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Adsorption and Desorption Metal Cu(II) using Zeolite Synthetic by Bottom Ash Coal Modified Dithizone

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Abstract

Zeolite synthetic and zeolite modified dithizone has been successfully created by hydrothermal method. The aim of this research is to know the characteristics of zeolite synthetic, and zeolite modified dithizone and to know capacity of adsorption and desorption. The effect of various variables, such as pH, concentration of Cu(II), contact time and temperature was investigated using batch process, characterization zeolite modified dithizone and zeolite synthetic using XRD, XRF, FTIR and GSA. The result of characterization bottom ash coal by hydrothermal reaction using XRF, be discovered composition Si as many 82,01% and Al 8,54%. product of melting hydrothermally indicates a specific zeolite IR absorption at a wavelength of 300-1250 cm-1. The result XRD showed that be found zeolite-X, zeolite-A, zeolite sodalite and diffractogram of dithizone. Zeolite modified dithizone has been successfully synthesized with a marked presence group of -NH and -SH by using FTIR. Zeolite modified dithizone surface area change from 160,262 m2/g to 69,609 m2/g. The best adsorption metal Cu(II) by zeolite synthetic is pH 7. Kinetics adsorption zeolite synthetic and zeolite modified dithizone follow kinetics of pseudo second order, with R2 respectively 0,7378 and 0,8689, rate constant of pseudo second order adsorption at zeolite synthetic is -0,017 g/mg.min-1 and zeolite modified dithizone -0,013 g/mg.min-1. Isotherm type for both of adsorbent follow Langmuir isotherm. Desorption of metal Cu(II) on zeolite modified dithizone and zeolite synthetic a lot off obtained using HCl at level 47,08% and 41,49% respectively.

Keywords: Zeolite synthetic, diphenyltiocarbazone, desorption, metal Cu(II)

INTRODUCTION

Bottom ash is a coal combustion residue used as fuel. One use is factory Spiritus Madukismo Yogyakarta. According to (Gupta et al., 2006) Major chemical composition of bottom ash coal is at 45.4 SiO_2 and Al_2O_3 19.3%, while the composition of the minor is 15% moisture content; Fe_2O_3 9.7%; CaO 5.3%; MgO 3.1%; and Na_2O 1.0%. Bottom ash waste will normally be transferred to localized accumulation in vacant land (landfills) that in time they will accumulate in huge quantities and raises new problems for the environment. If waste bottom ash carried by the wind will cause air pollution, and if exposed to rain, bottom ash carried by rainwater entered the aquatic environment polluting the aquatic environment. Therefore, the need to make use of bottom ash waste to address the pollution.

Utilization of coal bottom ash to synthesize zeolite can be done because the content of Si and Al has, Mineral Si and Al is the main component constituent zeolite so with a certain treatment of bottom ash can be converted into a zeolite. Zeolite synthesis is generally made hydrothermally. According to (Shigemoto et al., 1995), zeolite synthesis through fusion method followed by hydrothermal process can significantly improve the process of formation of zeolite compared with alkaline hydrothermal method. In addition, the zeolite produced has high crystallinity.

Zeolite is defined as a hydrated aluminosilicate consisting of SiO4 tetrahedral units and AlO4 with hollow structural framework which is occupied by water molecules and cations. Cations in the zeolite cavities can move freely to enable the exchange of ions without damaging the structure of the zeolite(Ming & Mumpton, 1989). Zeolites as support materials are often modified with a variety of ligands to improve capacity retention and selectivity. Difeniltiokarbazon (dithizone) is a chelating agent that shows sensitivity and good selectivity towards Pb 2+ ions under alkaline conditions (Rajesh & Manikandan, 2008).

Difeniltiokarbazon (dithizone) is a reagent that is already known and is still used as a chromogenic agent for the determination of heavy metal with classical extraction of an analyte in a medium of organic solvent (Nezio et al., 2005). Dithizone a black - purple solids that do not dissolve in water, soluble in a solution of ammonia and dissolved in chloroform and carbon tetrachloride to produce a green solution. These reagents both for the determination of metals in small quantities (Rajesh et al., 2003). Ditizon has two active hydrogen atoms which can be substituted with cations. In addition, ditizon also molecules which have atomic electron donors, namely sulfur and nitrogen that can react with cations such as Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn, Pt, Au, Hg, Ti, Pb, Bi, Se, Te, and Po. (Costa et al., 2002). Research on zeolite modified dithizone also been done with adsorbent Amberlite XAD-16. (Yu et al., 2011) using silica gel modified with dithizone to online pre-concentration metal ion Cu. While (Anaraki & Alireza, 2014) using clinoptilolite nanoparticles by cationic surfactants and ditizon solution to eliminate Pb(II) and stated that the nanoparticles modified cationic surfactants and dithizone can increase the surface area effectively and significantly improving the removal of Pb(II).

In this study, zeolite synthesis of bottom ash coal modified with dithizone aims to determine the amount of dithizone adsorbed on zeolite that can be used to adsorb pollutants Cu(II). Cu(II) are common in the waters of both natural and due to the contaminants, that come from industries such as iron and steel processing. If the concentration of copper in our bodies high enough to cause respiratory and neurological damage. Further characterization of bottom ash, zeolite synthesis and zeolite modified dithizone, and determine the optimum conditions of the entrapment of Cu(II) by zeolite synthesis and zeolite modified dithizone to determine the kinetics of adsorption, adsorption isotherm and thermodynamics, as well as knowing as desorption from zeolite synthesis and zeolite modified dithizone.

RESEARCH METHODS

Research Tools

The tools used in this study is a set of tools beaker, tool reflux, Whatman filter paper 42, the pH paper, a centrifuge, a mortar and pestle porcelain, crucible of nickel, vessel Teflon, magnetic stirrer, a sieve of 250 mesh, pH meter, analytical balance, hot plate, centrifuges, shakers water batch, shaker incubator, furnace, oven, XRF, (XRD) Shimadzu 6000, (FTIR) Shimadzu Prestige-21, (GSA) Quantachroome NovaWin2 and AAS.

Research Materials

Materials used in the study include coal bottom ash, dithizone, concentrated HCl, distilled water, pellets NaOH, sodium silicate, 96% ethanol, diethyl ether and copper (II) 1000 ppm.

Initial Preparation of Bottom Ash Coal

Coal bottom ash originating from the plant Spiritus Madukismo Yogyakarta crushed using a porcelain mortar until small size and then sieved with a sieve to qualify for > 106μm. Bottom ash that has escaped the sieve is then weighed as much as 10 grams, plus 100 mL of concentrated HCl, and refluxed at a temperature of $80°C$ for 4 hours. Results reflux then filtered and washed with distilled water to 7 pH. The resulting solid was then put into oven at a temperature of $160°C$ for 8 hours, bottom ash of the results reflux (AD) obtained were then characterized using XRF, XRD and FTIR. The second stage is melting with NaOH. This stage is done by AD 2.5 grams and 2.5 grams of NaOH pellets crushed using a porcelain mortar until smooth, put in a nickel crucible and melted at a temperature of $550°C$ for 60 minutes. AD remelting cooled and crushed and then proceed with the synthesis of zeolites using a hydrothermal reaction. Bottom ash (AD) obtained from remelting with NaOH, was put in a Teflon vessel, added with 10 mL of sodium silicate and 15 mL of distilled water, and then stirred with a magnetic stirrer for 24 hours. The results are then reacted hydrothermally at a temperature of $100°C$ for 24 hours. The solids are separated hydrothermal results with filter paper, neutralized with distilled water and dried in an oven at $100°C$ for 1 hour. Results obtained in the form of synthetic zeolite obtained were then characterized using XRF, XRD, FTIR, and GSA respectively.

Modification Zeolite with Dithizone

Difeniltiokarbazon (dithizon) of 2.56 g (10.0 mmol) put in a 500 mL round flask and completely dissolved in 400 mL of 96% ethanol by heating at $50°C$. The solution is then supplemented with 10 grams of Z-AD and reacted for 6 hours at that temperature. The modified zeolite phase was filtered and washed using 50 mL of ethanol three times repetition is then washed with 50 mL of diethyl ether. The results produced and then aired dried overnight. Zeolite dithizone (ZD) obtained were then characterized using XRF, XRD, FTIR, and GSA

Study of adsorption includes adsorption at various pH, the interaction time, initial concentration of metal ions and temperature. Adsorption of pH is done by means of 10 ml of Cu(II) 10 ppm and regulated pH of the solution by adding HCl or NaOH into a solution of Cu(II) at pH 4, 5, 6,7 and 8. Each solution in the insert into 50 mL erlenmeyer and added as much as 0.01 gram of zeolite synthesis. Then do adsorption using a shaker water bath at a speed of 125 rpm for 60 minutes. Adsorption resulting solution is filtered using a filter paper. Then, the filtrate was analyzed using AAS to determine the concentration of Cu(II). The same treatment was also carried out on a zeolite modified dithizone adsorbent.

Adsorption time interaction is done by means of 10 ml of Cu(II) 10 ppm each put in a 50 mL Erlenmeyer 5 pieces different. Then each erlenmeyer was added 0.01 gram of zeolite synthesis and adsorption performed using a shaker water bath at a speed of 125 rpm for 30 minutes, 60 minutes, 90 minutes, 120 minutes, and 150 minutes. Adsorption resulting solution is filtered using a filter paper. Then, the filtrate was analyzed using AAS to determine the concentration of Cu(II). The same treatment was also carried out on a zeolite modified dithizone adsorbent.

Adsorption initial concentration of metal ions do by way of standard solution of Cu(II) made variations of the initial concentration of the solution of Cu(II) 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm. Each pipette as much as 1 mL, 2 mL, 3 mL, 4 mL, and 5 mL standard solution Cu(II) 1000 ppm in a 100 mL volumetric flask. The solution was diluted using distilled water and shaken until homogeneous. Furthermore, 10 mL solution of Cu(II) of various concentrations was took into the erlenmeyer. Then did adsorption using a shaker water bath at a speed of 125 rpm for 120 minutes by adding 0.01 gram of zeolite synthesis. Adsorption resulting solution filtered using a filter paper. Then, the filtrate was analyzed using AAS to determine the concentration of Cu(II). The same treatment was also carried out on a zeolite modified dithizone adsorbent.

Adsorption temperature variation is done by means of 10 ml of Cu(II) 10 ppm each put in a 50 mL Erlenmeyer 5 pieces different. Then each erlenmeyer was added 0.01 gram of zeolite synthesis. The mixture was stirred using a shaker incubator and heated at a temperature of 30, 33, 40, 50 and $60°C$ for 60 minutes. Adsorption resulting solution was filtered using a filter paper. Then, the filtrate was analyzed using AAS to determine the concentration of Cu(II). The same treatment was also carried out on a zeolite modified dithizone adsorbent.

Desorption

A total of 2.5 grams of synthetic zeolite and modified zeolite ditizon included in erlenmeyer, and immersed in 50 mL of Cu(II) 57.457 ppm then performed using adsorption Shaker water bath using a speed of 125 rpm for optimum time, then the mixture was filtered and the filtrate was analyzed levels copper using AAS. The residue is then dried, then put in a 3 Erlenmeyer flask 0.05 gram respectively, and then soaked with 10 mL of distilled water at first Erlenmeyer, 10 ml of HCl on the second Erlenmeyer, 10 mL Erlenmeyer Na_2EDTA in the third, then in Shaker back during the optimum time, after which the solution was filtered again and the filtrate was analyzed levels of Cu(II), then the calculated % adsorption for each solution.

RESULTS AND DISCUSSION

Some of the unwanted components can be reduced with adding, of such acid HCl (Ojha et al., 2004). Therefore, coal bottom ash samples refluxed in advance using HCl to remove impurities contained therein. Results characterization of bottom ash reflux using XRF results are presented in Table 1.

Based on the results obtained in Table 1 treatment of reflux in bottom ash with HCl can lead to reduced components in the form of metal impurities of iron and calcium which is located on the outside of the ash particles Al_2O_3 number (Natusch & Taylor, 1980). Based on the data obtained, Ash coal base containing 82.01% SiO_2 and 8.45% Al_2O_3 molar ratio of about 9.6: 1. SiO_2 content is largely due to the influence of reflux. Increasing the percentage composition of silica occurs because of the dealumination process (Wardani, 2013).

Fourier Transformation Infra Red (FTIR) strengthening characterization owned by x-ray diffraction (XRD), the results of Fourier Transformation InfraRed (FTIR) can be seen. The results of spectroscopic analysis of bottom ash reflux results are presented in Figure 1.

Based on the results of the characterization of FTIR in Figure 1 shows that the bottom ash that has refluxing with HCl can be observed at wavenumber 1087.85 cm-1 and 470.63 cm-1 shows the peak of Si-O-Si which is the main constituent of the zeolite as a component. At wavelengths of 300 cm-1 - 1300 cm-1 which is located in the central part of IR provides information on the composition and how each tetrahedral SiO_4 and AlO_4 are bonded to each other. In addition to the central part of the IR also obtained information composition Si / Al and formation of pores in zeolite resulting H+ ion from HCl removes impurities at the time of the reflux.

Table 1: The composition of the compounds in the bottom ash results reflux

Compound	Content (% weight)	Compound	Content (% weight)
SiO_2	82,1	P_2O_5	0,58
Al_2O_3	8,45	CaO	0,31
TiO_2	3,74	ZrO_2	0,09
Fe_2O_3	1,31	Cr_2O_3	0,09
SO_3	1,23	NiO	0,02
Cl	1,18	MnO	0,02
K_2O	0,87	CuO	0,01

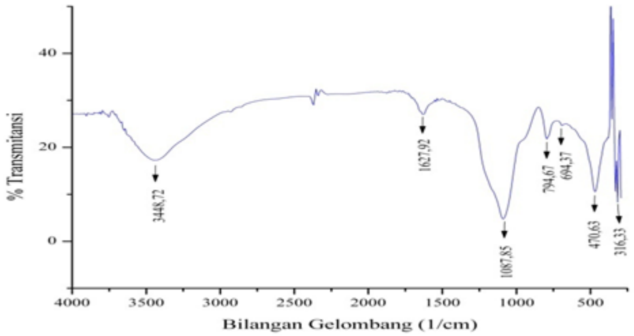

Figure 1: The results FTIR of bottom ash

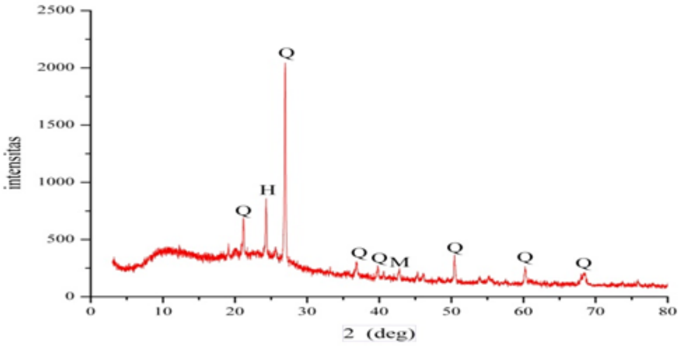

Figure 2: X-ray Diffractogram bottom ash reflux result.

Based on the results of IR data on the basis of the results reflux ash minerals that amount of impurities contained in zeolite reflux, and the emergence of absorption -IR absorption of the higher intensity at wavelengths characteristic indicates that there is a component that is main constituent of the zeolite framework SiO-Si so that it can be concluded that the material can be synthesized was a zeolite.

Identify the type of minerals in the bottom ash is obtained by comparing diffractogram with standard database Powder Diffraction File (PDF) obtained from the Joint Committee for Powder Diffraction Standards (JCPDS) using software version 2.3 PCPDFWIN. X-ray diffraction pattern of bottom ash reflux results are presented in Figure 2.

Based on Figure 2 taken from diffraction at the bottom ash reflux results can be seen the sharpest peaks can be observed in 2Θ = 26,92° (d = 3,30Å, 101) followed by other peaks 2Î¸ = 24,29° (d = 3,66Å, 012), 2Θ = 21,14° (d = 4,19Å, 100), 2Θ = 39,73° (d = 2,26Å, 102), 2Θ = 42,71° (d = 2,11Å, 206), 2Θ = 50,40° (d = 1,80Å, 112), 2Θ = 60,20° (d = 1,53Å, 121), 2Θ = 36,82° (d = 2,43Å, 130), 2Θ = 68,38° (d = 1,37Å, 023), 2Θ = 40,58°.

Characterization by XRF aims to look compounds contained in a material. Characterization is conducted on zeolite synthetic from coal bottom ash by hydrothermal fusion method and a zeolite modified dithizone. Characterization of zeolite synthesis by XRF are shown in Table 2.

Based on Table 2, it can be seen the elements contained in zeolite synthesis and modified zeolite dithizone. In the synthetic zeolite seen that the Si / Al ratio decreases. The ratio of Si / Al according possible because the addition of NaOH pellets in zeolite synthesis.

The addition of NaOH can alter the composition of bottom ash by damaging the outer layers of bottom ash so as silica and alumina contained in the bottom ash bottom ash to the surface and cause changes in the percentage of the number of elements or compounds contained in bottom ash during zeolite synthesis.

Zeolite synthesis and zeolite modified dithizone having specific spectra. Characterization of zeolite synthesis and zeolite modified dithizone done using FTIR at wave number 400-40 cm-1 to determine the functional groups on the zeolite synthesis and zeolite modified dithizone. In this study, zeolite synthesis and zeolite modified dithizone characterized using FTIR. Results of FTIR characterization of zeolite synthesis and zeolite modified dithizon presented in Figure 3.

Table 2: The composition of the compound in the zeolite synthtic and zeolite modified dithizon.

No	**Compound**	**Level of zeolite (%)** **Zeolite synthesis**	**Zeolite modified dithizon**
1	SiO_2	65,79	64,00
2	Al_2O_3	18,00	19,01
3	TiO_2	7,07	5,66
4	Fe_2O_3	2,80	2,35
5	SO_3	1,12	6,47
6	MgO	1,09	-
7	K2O	0,90	0,63
8	Cl	0,83	0,52
9	CaO	0,66	0,34
10	P_2O_5	0,51	0,29
11	La_2O_3	0,41	0,18
12	ZrO_2	0,32	0,24
13	CrO_3	0,22	0,11
14	NiO	0,06	0,05
15	CuO	0,04	0,02
16	MnO	0,03	-
17	Y_2O_3	0,02	0,01
18	SrO	0,02	0,02
19	ZnO	0,02	0,02
20	PbO	0,02	-

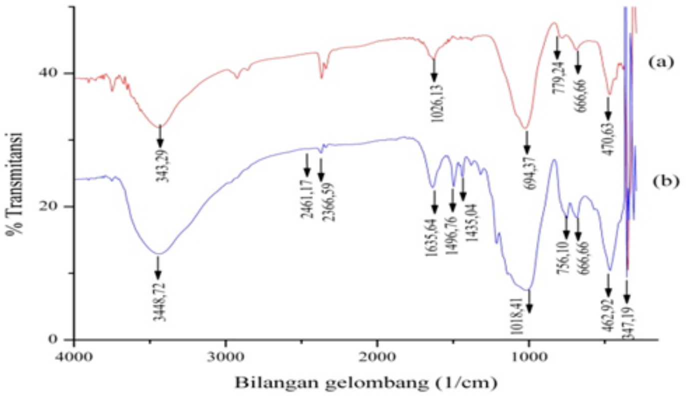

Figure 3: Result of FTIR: (a) Zeolite synthesis and (b) Zeolite modified dithizone.

Based on Figure 3 IR spectra of zeolite synthesis and dithizone modified zeolite can be observed. Zeolite synthesis from coal bottom ash was synthesized, as shown by their spectra which appear at a wavelength of 300-1300 cm - 1. The range is the wavelength range that is typical of the components of the zeolite and explain the composition and how each tetrahedral SiO_4- and $(AlO_4)_5$- bonded to one another (Agustiningtyas, 2012).

Based on Table 3 in wave numbers 347.19 and 339.47 cm-1 known of the opening pore zeolites and zeolite modified dithizone. This is caused by the reflux treatment will lead to H+ and HCl will protonation functional groups adsorbent, and removes the impurities inherent in the adsorbent, causing the pore opening.

The structure of zeolite is crystal atoms are arranged regularly and repeatedly, so that the resulting radiation from X-rays to be diffracted when worn on the structure of the zeolite. Characterization using XRD is also used to determine whether the process of modifying zeolite with dithizone can alter the framework of the zeolite synthesis or not. Based on Figure 4, seen the peaks and bumps that show crystalline and amorphous phases.

Based diffractogram in Figure 4 the diffraction patterns of zeolite synthesis has sharp peaks at 2Θ = 26,76° (733); 20,98 (531); 2Θ = 36,64° (268). The peaks of these are characteristic peaks of zeolite X (PDF 39-0218). Crystallinity of the sample height of a diffraction peak indicated by a narrow diffraction peaks, sharp or strong in its diffraction pattern. The higher the crystallinity was the sharper intensity (Trisunaryanti, 2006).

Characterization using sorption Gas Analyzer (GSA) provides information on the analysis of surface area, pore volume, mean pore and pore size distribution . Characterization is based on the adsorption - desorption of nitrogen gas by synthetic zeolite samples and a modified zeolite dithizone previously undertaken degassing process.

Based on Table 4 shows that the addition of dithizone into synthetic zeolite causes a decrease in specific surface area and total pore volume. This is because the modified dithizone compounds on the surface of the zeolite will cover the pores so the smaller the pore size and produce a smaller surface area. The more compounds modified dithizone the less specific surface area.

This was confirmed by previous research as the reduction in the total pore volume that may occur due to the insertion of dithizone molecules into the pore. The insertion of this molecule is accompanied by the possibility of interaction between groups of dithizone with zeolite active sites that cause pore zeolites undergo dilation (increase in average pore) (Handayani & dkk, 2014).

Based on Table 5 shows that the addition of synthetic zeolite dithizone into the lead broad decline specific surface and total pore volume. This is because the compound dithizone immobilized on zeolite surface will cover the pores so the smaller the pore size and produce a smaller surface area. The more compounds is immobilizeddithizone that the smaller the surface area specific. These results reinforce previous research that has been done by (Suseno, 2010) shows the natural zeolite after immobilized with ditizon provide surface area and total volume pore was lower.

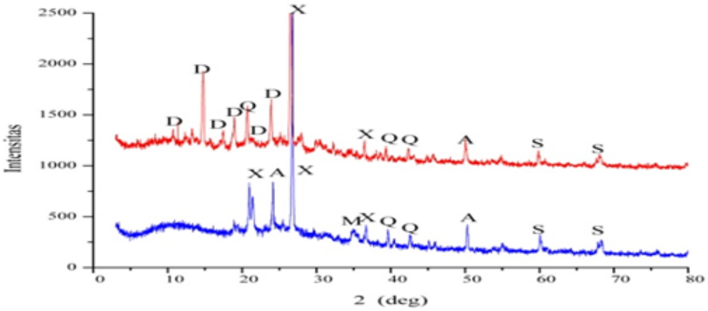

Figure 4: Diffractogram zeolite synthesis (red) and zeolite modified dithizone (blue)

Table 3: Interpretation of IR spectra and vibration types of synthetic zeolite and modified zeolite ditizon

Interpretation of vibration	**Wave number (cm^{-1})**	
	Zeolite synthetic	**Zeolit modified dithizone**
stretching O-H	3433,29	3448,72
Stretching aromatic bond -CH	-	2970,38
stretching -SH	-	2461,17
stretching C=N	-	2276,00
bending O-H	1635,64	1635,64
bending NH	-	1496,76
stretching -N=N-	-	1435,04
stretching asimetric Si-O-Si	1026,13	1018,41
External symmetric stretching O-Si-O/Al-O-Al	-	756,10
Internal symmetric stretching O-Si-O/Al-O-Al	686,66	686,66
bending Si-O/Al-O	470,63	462,92
Pore opening	347,19	339,47

Table 4: Data specific surface area, total pore volume and average pore zeolite synthesis (ZAD) and zeolite modified dithizone (ZD)

Types of samples	**Specific surface area (m2/g)**	**Total pore volume (cc/g)**	**Pore radius (Å)**
Zeolite synthesis	160,262	2,188x10-1	2,73065x 101
Zeolite dithizone	69,609	1,84x10-1	5,30304x101

Table 5: Percentage distribution of pore zeolite synthesis and zeolite modified dithizon.

Types of samples	**Mesopore (%)**	**Macropore (%)**
Zeolite synthesis	73,84	21,26
Zeolite dithizone	79,68	15,63

Effect of pH on the adsorption of Cu(II) using a zeolite synthesis and zeolite modified dithizone presented in Figure 5.

Figure 5 shows the effect of pH on the adsorption of Cu(II) using a zeolite and modified zeolite dithizone. At low pH, namely at pH 4 looks percent adsorption of Cu(II) is low . Adsorbent positive because the surface of the adsorbent in acidic conditions, which may cause repulsion between the adsorbent surface with metal ions, so that the percent adsorption becomes low (Oscik, 1982). Says that at low pH, the amount of H+ ions in the solution system became a lot, so that competition among cations binding to the active site of the zeolite will be even greater.

Model equation of kinetic adsorption pseudo first order and pseudo second order made by plotting between t vs ln (qe - qt) (Figure 6) and t vs. t / qt (Figure 7) as the equation Lavergne , so it can be determined the value of linearity (R2) , the adsorption rate constant (k) , and the adsorption capacity (qe) . It can be concluded that the two adsorbents tend to follow the pseudo second-order kinetic model.

In this research, the initial concentration variation for each adsorbate 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm with a mass of adsorbent used as much as 0.01 grams. Can be seen in Figure 8 the effect of variations in the initial concentration of Cu(II).

At high concentrations, the amount of metal ions in the solution are not comparable with the availability of the active adsorbent so that the surface of the adsorbent will reach a saturation point that may affect the decline % adsorption (Putra, 2015).

In this study, used two models namely the adsorption equilibrium isotherm model of Langmuir and Freundlich isotherm can be studied to determine the adsorption isotherm models corresponding to the Cu metal adsorption by zeolite synthesis and zeolite modified dithizone.

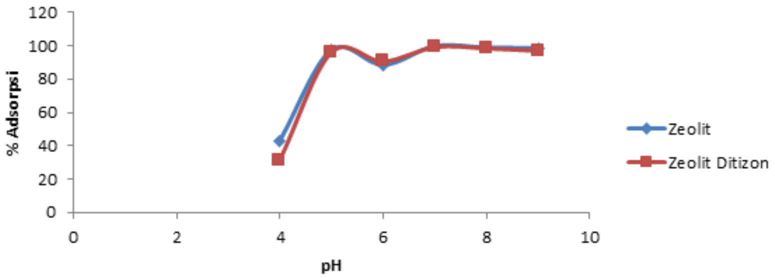

Figure 5: Graph of the effect of pH on the adsorption of Cu(II)

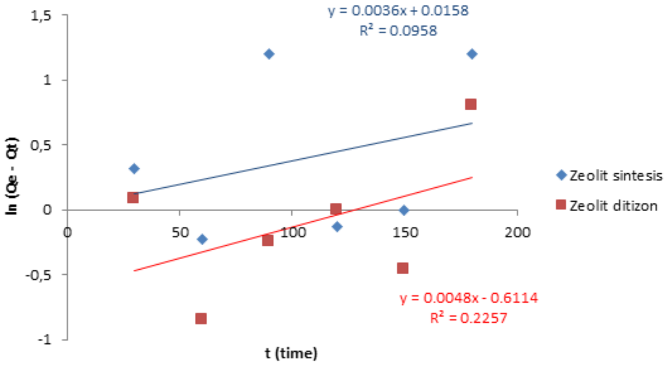

Figure 6: graphs pseudo first order of zeolite synthesis and zeolite modified dithizone.

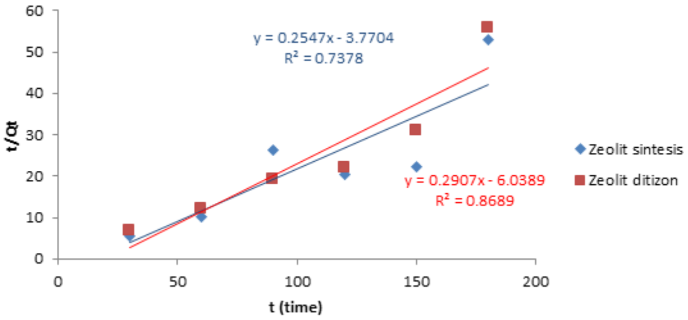

Figure 7: Graph pseudo second order of zeolite synthesis and zeolite modified dithizone.

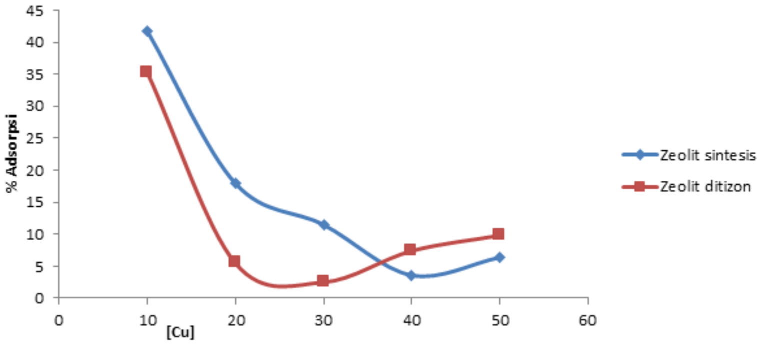

Figure 8: graphs the relationship between the initial concentration of Cu% solution adsorption.

Based on the linearity of synthetic zeolite and zeolite modified dithizone. On the surface of the Langmuir isotherm zeolite synthesis and zeolite modified dithizone has a number of specific active sites that are comparable to the surface area of the adsorbent. On each side of the active only one molecule that can be absorbed. Therefore, the Langmuir isotherm models suitable for monolayer adsorption on the surface with a limited number at the same place. Langmuir Model also indicates that the bonding that occurs when the adsorption is a chemical bond because of their chemical bond between the adsorbate with adsorbent surface.

This result indicates that the affinity of Cu(II) of zeolite modified dithizone greater than its affinity of zeolite synthesis. In addition, the adsorption capacity of Cu(II) increases due dithizone active groups attached to the surface of the zeolite synthesis. As research conducted by (Mudasir, 2007), zeolite modified dithizone can be used as a selective adsorbent to remove heavy metals that react specifically with the ligand ditizon.

This research was done by varying temperatures 30$^{\circ}C$, 33$^{\circ}C$, 40$^{\circ}C$, 50$^{\circ}C$, dan 60$^{\circ}C$ This research was done by varying the temperature is 30$^{\circ}C$, 33$^{\circ}C$, 40$^{\circ}C$, 50$^{\circ}C$, and 60$^{\circ}C$ with a concentration of 10 ppm metal. Results of the effect of temperature on adsorption of Cu(II) can be seen in Figure 9.

Thermodynamics of adsorption is used to show the relationship between changes in temperature on adsorption capacity of the adsorbate metal by zeolite synthesis and zeolite modified dithizon. To determine the value of the thermodynamic parameters of adsorption can be done through the connection between the adsorption equilibrium constants (Kads) with temperature. Graph of the relationship between ln Kads with 1/T can be seen in Figure 10.

Based on Figure 10 shows a graph of 1/T against ln Kads in which linearity can be used to calculate the enthalpy (ΛHo), entropy (ΛSo), and the Gibbs free energy (ΛGo). Based on calculations, ΛHo on synthetic zeolite is negative, it can be concluded the reaction is exothermic, while the zeolite modified ΛHo dithizone is positive, it indicates the reaction to take place dithizone modified zeolite endothermic. This means that the heat of reaction moves from the environment to the system.

Desorption is the process of re-release of ions or molecules that have bonded to the adsorbent. Desorption results by using HCl, Na_2EDTA and distilled water on the synthetic zeolite and modified zeolite dithizone presented in Table 6.

Desorption using HCl will be greater due to its binding occurs chemically. This is supported by data that follow the kinetics of adsorption kinetics model adsorption isotherm following the second order with the Langmuir isotherm models, so the bonding that occurs involving chemical bond, on the other side of H+ ions in HCl can be protolyzed functional groups on the adsorbent zeolite and modified zeolite dithizone, that will cause ion exchange between H+ and Cu2+ metal ions that bind the adsorbent. Although the amount of Cu2+ ions on the adsorbent mostly be desorbed using HCl, the solvent is not selected as a solvent of desorption. This is because the danger of contamination when ionized HCl solvent release of Cl- ion as an oxidizing agent that can cause toxicity compared with distilled water that are environmentally friendly.

Table 6: Results of desorption of Cu(II) on the synthetic zeolite and zeolite modified dithizone.

Adsorbent	**Desorption Number of Cu(II) (%)**		
	HCl	**Na_2EDTA**	**H_2O**
Zeolite sintesis	41.49	29.36	< 0,01
Zeolite modified dithizone	47.08	36.75	< 0,01

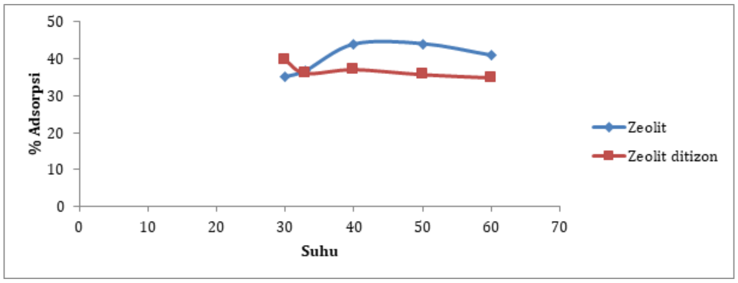

Figure 9: Graph effect of temperature on adsorption of Cu(II)

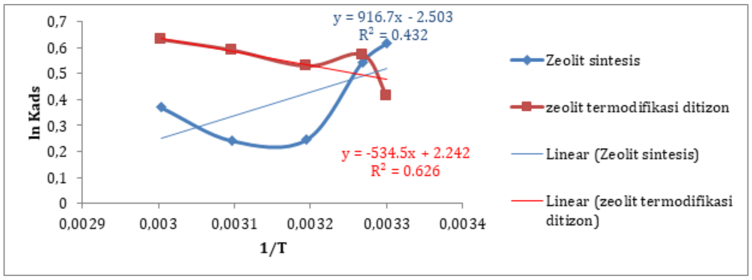

Figure 10: Graph of 1/T against ln Kads.

CONCLUSION

Based on research that has been done, it can be concluded synthesis of zeolite from coal bottom ash with a smelting - hydrothermal method has been successfully carried out zeolite synthesis zeolite obtained similar material (zeolite -like) is zeolite Y , sodalite , zeolite Na - P and zeolite X. The modified zeolite showed dithizone successfully synthesized with -NH and -SH group at wave number 1496.76 and 2461.17 cm-1. The results obtained in the characterization dithizone GSA reflect the addition of zeolites to lower the specific surface area of 160.262 m2/g to 69.609 m2/g. Based on the adsorption kinetics model, modified zeolites and zeolite synthesis dithizone followed pseudo second-orde, kinetic model with R2 respectively 0.7378 and 0.8689. The second-order rate constant pseudo synthetic zeolite is -0.017 g/mg.min-1 and modified zeolite dithizone of -0.013 g/mg.min-1. Ion adsorption isotherms of Cu(II) using a synthetic zeolite and modified zeolite dithizone follows the Langmuir isotherm models, with R2 respectively 0.9983 and 0.9897. Rated maximum adsorption capacity of zeolite synthesis is 0.975 mg/g and a zeolite modified dithizone amounted to 1,060 mg/g. Thermodynamic models adsorption of Cu(II) by synthetic zeolite and modified zeolite dithizone generating Gibbs free energy is positive (endothermic reaction). Energy entropy negative value indicates the regularity of the adsorbent and adsorbate systems. The optimum condition of adsorption of Cu(II) by zeolite synthesis is pH 7, a time of 150 minutes, the concentration of 10 ppm and a temperature of $50^{\circ}C$ while the adsorption of Cu(II) by zeolite modified dithizone pH, 120 minutes, the concentration of 10 ppm and temperature $30^{\circ}C$. Desorption results on zeolites and zeolites modified dithizone. Desorption results using HCl, Na_2EDTA and distilled water are respectively 41.49; 29.36; and < 0.01%. While the modified zeolite dithizone amounted to 47.08; 36.75; and < 0.01.

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