Effectivity of Zeolite as An Adsorbent for Methyl Violet Adsorption

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ABSTRACT
The textile industry in Indonesia is developing. This development aligns with the amount of waste produced, such as dyes and metal waste, which can harm the environment and must be processed. One of the waste treatment methods that can be used is adsorption using zeolite. This study aims to determine the absorption effectiveness of Bayah natural zeolite adsorbents on lead and methyl violet waste. The zeolite was mashed and uniformed in size up to 80 mesh and then washed and heated to 120℃ to remove impurities in the zeolite. Then the zeolite was activated using 1 M HCl and 1 M NaOH activators and calcined at 500 ℃ for 4 hours. This research was carried out by varying the mass of the adsorbent as much as 0.5 and 1 g and the adsorption stirring time for 30 and 60 minutes. The results show that the maximum adsorption capacity was 181.84 mg/g with an efficiency of 91% for methyl violet adsorption and 198.7 mg/g with an efficiency of 99.57% for lead adsorption. The adsorption of natural zeolite on methyl violet and lead metal followed the Langmuir isotherm pattern with adsorption capacity of 23.04 mg/g and 87.72 mg/g, respectively.

Keywords: adsorption, methyl violet, natural zeolite

1. INTRODUCTION
The development of the textile industry in Indonesia is very rapid. According to the Central Bureau of Statistics, 2016, the number of textile industries in Indonesia was 5,900, then in 2018, it increased by 8.73%, and in 2019, it increased rapidly to 18.9% (Watini, 2009). One of the textile industries in Indonesia is the batik industry. The batik industry is a relatively large producer of liquid waste. The amount produced reaches 80%. Batik industry waste is dominated by natural and synthetic dyes in the production process. Using synthetic textile dyes often causes problems. The waste is still colored and difficult to degrade.

Adsorption is one of the most commonly used methods because it has a more straightforward and economical concept (Suhud et al., 2012). Various adsorbents often used include activated carbon, fly ash, biomass, and zeolites, referred to as biosorbents. Zeolite is a porous material with several dominant minerals, such as silica and alumina (SiO₂ and AlO₃).

Natural zeolite utilization as a dye adsorbent has been done by some researchers. Ngapa & Ika (2020) carried out the adsorption of methylene blue and methylene orange using Ende’s natural zeolite. Atikah (2017) used Gunung Kidul natural zeolite to adsorb mono chloro triazine.

Zeolite is usually used as an absorbent, but still not maximized because the cavities or pores in the zeolite are generally not fully opened because there is water and impurities in the form of alkali metals Ca²⁺, K⁺, and Mg²⁺ covering the pores. Therefore, the adsorption ability of zeolite can be increased by activation using a strong acid solution. The activation process can be done both physically and chemically. Chemical activation can be done using acids or bases, while physical activation is done by heating at high temperatures (Ginting, 2003).

Arnelli & Arthono (2002), stated that calcination of zeolites is required at 550°C to absorb anions and only at 300°C to absorb organic compounds. The adsorption process is influenced by the type of adsorbent and adsorbate. Another study conducted by (Permana,
Concerning the analysis of the effect of zeolite grain size on the reduction of color and chromium (Cr) in textile industry wastewater used a grain size ratio of <0.5 cm and >0.5 cm. This study showed that zeolite with a diameter of <0.5 cm was more effective than zeolite with a diameter of >0.5 cm in reducing color and chromium content in textile industry wastewater. This means that the smaller the diameter of the zeolite, the greater the degree of settlement obtained. In this study, adsorption was conducted using Bayah natural zeolite to remove methyl violet, which has not been done before.

2. METHODS

2.1 Zeolite and Dye Waste Sample Preparation

Zeolite was obtained from Bayah, Banten Province. First, it was reduced to a size of 80 mesh (Aidha, 2013). Then soak the zeolite using distilled water for one day. Furthermore, drying the zeolite using an oven at 120°C for 4 hours (Anggara et al., 2013). After that, it is stored in a closed airtight container. After that, 50 g of pretreated zeolite powder was activated by mixing 250 ml of 1M NaOH solution, which was stirred using a magnetic stirrer at 100 rpm for 3 hours (Manatap et al., 2016).

The zeolite biosorbent was filtered with filter paper and washed using distilled water. The washed zeolite was calcined at 500°C for 4 hours (Banon & Suharto, 2008), and the activated zeolite was then analyzed with FTIR. The zeolite is stored in a closed, airtight container. This process was repeated using 1M HCl for the activation process.

The dye used in this research is methyl violet textile dye. The dye waste sample solution was prepared by weighing 1 g of methyl violet powder and dissolving it with distilled water in a 1000 ml volumetric flask to obtain 1000 ppm methyl violet.

2.2 Adsorption Process

50 ml of the dye waste sample (methyl violet) with a concentration of 100 ppm was put into a 250 ml beaker glass, and then adsorbent was added to the samples. The mass was varied at 0.5 and 1 gram. The samples were stirred at 300 rpm for 30 and 60 minutes. The samples were then analyzed using a UV-Vis spectrophotometer.

3. RESULT

3.1 FTIR Analysis Results

Figure 1 and Table 1 showed that natural zeolite without activation (ZAT) shows a broad peak at 3378.98 cm⁻¹ related to the presence of stretching OH vibrations, although it does not yet appear sharp. In the area of 400 – 1600 cm⁻¹, some peaks were seen, at an absorption area of 1631.84 cm⁻¹, the presence of OH bending vibrations, the area of 1031.18 cm⁻¹, the presence of Si/Al asymmetric stretching vibrations, the area of 792.78 cm⁻¹ there is a Si/Al symmetric stretching vibration, and in the absorption area 454.72 cm⁻¹ there is an O-Si-O / O-Al-O bending vibration.

The Acid Activated Zeolite (ZAA) peaks are visible at 1035.29 cm⁻¹ (Si/Al asymmetric stretching vibration), which is broader than that of ZAT. This occurs due to a shift in wave number due to acid treatment, which causes the dealumination of the activated zeolite solids. The dealumination process releases Al from within the zeolite framework to become Al outside the zeolite framework so that the decreased amount of Al affects the Si/Al ratio in ZAA.

In the Base Activated Natural Zeolite (ZAB), the wavelength decreased to 1028.88 cm⁻¹ (Si/Al...
The two groups decreased due to bond breaking due to Si extraction (desilication) after NaOH solution activation. In the activation process, there is desilication of the zeolite framework with alkaline media. The Si atoms in Si-O-Si were extracted earlier in the base treatment compared to Si-O-Al. This is due to the presence of AlO-, which can stabilize the surrounding Si atoms by repelling OH- so that Si-O-Al is not attacked by OH- compared to Si-O-Si (Sadowska et al., 2013). From this statement, it can be concluded that the greater the Al which can replace Si, the lower the Si/Al value and the greater the zeolite's negative charge. The greater the surface area of the contact area and the formation of a more negative zeolite surface charge will maximize the performance of zeolite as an adsorbent for methyl violet dye (Wang et al., 2012).

**Table 1.** FTIR analysis results of bayah natural zeolite adsorbents

<table>
<thead>
<tr>
<th>Functional type</th>
<th>Wave number (cm⁻¹)</th>
<th>Range*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric T-O stretching vibration - OSI-O - OAI-O</td>
<td>1031.18 1035.29 1031.18</td>
<td>1250–950</td>
</tr>
<tr>
<td>Symmetrical stretching vibration O-Si-O / OAI-O</td>
<td>792.78 790.00 792.78</td>
<td>820–650</td>
</tr>
<tr>
<td>Internal T-O bending vibration O/Si-O / OAI-O</td>
<td>454.2 452.98 454.72</td>
<td>500–420</td>
</tr>
</tbody>
</table>

**3.1 Methyl Violet Adsorption**

Table 2 shows that the final concentration of methyl violet solution underwent various degradation ranging from 72.64 ppm to 9.08 ppm.

**Table 2.** Results of adsorption of methyl violet by zeolite adsorbents

<table>
<thead>
<tr>
<th>Activator</th>
<th>Mass (g)</th>
<th>Time (minutes)</th>
<th>Final concentration (ppm)</th>
<th>Efficiency (%)</th>
<th>Q (mg/g adsorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 1M</td>
<td>0.5</td>
<td>30</td>
<td>42.15</td>
<td>58</td>
<td>115.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>10.90</td>
<td>89</td>
<td>178.20</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>30</td>
<td>38.67</td>
<td>61</td>
<td>61.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>21.46</td>
<td>79</td>
<td>78.54</td>
</tr>
<tr>
<td>NaOH 1M</td>
<td>0.5</td>
<td>30</td>
<td>23.88</td>
<td>76</td>
<td>152.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>9.08</td>
<td>91</td>
<td>181.84</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>30</td>
<td>72.64</td>
<td>27</td>
<td>27.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>17.34</td>
<td>83</td>
<td>82.66</td>
</tr>
</tbody>
</table>

The research was carried out starting from a concentration of 100 ppm methyl violet (Figure 2), which produced a concentrated solution that was difficult for light to penetrate. After that, adsorption was carried out by natural zeolite adsorbents so that the sample underwent a gradual color change, as shown in Figures 3 and 4. Compared to other adsorption samples, the sample with the lowest color level was NaOH-activated adsorbent with an adsorption capacity of 181.4 mg/g and an efficiency of 91%. The adsorbent activated by NaOH reduced the sample concentration from 100 to 9.08 ppm. This result is better than other study using activated carbon from pineapple leaves which has an adsorption capacity of 73.55 mg/g of methyl violet.

This is because the activation process provides a tremendous change due to the striking difference in adsorption capacity. The results showed that the natural zeolite have fewer impurities with the activation treatment, so the natural zeolite pores are more open, and its ability to adsorb methylene violet is also great (Wiyantoko et al., 2017).

In addition, the mass of the adsorbent and the stirring time also affect the absorption efficiency. Zeolite has an open pore structure with a large surface area, allowing higher dye molecule absorption. So that if the adsorbent mass is more significant with a longer stirring time, the adsorption process will be more effective. This is proven by the highest efficiency obtained from absorption with a mass of 0.5 g of zeolite with a stirring time of 60 minutes. When zeolite was activated using HCl, methyl violet’s absorption efficiency decreased. The adsorbent showed the most efficient adsorption with a mass of 1 g of zeolite with a stirring time of 60 minutes. The adsorbent added with HCl is different from the adsorbent added with NaOH, which has an open pore radius, the adsorbent with the HCl activator has a lower pore radius so that the desorption process is likely to occur because the absorption takes place on the surface-active site, not on the active pore site (Alimano et al., 2014).
The most ineffective adsorption results were obtained with an adsorbent with a mass of 0.5 g of zeolite and a stirring time of 60 minutes with an adsorption capacity of 27.36 mg/g. This is because the adsorbent in these conditions has the lowest surface area and pore volume compared to other samples, so the absorption of methanol violet that occurs is less effective. The results of this study were better than some previous studies, namely the absorption of natural zeolite on methylene blue dye with variations in acid-base activation, where the maximum adsorption capacity obtained was 19.98 mg/g with 3 M NaOH activator, while the adsorbent which 3 M HCl activated obtained an adsorption capacity of 18.38 mg/g (Al-Duri, 1995). Other studies have also shown that natural zeolite that has been physically activated can adsorb 75.77 mg/g of methylene blue at a concentration of 200 mg/L, and the mass of zeolite used is 20 mg (Wiyantoko et al., 2017).

From Figure 5, it can be seen that the pH value is exceptionally fluctuating. The adsorbent activated by HCl has a lower pH value than the adsorbent activated by NaOH. This causes the absorption efficiency of methyl violet to decrease because methyl violet is a cationic dye that is more easily absorbed in alkaline solution conditions. When the adsorbent is added to the NaOH solution, the adsorbent conditions will be more alkaline. Thus, the absorption process will be more efficient.

4. CONCLUSION

The results of the characteristics of Natural Zeolite Without Activation (ZAT), Acid Activated Zeolite (ZAA), and Base Activated Zeolite (ZAB) using FTIR spectrophotometer showed the presence of Si-O-Si / Al-O-Al asymmetric stretching vibration at a wavelength of 1031.18 cm⁻¹; 1035.29 cm⁻¹; 1028 cm⁻¹; symmetrical stretching vibration Si-O-Si/Al-O-Al at a wavelength of 790.78 cm⁻¹; 790 cm⁻¹; 790.07 cm⁻¹. Based on these data, the activation process with 1M NaOH is better due to a larger contact surface area to maximize the adsorption process. Mixing the zeolite with other materials is suggested, which can further degrade the adsorbed methyl violet to improve the effectiveness.

5. REFERENCES


