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Comparative Study of The Absorption of Active Zeolite and Ethylenedimintetraacetate (EDTA) Modified Zeolite as Absorbent in a Mixture of Copper (II), Nickel (II), and Zinc (II) Ions

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Abstract. Research about the absorption of activated zeolite and EDTA-modified zeolite has been successfully conducted to absorb Cu^{2+}, Ni^{2+}, and Zn^{2+} ions. Natural zeolite used from Sarulla, Pahae Jae, North Sumatera. This research aims to determine the effect of activated zeolite and EDTA-modified zeolite to absorb Cu^{2+}, Ni^{2+}, and Zn^{2+} ions in the mixture. In this research, natural zeolite was sifted with a 120 mesh sieve, then calcinated at 300ºC, and activated with HCl 15%. The natural zeolite was modified with EDTA 0,1 M that was applied as an absorbent on Cu^{2+}, Ni^{2+}, and Zn^{2+} ions which each of the initial concentrations was 50 mg/L with variations of contact time were 1, 2, and 3 hours and weight of adsorbent were 0,25 g/25 mL, 0,5 g/25 mL, and 1 g/25 mL and also the determination of metal concentration was used ICP-OES method. The results obtained showed that EDTA-modified zeolite and activated zeolite were able to decrease the concentration of metal, but the absorption ability of EDTA-modified zeolite was bigger than activated zeolite. The result of the absorption experiment of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions showed that the best absorption has been carried out with a contact time was 3 hours and the weight of absorbent was 1 g/25 mL. The percentages of decrease in this research by adding activated zeolite as an absorbent on Cu^{2+}, Ni^{2+}, and Zn^{2+} ions were 95.99.77.92, and 81,62%, respectively. In addition, the percentages of decreasing by adding EDTA-modified zeolite as an absorbent Cu^{2+}, Ni^{2+}, and Zn^{2+} ions were 98.79, 96.07, and 97,54%, respectively.

Keywords: Zeolite, EDTA Modified Zeolite, ICP-OES, FTIR, Absorption

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1 Introduction

Development in the industrial, transportation sectors, and other types of human activities, the level of pollution in the environment, and water pollution is also increasing. Pollution occurs due to toxic and hazardous materials in the environment, resulting in changes in environmental

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quality. Air is often polluted by various inorganic components, such as mercury (Hg), lead (Pb), arsenic (As), nickel (Ni), iron (Fe), copper (Cu), and zinc (Zn).

Copper, nickel, and zinc are components that are widely used for industrial purposes. Nickel is commonly used in the manufacture of stainless steel and other alloys while copper is widely used in the electronics and textile industries. In addition, zinc is also used in the paint coating and alloy manufacturing industries (Widowati, 2008).

In Kep-202/MENLH/10 / 1995, the maximum permissible levels for industrial wastewater for copper are 2 mg/L, Nickel 0.5 mg/L, and zinc 10 mg / L. These heavy metals can accumulate in the human body over a long time which can be toxic and have a negative influence on health (Kristansto,2004). Due to the nature of the toxicity of heavy metals, it is recommended that the disposal of waste into the environment must meet the established threshold.

In order to the level of heavy metals in liquid waste, several methods can be used such as membrane separation techniques, cation exchangers, chemical precipitation, electrolysis deposition, and absorption techniques using absorbent, especially activated carbon and zeolite.

Sarulla area Pahae Jae District, North Sumatra is one of the areas that have the potential of natural zeolite availability is very large but the management has not been optimally conducted so that the desire arises to use natural zeolite as a heavy metal absorbent. Natural zeolite has the ability of adsorption and ion exchange very high but natural zeolite has several disadvantages that contain many impurities such as Na, K, Ca, and Mg, and crystallinity is not good (Yuanita, 2010). Therefore, zeolites must be activated both physically and chemically to increase their absorptivity.

The use of active zeolite as a heavy metal absorbent has been performed in previous studies where the results showed that zeolite can reduce zinc and iron levels in the liquid waste of the rubber gloves industry with the optimum activation temperature of zeolite being 300ºC (Simangunsong,2011).

Currently, many studies have been conducted to further improve the quality of absorption and selectivity of zeolite by modifying it. Rina (2012) reported modified natural zeolite with nano chitosan as a heavy metal ion adsorbent and kinetics study of PB(II) ions. Moreover, optimization of PB (II) ion adsorption using citizen-modified natural zeolite had been also notified by Zurida (2012). In the study, it turned out that the modified zeolite influences the absorption of heavy metals. Other researchers have also studied the modification of natural zeolite by using EDTA for the absorption of PB and Cd ions (Sriatun,2008). The results showed that EDTA-modified zeolite can improve the adsorption ability of heavy metals Pb and Cd. EDTA is a chelating agent that can form stable complexes against almost all metals such as Ni, Cu, Fe, Zn, Co, Ca, Mg, etc which are EDTA coordinates with an ion through two nitrogen groups and four carboxyl groups (Day, 2002).

Therefore, it is necessary to research to compare the absorption of heavy metals Cu, Ni, and Zn with EDTA-modified zeolite and activated zeolite by various contact times and zeolite weight. The formed activated zeolite and EDTA-modified zeolite was analyzed and its potential as an absorbent using fourier transform infrared (FTIR), inductively coupled plasma-optical emission spectrometry (ICP-OES).

2 Materials and Methods

2.1 Equipments

In this study, the equipments used were analytical balance, porcelain dish, furnace, magnetic stirrer, oven, mortar, pestle, wash bottle, Whatman filter paper no.42, and siever 120 mesh.

2.2 Materials

Materials used were natural zeolite from Sarulla, hydrochloric acid (HCl), $ZnSO_4.7H_2O$, $NiSO_4.6H_2O$, $CuSO_4.5H_2O$, disodium ethylenediamine tetraacetate dihydrate, sodium hydroxide (NaOH) and distilled water.

2.3 Zeolite Preparation

As much as 150 g of Sarulla natural zeolite was put in a porcelain dish and then heated at 105±5ºC for 3 hours in the oven, then cooled in the desiccator for 1 hour, and sifted with a 120 mesh sieve.

2.4 Zeolite Activation

Sarulla natural zeolite with a size of 120 mesh was activated physically by heating at 300ºC for 3 hours and cooled in a desiccator. Next, transfer as much as 50 g of zeolite into beaker glass then mixed with 250 mL HCl 15% to be activated chemically. Stirred for 12 hours and filtered. The residues obtained were washed with distilled water to reach free chloride and dried at 105± 5ºC.

2.5 Modification of Zeolite

As much as 10 g activated zeolite was mixed with 100 mL EDTA solution and stirred while heating at 50ºC for 6 hours and filtered. The residues obtained were washed with 50 mL distilled water 3 times and then dried at 100ºC for 3 hours.

2.6 Absorption of Mixture of Cu(II), Ni(II), and Zn(II) Ions by EDTA Modified Zeolite

As much as 5 mL of each standard solution of Cu(II), Ni(II), and Zn(II) (1000 mg/L) ions were done by pipetting, into a 100 mL volumetric flask and then added to the distilled water until the

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marked line till the concentration of each ion in the mixture becomes 50 mg/L. Next, as much as 25 mL of each solution and pH reach 5 and then put into a column containing 0.25 g EDTA-modified zeolite. Allowed to stand for 1 hour. A clear solution was filtered. The intensity was determined using ICP-OES with wavelength Cu = 324.754 nm, Ni = 221.647 nm, and Zn = 213.856 nm and calculated ion concentration after the absorption process. The same treatment was carried out for EDTA-modified zeolite and activated zeolite with zeolite weight variations of 0.25, 0.5, and 1.0 g with a contact time of 1 2, and 3 hours.

3 RESULT AND DISCUSSION

3.1 Preparation of Copper, Nickel, and Zinc Metal Calibration Curves

Based on the research conducted, the calibration curve of the standard solution of Copper (II) was made by varying the concentration of the standard solution of Cu^{2+} by using the Least Square method so obtained the equation of the linear line Y = 804.8263 x + 36.9168. The same method was also carried out for the standard solution of Ni^{2+} was y = 10790.7495 x + 42.8098 and Zn^{2+} was y = 35254.8765 x + 2764.7744. In addition, the value of the correlation coefficient (r) for the three metals is 0.9999. They show a positive correlation between concentration and intensity which good calibration curves are analytically shown with the price R of 0.99. The calibration curves are shown in figure 1.

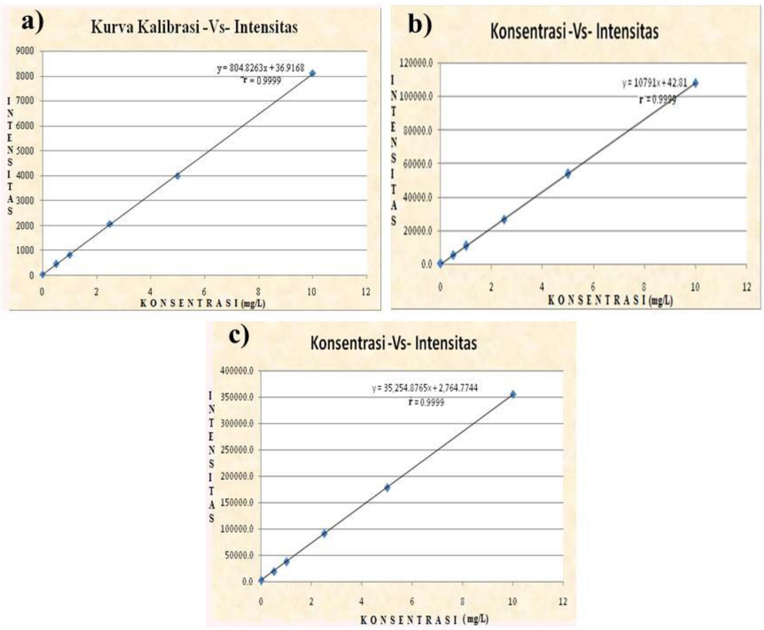

Figure 1. Calibration curve of the standard solution of (a) Cu^{2+}, (b). Ni^{2+}, (c) Zn^{2+}

3.2 Zeolite Activation

The zeolite used in this study was obtained from Sarulla district Pahae Jae, North Tapanuli which has the mineral composition of anornite and monmorilonite. Sarulla natural zeolite was taken purposively and the zeolite obtained has the physical properties of gray and yellow. The

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yellow color of this zeolite indicates that zeolite still contains impurities metals in its pores so it must be activated both chemically and physically to remove impurities and increase its absorptivity power.

Firstly, zeolite was dried at 100ºC to remove the moisture content of the zeolite, then smoothed with a pore size of 120 mesh. Furthermore, zeolite was chemically activated by using HCl 15% which aims to clean the pore surface and remove impurities compounds and regulate the location of atoms in the zeolite. The zeolite was then washed with distilled water until it is free of chloride. After that, zeolite was activated physically with a calcination process at 300ºC which aims to remove water content that is still left in the pores of zeolite and evaporate organic compounds attached to zeolite.

3.3 Modification of Zeolite

In this study. Zeolite was modified using EDTA. This is expected to improve the quality and absorption capacity of zeolite as an adsorbent to absorb Cu^{2+}, Ni^{2+}, and Zn^{2+} ions with the formation of a more stable complex with EDTA on the surface of zeolite pores. Based on the results of research that had been done by Sriatun (2008) reported that characterization results obtained using FT-IR that the interaction that occurs between zeolite with EDTA is a physical interaction where there are no chemical or structural changes in zeolite although it had interacted with EDTA (Sriatun,2008). The FT-IR spectra of ZA and ZA-EDTA were presented in figure 2.

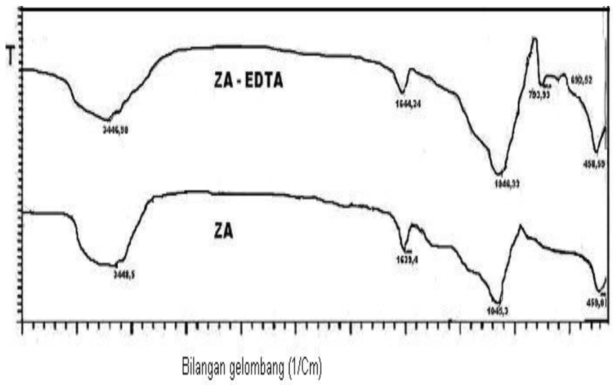

Figure 2. FT-IR spectra of ZA and ZA-EDTA (Sriatun,2008)

Tabel 1. The standard solution for Fe

Absorption Band of ZA	Absorption Band of ZA-EDTA	Description
459.0	458.59	Si-O or Al-O bending
1045.3	1046.33	O-Si-O or O-Al-O asymetric
1639.4	1644.24	H-O-H bending
3448.5	3446.90	OH stretching
-	793.93	O-Si-O or O-Al-O symetric

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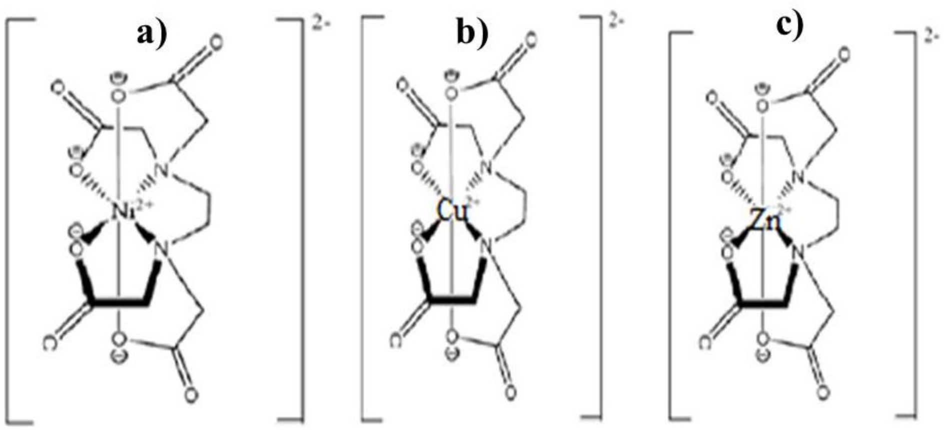
-	692.52	O-Si-O or O-Al-O symetric

EDTA is potential as a sexidentate ligand that can coordinate with metal ions through its two nitrogen and four carboxyl groups. (Day, 1998). The absorption of zeolite after modification with EDTA to Cu^{2+}, Ni^{2+}, and Zn^{2+} ions is increasing compared to zeolite without modification. Due to ion absorption through interaction with carboxyl groups in EDTA and cation exchange reaction with balancing cation in the zeolite. Based on stoichiometry, a metal ion can generally



be bound by one EDTA molecule (1:1). The complex compounds $[Ni(EDTA)]^{2-}$, $[CuEDTA)]^{2-}$ and $[Zn(EDTA)]^{2-}$ have an octahedral structure, as shown in figure 3.

Figure 3. . Complex structure of (a)$[Ni(EDTA)]^{2-}$, (b) $[Cu(EDTA)]^{2-}$, (c) $[Zn(EDTA)]^{2}$ (Day,1998)

3.4 Effect of Contact Time

In this study, the maximum contact time that was obtained between absorbent and absorbate to remove these ions occurs with a contact time of 3 hours. It shows that the ions can be retained well in the pores of the activated zeolite and EDTA-modified zeolite where almost all the ions can be absorbed on zeolite. At the contact time of 3 hours with 1 g absorbent obtained percentage reduction in ion levels of Cu^{2+}, Ni^{2+}, and Zn^{2+} are 95.99, 77.92, and 81.62%, for activated zeolite, respectively. In contrast, percentage reductions by EDTA-modified zeolite are 98.79, 96.07, and 97.54%, respectively. The percentage reduction is indicated in Table 1 and figure 4.

Table 1. The percentage reduction data of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions with various contact time

Contact Time (hour)	Cu-ZA	Cu-ZeoEDTA	Ni-ZA	Ni-ZeoEDTA	Zn-ZA	Zn-ZeoEDTA
1	55.59	86.66	36.12	72.95	39.11	77.66
2	86.07	89.83	69.89	77.53	69.25	83.13
3	95.99	98.79	77.92	96.07	81.62	97.54

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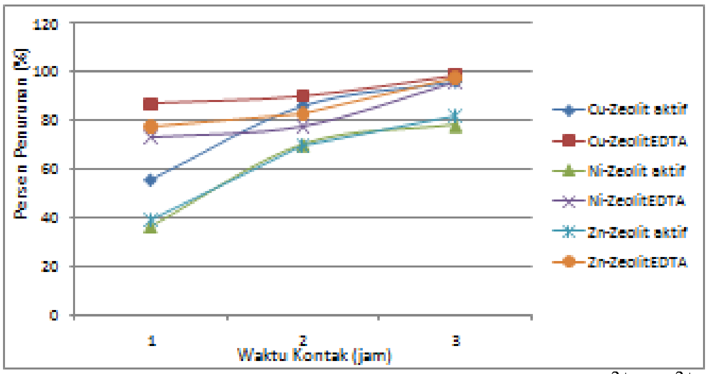

Figure 4. Graph of the effect of contact time on absorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions

3.5 Effect of Weight Adsorbent

The results showed the largest percentage reduction in ion levels occurred with the addition of activated zeolite and EDTA-modified zeolite is 1 g. It can be due to the increasing number of absorbents till the greater the amount of adsorbate that can be absorbed by the pores of the zeolite. The percentage reduction of Cu^{2+}, Ni^{2+}, and Zn^{2+} concentration ions using absorbent weight variation are 0.25, 0.5, and 1.0 g with optimum contact time for 3 hours shown in Table 2 and figure 5.

Table 2. The percentage reduction data of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions with various absorbent weight

Weight of Zeolite (g)	Cu-ZA	Cu-ZeoEDTA	Ni-ZA	Ni-ZeoEDTA	Zn-ZA	Zn-ZeoEDTA
0.25	88.28	96.13	61.44	82.42	65.62	86.87
0.5	84.75	96.72	62.76	85.65	65.89	90.40
1.0	95.99	98.79	77.92	96.07	81.62	97.54

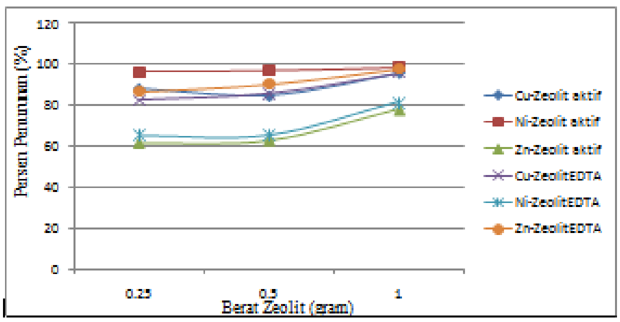

Figure 5. Graph of the effect of absorbent weight on the absorption of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions

4 Conclusion

In conclusion, the adsorption capacity of Cu(II), Ni(II), and Zn(II) ions by EDTA-modified zeolite is higher than that of unmodified zeolite. A contact time of 3 hours is the best variation to absorb Cu(II), Ni(II), and Zn(II) ions by using EDTA-modified zeolite and activated zeolite. Besides that, the zeolite weight of 1 g obtained percentage decrease produced by the addition of activated zeolite for Cu(II), Ni(II), and Zn(II) ions are 95.99, 77.92, and 81.62%, respectively. Furthermore, the percentage decrease produced by the addition of EDTA-modified zeolite for Cu(II), Ni(II), and Zn(II) ions are 98.79, 96.07, and 97.54%, respectively.

References

Alicia, A.2012. Pb(II) adsorption optimization using ditizon modified zeolite. Thesis. Bogor: IPB.

Day, R.A.1998.Quantitative Chemical Analysis. Sixth Edition.Jakarta: Erlangga.

Kristanto, P.2004.Itndustrial Ecology.Yogyakarta: Andi printing.

Narita, I.2012.Immobilization of Nano Au in natural zeolite and its modification with 11-Mercapto Undecanoic acid and L-Cysteine for adsorption of heavy metal ions.Thesis Department of Chemistry Faculty of Mathematics and Natural Sciences. University of Indonesia.

Rina, U.2012.Modification of Natural zeolite with Nano chitosan as adsorbent of heavy metal Ion and Kinetics study of PB(II) Ion. Thesis. Depok: University of Indonesia.

Simangungsong, V.2011. Optimization of activation temperature and dosage of zeolite as adsorbent of zinc and iron contained in industrial waste liquid rubber gloves. Thesis Department of Chemistry Faculty of Mathematics and Natural Sciences. University of North Sumatera.

Sriatun, O .2008.Modification of Natural zeolite with EDTA for adsorption of metal ions Pb^{2+} and Cd^{2+}.Thesis Department of Chemistry Faculty of Mathematics and Natural Sciences.Diponegoro University.

Widowati, W. et al. 2008. Toxic effects of metal pollution prevention and countermeasures. Yogyakarta: ANDI.

Yuanita, D.2009.Catalytic Hydrogenation Of Methyl Oleate Into Stearyl Alcohol Using Natural Ni/Zeolite Catalysts.Proceedings of the National Seminar UNY.