized all have similarities with Kiesel gel 60G E'Merck as a comparison. Qualitative analysis by FTIR indicates that it has formed a bond of Si-O-Si and Si-OH. The optimum adsorption efficiency of the metal ion Zn(II) obtained from AK-HNO<sub>3</sub>-3 M adsorbent is equal to 63.24% for electroplating waste and the optimum adsorption efficiency of the Cr(VI) metal ion obtained from the adsorbent AK-HNO<sub>3</sub>-3M is equal to 64.01% for tannery waste.

## INTRODUCTION

The main component constituent Kelud volcanic ash is silica (SiO<sub>2</sub>) that is equal to 70.6% [1]. Therefore, the content of silica is large enough to allow Kelud volcanic ash to be synthesized into a silica gel adsorbent. Preliminary research on the synthesis of silica gel of Kelud volcanic ash for adsorption of heavy metal ions of Cr (VI) and Pb (II) was conducted by some researchers [2,3,4,5]. The results showed that the optimum concentration of HCl for synthesis was 3 M with the efficiency adsorption to Cr(VI) about 15%; the optimum of H<sub>2</sub>SO<sub>4</sub> for synthesis was 5 M with efficiency adsorption to Cr(VI) about 5% and that of HNO<sub>3</sub> for synthesis was 3 M with efficiency adsorption to Cr(VI) about 12%. The optimum adsorption efficiency for Cu(II) obtained from the adsorbent AK H<sub>2</sub>SO<sub>4</sub>-5M was 93.2617% and the optimum adsorption capacity of Cu(II) obtained from the adsorbent AK-CH<sub>3</sub>COOH-3M was 2.4919 mg/g [5].

Therefore, the study of adsorption efficiency obtained is still too small compared to kiesel gel 60G E' Merck, and there is no work on the adsorption of Cr(VI) and Pb (II), and Cu(II). The research on the synthesis of the adsorbent of volcanic ash Kelud, hence still needs to be developed, by continuing the previous research on various variables. The utilization of silica gel adsorbents is relatively cheaper compared to activated carbon. This is because silica gel has several advantages that are stable in acid conditions, non swelling, high porosity, large surface area and resistant to high temperatures [6]. This research will be one of the utilization of volcanic ash Kelud as a source of silica for the selective adsorbent metal ions, Zn(II) and Cr(VI), including by the use of hydrochloric acid and nitric acid, followed by characterization, and test its adsorption on Zn(II) and Cr(VI). Silica gel is one of the inorganic solids which can be used for heavy metal adsorption. This is because the silica gel has an active side, i.e. siloxane groups (-Si-O-Si) and silanol (-Si-OH) and has a large surface area. Oxygen atoms contained in the siloxane groups (-Si-O-Si) and silanol (-Si-OH) is used as a surface active sites of silica gel, in this case as an electron-pair donor. This silanol group will be protonated at pH 2-3 Si-O- [7].

The extent of the use of silica gel due to its properties, among which are inert, neutral and reactivity of surfaces that have fairly large adsorption capacity [8]. Silica gels, which are known for their high specific surface area and their good gas adsorption capacities, could be produced from sodium silicate solutions by hydrothermal methods using sol-gel processes [9] and generally divided into three stages, namely the preparation of the gel, the gel ripening and the gel drying [10]. In addition, the sol-gel process is relatively cheap, and the products such as silica xerogel produces non-toxic [11]. Silica gel can be prepared by the polymerization of silicic acid by mixing a solution of sodium silicate with a mineral acid, and pH is very important in the polymerization process [12]. The adsorbent synthesized were analyzed qualitatively and quantitatively. Qualitative analysis by the FTIR spectra and XRD. The quantitative analysis in the form of moisture, acidity, adsorption capacity and adsorption efficiency to the metal ions Zn(II) and Cr(VI).

## EXPERIMENTAL

The procedure referring to the previous studies [5,13,14] was conducted through three steps: synthesis of Kelud volcanic ash adsorbent with various kinds of acids, characterization of the adsorbent synthesized and determination of the adsorptive properties of the adsorbent synthesized to Zn(II) and Cr(VI).

Step 1, the synthesis of the adsorbent. Kelud volcanic ash samples taken from Minomartani Sleman by "purposive sampling" on February 2014. Kelud volcanic ash was sieved using a 200mesh sieve as many as 50 grams, and then calcined using a muffle furnace at 700 °C for 4 hours. Fine ash as much as 25 g was washed using 150 mL of 0.1 M HCl solution with stirring for 1 hour and allowed to stand overnight. Then the ash was filtered with Whatman filter paper no. 42 and rinsed with aqua DM to neutral. Fine volcanic ash was then dried in an oven at 110°C for 2 hours. About 6 g of the dry ash was dissolved in 200 mL of 3 M NaOH solution, stirring and heating until boiling for 1 hour and then allowed to stand for 24 hours. Sodium silicate solution that was formed was filtered using Whatman 42 filter paper. About 20 mL of sodium silicate solution was placed in a plastic container, and 3 M HCl was dropwise added while stirring with a magnetic stirrer to form a gel at pH 7, and then allowed to stand for one night. Then the gel formed was filtered with Whatman 42 filter paper and washed with aqua DM until neutral. Then it was dried in an oven at 120°C for 2 hours. Silica gel was then crushed using a mortar and sieved using a 200 mesh sieve. The similar procedure was performed for nitric acid.

Step 2, the characterization of silica gel adsorbent. This was performed using FTIR and XRD, furthermore was also determined acidity, and moisture content, after the functional groups of silica gel were characterized using FTIR and compared with the FTIR spectra Kiesel Gel 60G E' Merck.

Step 3, the determination of the adsorptive properties of the adsorbent synthesized on Zn(II) and Cr(VI) in electroplating and tannery waste by AAS. The adsorptive properties of the adsorbent studied were adsorption efficiency (Ep) and the adsorption capacity (D) was calculated by the formula:

$$E_p (\%) = \frac{C_0 - C_1}{C_0} \times 100\%$$

$$D = \frac{C_0 - C_1}{m} \times V$$

Where:

D= adsorption capacity (mg / g)

C<sub>0</sub>= concentration of metal ions Zn, Cr initialy (ppm)

C<sub>1</sub>= concentration of metal ions Zn, Cr after process adsorption (ppm)

V= volume of metal ions Zn, Cr (L)

m= mass of adsorbent (g)

E<sub>p</sub> = adsorption efficiency of the Zn(II) and Cr(VI)

## RESULTS AND DISCUSSION

Processing of ash at a temperature of 700 °C will produce an ash with textured amorphous silica, whereas that at temperatures of 800 and 900°C will produce ash with a textured crystalline silica [14]. Ash with the amorphous structure would be more easily melted and optimize the resulting silica [15]. Silica gel produced is white and smooth. The preparation of sodium silicates are commonly used as a precursor to prepare silica gel. In this research sodium hydroxide was heated at 700 °C to prepare sodium silicates, but at the other research a siliceous sand

sample was mixed with sodium carbonate and heated at a high temperature (1060°C) to prepare sodium silicates [9]. At the other research the silica nanospheres were successfully synthesized by using sol-gel method with the optimum parameters of 700 °C in calcination temperature with 2 h of aging time [16]. Hydrogel formation starts to occur when the pH value ranging between 8-10 and forms a stiff gel at pH 7. This is consistent with previous research which reported that the hydrogel can be formed in the range of 3-10 pH value and is not produced when the pH value is less than 3 [17, 18]. Hydrogel that has been formed was then allowed to stand for overnight at room temperature to have maturation gel. At this stage of maturation, strength and rigidity of silica gel will increase and the particle size and pore become larger and homogeneous [19]. Increasing strength and rigidity of silica gel is the result of the process of hardening gel syneresis which is a process that occurs spontaneously without the evaporation process. Syneresis process occurs due to the formation and growth of the surface of the gel which is accompanied by the release of H<sub>2</sub>O molecules from the pores of silica gel [20]. In this research silica gel was neutral then dried in an oven at a temperature 110°C for 2 hours to remove H<sub>2</sub>O molecules to form xerogel namely silica gel produced by removing water from the pore through the process of evaporation [21]. During the drying process, the size of the silica gel shrinks due to loss of fluid mass in large enough quantities. This process is influenced by the pore size and pore size distribution of gel [22]. The most resulting adsorbent from modifications with 3 M HCl is 25.5%.

Hydrochloric acid 3 M was the most prevalent used in this process to transform silicate into silicic acid [23]. The addition of acid formed aqua gel which would then form balls of polymer and shrinking volumes accompanied by the release of the sodium salt and thus produced hydrogel [20]. To get rid of the salt that was still attached to the hydrogels washing the gel was necessary until aqua DM rest of the washing was neutral. pH is very important in the polymerization process. Coagulation stage involves aggregation of colloidal particles of silica sol with a uniform size [12].

This suggests that salt of by products were exhausted and soluble aqua DM. The final pH of sludge tends to increase in the washing process. This is because H<sup>+</sup> in the sediment tends to be less then the reaction rate of Si-O-Si formation is relatively fast, so the gel formed is solid and rigid [24]. Synthesis of silica gel with a variation of the acid is not optimum because it is influenced by many factors. One factor is the calculation of the ratio of SiO<sub>2</sub> / Na<sub>2</sub>O which must be close to 1 in order to form sodium meta silicate in the optimum amount [25]. Sodium silicate and sodium tetra silicate are formed at a ratio of SiO<sub>2</sub>/Na<sub>2</sub>O more than 1. If the ratio of SiO<sub>2</sub>/Na<sub>2</sub>O is less than 1 it will form 2Na<sub>2</sub>O.SiO<sub>2</sub> (sodium ortho silicate). These compounds are less reactive in the formation of silica gel, so it takes more time in the process of condensation and polymerization [25]. The chemical formula of the adsorbent of the synthesis and its comparative results is obtained from the water content test. In this research, the chemical formula of adsorbent is SiO<sub>2</sub>.0,329H<sub>2</sub>O (AK-HNO<sub>3</sub>) and SiO<sub>2</sub>.0,175H<sub>2</sub>O (Kiesel gel 60 G). Graph of acidity, water content of synthesized adsorbent and its comparative results (Kiesel Gel 60G E' Merck) is shown in Figure 1.

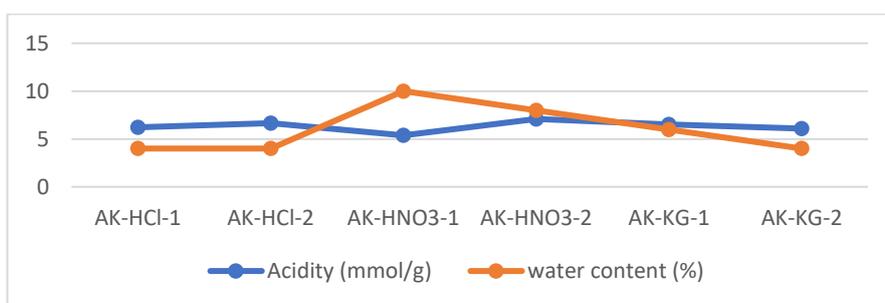


FIGURE 1. Graph Acidity and Moisture Content of Adsorbent Kelud Results Synthesis and Comparison.

Information:

- AK-HCl : Adsorbent of Abu Kelud results synthesis with HCl
- AK -HNO<sub>3</sub> : Adsorbent of Abu Kelud results synthesis with HNO<sub>3</sub>
- AK-KG : Kiesel Gel 60G E' Merck

FTIR spectra of volcanic ash from Kelud before and after washing, can be seen in Figure 2.

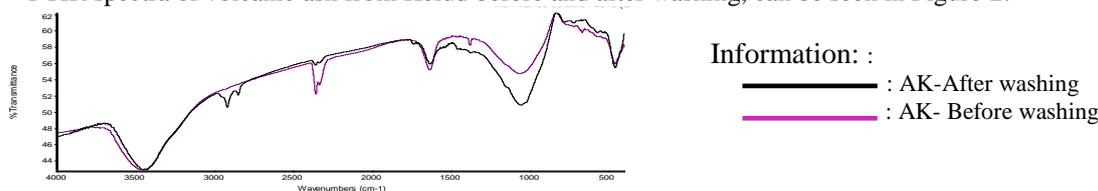
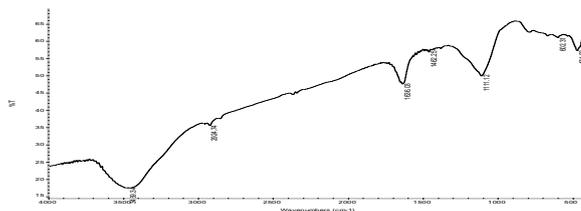


FIGURE 2. FTIR spectra Abu Kelud Before and After washing with 0.1 M HCl

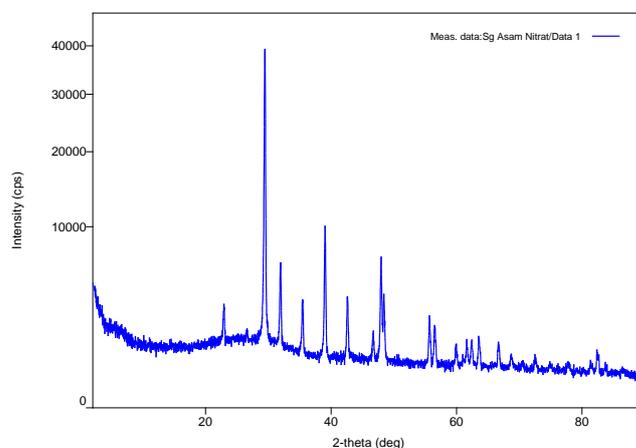
Whereas the FTIR spectrum of Kiesel Gel 60G is shown in Figure 3.



**FIGURE 3.** FTIR spectrum Kiesel Gel 60G E'Merck

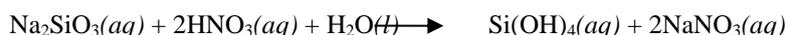
Based on these results it can be said that the greater the concentration of acid used in the synthesis of silica gel, the higher the acidity, as more and more of silanol owned by silica synthesized. The silanol group will be increased by the effect of  $H^+$  ions used during synthesis. The acidity value of the comparative silica gel (kiesel gel 60G E' Merck) was 6 mmol/g. Therefore, the higher the acidity, the more the number of silanol (Si-OH) so the greater its ability to donate protons. Thus, it is estimated that the silica gel with a higher acidity will bind more metal ions to be adsorbed [5].

The acidity of the silica gel adsorbent synthesis results are not much different (similar) with Kiesel gel 60G E'Merck. Acidity of AK-HCl-3M, AK-HNO<sub>3</sub>-3M and AK-KG are 6.446; 6.231 and 6.302 mmol/g, respectively. AK-HNO<sub>3</sub>-3M has acidity similar to kiesel gel 60G E' Merck . This is supported by the XRD results of the synthesis adsorbent as shown in Figure 4 [5]. Diffractogram XRD shows a sharp peak with high intensity at an angle of  $2\theta$  and a certain spacing  $d$  value. The peak shows that AK-HNO<sub>3</sub>-3M is a crystalline phase. The crystalline phase is derived from the NaNO<sub>3</sub> salt crystals. The existing NaNO<sub>3</sub> salts are formed from the reaction between HNO<sub>3</sub> and the residual NaOH from the synthesis of sodium silicate, according to the following reaction [26]:

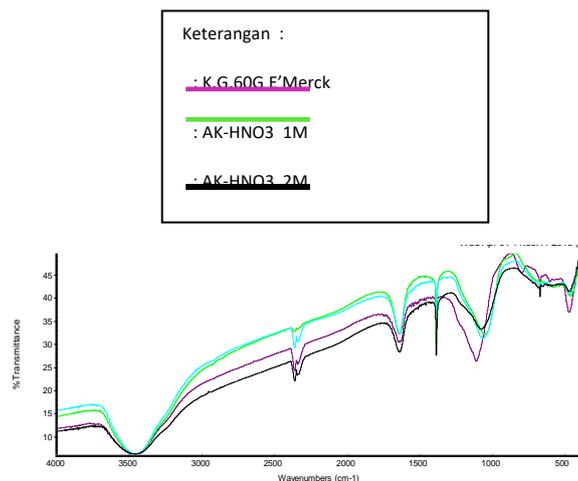


**FIGURE 4.** Adsorbent diffractogram Kelud synthesized with HNO<sub>3</sub>

Nitric acid is a strong inorganic acid which has a  $pK_a = -1.34$  and donates one proton in the solution. NaNO<sub>3</sub> contained in AK-HNO<sub>3</sub> is also derived from the reaction between HNO<sub>3</sub> with Na<sub>2</sub>SiO<sub>3</sub> precursor. The reaction is:



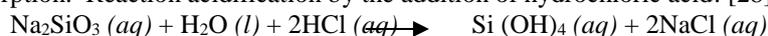
The dissolved NaNO<sub>3</sub> will be adsorbed by AK-HNO<sub>3</sub> when the process of extinguishing is too long which then the NaNO<sub>3</sub> salt crystallizes [27]. The presence of NaNO<sub>3</sub> is reinforced by the FTIR spectra of AK-HNO<sub>3</sub> (Figure 5) indicating the presence of a sharply sloping upshift of the N = O group in the region of about 1384 cm<sup>-1</sup>. This occurs because of the effect of the use of nitric acid for the synthesis of silica gel [3,5].



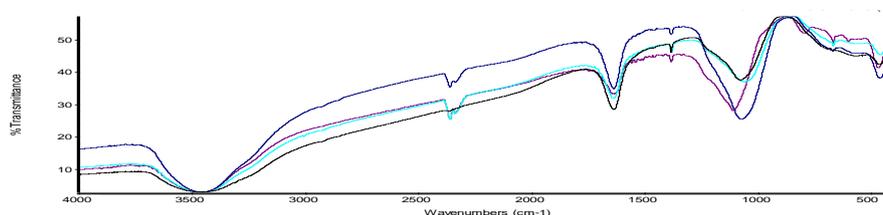
**FIGURE 5.** FTIR spectra of the adsorbent synthesized with HNO<sub>3</sub>

Based on the FTIR spectra of the synthesized adsorbent and kiesel gel 60G E'Merck (Fig. 5) showed widespread uptake in the area of 3462.29 cm<sup>-1</sup>; 3459.94 cm<sup>-1</sup>; 3448.92 cm<sup>-1</sup>; and 3459.61 cm<sup>-1</sup>. This region of absorption shows the stretching vibration of the -OH (Si-OH) group. The presence of -OH is confirmed by the absorption bands in 1636,79 cm<sup>-1</sup>; 1637,96 cm<sup>-1</sup>; 1636,83 cm<sup>-1</sup>; and 1637,19 cm<sup>-1</sup> indicating the bending of the -OH group (Si-OH). In absorption of 1110.63 cm<sup>-1</sup>; 1637,96 cm<sup>-1</sup>; 1066.20 cm<sup>-1</sup>; and 1077.26 cm<sup>-1</sup> show the vibration of the asymmetric strain of Si-O (Si-O-Si) groups. Si-O bonds appear at 670,01 cm<sup>-1</sup>, whereas in AK-HNO<sub>3</sub>-2M and AK-HNO<sub>3</sub>-3M appear on wave numbers 668,60 cm<sup>-1</sup> and 668,68 cm<sup>-1</sup>. The absence of Si-O uptake in AK-HNO<sub>3</sub>-1M is caused by the absorption intensity so weak that it can't be read. Other absorption bands which confirm the presence of Si-O groups are at wave numbers 470.58 cm<sup>-1</sup>; 463.45 cm<sup>-1</sup>; 465.14 cm<sup>-1</sup>; and 463.96 cm<sup>-1</sup> show the bending vibrations of Si-O-Si.

Adsorbent of synthesis which has water content similar to Kiesel Gel 60G is AK-HCl-3M which is 4%. The order of water content is AK-HNO<sub>3</sub> > AK-KG > AK-HCl. The highest water content of 9% is obtained from AK-HNO<sub>3</sub>-1M, and at least 4% is obtained from AK-HCl-3M. This is probably due to the drying process is still less long time so that the water content is still quite high. The absorption of volcanic ash characteristics before and after washing at wave numbers 1639,19 cm<sup>-1</sup> and 1635,64 cm<sup>-1</sup> shows the bending that asserts the OH-group of Si-OH. The asymmetry strain vibration of Si-O groups of Si-O-Si from volcanic ash before and after washing was shown in 1071.45 cm<sup>-1</sup> and 1057.66 cm<sup>-1</sup>. The absorption bands at 462.44 cm<sup>-1</sup> and 461,37 cm<sup>-1</sup> are the bending vibrations of Si-O-Si from each volcanic ash before and after washing. FTIR spectra results of volcanic ash before washing there are absorption bands in the area of 2361,35 cm<sup>-1</sup> and 1383,14 cm<sup>-1</sup> and after washing the absorption band tends to disappear or the intensity is very small. The absorption band is probably an impurity group dissolved in 0.1 M HCl. The apparent difference in the volcanic ash spectra after and before washing is the increase in the intensity of the absorption. Reaction acidification by the addition of hydrochloric acid: [28]



FTIR spectra of silica gel with HCl synthesis results are shown in Figure 6.



**FIGURE 6.** FTIR spectra of silica gel adsorbent synthesized with HCl.

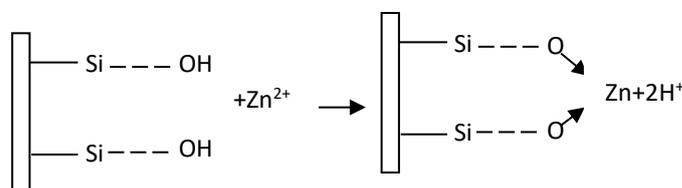
FTIR spectra of AK-HCl (Fig. 6) has an absorption at almost the same area. The presence of widespread uptake in 3460,36 cm<sup>-1</sup>, 3455,43 cm<sup>-1</sup> and 3454,49 cm<sup>-1</sup> shows the vibration of the -OH group strain of Si-OH. The presence of siloxane groups is confirmed by the presence of a -OH bending vibration of the Si-OH groups at wave numbers 1637.21 cm<sup>-1</sup>, 1639.44 cm<sup>-1</sup>, and 1638.09 cm<sup>-1</sup> respectively. Si-O asymmetry strain strains of Si-O-Si also appear on each of the resulting silica gel FTIR spectra results, at 1060,65 cm<sup>-1</sup>, 1074,00 cm<sup>-1</sup>, and

1079,40  $\text{cm}^{-1}$  and is confirmed by the appearance of Si-O-Si bends in each of the synthesized silica gel spectra, in the wavelength numbers 470.58  $\text{cm}^{-1}$ , 464.72  $\text{cm}^{-1}$ , and 469.80  $\text{cm}^{-1}$  respectively. Silica gel of the synthesis product is a silanol and siloxane group which is a typical group for silica gel. This indicates that the synthesized adsorbent silica gel already exhibits a bonding character in accordance with the gel comparative kiesel gel 60G E' Merck.

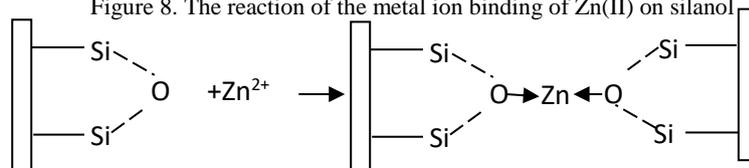


**FIGURE 7.** Graph adsorption efficiency (Ep) of adsorbent modified to Zn(II) in electroplating wastewater (mean from triplo)

In this research, the test of adsorptivity was conducted on electroplating waste and tannery waste with adsorbent and adsorbate ratio of 1:50 and 1: 100 (w/v). Based on Figure 7 it was found that the adsorption efficiency of the synthesized adsorbent on Zn(II) ion from AK-HNO<sub>3</sub>-3M, AK-HCl and kiesel gel 60G E' Merck were 63.24%, 48.93% and 55.16% respectively (in electroplating waste with a ratio of 1:50 w/v). The optimum adsorption of Zn(II) ion is obtained from AK-HNO<sub>3</sub>-3M. Similarly, it occurs in the ratio of adsorbent and adsorbate (1:100) (w/v). This shows that the type and concentration of acids used to different the adsorption capacity of Zn(II) metal ion. The amount of Zn(II) metal ion adsorbed is generally proportional to the number of active sites of adsorbent. The more H<sup>+</sup> ions are added, the more protonation and species of silicon ions are formed, resulting in faster siloxane bond formation. The more active sites the adsorbent surface becomes, the more effective the adsorbent is in adsorbing the Zn(II) metal ion. The binding reaction of Zn(II) metal ion in the silanol and siloxane groups is estimated as in Figures 8 and 9 [5].

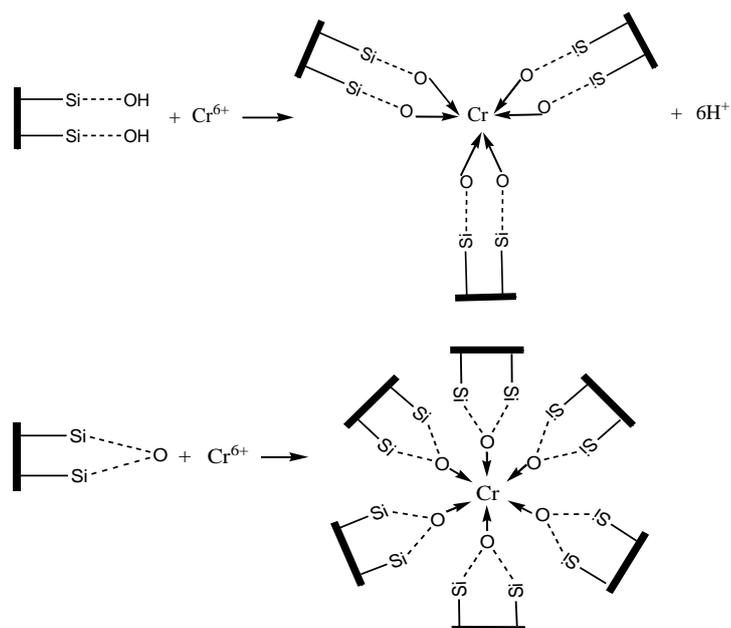


**Figure 8.** The reaction of the metal ion binding of Zn(II) on silanol



**FIGURE 9.** The reaction of the metal ion binding of Zn(II) on the siloxane groups

The adsorption efficiency of the synthesized adsorbent on Cr(VI) ion in the 1:50 (w/v) tannery waste of the AK-HNO<sub>3</sub>-3M adsorbent, AK-HCl and kiesel gel 60G E' Merck were 64.01%, 62.64%, and 58.59% respectively. The optimum adsorption efficiency of Cr(VI) ion is obtained from AK-HNO<sub>3</sub>-3M, which is 64,01% (ratio 1:50w/v). Similarly, it occurs in the ratio of adsorbent and adsorbate (1:100 w/v). This indicates that the type and concentration of acids used on different adsorption capacity of Cr(VI) metal ion. In this research there was an increase of Ep 47.64% for AK-HCl and 52.01% for AK-HNO<sub>3</sub> when compared with the previous research [2,3,4,5]. In the previous research only obtained Ep 15% for AK-HCl and 12% AK-HNO<sub>3</sub>. Thus it can be said that the synthesized adsorbent has the ability of adsorption to Cr(VI) ion is higher than before. The Cr(VI) metal ion binding reaction by the silanol group and the siloxane group can be assumed as in Figure 10 [3,5].



**FIGURE 10.** The reaction of the metal ion binding of Cr(VI) by silanol and siloxane Cluster

Adsorptive property test towards metal ion of Cr(VI) is committed against a tannery wastewater and electroplating waste. The amount of Cr(VI) ion after adsorption in electroplating waste is very small that is below the device detection limit of 0.015 ppm. Because of the very small Cr(VI) content in the residual solution, the adsorption efficiency is close to 99%. Almost all Cr ions in the solution are adsorbed by synthesized adsorbents.

## CONCLUSION

Based on these results, it can be drawn some conclusions. The modified adsorbent can be synthesized from Kelud volcanic ash by using sol-gel method. The type of acid producing optimum adsorbent is AK-HCl 3M ie 25.5%. The characters of functional groups of all silica gel synthesized have similarities with Kiesel gel 60G E' Merck. The acidity of the synthesized adsorbent silica gel all have similarities with Kiesel gel 60G E' Merck ie 6.302 mmol/g and the water content of the silica gel adsorbent synthesized similar to Kiesel gel 60G E' Merck i.e adsorbent AK-HCl-3M. The optimum adsorption efficiency of the metal ion Zn(II) obtained from the adsorbent AK-HNO<sub>3</sub>-3 M is equal to 63.24% for electroplating waste and the optimum adsorption efficiency of the Cr(VI) metal ion obtained from the adsorbent AK- HNO<sub>3</sub>-3M is equal to 64.01% for tannery waste.

## ACKNOWLEDGMENT

The authors thank to the Faculty of Mathematics and Science, YSU, due to the funding of DIPA-2016 for this work. We also thank to students who assist in the implementation of this study (Nurul and Ruri).

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