The effect of alkaline activation on the zeolite binding properties toward dissolved irons

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Abstract. This research aims to determine the effect of alkaline activation on the zeolite binding properties toward dissolved irons. Natural zeolite was activated by reflux using NaOH with various concentrations (2 N, 4 N, and 6 N). Furthermore, the activated zeolite was mixed into a solution of FeSO₄·₇H₂O 0.5 M. Zeolite-Fe then characterised using FTIR, XRD, and SEM. The optimum contact time and the adsorption of irons by activated zeolite were studied. The result shows that alkaline activation in zeolite caused a change in structure zeolite as evidenced by FTIR spectra. The data from XRD result have also identified diffraction patterns of alkali activated zeolites run into differences in the peak characteristics of their constituent and changing the degree of crystallinity of the mineral structure in zeolites. Besides, it also observed that NaOH activation of zeolites increased the amount of Fe bound to zeolite as evidenced by changes in colour and SEM results. The optimum contact time is 2 minutes and the adsorption kinetics of irons were fitted well with the pseudo-second-order kinetic model.

1. Introduction
Zeolite is a hydrated aluminosilicate that belongs to tectosilicate, where SiO₄ tetrahedral is in the form of three-dimensional supercage. In the structure of zeolites, some of Si is replaced by Al atoms, resulting in a negatively charged structure derived from the structural differences between tetrahedral (AlO₄)⁵⁻ and (SiO₄)⁴⁻. The negatively-charged sites in the zeolite framework are balanced by the opposite ions, usually alkaline and alkaline earth ions, which can be replaced by other cations. Thus, zeolites can be used as ion exchangers [1].

Some treatments or modifications to zeolite can be done to obtain zeolites with different forms or Si/Al ratios as needed. This modification is intended to change the structure of zeolites, replacement cations, pore or cavity sizes and the ratio of silica-alumina. Alkaline treatment is one of the modification techniques to reduce Si content from the zeolite framework which aims to obtain zeolites which have a low Si/Al ratio and are hydrophilic. This process with alkaline treatment is called disilicate. The disilicate process occurs when the framework of silica-alumina is cut off so that amorphous alumina and dissolved amorphous silica form silicate and aluminate ions in the solution system [2].

The activation of zeolite is also needed to improve the special properties of zeolites and eliminate impurities. The activation process can also change the type of cation, Si/Al ratio and zeolite characteristics to match the material to be absorbed. In the activation of zeolites with NaOH, silica dissolution process will occur which causes changes in zeolite structure and the reduction of silica in
zeolite framework thereby reducing the Si/Al ratio. Decreasing this ratio will increase the adsorption capacity and selectivity of zeolites to polar molecules such as water vapor [3].

Zeolite modification was carried out in order to increase the number of micronutrients bound to zeolite and its released. One modification was carried out through chemical activation of zeolites using sodium hydroxide (NaOH). NaOH activated zeolite is expected to be able to bind more Fe than zeolite without activation.

2. Methods

2.1 Activation of natural zeolite
A 25 g of natural zeolite from Klaten which passes 200 mesh sieve was refluxed using 100 mL of 2, 4, and 6 M NaOH solutions for 8 hours at a temperature of 85-90°C. The zeolite is then filtered and dried in an oven. Furthermore, zeolite activated NaOH followed by characterisation using an infrared spectrophotometer and X-ray diffractometer.

2.2 Synthesis zeolite-Fe and determination of optimum contact time
A 3 g of activated zeolite was dispersed in 10 mL of distilled water and then added into 60 mL of FeSO₄·7H₂O 0.5 M and stirred for 1 minute. The previous steps were repeated for stirring time 2, 3, 4, 5, 6, 7, 8, 9, and 10 minutes. The suspension was then filtered to separate from the filtrate zeolite. Zeolite-Fe is then dried in an oven at a temperature of 50°C for 24 hours. The previous steps were repeated for alkaline activated zeolites with variations of NaOH concentrations of 2, 4, and 6 M. The resulting composites were then characterised using FTIR, X-ray diffractometer, and SEM.

3. Result and discussion

3.1 Characterization of natural zeolite and activated zeolite
In this study, zeolite used was natural zeolite from Klaten. Zeolites that succeeded in forming the powder passed by a 200 mesh filter. Zeolite characterisation using FTIR spectrophotometry to determine the types of active sites that make up zeolite. The results of the characterisation of natural zeolites and activated zeolites by FTIR spectroscopy are shown in Figure 1.

![Figure 1. Spectra of natural zeolite and activated zeolite.](image)

Based on Figure 1, for natural zeolite spectra, there is a peak at wave number 1049 cm⁻¹ which refers to the internal Si-O or Al-O asymmetric stretching vibration at TO₄. However, the alkaline activation treatment showed that peaks in the 900-1250 cm⁻¹ area shifted to smaller wavenumbers by increasing
NaOH concentration. At the concentration of NaOH 2 M, the peak shifted to 1018 cm$^{-1}$ and in NaOH 4 M and 6 M shifted to 1003 cm$^{-1}$, accompanied by a decrease in intensity. This is in accordance with the opinion of [4] [5] which stated that the shift of absorption peak in the area of 1051 cm$^{-1}$ to a smaller number was because of the treatment of alkaline activation of zeolite is the overhaul of covalent Si-O-Si and Al-O-Si bonds to silicate and aluminate.

Alkaline activation is not only caused by the structure of siloxane and silanol presented in zeolites but also caused by remodelling the structure of quartz, i.e. a silica mineral. This is indicated by the decreasing and shifting of peaks in the area of 795 cm$^{-1}$ to smaller numbers, there are 779 cm$^{-1}$ (2 M NaOH), 741 cm$^{-1}$ (4 M NaOH), and 664 cm$^{-1}$ (6 M NaOH). In addition, alkaline treatment of zeolites gives rise to a new peak which can be seen at wavenumbers 1474 cm$^{-1}$ for 2 M NaOH, and 1427 cm$^{-1}$ for 4 M and 6 M NaOH with increasing intensity. The peak at the wave number indicates the appearance of hydrated carbonate or hydrated aluminates on the surface of the zeolite [6].

XRD analysis aims to determine changes due to the activation process of the crystallinity of zeolite structures. The diffractogram for natural zeolites and alkaline activated zeolites with variations in concentration are shown in Figure 2.

![Figure 2](image.png)

**Figure 2.** (a) Diffractogram natural zeolite and (b) activated zeolite (C = Clinoptilolite, M = Modernite, Q = Quartz).

In Figure 2 (a) for a natural zeolite diffractogram, characteristic peaks appear at $2\theta=9.86$ (d=8.96 Å) and 22.37 (d=3.97 Å) which indicate the clinoptilolite mineral. The emerging peaks correspond to the value of d-spacing on JCPDS 25-1349 for clinoptilolites with a value of d = 8.99; 3.91. Therefore, the peak can be identified as the peak of the clinoptilolite mineral.

Peak at $2\theta=13.55$ (d = 6.52 Å), 19.75 (d = 4.49 Å), 23.24 (d = 3.82 Å), 25.75 (d = 3.46 Å), 26.42 (d = 3.37 Å), 27.84 (d = 3.20 Å) are indicated as a modernite mineral peak. The peaks are compatible with d-spacing with JCPDS 6-239 for d = 6.61; 4.53; 3.84; 3.48; 3.39; 3.22. Peak $2\theta=26.7$ (d = 3.33 Å) indicates the presence of quartz minerals in zeolites (JCPDS 5-0490). Based on the results of XRD analysis, it can be seen that the types of minerals present in Klaten's natural zeolite are clinoptilolite, modernite, with quartz as an impurity.

Based on Figure 2 (b) for the base-activated zeolite diffraction pattern, it shows the change at the peak of its constituent material characteristics. Activation of bases using NaOH changes the degree of crystallinity of natural zeolite constituents. This can be seen from the clinoptilolite peak as one of the main zeolite mineral types at $2\theta=9.86$ which disappeared and at $2\theta=22.37$ which decreased in intensity due to alkaline activation used in zeolites. Data from the XRD results confirm and reinforce the results of FTIR characterization for previously activated zeolites, which stated that alkaline activation in natural zeolites caused a change in silanol, aluminol and siloxane bonds to silicate and aluminates. Characterization using SEM was also carried out in order to determine the surface morphology for Fe-activated zeolites. SEM results can be observed in Figure 3.
Figure 3. The surface morphology of Fe-activated zeolite: (A) 2M; (B) 4 M; and (C) 6 M.

SEM zeolite-Fe photos (Figures 3A to 3C) show surface morphology that tends to be rough and in accordance with SEM photos from modernite [7]. Physical comparison of natural zeolite-Fe and activated zeolite-Fe can be seen by colour as shown in Figure 4.

Figure 4. Colour difference between: (a) Natural zeolite-Fe, (b) Activated zeolite-Fe (2M); (c) Activated zeolite-Fe (4M); and (d) Activated zeolite-Fe (6M).

Figure 4 shows that alkaline activation causes the zeolite-Fe colour to be more yellow than zeolite without activation. The greater the concentration of alkaline used, the more yellow-brown colour. It indicates that the amount of Fe bonded to the zeolites increases with the added alkaline concentration. Besides that, the yellow colour formed is also possible because of the Fe(OH)$_3$ formed.

3.2 The effect of alkaline concentration on activated zeolite versus the amount of Fe
In this study, zeolites were used as carriers of Fe. In zeolites, activation was carried out by using NaOH 2, 4 and 6 M to determine the effect of zeolite activation on the amount of Fe bound to zeolites. The curve effect of NaOH concentration on zeolite on the amount of Fe is presented in Figure 5. The data displayed has been corrected with the amount of Fe(OH)$_3$ formed.
Figure 5. The effect of NaOH concentration on zeolite on the amount of Fe.

Figure 5 shows that the greater the NaOH concentration used for zeolite activation, the more the amount of Fe bound by zeolite. Alkaline activation causes the zeolite framework becoming increasingly negatively charged through the termination of Si-O-Si and Al-O-Al covalent bonds to form silicates and aluminate [8]. The greater the concentration of alkaline used, the more silanol and aluminol groups and siloxanes are used, so that more silicate and aluminate groups are formed. As a result, the zeolite framework becomes increasingly negatively charged. This will increase the possibility of interaction between zeolite and Fe.

In alkaline activated zeolites, there are two active sites, that are the silicate-aluminate active site and \( \text{HO}^- \). When the alkaline activated zeolite is added by Fe, the active silicate-aluminate site or \( \text{HO}^- \) can interact with this Fe. The interaction between Fe and zeolite is slower than the interaction Fe and \( \text{HO}^- \). As a result, Fe is not only filled the room in zeolite but also disperses on the surface of zeolite in the form of \( \text{Fe(OH)}_3 \). The large size of \( \text{Fe(OH)}_3 \) causes it unable to enter the zeolite structure so that the result of this filtration is zeolite-Fe and \( \text{Fe(OH)}_3 \). Consequently, the total Fe measured from destruction is Fe derived from zeolite-Fe and \( \text{Fe(OH)}_3 \). For this reason, it is necessary to control the amount of \( \text{Fe(OH)}_3 \) formed with no more than zeolite-Fe.

3.3 Effect of contact time on adsorption capacity

Experiment representing contact time variation between activated zeolite was dispersed in distilled water and \( \text{FeSO}_4\cdot7\text{H}_2\text{O} \) 0.5 M for 1 to 10 minutes. The result is depicted in Figure 6.

Figure 6. Activation zeolite adsorption capacity versus time
Figure 6 shows that the adsorption process attains equilibrium at 2 minutes. The increase of the shaking time for more than 2 minutes has no significant effect on the adsorption of iron. The initial adsorption was rapid due to the adsorption of iron onto the exterior surface, after that the metals ions enter into pores (interior surface) with relatively slow process[9].

3.4 Kinetics of adsorption
The kinetic data of the adsorption of iron onto zeolite is evaluated using pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order is determined by the equation of Lagergren[10]:

$$\ln(q_e - q_t) = \ln q_e - kt$$

(1)

where $q_e$ and $q_t$ are the values of the amount of adsorbed per unit mass at equilibrium and at any time $t$, respectively. The kinetic adsorption model of the pseudo-second-order model is defined by the equation [11], [12]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e t}$$

(2)

Where $k_2$ is the rate constant pseudo-second-order (g.mg⁻¹.min⁻¹) which describes the number of irons adsorbed by the zeolite at time $t$. From the plot between ln$(q_e - q_t)$ versus time and the plot of $t/q_t$ versus time $t$, the rate constants of first and second adsorption, also $R^2$ were determined.

Table 1. Pseudo-first order and Pseudo-second order kinetics rate constant for irons in the zeolite.

| First-order kinetic model | Second-order kinetic model |
|---------------------------|---------------------------|
| $R^2$         | $k_1$ (min⁻¹) | $R^2$        | $k_2$ (g.mg⁻¹.min⁻¹) |
| 0.31         | 3.9669       | 0.9997       | 0.0012          |
| 0.3782       | 3.3684       | 0.9995       | 0.0010          |
| 0.4771       | 3.2927       | 0.9990       | 0.0014          |

Table 2 shows the kinetic parameters of adsorption of irons onto zeolite. The kinetic model with a higher $R^2$ was selected as the most suitable one. The results show that the adsorption kinetics of irons were fitted well with the pseudo-second-order kinetic model.

4. Conclusion
Alkaline activation in zeolites causes a change in silanol, aluminol, and siloxane bonds to silicate and aluminate as evidenced by FTIR spectra. The data of XRD results have also identified diffraction patterns of alkaline activated zeolites run into changes in the peak characteristics of their constituent materials and change the degree of crystallinity of the mineral structure in zeolites. In addition, alkaline activation in zeolites can increase the amount of Fe bound to zeolites as evidenced by changes in colour and SEM results. The optimum contact time is 2 minutes and the adsorption kinetics of irons were fitted well with the pseudo-second-order kinetic model.

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