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Physical Characterization of a Natural Zeolite using a Scanning Electron Microscopy: A Preliminary Study

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Abstract

Zeolite is one of important non-metallic mineral deposites in Indonesia. It has been used for various purposes, including as an adsobent in environmental protection, industry, and agriculture. The most important characteristics of zeolit to be an adsorbent is its surface area and crystal structure. To optimally use zeolite as an adsorbent, it is necessary to understand its physical characteristics. This preliminary study was aimed to characterize physical properties of a natural zeolite obtained from Tasikmalaya, West Java, Indonesia. The zeolite material was crushed into <0.5 mm diameter and divided into two sets of samples. One set of samples was heated in a muffle furnace at 250 ^{o}C for two hours and the other set was left untreated. All samples were then observed using a Scanning Electron Microscopy (SEM). The SEM micrographs showed rough and porous structure and defined crystallinity of the zeolite. Thermal treatment at 250 ^{o}C increased zeolite crystallinity. These results confirm that this natural zeolite is potential to be used as an adsorbent to remove dissolved metals from acid mine drainage.

Keywords: Natural Zeolite, Adsorbent, Physical Characterization, Scanning Electron Microscopy

INTRODUCTION

Natural zeolite is one of important non-metallic minerals and multi-use industrial minerals in Indonesia (Kusdarto, 2008; Kadja and Ilmi, 2019). It has been used for various purposes, including environmental protection and industry. Various types of zeolite have been used as adsorbents, molecular sieves, membranes, ion-exchangers, and catalysts (Kusdarto, 2008; Masoudian et al., 2013; Atikah, 2017; Bakalar and Pavolova, 2018). It is also particularly suitable for removing undesirable heavy metals (Zendelska et al., 2014; Atikah, 2017; Bakalar and Pavolova, 2018; Kadja and Ilmi, 2019).

A number of reports (Kabwadza-Corner et al., 2015; Krol, 2020) indicated that the most important characteristics of zeolite are its surface area and crystal structure. Zeolite has a complex three dimensional network of tetrahedrous SiO4 and $AlO4^{-}$ which creates lattices or cavities that can trap various ionic pollutants and organic molecules (Atikah, 2017; Belova, 2019). The isomorphic substitution of Al^{3+} for Si^{4+} generates a negative charge density in the zeolite latttice counterbalanced by cations. These cations can be removed or exchanged with other cations without structural damage. With a such structure and behaviour, therefore, zeolite can be utilized for different purposes, including adsorbent of metal elements (Masoudian et al., 2013; Atikah, 2017). The size and structure/shape of zeolite particles highly determine zeolite stability, chemical reactivity and physical strength. Therefore, the use of natural zeolite usually involves physical as well as chemical activation processes that cause changes in zeolite properties. This preliminary study was aimed to investigate the effects of thermal treatment on some physical characteristics of a natural zeolite from Tasikmalaya, West Java, Indonesia. The results of this study will be considered for a further study on the use of natural zeolite to remove dissolved manganese (Mn) from acid mine drainage collected from mine a coal mine site.

LITERATURE REVIEW

Natural Zeolites

Natural zeolites are well defined crystalline aluminosilicate minerals in nature (Dyer, 1988; Kadja and Ilmi, 2019). They are hydrothermal and of mainly volcanic origin (Kusdarto, 2008; Krol, 2020). The zeolite struture consists of an assemblage of $[SiO4]^{4-}$ and $[AlO4]^{5-}$ tetrahedral (Figure 2.1) that join

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together in various arrangements through shared oxygen atoms to form open crystal spaces in molecular dimensions into which water and cations can penetrate (Mortier et al., 1982; Atikah. 2017).

Zeolite particles usually have net negative charges in their structure. These charges originally come from the isomorphous substitutions of Al^{3+} for Si^{4+} in the mineral structure, and the negative charges can be counterbalanced by cations. Therefore natural zeolite has a high cation exchange capacity (Alvarez et al., 2003; Iskander et al., 2011; Masoudian et al., 2013; Atikah, 2017; Belova, 2019; Kadja and Ilmi, 2019). This cation exchange capacity play an important role in determining the adsorptive capacity of zeolite.

Such a unique structure of natural zeolite shows a number of propertie, including low density and large free spaces, the existence of channels and pores, high degree of hydration, high crystallinity, and possibility ionic and molecular sorption, and catalytic properties (Krol, 2020).

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a relatively new techniques, compared to optical microscopy (OM), but it has been used worldwide in various disciplines. This is an instrument that can produce a largely magnified image by using electrons (Motsi, 2010). The SEM can magnify images to 300.000 times and even 1000000, so it is regarded as an effective method in analysis of organic and inorganic materials on a nanometer to micrometer scale (Mohammed & Abdullah, 2018).

The principle analysis of SEM is based on a beam of electrons having high-energy produced at the top of the microscope by an electron gun (Motsi, 2010; Mohammad & Abdulah, 2018). This electron beam travels down through electromagnetic fields and lenses onto the sample. Once the beam hits the sample, electrons and X-rays are reflected from the sample, causing interactions with the atoms from the sample which then generate signals consiting of information about the sample's surface morphology and topography and appearance. The electron detectors collect these scattered electron and X–Rays and convert them into a signal that can be displayed as a greyscale SEM image on a computer (Motsi, 2010; Mohammed & Abdullah, 2018). This technique is very powerful (Yokoi, 2021); and therefore SEM is helpful for characterizing physical properties of minerals such as natural zeolites.

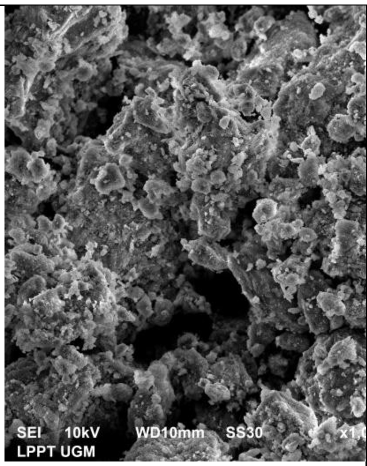
RESEARCH METHODOLOGY

This preliminary study is part a research project using a natural zeolite to remove dissolved manganese (Mn) from acid mine drainage. In order to properly use this material, therefore, characterizaion of the zeolite is an important step of the study. The results of this study will be further used in the research project.

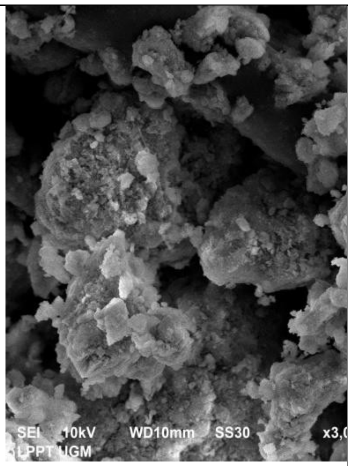
In this study natural zeolite samples from Tasikmalaya, West Java, Indonesia were used and supplied by ADY WATER CV in Bandung, Indonesia. The original zeolite materials were divided into three diameter classess: <0.5 mm, 1-2 mm, and > 2.0 mm. For this study so-called a preliminary study, however, only the <0.5 mm class diameter was used. The <0.5 mm class diameter was divided into two sets of samples, one set of samples was thermally treated or activated at 250^{o} C in a muffle furnace for two hours and the other set of samples was left untreated. These two sets of samples were characterized using a Scanning Electron Microscopy (SEM).

FINDING AND DISCUSSION

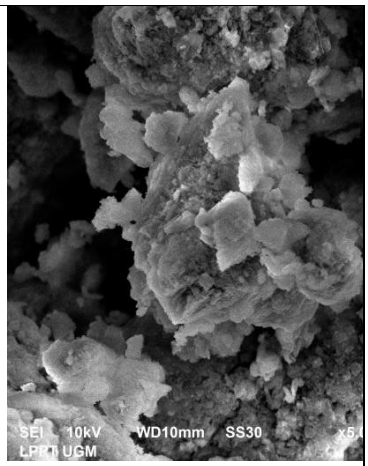
The micrographs of the natural zeolite samples obtained from the Scanning Electron Microscopy (SEM) analysis are shown in Figure 1. The micrographs clearly show rough surfaces and a number of macropores in the zeolite structure. The micrographs also show well defined crystals of minerals. The thermal treatment at $250^{o}C$ for two hours in a muffle furnace show much more defined structures of the zeolite particles. Neag et al. (2020) stated that rough surfaces were favorable for the adsoption of metals.



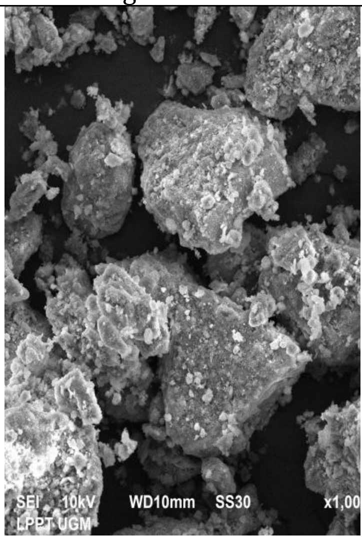
a. Natural zeolite, original at 1000 x magnification



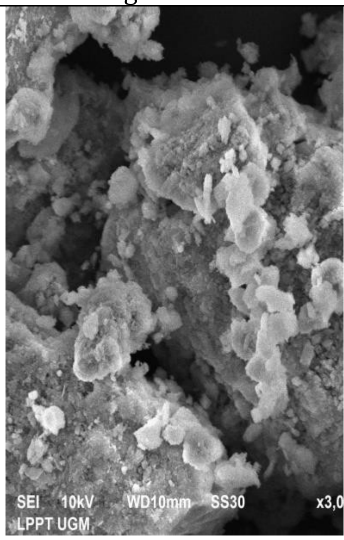
b. Natural zeolite, original at 3000 x magnification



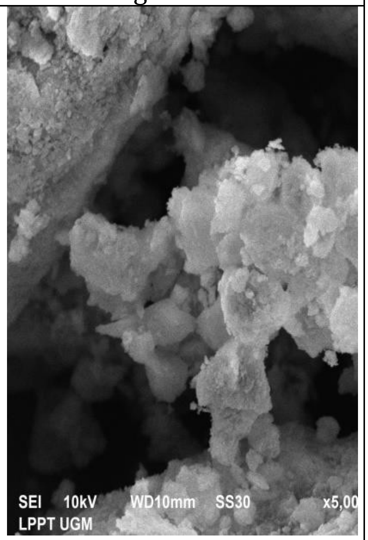
c. Natural zeolite, original at 5000 x magnification



d. Natural zeolite thermally-pretreated at 250°C, 1000 x magnification



e. Natural zeolite thermally-pretreated at 250°C, 3000 x magnification



f. Natural zeolite thermally-pretreated at 250°C, 5000 x magnification

Figure 1. SEM micrographs of original natural zeolites (a, b, and c) and thermally-treated natural zeolites at 250° C for two hours (d, e, and f) at three different magnification levels.

Results of on thermal treatments of natural zeolites have been widely reported by other authors from different parts of the world (Motsi, 2010; Neag et al., 2020; Cadar et al., 2020). In general they observed that the effects of thermal treatment have been more on structural changes, particularly the degree of cristallinity, and not on chemical composition of natural zeolites (Cadar et al., 2020). The thermal treatment results in loss of the zeolite crystallinity. Most authors suggested that such structural modifications had been associated with the loss of water molecules, followed by cation retention balancing negative charged left by water molecules.

In his work with natural zeolites (clinoptilolite) from Turkey, Motsi (2010) found that heating natural zeolites at 200 °C did not significantly change mineral structure, However, he observed that heating upto 400 °C had damaged their crystalline structures and collapsed the macro-pores of the zeolites. He further reported that after being heated in a microwave for 15 minutes, natural zeolites still had porous structure, but showed reduced the degree of their crystallinity, and had “plate” structures. He attributed this to the collapsed macro-pores and crystals.

Neag et al. (2020) reported that thermal activation of natural zeolites from Rupea Quarry, Brasov County, Romania at 250 °C was optimal to remove Fe and Mn from artificial solution, and this had been associated with rough surfaces after the activation. In a more recent study on Romanian clinoptiloliterich zeolites, Cadar et al. (2020) who worked on much higher thermal treatment found that crystallinity of the zeolites progressively decreased by increasing thermal treatment. At that 600 ^oC the structure started to collapse and completely collapsed at at 800 ^oC resulting in trasformation of clinoptilolite into an amorphous.

CONCLUSION AND FURTHER RESEARCH

The natural zeolites used in this study showed a number physical characteristics, including large volume of free space and a high degree of crystallinity. Thermal treatment at 250 ^oC had increased the crystalinity of the natural zeolites and their pore spaces. Therefore, this zeolite will be used as an adsorbent for a further research on removal of manganese (Mn) from acid mine drainage.

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