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**THE FABRICATION OF NATURAL ZEOLITE VIA  
CO-PRECIPIATION METHOD AS Cu, Pb AND Zn  
METAL ADSORBENT**

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Heavy metal waste is very dangerous, which can change the condition of water into a solid substance that can be suspended in water and can reduce the cleanliness level of water consumed by living things. To date, heavy metals can be managed through several processes, namely physics, biology or chemistry. One of the ways to overcome heavy metal pollution is to use natural zeolite applying a co-precipitation method, as it is known that zeolite is a powerful natural material to be used for certain purposes. In order to justify the research results, several analyses have been performed, such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Surface Area Analyser (SAA), and Atomic Adsorption Spectrophotometric (AAS). From the XRD results, it has been found out that the size of each zeolite with variations in size of 150 mesh, 200 mesh, and 250 mesh is 29.274 nm, 38.665 nm and 43.863 nm, respectively. Moreover, the SEM-EDX has shown that the zeolite under consideration is a type of Na-Zeolite and that the co-precipitation method successfully removes impurity elements, namely, Fe, Ti, and Cl. The results of SAA testing have indicated that the total surface area for each variation of zeolite sizes is 63.23 m<sup>2</sup>/g, 45.14 m<sup>2</sup>/g and 59.76 m<sup>2</sup>/g. The results of the AAS test analysis have demonstrated that the optimal absorption of metal content is observed in a size of 150 mesh zeolite with adsorption power of 99.6 % for Pb metal, 98 % for Cu metal, and 96 % Zn metal.

**Keywords:** Co-precipitation method, metal adsorbent, natural zeolite

## 1. INTRODUCTION

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Aquatic environment pollution caused by heavy metals is transforming into a serious problem in public health and significant environmental issues. Mining activities, household waste liquids, industrial waste and agricultural waste are reported to be the main contributors to pollute the aquatic environment [1]–[4]. Natural zeolite is formed due to the existence of complex chemical and physical processes from rocks, which experience various kinds of changes in nature. Geochemists and mineralogists estimate that zeolites are frozen volcanic products, which then turn into volcanic rocks, sedimentary rocks and metamorphic rocks. Then, they subsequently undergo weathering due to the effects of heat and cold. Zeolite structures can be divided into three components, namely, aluminosilicate frame, empty space interconnected containing metal cations and water molecules in the occluded phase [5].

One way to overcome heavy metal pollution is by applying natural zeolite. Zeolite is commonly used as a catalyst in various acid catalyst reactions [6]–[9]. The adsorption method is an alternative method to

minimize the presence of pollutants in the environment [10]–[14]. Moreover, by synthesizing the zeolite via co-precipitation method and combining it with the acid, such as hydrochloric acid (HCl), it can give a significant effect, since hydrochloric acid is known as an acid capable of dissolving inorganic compounds [15], [16].

The co-precipitation method is a bottom up synthesis method that is used to obtain small nanometer sized particles [17]. This method has the principle of removing the continuous bond that is owned by a metal compound in the form of liquid without considering the specific mechanism that occurs. By using the co-precipitation method, a solid material is obtained from its aqueous precipitate [18].

Finally, it is necessary to investigate and research an active natural zeolite to be more optimal and efficient in its performance as an adsorbent. This adsorption property will be focused on removing metals as pollutants such as copper (Cu) and lead (Pb). Adsorption has been chosen as the best method for it is efficient and reliable.

## 2. EXPERIMENTAL

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Concentrated hydrochloric acid, copper metal, lead metal, zinc metal and distilled water were purchased from Merck and used for the research. Moreover, ball mill and several characterisation and analysis equip-

### 2.1. The Synthesis of Zeolite

Natural zeolite was dried in the furnace with various temperature levels. The first heating was reaching at 200 °C for 30 minutes, then it was increased to 400 °C for 30

minutes, namely X-ray Diffraction (XRD), Atomic Absorption Spectroscopy (AAS), Surface Area Analyser (SAA) and Scanning Electron Microscopy (SEM) were utilised.

minutes. Finally, the heating temperature was increased to 600 °C for 1 hour, which aimed at removing the water content in the zeolite to ease the grinding process.

Zeolite was crushed to break the zeolite stones and then sieved with 200 mesh sieves. Furthermore, zeolite powder was treated with ball mill type planetary ball mill for 2 hours with 400 rpm rotation and sieved with 200 mesh sieve to produce a smoother powder zeolite. Finally, it was characterised by using SEM-EDX and XRD method.

As much as 20 g of zeolite powder from the previous treatment was put into a beaker glass and then dissolved in 100 ml of 12 M HCl, then heated in a magnetic stirrer at the temperature range of 70 °C–90 °C for 120 minutes. Then, it was stirred at 350 rpm,

## 2.2. The Metal Adsorbent Test

As much as 0.2 g of Pb, Cu and Zn were weighed and then poured into a beaker glass and added with 1200 mL of distilled water. Then, it was stirred at room temperature at a rotation speed of 300 rpm until mixed evenly. After that, as much as 1 g of zeolite combined with HCl with various particle size of 150, 200 and 250 mesh was put in three beaker glasses. Then, as much as 300 mL of the solution containing metals was

and also heated at the temperature range of 70 °C–90 °C for 120 minutes. The mixture was then neutralised with distilled water.

The mixture was dried in the oven for 5 hours at the temperature of 100 °C. The dried mixture was crushed using a mortar to smoothen and turn it into powder. The zeolite powder was calcined in a furnace at the temperature of 600 °C. After calcination process, zeolite powder was milled using a ball mill at a speed of 100 rpm for 30 minutes, and sieved to produce zeolite. Zeolites combined with HCl solvents were tested by SEM-EDX, XRD, and SAA method.

poured into each of zeolite with various particle size and into one beaker glass that did not contain zeolite (blank).

The solution mixed with zeolite was stirred at a room temperature at a rotation speed of 300 rpm for 1 hour. The mixtures were filtered with Whatman paper to separate the solution and adsorbent materials. Finally, it was characterised by using the AAS method.

## 3. RESULTS AND DISCUSSION

Zeolites in the form of chunks were first put in the furnace at the temperature of 600 °C for 4 hours. The zeolite chunks were crushed with mortar and then sieved with 150 mesh, 200 mesh, and 250 mesh sieves. The sieve results were milled with the planetary ball mill at a rotation speed

### 3.1. XRD (X-Ray Diffraction) Analysis

X-ray diffraction method is an analytical method based on the interaction between matter with X-ray electromagnetic radiation (having  $\lambda = 0.5\text{--}2.5 \text{ \AA}$  and energy  $\pm 107 \text{ eV}$ ), which is the measurement of diffracted X-ray radiation by the field crystal.

of 300 rpm for 2 hours to produce zeolite powder.

Then, the size variations were carried out with the aim of discovering which zeolite would have optimum adsorption of heavy metal ions and have the largest surface area.

Moreover, in the present research, the XRD characterisation used the Shimadzu type XRD tool with  $K\alpha$  wavelength of  $1.541862 \text{ \AA}$  and speed (scan speed) of 2 degree/min. The XRD characterisation results are displayed in Fig. 1.

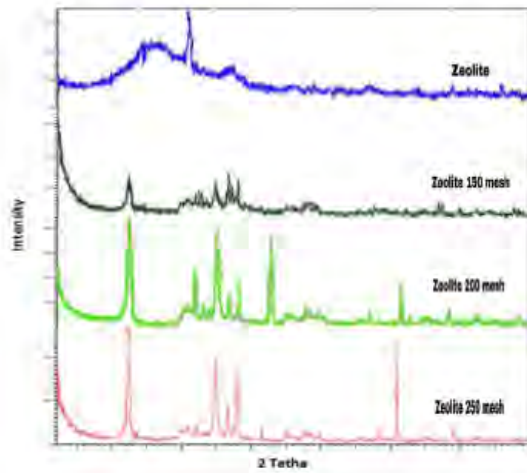


Fig. 1. The XRD result of: Zeolite after milling process, zeolite 150 mesh, zeolite 200 mesh and zeolite 250 mesh.

Based on the XRD results, it can be seen that the size of each zeolite with variations in the size of 150 mesh, 200 mesh, and 250 mesh is 29.274 nm, 38.665 nm and 43.863 nm, respectively. Furthermore, the crystal structure of zeolite after milling process, zeolite 150 mesh, zeolite 200 mesh, zeolite 250 mesh are trigonal, tetragonal and cubical, respectively.

Particle size can affect material properties; a smaller size affects a larger surface area causing greater or more responsive reaction power [19], [20]. Furthermore, changes in material properties (chemical properties and thermal properties) lead to changes in the structure of the material; this structure also illustrates the strength of the material [21].

### 3.2. Scanning Electron Microscope (SEM) Analysis

The characterisation using Scanning Electron Microscopy (SEM) is expected to determine the morphological structure of a material. Through SEM analysis, the pore particle size can be seen in the sample with a certain magnification; besides, the composition of the material can be determined through an EDX tool that is integrated with the SEM.

The smaller the size of the adsorbent pores, the higher the surface area so that

the number of molecules adsorbed will increase. From the results of the analysis of the composition of the SEM-EDX compound, it is known that zeolite under consideration was Na-Zeolite type. Zeolite before being co-precipitated had a rough surface and agglomerated, whereas zeolite that was co-precipitated had a smooth surface and less agglomeration. The zeolite synthesis of the co-precipitation method succeeded in removing impurities, namely, Fe.

Table 1. The Element Composition Obtained from the EDX Analysis

Chemical Elements	Mass [%]			
	Zeolite	Zeolite 150 mesh	Zeolite 200 mesh	Zeolite 250
Si	14.40	15.10	18.71	30.65
Al	32.86	15.09	17.49	16.33
Fe	10.04	1.20	0.74	-
Ti	-	0.13	0.34	-
C	4.80	8.73	7.56	4.64
Cl	3.31	0.61	0.84	-
O	34.58	58.91	52.85	48.38

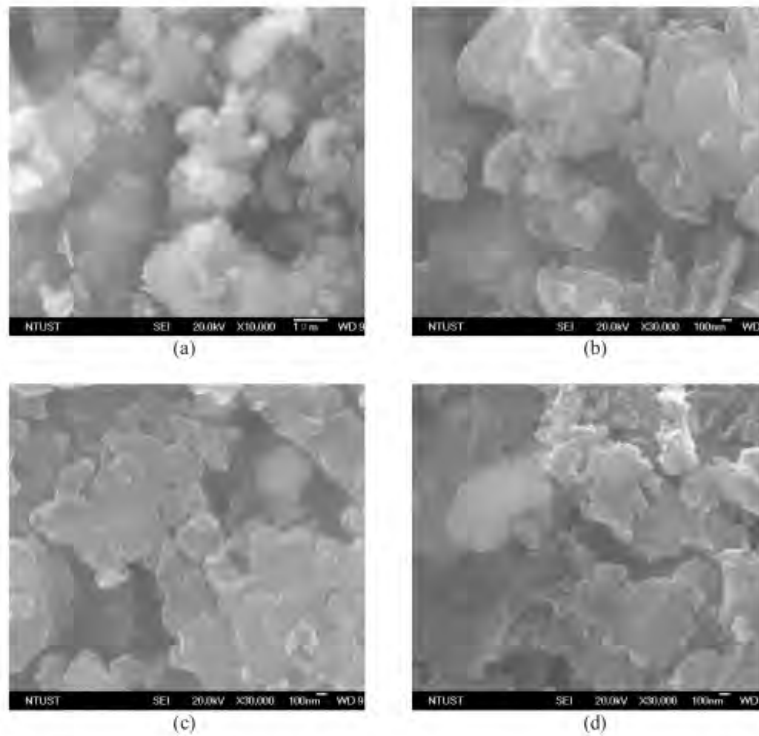


Fig. 2. The SEM result of: (a) zeolite after milling process, (b) zeolite 150 mesh, (c) zeolite 200 mesh and (d) zeolite 250 mesh.

### 3.3. Analysis of Surface Area Analyser (SAA)

Surface Area Analyser has several methods with one of them in the form of Gas Surface Analyser, which uses gas to analyse the surface area of a porous material with desorption adsorption techniques applying adsorbate inert gases such as nitro-

gen or helium and adsorbent in the form of porous material. Zeolite is said to be physically adsorbed, which only occurs in the interaction between the molecule adsorbent and the adsorbate.

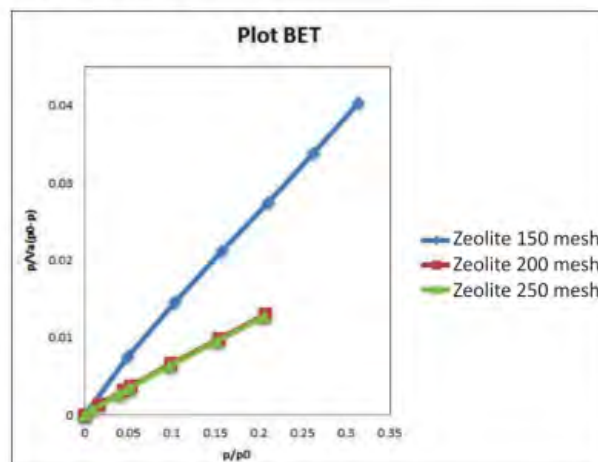


Fig. 3. The BET plot result of zeolite 150 mesh, zeolite 200 mesh and zeolite 250 mesh.

The SAA test results revealed that the total surface area of the zeolite variation of 150 mesh, 200 mesh, 250 mesh were 32.07 m<sup>2</sup>/g, 65.36 m<sup>2</sup>/g and 65.06 m<sup>2</sup>/g, respectively, with specific surface area (BET)

variations in each size – 323.95 m<sup>2</sup>/g, 660.26 m<sup>2</sup>/g and 157.18 m<sup>2</sup>/g. Furthermore, the calculation results of BET analysis on the surface area of each zeolite size are as follows (see Table 2).

**Table 2.** The Calculation Result of BET Analysis

Sample	Zeolite 150 mesh	Zeolite 200 mesh	Zeolite 250 mesh
Slope	1.22 x 10 <sup>-1</sup>	5.99x 10 <sup>-2</sup>	6.05x 10 <sup>-2</sup>
Intercept	2.04x 10 <sup>-3</sup>	7.07x 10 <sup>-4</sup>	4.00x 10 <sup>-4</sup>
Surface Area	3.52x 10 <sup>1</sup>	7.18x 10 <sup>1</sup>	7.15x 10 <sup>1</sup>
Wm (m <sup>2</sup> /g)	8.09	1.65x 10 <sup>1</sup>	1.64x 10 <sup>1</sup>
St (m <sup>2</sup> /g)	3.21x 10 <sup>1</sup>	6.54x 10 <sup>1</sup>	6.51x 10 <sup>1</sup>
S (m <sup>2</sup> /g)	3.24x 10 <sup>2</sup>	6.60x 10 <sup>2</sup>	6.57x 10 <sup>2</sup>
Error (%)	8.9761	8.9718	8.9714

### 3.4. Atomic Adsorption Spectrophotometric (AAS) Analysis

The results of the AAS analysis showed that the optimum adsorption of metal content was using zeolite variations in size of 150 mesh with adsorption power of 99.6 % for Pb metal, 98 % for Cu metal, and 96 % Zn metal. The zeolite 200 mesh adsorption power was Pb 96.97 %, Zn 99.694 %, and Cu 97.51 %, while zeolite 250 mesh adsorption power was Pb 99.92 %, Zn 99.684 %, and Cu 99.978 %.

At the time of exchange of heavy metal ions with zeolites, it will be confused with zeolite elements which have weak ionization, so that zeolites can absorb the metal ions. The second indicator that causes high absorption results is because the small particle size will increase the surface area, causing higher absorption properties.

**Table 3.** The Metal Content of Each Size Variation of Zeolite

Sample	Pb (mg/L)	Zn (mg/L)	Cu (mg/L)
Without indicator	591.6	0.5264	0.2709
Zeolite 150 mesh	0.1051	0.1636	<0.006
Zeolite 200 mesh	6.49	0.1611	0.6734
Zeolite 250 mesh	<0.005	0.5880	<0.006

Based on the table above, it can be seen that there is a decrease in metal content when using nano zeolite. The optimal metal absorption uses HCl solvent where there is a decrease in metal content for all Pb, Zn

and Cu metals. It can be inferred that the co-precipitation method applied to natural zeolite and converted to several size variations is proven to be able to show a good performance for metal adsorbent.

## 4. CONCLUSION

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The fabrication of natural zeolite via the co-precipitation method has been successfully performed. Furthermore, this material

shows an impressive capability as a metal adsorbent, particularly copper, lead and zinc.

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