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# Removal of Cu and Pb from Wastewater Using Modified Natural Zeolite

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**ABSTRACT**

In this article, the copper and lead adsorption process using Indonesian Natural Zeolite (INZ) is studied as an adsorbent. INZ samples were obtained from Sumbermanjing Wetan, Malang district, East Java. The influence of activating acid concentration and different types of acid on the removal of copper and lead were evaluated. The activated INZ was used for adsorption of Cu and Pb from chemistry laboratory wastewater of State Islamic University of Maulana Malik Ibrahim Malang. INZ were characterized by X-ray diffraction and X-ray fluorescence spectroscopy. Characterization using XRD indicated that the activation does not affect structural changes and the diffraction pattern showed that INZ had a mordenite phase. The XRF spectra showed that increasing concentration of the activating acid simultaneously reduces undesired metal content in INZ. Determination of Cu and Pb content using Atomic Absorption Spectroscopy on wastewater showed that increasing concentration of the activating acid decreases the concentration of Cu and Pb in wastewater. The removal of Cu and Pb using INZ activated by HCl reached 61.56 % and 71 % respectively, while the removal of Cu and Pb using INZ activated by $H_2SO_4$ reached 32.86 % and 73.14 % respectively.

*Keywords: Indonesian Natural Zeolite, acid activation, Cu, Pb, chemical laboratory wastewater*

## 1. INTRODUCTION

Rapid industrialization throughout the world has generated a huge volume of wastes containing toxic materials such as metal ions. The presence of heavy metals in wastewater and surface water is the major concern of the public health and environment [1][2] and [3]. Metal toxicity poses great danger and has been the cause of many human diseases, e.g., cancer, nervous disorder, organ failure, and growth reduction healthy living [4]. In the environment, metal content such as copper is an essential element for living organisms, but at high concentrations it turns dangerous. Several methods have been developed to treat wastewater, including physical, chemical and biological techniques [5].

Chemistry laboratories of universities produce liquid waste which is sorted according to its contents. One type of liquid waste is liquid containing heavy metals in high concentration. Conventional techniques are more common used in the removal of heavy metal from wastewater including ion-exchange, membrane, filtration, electrolysis, coagulation and flotation. Among all these techniques, adsorption is more efficient, low cost, simple, rapid and effective at lower concentrations [4]. The adsorption of $Cu^{2+}$ on natural substances combined with zeolites and clays is considered, and modified natural materials are also in use because they enhance ion-exchange capacity [5].

One type of natural adsorbents which is considered to be capable of being used as a cheap and effective adsorbent is natural zeolite [4] and [6]. Zeolite has physical or chemical properties capable of adsorbing inorganic or organic substances, act as an ion exchanger, catalyst, and filter delicate molecules [7].

Adsorption of Fe, Zn and Mn in palm oil industrial wastewater has been carried out with natural zeolite and proven to be very effective. Equilibrium is achieved at 180 minutes, second pseudo order, equilibrium

adsorption follows the Langmuir law by absorbing more than 50% of metal in waste [4].

The use of natural zeolite adsorbent cannot be done directly because natural zeolite still contains lots of dopants such as Na, K, Ca, Mg and Fe, so there is a need for activation [3],[8]. Activation can be done by acid, i.e. soaking natural zeolite with an acid solution such as HCl, HNO₃, and H₂SO₄ [4],[8].

There are two methods of treating zeolite in HCl. Both strategies cause a dealumination in zeolites. Both methods have an effect on the surface area and acidity of zeolite surface [9]. HCl activation shows that the higher the concentration of HCl used, the higher the degree of dealumination will extend and will expand the micropore and surface area. This resulted in an increased capacity to adsorb water vapor [10].

The acid-modified Ukrainian Transcarpathian clinoptilolite shows that this nanomaterial most successfully sorbs cationic aqua hydroxo complexes of Pb(II) ions. The maximal absorption capability toward Pb(II) is 4.5 times greater than the natural shape of this zeolite [11].

In this study, natural zeolite from Malang city East Java Indonesia was activated using HCl and H₂SO₄ (1, 3, and 7 M). Characterization of activated natural zeolites was performed using XRF (X-ray Fluorescence), XRD (X-Ray Diffraction) and AAS (Atomic Absorption Spectroscopy) instruments. Furthermore, zeolite was used as an adsorbent for Cu and Pb in liquid waste of chemistry laboratory.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Natural zeolite was obtained from Sumbermanjing Wetan, Malang district, East Java, Indonesia. HCl p. a (1, 3, 6 and 7 M), $H_2SO_4$ p.a (1, 3, 5 dan 7 M), HNO₃, metal wastewater originated from chemistry laboratory of UIN Maulana Malik Ibrahim Malang.

### 2.2. Methods

#### 2.2.1. Preparation of natural zeolite

Refined natural zeolites as much as 250 gram were soaked in 500 mL distillated water and continuously stirred with magnetic stirrer for (24 hours) at room temperature (± 25 ° C), and then filtered. The deposition obtained was dried in oven at 100 ° C for 24 hours.

#### 2.2.2. Modification of natural zeolite

As much as 50 grams of prepared zeolites were put into 100 mL (1:2 b/v) aqueous solution of HCl in varying concentrations (1, 3, 6, and 7 M), then soaked

for 4 hours without stirring. Furthermore, the activated zeolite was filtered and washed by distilled water until the pH reaches ± 7, and then dried at 110 ° C for 12 hours.

The same treatment was carried out with H₂SO₄ as an activator in varying concentrations (1, 3, 5, and 7 M).

#### 2.2.3. Characterization

*A. Cappello analysis of XRF (x-ray Fluorescence)*

Characterization using XRF was carried out on modified natural zeolite using variations in HCl and H₂SO₄ concentrations. The characterized sample is ground out and then placed in a sample holder. Then, the sample is irradiated with X-rays.

*B. XRD Analysis (X-ray Diffraction)*

Characterization using XRD was carried out on modified natural zeolite using a variation of HCl and H₂SO₄ concentrations. At first, the sample was smoothed to acquire fine powder and then settled in a preparation plate and processed. Next, it was placed on a sample holder and irradiated with X-rays with Cu Kα radiation at λ of 1.541 Å, angle 2 θ of 5-60 ° and 0.02 ° / second scan speed.

*C. Adsorption of metals Pb and Cu On Laboratory Waste With Activator H-ZA*

As much as 50 mL of metal wastewater was put in a beaker glass and then stirred until homogenized. After that, the mixture containing beaker glass was covered with aluminum foil and followed by the destruction of metal wastewater with 10 mL of 65 % HNO₃ and heated at 100 ° C until there was 25mL solution remained. Sample was then analyzed by AAS (Atomic Absorption Spectroscopy).

As much as 250 mL of wastewater sample produced was interacted with 25 g of activated zeolite. The solution was subjected to shaking at 180 rpm for 180 minutes [4]. After that, it was filtered and the filtrate was destructed by 65 % HNO₃ and heated at 100 ° C until the solution is clear. Cu and Pb content were measured with AAS (Atomic Absorption Spectroscopy).

*D. Metals analysis of Cu and Pb with AAS*

Wastewater sample was destructed by 65 % HNO₃. The characterization by Atomic Absorption Spectroscopy (AAS) was carried out to determine the concentration of Cu and Pb in the sample. Metal content was determined by inserting sample absorption into the regression equation of the elements Cu and Pb.

## 3. RESULT AND DISCUSSION

### 3.1. Natural Zeolite Modified with Inorganic Acid

Natural zeolite contains undesired components such as metal oxides. The metal oxides are trapped in the

frame of zeolite when it is formed naturally, and it can decrease pore size and thereby decrease the capability of zeolite matrices as adsorbent. By activating zeolite, the undesired components could be discarded from the natural zeolite matrices. Acid treatment can improve the adsorption ability and enlarge the pore system [12]. Natural zeolite was activated by acid (HCl and $H_2SO_4$) solution in varying concentrations of 1, 3, 6 and 7 M for HCl and 1, 3, 5 and 7 M for $H_2SO_4$.

It was determined that by activating zeolite using 1, 3, 5 and 7 M HCl and $H_2SO_4$ for 4 hours at room temperature, zeolite was subjected to de-alumination without destructing the crystal lattice. Increasing concentration of the activating acid simultaneously reduces undesired metal content in natural zeolites.

The use of HCl and $H_2SO_4$ in the activation of natural zeolite of Malang has caused zeolite surface to be more accessible due to the loss of metal impurities that have been exchanged with $H^+$ ions of HCl and $H_2SO_4$. Strong acids can easily dissolve metal elements on zeolite surface and replace it with $H^+$. Based on

researches [13], the addition of acid can lead to de-cationization, which is the exchange of cation on zeolite surface with $H^+$.

Analysis on the type and percentage of the composition of natural zeolite can be observed through XRF (X-Ray fluorescence). Table 1 shows that there are several metal impurities reduced; Cr, Mn, Fe, Zn and Eu due to activation treatment using acid, but they tend to remain as in the case of V, Ni, Cu and Re. The metal selectivity series is $Cs^{+1} > Rb^{+1} > NH^{+4} > Ba^{+2} > Sr^{+2} > Na^{+1} > Ca^{+2} > Fe^{+2,+3} > Al^{+3} > Mg^{+2} > Li^{+1}$ [14]. Based on the selectivity series it is known that high-valence and small-sized metal cations are relatively less selective to the cation exchange in the zeolite framework. The charge difference factor is suspected to affect the power of electrostatic interactions between the negative charge of zeolite $AlO_4$ with the balancing cation or impurities on zeolite surface.

**Table 1.** XRF analysis on natural zeolite of Malang before and after activation using inorganic acid

| Metals | Before activation (%) | Activated Indonesian Natural Zeolite | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | HCl | | | | $H_2SO_4$ | | | |
| | | 1 M (%) | 3 M (%) | 6 M (%) | 7 M (%) | 1 M (%) | 3 M (%) | 5 M (%) | 7 M (%) |
| Al | 9.5 | 9.7 | 9.1 | 10 | - | 9.3 | - | - | 10.0 |
| Si | 37.3 | 44.4 | 43.1 | 54.5 | 58.2 | 44.6 | 51.8 | 60.8 | 58.0 |
| K | 5.16 | 1.87 | 5.09 | 7.48 | 9.05 | 5.14 | 6.67 | 9.09 | 8.79 |
| Ca | 5.57 | 4.90 | 2.94 | 3.80 | 4.77 | 3.55 | 4.53 | 6.55 | 6.30 |
| Ti | 1.64 | 3.35 | 1.90 | 2.66 | 3.33 | 1.88 | 2.62 | 3.57 | 3.34 |
| V | 0.045 | 0.05 | 0.065 | 0.086 | 0.09 | 0.063 | 0.064 | 0.09 | 0.08 |
| Cr* | 0.072 | 0.080 | 0.071 | 0.064 | 0.59 | 0.067 | 0.075 | 0.31 | 0.061 |
| Mn* | 2.21 | 1.58 | 1.61 | 0.74 | 0.085 | 1.4 | 1.2 | 0.073 | 0.27 |
| Fe* | 35.9 | 30.3 | 33.5 | 21.7 | 20.9 | 30.6 | 29.9 | 17.1 | 14.3 |
| Ni | 1.11 | 2.58 | 1.41 | 1.15 | 1.92 | 1.54 | 1.8 | 1.48 | 1.35 |
| Cu | 0.21 | 0.31 | 0.24 | 0.21 | 0.32 | 0.26 | 0.31 | 0.27 | 0.25 |
| Zn* | 0.70 | 0.49 | 0.55 | 0.36 | 0.37 | 0.50 | 0.54 | 0.36 | 0.27 |
| Eu* | 0.5 | 0.3 | 0.3 | 0.2 | 0.16 | 0.2 | 0.2 | 0.2 | 0.1 |
| Re | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.3 | 0.2 | 0.2 |

* Decreasing in undesired ions resulting in increases of other metal ions in natural zeolite of Malang activated by inorganic acid

The metal that has significantly decreased as the concentration of acid as zeolite's activator increased is Fe. The decline might occur because Fe has high valence, so the power of the electrostatic interaction between Fe and $AlO_4$ metals is too weak. Moreover, Fe is the main and most important impurities in natural zeolite of Malang which is accounted to 35.9 % of total impurity content, therefore the interaction between Fe and acid will be greater.

Activation of natural zeolite using 7 M HCl and 5 M $H_2SO_4$ caused de-alumination. The occurrence of de-alumination can be attributed to the acid concentration that is too high, thus dissolving alumunium [15]. The excess $H^+$ ions of acid will be attacked by oxygen atoms tied to Si and Al. Based on the bond dissociation energy of Al-O (116kkal/mol), it has much lower value than the bond dissociation energy of Si-O (190 kcal/mol), so the Al-O bond is much easier to break compared to Si-O [16]. Therefore, $H^+$ ions will tend to cause termination

of Al-O bond to form Silanol group. Meanwhile, Cl⁻ ion from decomposed HCl will also affects the strength of Al-O and Si-O bonds. Ion Cl⁻ has high electronegativity (3.16) and is small in size (R = 0.97 Å), causing this ion to bind to a high-valence cation such as $Si^{4+}$ and $Al^{3+}$. However, Cl⁻ ion tend to bind to Al atoms because the electronegativity of Al is smaller (1.61) than that of Si (1.90) [17].

Characterization using XRD (X-Ray Diffraction) plays a role in the process of crystalline solids analysis. This qualitative analysis uses X-ray with a reduced operating condition of 1.540 Å with an angle of 2 θ, 5-60 ° to identify crystal phase and determine the minerals composition of sample. The diffraction pattern of the samples will then be compared with Standart Collection of Simulated XRD powder Patterns for Zeolites [18].
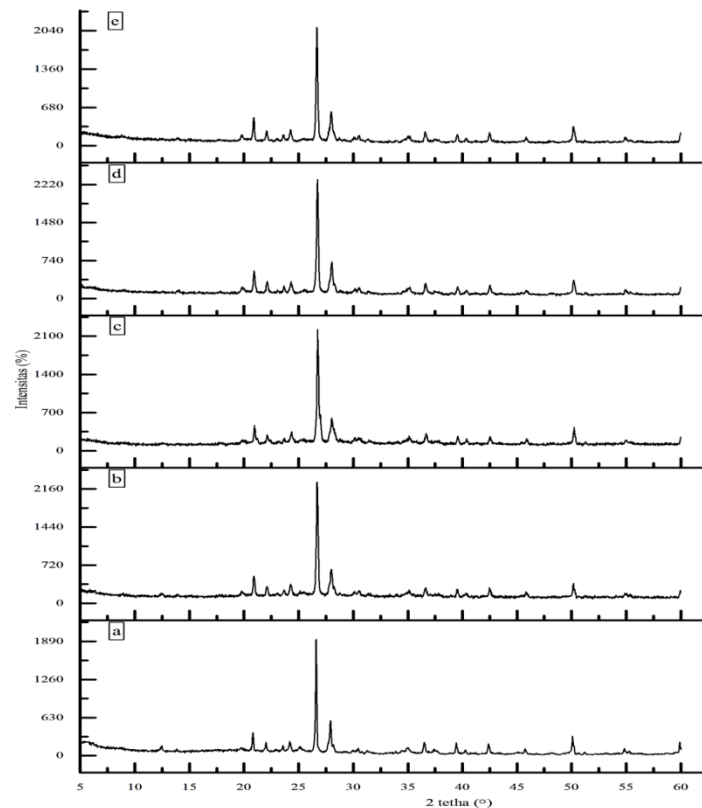
## 3.2. X-ray Diffraction Analysis



**Figure 1**. X-ray diffraction pattern of: a = natural zeolite, b = natural zeolite activated with HCl 1 M, c = natural zeolite activated with HCl 3 M, d = natural zeolite activated with HCl 6 M, e = natural zeolite activated with HCl 7 M

Figure 1 and Figure 2 show that the addition of acid does not significantly affect the structure of natural zeolite of Malang. Similarly, the addition of 7 M HCl and 5 M H2SO4 does not affect the structure of zeolite despite causing de-alumination. The diffraction pattern of Indonesian Natural Zeolite, which was activated with varying concentrations of acid, is clearly seen as having

the highest peak intensity with the position of 2 θ almost equal to that of natural zeolite of Malang before activation. Changes in relative intensity might occur due to the addition of acid in varying concentrations.
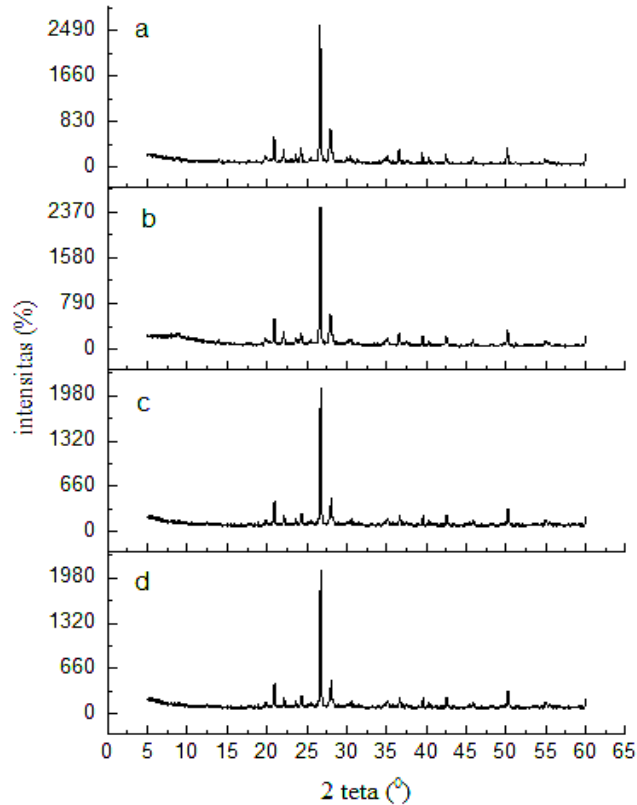
**Figure 2**. X-ray diffraction pattern of modified INZ: a = by 7 M $H_2SO_4$, b = by 5 M $H_2SO_4$, c = by 3 M $H_2SO_4$, d = by 1 M $H_2SO_4$

Natural zeolite of Malang consists of mordenite phase [19]. Mordenite has silica-rich frameworks based on five-oxygen rings linked together [20]. Industrially, mordenite phase has a good performance due to its wide micropore aperture with 12-R (0.57–0.70 nm), which is convenient for access of the reactant [21].
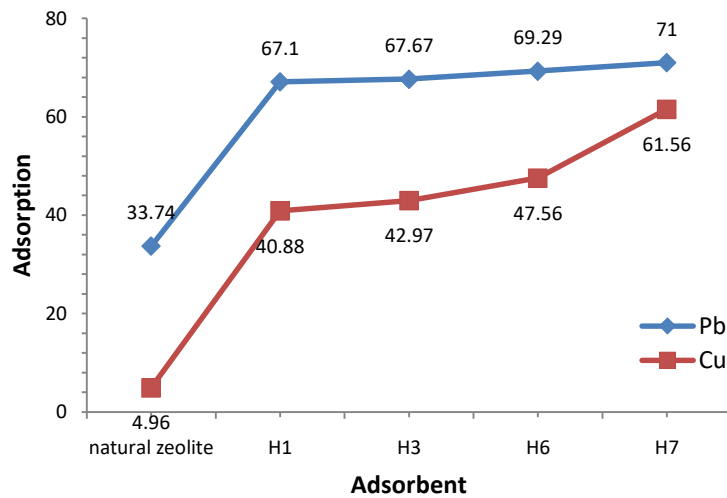


**Figure 3.** Adsorption of Cu and Pb using INZ modified with HCl

### 3.2.1. Adsorption of Cu and Pb Using Zeolit

Figure 3 and Figure 4 show that natural zeolite activated with inorganic acid is more effective for reducing Cu and Pb metal on waste. The higher the concentration of acid, the higher the adsorption of Cu and Pb metal. This is due to the surface area of the natural zeolite which is greater after the loss of impurities caused by the treatment of acid activation. Thus, the adsorption becomes higher.
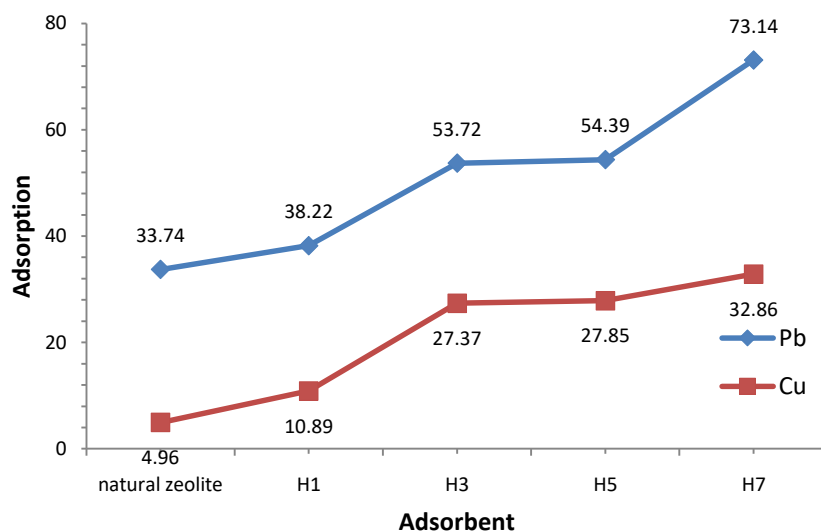
**Figure 4.** Adsorption of Cu and Pb using modified INZ by $H_2SO_4$

The selectivity of $Pb^{2+}$ is greater than that of $Cu^{2+}$. Selectivity of natural zeolite for heavy metal ions is caused by the hydration radii. The hydration radius of the cation is: $rHCu^{2+} = 4.19Å$, $rHPb^{2+} = 4.01Å$ [22]. Smaller cations get adsorbed faster and in greater amounts compared to larger cations because smaller cations can pass micropore and zeolite channels structure easily [23].

Adsorption can also be explained using enthalpy of hydration, which is the energy that permits the detachment of water molecules from cations and thus reflects the ease with which the cation interacts with the adsorbent. Therefore, the more a cation is hydrated, the stronger its hydration enthalpy and the less it can interact with adsorbent [23]. Divalent cations with low hydration energies are sorbed preferably compared to cations with high hydration energies. The hydration energy of the cation is; -2010, and -1481 $kJmol^{-1}$ for $Cu^{2+}$ and $Pb^{2+}$ respectively [22]. According to the hydration radii, the order of adsorption should be $Pb^{2+} > Cu^{2+}$.

## 4. CONCLUSIONS

The resulting natural zeolite after activation using HCl indicates that as the concentration of HCl increases, the percentage of the undesired ions that covers the pores of zeolite increasingly decreases. The activation of natural zeolite using HCl (1, 3, 6 and 7 M) does not affect the structure of zeolite, although natural zeolite activated using HCl 7 M underwent de-alumination. The best concentration of HCl for zeolite activation for Cu and Pb adsorption is 7 M.

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