Modification of Natural Zeolite with Fe(III) and Its Application as Adsorbent Chloride and Carbonate ions

Suhartana*, Emmanuella Sukmasari, Choiril Azmiyawati
Diponegoro University, Department of Chemistry, 50275 Semarang, Indonesia.

*E-mail: suhartana@live.undip.ac.id

Abstract. The aim of the research is to natural zeolite with Fe(III) using anion exchange process to improve the anion exchange capacity. Natural zeolite was activated using HNO₃ 1 N and then mixed with FeCl₃ solution and refluxed followed by oven and calcination at a temperature of 550°C. The influence of Fe(III) to zeolite was characterized by FTIR while presence of Fe in zeolite characterized by AAS. Zeolite and Zeolite-Fe adsorption capacity of chloride and carbonate anions were determined through adsorption test by variation of pH and contact time. In advanced, and then to determining the Fe adsorbed concentration at Zeolite using UV-Vis spectrophotometer. FTIR analysis result showed that the addition of Fe does not affect the zeolite’s structure but change the intensity of the zeolite spectra. The Fe concentration in Zeolite-Fe of 714 mg L⁻¹, indicate that Fe was present in the zeolite. Both Zeolite and Zeolite-Fe adsorption results showed that optimum pH of Chloride anion is 2, with adsorption capacity 2.33 x 10⁻³ g⁻¹ and optimum contact time is 8 minutes. While Zeolite and Zeolite-Fe adsorption results showed that optimum pH of Carbonate anion is 5, with adsorption capacity 5.31 x 10⁻³ g⁻¹ and optimum contact time is 8 minutes.

1. Introduction
Zeolite is a natural compound found in many parts of Indonesia. Zeolite consists of a cluster of alumina and a group of silica-oxide, each of which is tetrahedral and interconnected by the oxygen atom to form a three-dimensional framework. Zeolite is used as a carrier molecular because its crystal structure is porous and has a large surface area, composed by a silica-alumina skeleton, has high thermal stability, is cheap, and its presence is quite abundant [1].

The best method to look at the ability and quality of zeolites is from ion exchange capabilities. This capability is expressed as the value of cation exchange capacity. The value of cation exchange capacity depends on the degree of substitution of the number of Al³⁺ and Si⁴⁺ atoms which results in a negative charge on the zeolite framework. Although the capacity of zeolite adsorption capacity against large cations, natural zeolites do not show any affinity for anions [1]. The negative charge on the zeolite structure causes the zeolite to have a small ability to absorb the anion. One way of modifying zeolites to improve the anion exchange properties is by
modification with transition metal cations, one of which is Fe(III). Ion Fe(III) can enter empty zeolite cavities and replace balancing cations in interchangeable zeolites [2]. The modified zeolite with Fe(III) is no longer negatively charged because it has binds to Fe so it can be used to absorb the anions [3].

Chloride and bicarbonate is one of the causes of water hardness, whether it is permanent hardness (CaCl₂, MgCl₂, and CaSO₄, MgSO₄), as well as the temporary hardness (Ca(HCO₃)₂, and Mg(HCO₃)₂). In industrial boilers (boyler, boil feed water), water is highly avoided because it will result in crust on the pipe / boiler, so its existence should be handled properly. Anion chloride and bicarbonate are present in ground water as soluble salts, both from cations derived from alkali metals, alkaline earths and transition metals [4, 5].

The objective of this study was to obtain Fe(III) modified natural zeolite and to determine the optimum adsorption capacity chloride and bicarbonate anion. Interaction Fe zeolite with chloride and bicarbonate anion based on pH variation and contact time.

2. Experimental Section

2.1. Materials

The materials used in this research are Bayat natural zeolite, HCl 6 N, FeCl₃.6H₂O, aquades, 0.1 M HCl, 0.1 M NaOH. The equipment used is a set of glass tools, erlenmeyer, mistype glass, a mesh size of 100 mesh, an analytical balance, oven, vacuum pump, shaker, reflux apparatus, pH meter, filter paper, micro biuret, furnace, Fourier Transform Infrared Spectroscopy (Shimadzu Prestige 21), Atomic Absorption Spectrophotometry (Perkin Elmer 1300).

2.2. Preparation of Zeolite

Natural zeolite from Bayat of Klaten Regency was crushed then sieved with 100 mesh strainer to homogenize the size then washed with distilled water. After washing with distilled water several times, the zeolite is filtered and then dried with oven at 110°C for 4 hours. Zeolite mashed by crushing until obtained powder back.

2.3. Activation of Zeolite

Zeolite which passes 100 mesh sieve added HCl 6 N solution with ratio 1:10 and soaked for 24 hours. The zeolite is then filtered and rinsed with distilled water to a neutral pH (equal to pH of aquadest). Furthermore, the zeolite was dried with oven at 110°C for 4 hours.

2.4. Modification of Zeolite

A total of 20 grams of zeolite plus 100 mL FeCl₃ 0.2 M then the solution was refluxed for 4 hours at 85°C, the result was then filtered and dried in an oven at 110°C for 4 hours then calcined 550°C for 2 hours. To know the effect of adding Fe(III) to zeolite spectra, characterization using Fourier Transform Infrared (FTIR) instrument was done by comparing Fe(III) and zeolite activated zeolite spectra. In addition, AAS instruments are also used to determine Fe content in zeolite-Fe.
2.5. Adsorption of Anion chloride and carbonate

For the pH variation, 0.25 grams of Fe(III) modified zeolite were mixed with 10 mL Chloride anion concentration of 150 ppm or with 10 mL Carbonate anion concentration of 150 ppm. Furthermore, stirring using shaker with variations of pH 2, 4, 6, 8, and 10 for 60 minutes. Then the mixture was filtered, the filtrate and the starting solution were analyzed anion chloride concentration using a Mohr methods by AgNO₃ solution as standard.

Created the same treatment against activated natural zeolites. for variation of time. Furthermore, stirring using shaker with 10 mL Chloride anion concentration of 150 ppm or with 10 mL Carbonate anion concentration of 150 ppm variation of contact time 5, 10, 30, and 90 minutes at optimum pH then filtered. The filtrate and the starting solution were analyzed contain anion carbonate concentration using a titrimetric methods by EDTA solution as standard. Created the same treatment with activated natural zeolite.

3. Results and Discussion

This research was modified to natural zeolite from Bayat sub district, Klaten Regency with the addition of Fe₂O₃ as an adsorbent of Chloride and Carbonate ions. Stages of discussion include activation of natural zeolite, modification of active zeolite with Ferric Chloride and NaOH Solution, characterization of zeolite with FTIR spectrophotometer and its adsorbent ability test.

3.1. Activation of Natural Zeolite.

Natural zeolite carried out destruction and sieving measuring 100 mesh, with the aim of enlarge the surface area of natural zeolite so that the adsorption ability can be more optimal [6]. Then the zeolite was immersed in 3 M HF solution for 15 minutes. This is done to dissolve the remaining impurities on the zeolite [6]. Zeolite already soaked with 3 M HF solution having an acid pH of about 3-4, then pH zeolite neutralized to pH 7 by washing using aquadest and dried at 120°C. Zeolite which is free from impurity oxide, ion exchange process with ammonium ion. This ion exchange aims to form NH₄⁺ zeolite. The initial exchange occurs between the cations within the zeolite NH₄⁺ with of ammonium chloride (NH₄Cl). The ion exchange between the cations in the zeolite with NH₄⁺ aims to replace all the cations in the zeolite because in the zeolite there are still alkaline or alkaline earth cations such as K⁺, Na⁺, Ca²⁺ and Mg²⁺ which act as zeolite balancers [7]. Furthermore the alkali or alkaline earth may be interchangeable with the ammonium cation so that all of the cations will be converted to NH₄⁺. According to selectivity NH₄⁺ has a high selectivity value of NH₄⁺ > Ag⁺ > Ba²⁺ > Na⁺ > Sr²⁺ > Ca²⁺ > Li⁺ > Cu²⁺ [2, 8]. Then to form zeolite-H, after ion exchange process then heating at temperature 300°C because at that temperature NH₃ will loose and formed zeolite-H [2, 9].

3.2. Modified Zeolite with Fe₂O₃.

The activated zeolite formed into zeolite-H was dissolved into aquadest 70°C. This mixing process is intended to allow the zeolite and the material to be added to interact thoroughly and will speed up the reaction when FeCl₃ is added [10]. The next process is the addition of NaOH solution. Addition of NaOH in the solution is done dropwise and with stirring done. The water temperature is kept at 70°C intended. so FeCl₃ and NaOH immediately form Fe(OH)₃, because the Ksp price is very small [4]. The stirring process is done for 2 hours. This stirring is intended
to allow the zeolite and Fe (OH)$_3$ to react in a homogeneous manner [11]. After stirring, to remove NaCl then added aquades. This addition process is intended to allow the NaCl present in the mixture to dissolve with water. After this stage screening and washing using water at a temperature of 70°C. Washing is done to remove the NaCl still contained in the solution. To determine the presence of Cl$^-$ ion, it was tested with a silver nitrate solution (AgNO$_3$). AgNO$_3$ solution with Cl$^-$ will then form a white precipitate [5, 12]. The reaction is as follows:

$$\text{NaCl (aq) + AgNO}_3 \text{ (aq)} \rightarrow \text{AgCl (s) + NaNO}_3 \text{ (aq)}$$

(white)

The next stage of the Cl liberation process is drying. This drying process is done to remove water. The calcination process is carried out at 450°C. At that temperature is expected Fe(OH)$_3$ will be changed to Fe$_2$O$_3$. Fe$_2$O$_3$ will form at high temperatures which are then expected to bond with zeolites either physically or chemically. In its basic state, the zeolite has a balance cation on its skeleton. When the H-zeolite having a H-balancing cation has been modified with Fe$_2$O$_3$ to zeolite-Fe [13].

The comparison of physical appearance between natural zeolite, active natural zeolite and zeolite-Fe can be seen with different properties. Fe$_2$O$_3$ modified zeolite provides a more yellow-brown color than the unmodified zeolite. This confirms the formation of zeolite-Fe. Acquired natural zeolite, activated natural zeolite and Fe modified zeolite with differences in physical appearance are shown in Figure 1.

![Color difference between (a) Natural zeolite, (b) Activated natural zeolite, and (c) Zeolite-Fe](image)

Figure 1. Color difference between (a) Natural zeolite, (b) Activated natural zeolite, and (c) Zeolite-Fe

### 3.3. FTIR Analysis Result

An important method to characterize zeolite frame structure and to know the effect of Fe$_2$O$_3$ is by infrared spectra analysis, especially Fourier Transformation-Infra Red (FTIR). In general, the range of 300-1300 cm$^{-1}$ wave numbers are tetrahedral bonds, namely O-Si-O and O-Al-O. In the band 900-1250 cm$^{-1}$ is an asymmetric range, the symmetric range is shown on the band 650-850 cm$^{-1}$, the internal Si-O / Al-O (Fe-O) bends appear in the 410-500 cm$^{-1}$ region while External will appear at 700-780 cm$^{-1}$ [3]. The infrared spectra analyzed by FTIR of Fe zeolite and activated natural zeolite are shown in Figure 2.
The spectra produced by zeolite-Fe have a similar pattern with the activated zeolite. This shows that Fe$_2$O$_3$ reacted to zeolites does not alter the original structure of the zeolite. In the determination of existing functional groups in the structure of zeolite is divided into two [14]. The first functional group is the internal vibration associated with Fe$_2$O$_3$ which is the main structural unit. The second functional group is the external vibration associated with the tetrahedral connection [6].

FTIR spectra interpretation can be known from several absorptions. The absorption band of the wave number region 420-300 cm$^{-1}$, in the absorbed activated zeolite is at 324.04 cm$^{-1}$, which in which the absorption is included in the opening of the zeolite pore. The opening of the pore includes the external vibrational vibration spectra of the zeolite [14]. At ZA-Fe at 317.1 cm$^{-1}$ this shows the presence of a certain amount of Fe-O on the surface of the zeolite. Peak produced by FeO has a very large intensity and the resulting curve is very sharp. The decrease in absorption in wave numbers between 400-350 cm$^{-1}$ in ZA-Fe confirms the presence of van der walls forces between zeolites and FeO. When Fe$_2$O$_3$ is combined with zeolite via Fe-O-Si or Fe-O-Al, the presence of a Fe-O-binding force bounded by a surface bond on the zeolite structure causes the energy absorbed in FTIR become weak [13]. Another opinion of the region of the wave number also indicates the opening of zeolite pores [14].

The decrease in absorption also occurs not only in wave numbers between 400-350 cm$^{-1}$. In the uptake between 500-420 cm$^{-1}$ which is the Fe-O SiO / AlO bending Vibration also decreases.
between ZA and ZA-FeO. The size of the area produced in ZA-FeO (448.1 cm\(^{-1}\)) is smaller than that of ZA (455.20 cm\(^{-1}\)). This is due to the reduced bending between SiO / A1O. The amount of bending energy of SiO / A1O buckling is reduced, possibly due to Fe-binding of -O of SiO / A1O. Wavelength 790 cm\(^{-1}\) is the vibration of O-Si-O / O-Al-O symmetry. A stretching vibration involving a tetrahedral atom can be seen in the 650-820 cm\(^{-1}\) region. In ZA and ZA-Fe each have the same uptake at 794.67 cm\(^{-1}\). This resilient vibration shows the bonding composition of Si-Al zeolite framework [14].

### 3.4. AAS Analysis Result on Zeolite- Fe

To account Fe concentrations was bonding in zeolite should be analyzed by Atomic Absorption Spectroscopy (AAS). Result of the Fe in zeolites-Fe and activated natural zeolites are shown in Table 1.

### Table 1: Fe concentrations in zeolite-Fe and activated natural zeolite

| Adsorbent         | Concentration (mg L\(^{-1}\)) |
|-------------------|-------------------------------|
| Natural zeolite   | 2.164                         |
| Activated Zeolite-Fe | 11.786                       |

An increase in Fe concentration in Fe zeolite. The greater the concentration the amount of Fe in the zeolite is greater, it indicates that Fe(III) has entered into zeolite. In activated natural zeolites there is a high enough Fe concentration, probably because Fe is still present as an impurity in the zeolite.

### 3.5. Adsorption of Ion Chloride and Carbonate Using Zeolite-Fe.

Measurements taken to determine the results of these two variations using titrimetric methods. The principle of the titrimetric reaction is to react between the sample (which is not yet known) and the standard solution (which is already known). In the chloride ion analyzer, according to Vogel and Svehla [5], the prepared NaCl sample was analyzed with 3-5 drops of potassium chromate indicator (K\(_2\)CrO\(_4\)), then titrated with a silver nitrate solution (AgNO\(_3\)), in case of sediment color change from white precipitate to red brick, then the reaction has reached the equivalent point. The reaction is as follows.

\[
\text{NaCl (aq) + AgNO}_3 \text{(aq)} \rightarrow \text{AgCl (s) + NaNO}_3 \text{(aq)} \quad \text{(white)}
\]

\[
\text{K}_2\text{CrO}_4 \text{(aq) + AgNO}_3 \text{(aq)} \rightarrow \text{AgCrO}_4 \text{(s)} \quad \text{(red brownish)}
\]

In the analysis of carbonate ions, according to Vogel and Svehla [5] the carbonate ion sample is ready to be analyzed (CaCO\(_3\)) given 3-5 drops of Eriochrome Black T (EBT) indicator, then titrated with Ethylen Diamine Tetra Acetate (EDTA) solution. Titration has reached the equivalent point if there is a change of analytical solution, from red wine to sky blue [15, 16]. The reaction is as follows.
3.6. Adsorption Capacity of Zeolite-Fe on Anion Cl⁻

Curves effect of pH on the adsorption capacity of the zeolite-Fe and activated natural zeolite for anion Cl⁻ shown in Figure 3. To know and compare the adsorption capacity of zeolite activated Fe to chloride anion also measured the concentration of chloride ion adsorbed with various variations of pH. It is expected to obtain optimum pH conditions, whether in acidic, neutral or alkaline conditions.

![Graph](image)

Figure 3. Activated zeolite adsorption capacity and zeolite-Fe to Chloride anion versus variation of pH

To investigate and compare the adsorption capacity of zeolite activated Fe to the carbonate anion, also carried out exactly the same as the chloride anion. While the results obtained is also a graph, which states the relationship between pH and carbonate anion was adsorb.

The effect curve of pH variation on zeolite-Fe adsorption capacity and activated zeolite nature for CO₃²⁻ anions is shown in Figure 4.

\[
\begin{align*}
Ca^{2+} (aq) + H_2Y^{2-} (aq) &\rightarrow (CaY)^{2+} (aq) + 2H^+ (aq) \\
(red \ wine) \\
Ca^{2+} (aq) + EBT (aq) &\rightarrow (Ca - EBT)^{2+} (aq) \\
(blue \ sky)
\end{align*}
\]
Figure 4. Activated zeolite adsorption capacity and zeolite-Fe to $\text{CO}_3^{2-}$ anion versus variation of pH

It is seen that the adsorption of anion chloride and carbonate using Fe zeolite as well as activated zeolite reaches the highest adsorption capacity at different pH. At adsorption of chloride ions at pH 2-3, and adsorption of carbonate ions at pH 5. This difference is due to the different response, from both anions, in binding H-ions. after the optimum pH, the higher the pH of the solution, the adsorption capacity decreases. It shows that at pH 2-3 (for chloride) and pH 5 (for carbonate) is the optimum pH due to the highest adsorption capacity of anion chloride and carbonate both for activated zeolite and Fe-zeolites [10].

The optimal adsorption occurs at pH 2-3, according to Vogel and Svehla [5], at low pH (acid) chloride ions prefer to bind H ions in the form of HCl. While at higher pH (base) chloride ions will occur to compete H ions with iron ions in the form of divalent cations. At the high pH of the solution (base), the presence of hydroxyl ions (OH-) according to Crabtree and Hamilton [17], is likely to inhibit the interaction with Fe oxide on the zeolite surface. Since Ksp Fe(OH)$_2$ is very small ($2 \times 10^{-23}$) there may also be a precipitation reaction of Ferrohydroxide. So also for carbonate ions. The optimal adsorption occurs at pH 5, according to [5], at low pH (acid) carbonate ions prefer to bind H ions in the form of bicarbonate ions ($\text{HCO}_3^-$). While at higher pH (base) carbonate ions will occur to compete H ions with iron ions in the form of divalent cations. At the high pH of the solution (base), according to Crabtree and Hamilton [17], the presence of hydroxyl ions (OH-) is likely to inhibit the interaction with Fe oxide on the zeolite surface. Because Ksp FeCO$_3$ is very small ($2.1 \times 10^{-8}$ ) it is possible to have a precipitation reaction between the carbonate ion and the ferrous cation, forming a ferrocarbonate precipitate (FeCO$_3$) [16].
The curve effect of contact time variation on the adsorption capacity of the anion chloride and carbonate using the adsorption zeolite and the activated zeolite is almost the same, shown in Figure 5 and Figure 6.

**Figure 5.** Activated zeolite adsorption capacity and zeolite-Fe to Cl\(^-\) anions versus time

**Figure 6.** Activated zeolite adsorption capacity and zeolite-Fe to CO\(_3^{2-}\) anions versus time

It is seen that in general the adsorption of both anions (both chloride and carbonate) using zeolite-Fe and activated natural zeolite reached the highest adsorbed concentration at 5 minute for Cl\(^-\), after passing the 5th minute of constant adsorbed concentration. The results show that the contact time between the ion and the adsorbent will affect the amount of ions bonded to the
adsorbent, where the longer the contact time then the number of metal ions adsorbed also more and more [3]. Chloride anions and Carbonate anions is different result, because ionic radii from two anions is significant different [15, 18]. However, after exceeding the optimum time, the active side of the adsorbent has completely bonded with the ion and there is equilibrium. In both pH and contact time curves on the adsorbent adsorption capacity of both anions (both chloride and carbonate) it can be seen that the adsorption capacity between activated zeolite and zeolite-Fe has a relatively small difference. This suggests that the formation of iron oxide (Fe oxide) in zeolites has no significant effect on the adsorption capacity of the zeolites on the two anions [11].

4. Conclusions

Zeolite-Fe is obtained as evidenced by changes in spectral intensity of zeolite and Fe content in Fe zeolite is greater than activated natural zeolite. The zeolite-Fe adsorption capacity of chloride anion and carbonate is greater than activated natural zeolite, because 9.622 ppm of cations Ferrous was adsorbed at nature zeolite. For Chloride ions with an adsorption capacity of 5.7 ppm (Activated Zeolite) and 7.6 ppm (Zeolite-Fe) optimum adsorption at pH 3 contact time of reaction 5 minute and Carbonate ions with an adsorption capacity of 5.7 ppm (Activated Zeolite) and 7.6 ppm (Zeolite-Fe) optimum adsorption at pH 3 contact time of reaction 5 minute.

References

[1] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chemical Engineering Journal, 156 (2010) 11-24.

[2] D. Danabas, T. Altun, Effects of zeolite (clinooptilolite) on some water and growth parameters of rainbow trout (Oncorhynchus mykiss Walbaum, 1792), aquaculture, 6 (2011) 10.

[3] H. Hamdan, Introduction to Zeolites: Synthesis, Characterization, and Modification, Universiti Teknologi Malaysia, Kuala Lumpur, (1992).

[4] J. Huheey, E. Keiter, R. Keiter, O. Medhi, Inorganic Chemistry, Pearson Education, New Delhi, 2011.

[5] A.I. Vogel, G. Svehla, Textbook of Macro and Semimicro Qualitative Inorganic Analysis, Longman Scientific & Technical, 1987.

[6] J.D. Sherman, Ion exchange separations with molecular sieve zeolites, in: Zeolites: Science and Technology, Springer, 1983, pp. 583-623.

[7] S.G. Poulopoulos, V.J. Inglezakis, Adsorption, ion exchange and catalysis: design of operations and environmental applications, Elsevier, 2006.

[8] P. Hemalatha, P.P. Rao, Adsorption of Cr (VI) ions from aqueous solutions using calcined brick powder (CBP), International journal of environmental sciences, 2 (2012) 2321.

[9] A. Joy, V. Ramamurthy, Chiral photochemistry within zeolites, Chemistry-A European Journal, 6 (2000) 1287-1293.
[10] M. Kragović, A. Daković, Ž. Sekulić, M. Trgo, M. Ugrina, J. Perić, G.D. Gatta, Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite, Applied Surface Science, 258 (2012) 3667-3673.

[11] G. Du, Z. Li, L. Liao, R. Hanson, S. Leick, N. Hoeppner, W.-T. Jiang, Cr (VI) retention and transport through Fe(III)-coated natural zeolite, Journal of hazardous materials, 221 (2012) 118-123.

[12] F.a.H. Treadwell, WT, Analytical Chemistry, John Wiley & Sons, New York, 1971.

[13] T. Perraki, A. Orfanoudaki, Mineralogical study of zeolites from Pentalofos area, Thrace, Greece, Applied Clay Science, 25 (2004) 9-16.

[14] L. De Araujo, C. Cavalcante Jr, K. Farias, I. Guedes, J.M. Sasaki, P.d.T.C. Freire, F.E.d.A. Melo, J. Mendes-Filho, Synthesis of cubic Y zeolite using a pulsed microwave heating system, Materials Research, 2 (1999) 105-109.

[15] D. Skoog, D. West, F. Holler, Fundamentals of analytical chemistry Saunders College Pub, Fort Worth, (1992).

[16] A. Vogel, 4 edition, The English Language Book Society and Longman, New York, A Textbook of Quantitative Inorganic Analysis, book, 4 (1978).

[17] R.H. Crabtree, D.G. Hamilton, H-H, C-H, and Related Sigma-Bonded Groups as Ligands, in: F.G.A. Stone, R. West (Eds.) Advances in Organometallic Chemistry, Academic Press, 1988, pp. 299-338.

[18] F.a.H. Treadwell, WT, Analytical Chemistry, John Wiley & Sons, New York, 1971.