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Analysis the Effect of Activated Natural Zeolites for Fe Metal Adsorption

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Abstract

Zeolite, as an adsorbent, can be improved by a chemical activation process. In this study, zeolite was activated using the acid activation method by soaking natural zeolite with HCl and HF, and the activated zeolite was then used to adsorb Fe metal. Zeolite was characterized using SEM and XRD, and the adsorption capacity of the zeolite was analyzed using AAS. The results of SEM analysis show that zeolite after activation has a more significant number of pores than zeolite before activation. The results of XRD analysis show that zeolite that has been activated has a higher content of quartz (SiO2) and clinoptilolite than zeolite that has not been activated. The results of the zeolite adsorption capacity and efficiency test on Fe metal showed that the most excellent adsorption capacity was when the contact time was 60 minutes, with adsorption capacity and adsorption efficiency values of 3.2403 mg/g and 97.21%.

Keywords: *Zeolite; activation; acid; Fe metal*

Introduction

Indonesia has a total resource of 447,490,160 tons of zeolite deposits, which are spread throughout almost the entire Indonesian archipelago. Volcanoes, the source of zeolite rocks that cause zeolite, can be found around the areas where Mount Merapi passes (Kusdarto, 2008; Marantos et al., 2012). Natural zeolite is an alumina silicate mineral crystal containing cations such as Na, Ca, K, Mg, and Fe (Ginting et al., 2007; Yuna, 2016). These crystals structurally form a three-dimensional framework and are acidic and porous in molecular size. Zeolite comes from the words zein," which means to boil, and "lithos," which means rock. This name is given because it looks like it is boiling when heated. This shows that the water content in the zeolite is relatively high because it is very porous. The amount of water content in the zeolite depends on the nature of the cations and their crystallization conditions (Akhtar et al., 2014; Jim'enez-Casta˜neda et al., 2017).

The zeolite used in this study is natural zeolite originating from Sukabumi, which has yet to be activated, so there are still many impurities. Impurities in zeolite will reduce the ability of zeolite to adsorb because it is covered by impurities (Liu and Jiaqi, Cheng, X., Zhang, Y., Wang, X., Zou, Q., Fu, 2017; Taneva, 2012). Zeolite can be activated because of its hollow 3-dimensional structure (Dionisiou et al., 2016; Irannajad et al., 2020; Reeve et al., 2018; Shi et al., 2018). Zeolite can be physically and chemically activated (Margeta et al., 2013, Wang, Y.F., Lin, F., Pang, 2007). The physical properties of the zeolite can be changed through a heating process to remove the water content from the structure (Fadliah *et al.*, 2021). Meanwhile, the chemical properties of the zeolite can be changed by removing impurities from the surface of the zeolite by reacting the zeolite with acid (Oztas¸ et al., 2008).

Several researchers have previously carried out the zeolite activation process both physically and chemically. Reka Oktaviani et al. (2018) modified and characterized natural zeolite with Fe2O3, which showed that natural zeolite that had been chemically activated using HCl would increase the SiO2 content from 78.26% to 87.69%. The results of the XRF analysis from this study showed reduced concentrations of impurities such as K, Zn, Mn, and others after activation. However, they had not completely disappeared, so physical activation was necessary for calcination (Oktaviani et al., 2019).

Indonesia's abundant natural resources have made mining activities very popular. Mining activities will have positive and negative impacts on the implementation process. The negative impact of the mining industry is the formation of waste from the process of mining activities. Waste from mining industry processes can be solids, liquids, or gases (Gutti et al., MM., Magaji, 2012). Liquid waste from the mining production process can be in the form of acid mine drainage, which contains dangerous heavy metals and can damage the environment due to decreased water quality (Renni, C. P., F. Widhi, W., dan Nuni, 2018).

According to research by (Fatimah et al., 2021), activated natural zeolite can absorb phosphate ions. Yulius Dala Ngapa researched in 2017 using natural zeolite, activated by acids and bases, to adsorb methylene blue dye. Therefore, in this study, chemical activation of zeolite will be carried out by soaking with HCl and HF and being physically activated through size reduction and calcination. The activated natural zeolite is then used as an adsorbent for heavy metals made artificially in the laboratory.

Methods

Tools and Materials

The tools used in this study were glassware commonly used in laboratories and zeolite characterization using SEM and XRD. Besides that, The adsorption analysis using AAS.

Natural zeolite activation

The natural zeolite comes from Sukabumi is activated by acid using HCl and HF. One hundred grams of 100-mesh natural zeolite was soaked in a 1% (v/v) HF solution for 30 minutes, filtered, and dried in the sun to dry. Then, the zeolite was refluxed in 6 M HCl for 5 hours at an operating temperature of 60°C. The zeolite was dried in an oven at 130°C for 3 hours. Calcination is carried out in a furnace at a temperature of 450°C. Natural zeolites before and after activation were characterized using XRD and SEM.

Adsorption of Fe metal with activated natural zeolite

Fe metal comes from $FeCl_3$ with a concentration of 100 ppm, which is put in 25 mL into 5 Erlenmeyers. Each is added with 1 gram of natural zeolite, which has been activated and adjusted to 4, then stirred using a magnetic stirrer with a stirring speed of 125 rpm with variations of 20, 40, 60, 80, and 100 minutes at room temperature. Then, the solution was filtered using Whatman 42 filter paper to separate the filtrate and residue. The filtrate obtained was then analyzed with AAS. Adsorption of Fe metal with activated natural zeolite.

Determination of Adsorption Capacity

$$qe = \frac{(Co - Ce)V}{m} \quad (1)$$

Determination of Adsorption Efficiency

$$EA = \frac{(Co - Ce)}{Co} x\ 100\% \qquad (2)$$

Results and Discussion

Natural zeolite activation

Characterization using SEM is used to see differences in the morphology and topology of the zeolite surface before and after activation by producing various signals (Wang et al., 2012; Rhodes & Christopher, 2010).

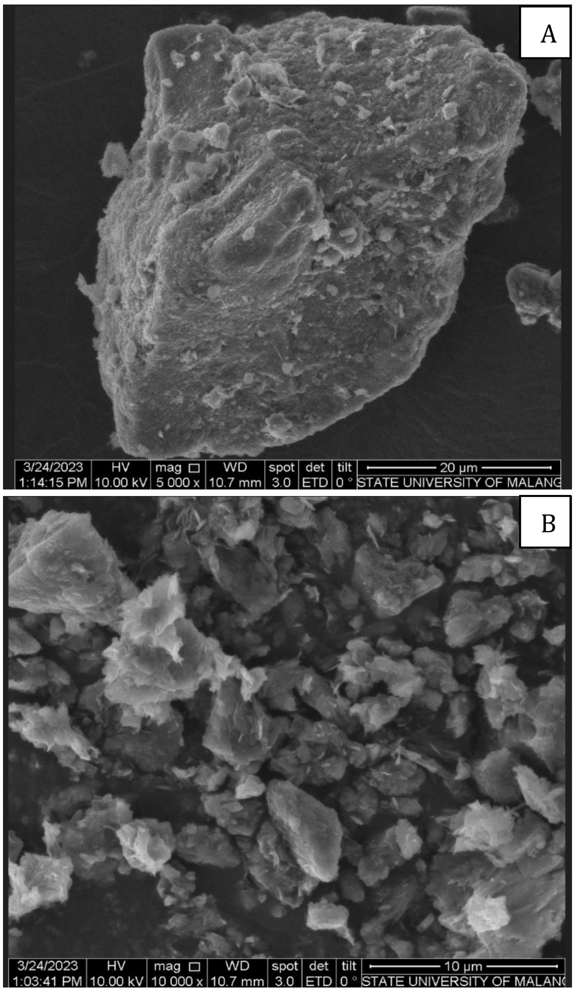

Figure 1. SEM analysis results of zeolite before (A) and after (B) activation

The results of SEM analysis on zeolite show differences in morphology before and after activation. The shape of the zeolite surface before activation shows closed pores; the large amount of impurities can cause this on the surface. Meanwhile, activated zeolite shows open pores without any impurities, which causes an increase in the zeolite's ability to adsorb metal because the surface of the pores formed becomes wider.

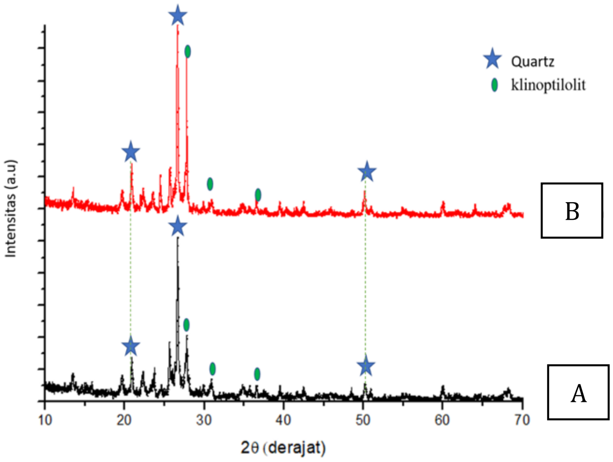

Figure 2. XRD analysis results of zeolite before (A) and after (B) activation

The XRD diffractogram in Figure 2 shows the presence of quartz (SiO_2) and clinoptilolite minerals. In the initial sample, the mineral content of quartz (SiO_2) and clinoptilolite was lower than in activated zeolite. This shows the increasing crystallinity of the zeolite after activation due to the loss of impurities on the zeolite surface.

Effect of Variation of Contact Time on Adsorption of Fe Metal

The ability of zeolite to adsorb Fe metal can be seen by varying the amount of zeolite added. The variation function of adding zeolite is to determine the optimal amount of zeolite that must be added to adsorb Fe metal. The adsorption capacity can be determined by performing an AAS analysis, which can reveal the Fe content in the sample.

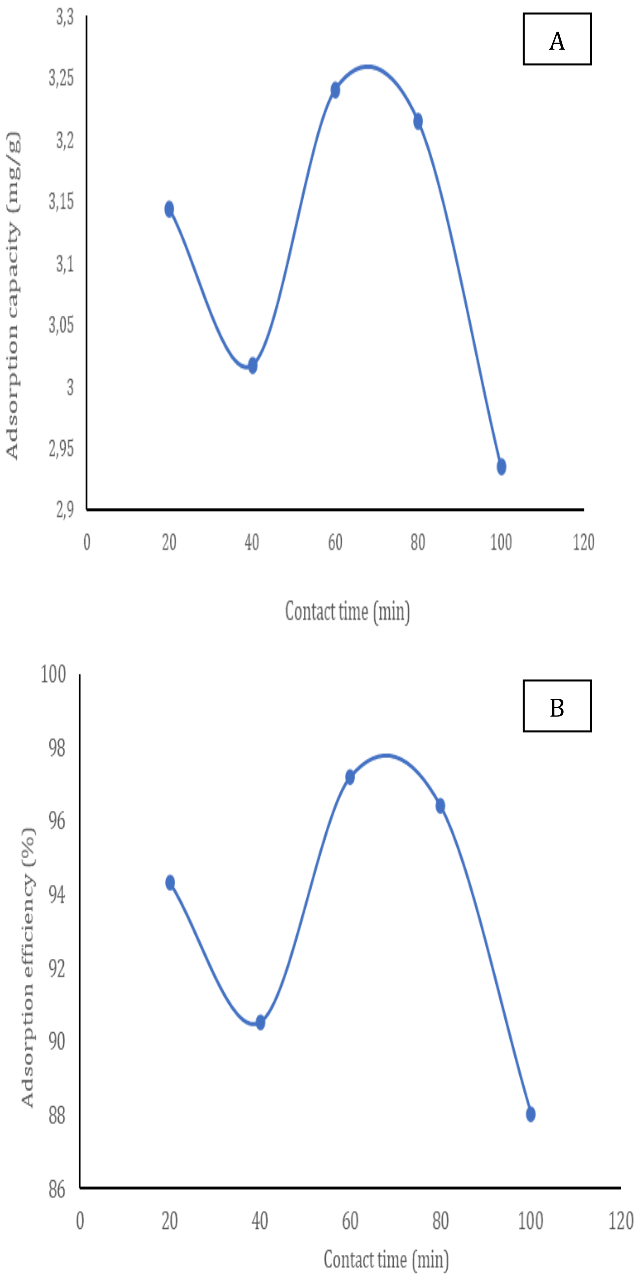

Figure 3. Effect of contact time on adsorption capacity (A) and adsorption efficiency (B) of zeolite

The duration of contact between Fe metal and zeolite reveals zeolite's capacity to adsorb the metal. The adsorption ability of different materials, including zeolite, is impacted by various factors, such as contact time. The effect of duration on achieving equilibrium between the adsorbate and zeolite can differ based on the type of adsorbate, zeolite, and experimental set-up. The longer the contact time, the higher the likelihood of attaining equilibrium between the adsorbate and zeolite. Adsorbate quantity can no longer be significantly altered by the zeolite. Moving forward, contact time has an impact on the speed at which the zeolite removes the adsorbate from the solution, also known as adsorption kinetics. Initially, the rate of adsorption can be quick, but it may gradually decrease as the adsorbate reaches saturation on the surface of the zeolite.

Zeolite's capacity to adsorb can be influenced by the duration of contact. As adsorbate accumulates, the initial contact time may increase the adsorption capacity. However, an equilibrium will eventually be reached, resulting in a constant adsorption capacity. According to Figure 3, the greatest adsorption capacity and efficiency was obtained at a contact time of 60 minutes, with an adsorption capacity value of 3.2403 mg/g, and an adsorption efficiency of 97.21%. When the optimal contact time is met, the amount of metal ions that can be adsorbed reduces. The Fe(III) metal ions filling the zeolite pores caused a decrease. Afterward, the Fe(III) ions left were unable to be adsorbed per Renni et al. (2018).

The diffusing of adsorbate into the zeolite structure can be impacted by the duration of contact time. The zeolite surface may initially allow for swift penetration of the adsorbate. Yet, as adsorbate increasingly fills the zeolite pores, the rate of diffusion may decelerate. If longer contact times are implemented, it is possible to augment zeolite selectivity in relation to specific adsorbates. Utilizing prolonged contact periods may prove beneficial in applications requiring separation or purification processes, as the zeolite becomes more discerning when extracting the desired adsorbate.

Conclusion

The results of SEM analysis show that the zeolite after activation has a broader number of pores than the zeolite before activation due to the loss of impurities on the surface. The results of XRD analysis show that the zeolite before and after activation has the same content, namely quartz (SiO_2) and clinoptilolite. However, activated zeolite shows a higher level of crystallinity. Adsorption capacity and efficiency tests show that contact time influences the ability of zeolite to adsorb Fe metal. The best adsorption capacity and efficiency were achieved at a contact time of 60 minutes, with an adsorption capacity value of 3.2403 mg/g and an adsorption efficiency value of 97.21%.

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