The influences of operating conditions on the removal of Fe(II) in water by adsorption using bentonite as a low-cost adsorbent

M Jannah¹, S Mulyati²*, C M Rosnelly², S Muchtar²
¹Graduate School of Chemical Engineering, Universitas Syiah Kuala University, Jl. Tgk. Chik Pante Kulu No. 5, Banda Aceh, 23111, Indonesia
²Department of Chemical Engineering, Syiah Kuala University, Jl. Syeh A. Rauf, No. 7 Banda Aceh, 23111 Indonesia

*E-mail: sri.mulyati@unsyiah.ac.id

Abstract. The contamination of Fe²⁺ in groundwater is a problem that needs to be handled seriously as it can cause health problems for humans. In this study, the adsorption process method is conducted by use of natural bentonite from North Aceh. This process is expected to reduce Fe²⁺ as effectively as possible. The adsorption process is carried out by varying the contact time, adsorbent dose, and pH of the sample. The most effective contact time is obtained at 160 minutes, the adsorbent dose is 1 g/L and the pH of the sample is in neutral condition. With the initial concentration of metal in the sample solution of 20 mg/L, the adsorption process is able to remove 85.5% of Fe with the remaining Fe in the water of only 2.82 g/L.

1. Introduction
Water pollution caused by toxic compounds is a major problem because it affects environmental quality such as plants, animals and human health. Heavy metals are toxic and dangerous substances even at very low concentrations[1]. The term heavy metals is described as pollutants that are discharged into the environment in the form of air, water, or soil [2]. Heavy metals are defined as elements with a density higher than 5 g/cm³ [3]. Heavy metals are dangerous because they are not biodegradable, accumulated in the food chain, and are persistent [4]. One of the heavy metals that are often present in water sources is ferrous (Fe). Although Fe is an essential mineral that helps transport oxygen in the blood, its presence in groundwater at a certain level makes water unusable due to change in taste, smell, and cloudiness [5]. Besides water hardness, the presence of Fe is the most common problem faced by consumers and water providers [6]. Fe which is deposited in the distribution system can increase the growth of microorganisms so that their concentration increases in the water. Fe is commonly found in groundwater supplies which are used as a source of raw water for clean water providers. If the content of this compound exceeds the maximum allowed, the water will visually change in color, which will result in poor piping and water quality. Therefore, the World Health Organization (WHO) has determined that the maximum permissible level of iron is 0.3 mg/L [7][8]. Measurement of iron content is particularly important in boreholes and other surface water sources. If the iron content exceeds 0.3 mg/L it is necessary to consider the most effective treatment that can be used.

Several methods have been used to remove iron compounds in water, including through the aeration process[9], oxidation-coagulation [10], chlorination[11], electrochemistry [12] and adsorption [13]. Of
all the methods, the adsorption process is an attractive option. This is due to the cost, flexibility, simplicity of design, ease of operation, insensitivity to toxic pollutants and better removal efficiency [4]. Activated carbon has been found to be the most effective adsorbent for removing metals from solution due to its high adsorption capacity. However, the costs involved are high, limiting their widespread use in most industries and developing countries. Many researchers have studied the use of low-cost adsorbents to remove metal ions from solutions, thereby minimizing the high cost problem. Some of the low-cost adsorbents that have been used include agricultural waste and biomass materials, clay, zeolite, silica, fly ash and bentonite. In this research, the natural bentonite acquired from local source (North Aceh Regency) is used. Besides its abundant availability, bentonite has also been reported to have a high adsorption capacity for heavy metals due to its high specific surface area, small particle size, high porosity and high cation exchange capacity [14]. Bentonite is used without chemical modification or maintenance to keep process costs low. The effects of pH, initial metal ion concentration, contact time, adsorbent dose.

2. Materials and methods
2.1. Materials
Natural bentonite acquired from North Aceh Regency was employed as the adsorbent material. Fe$_2$O$_3$ (Wako, Japan) was used as a model contaminant feed solution. HCl (Merck, Germany) and NaOH (Sigma Aldrich, Germany) were used as pH controller. Distilled water was used for solvent.

2.2. Preparation of bentonite adsorbent
The adsorbent used in this work was based of natural local bentonite. Natural bentonite in the form of rocks was cleaned of impurities. Natural bentonite was pounded with a stainless steel hammer to reduce the size and on the ballmill to obtain a size of 80 mesh.

2.3. Batch adsorption experiments
The adsorption experiments were carried out in batch reactor at a room temperature using bentonite adsorbent with particle size of 80 mesh. The experiment was conducted by studying various parameters such as contact time, adsorbent dose, and sample pH on the uptake of Fe (II) as a contaminant model solution. The Fe-containing feed solution was prepared in a concentration of 20 mg/L by dissolving 20mg of pure Fe in 1L of distilled water. A total of 100 ml feed solution was mixed with certain amount of adsorbent with continuous stirring. The pH was also continuously adjusted to the expected value using HCl and NaOH solutions. The concentration of the filtrate was analyzed using a UV-VIS spectrophotometer.

To study the effect of contact time on the adsorption of Fe(II), the experiment was carried out at a pH of 7, adsorbent dose of 1 g/L, and the stirring rate of 100 rpm. The effect of the adsorbent dose on the adsorption of Fe (II) was carried out by adding 0.25 g/L, 0.5 g/L, 0.75 g/L and 1.0 g/L in 100 mL of feed solution. Fe (II) with a concentration of 20 g/L.

To determine the effect of pH on Fe (II) removal, the pH of the sample was set to the range 2,3,4,5,6,7,8, and 9. The dose of adsorbent used was 1 g/L, the sample concentration was 20 g/L and stirring at 100 rpm.

3. Result and discussion
3.1. Influence of contact time on the removal of Fe (II)
The effect of contact time on the adsorption of Fe (II) by bentonite adsorbent was carried out by adding 0.1 gram of adsorbent into a beaker glass which filled with 100 ml of Fe (II) sample with a concentration of 20 mg/L. The mixture was then stirred at a speed of 100 rpm. Figure 1 shows the effect of contact time on Fe (II) metal removal. From Figure1, it can be seen that the effect of contact time on Fe (II) removal efficiency ranged from 0-20 minutes, the efficiency of the increase in metal removal was quite significant. In the next time interval, the elimination efficiency continued to increase, although it was not like in the 0-20 minutes interval range. The equilibrium condition is reached when the sample contact
time with the adsorbent is 180 minutes. At the beginning of the adsorption process, the surface area of the contact on the adsorbent surface is still sufficiently available so that there is no competition between metal ions on the adsorbent surface, but over time, the available space for ion absorption others become limited. Due to the repulsion between the metal ions absorbed on the adsorbent surface and the ions in the solution, further ion absorption becomes more difficult [14, 15]. Repulsion is when ions are separated having their core electron wavefunctions cannot overlap and have the similar quantum numbers. As the ions get closer, some of the ions might be forced into having higher state of energy due to the overlap of wavefunctions. Because the electrons cannot be in the same energy state some of the electrons are pushed into higher states and preventing the ions from approaching closer to each other [14, 15]. When the entire adsorbent surface is saturated, there is an equilibrium (steady state) condition, where the absorption efficiency will be constant even though the absorption time is longer. In this process the optimal efficiency is obtained at 160 minutes contact time, with an absorption efficiency of 84.35 percent.

![Graph](image)

**Figure 1.** Influence of contact time on Fe (II) removal
[[adsorbent] = 1 g/L; particle size 80 msh; [Fe (II)]0 = 20 mg/L; pH =7.]

### 3.2. Influence adsorbent dosage on the removal of Fe (II)

The effect of adsorbent loading on Fe$^{2+}$ adsorption by bentonite adsorbent is illustrated in Figure 2. From the results obtained, it can be concluded that the adsorbent dose greatly affects the removal performance. Increasing the adsorbent concentration to 1 g/L resulted in a large increase in the percentage of Fe uptake (0–80% Fe adsorption). The increase in the percentage of Fe removed by increasing the adsorbent dose can be associated with an increase in the surface area of the adsorbent, which can increase the number of available adsorption sites. A further increase in the concentration of the adsorbent is not significantly affecting the percentage of metal removal, probably because almost all ions of Fe have bonded to the adsorbent and on the formation of an equilibrium between the ions bound to the solid phase and those remaining in solution. The optimal adsorbent dose used in this study is 1 g/L.
Figure 2. Influence of contact time on Fe (II) removal. The contact time = 140 min; particle size 80 mesh; [Fe (II)]₀ = 20 mg/L; pH = 7.

Figure 3. Influence of pH of sample on Fe (II) removal. The contact time = 140 min; particle size 80 mesh; [Fe (II)]₀ = 20 mg/L; dosage adsorbent = 1 gr/L.

3.3. Influence of pH on the removal of Fe (II)

In the adsorption process, the pH of the solution is one of the main controlling parameters. The absorption capacity of metal ions and the adsorption mechanism are influenced by the pH of the solution [16]. The acidity or basicity of the solution affects the charge on the adsorbent surface as well as the chemical equilibrium, both on the adsorbate and on the adsorbent. The effect of pH of
the feed solution on the Fe$^{2+}$ absorption by bentonite adsorbent is illustrated in Fig. 3. From Figure 3, it can be seen that in acidic conditions the efficiency of Fe$^{2+}$ absorption is low. This is because in this condition the surface of the active side of the adsorbent is positively charged thus there is competition between hydronium ions and metal ions.[17]. The absorption efficiency increased at pH 7 and reached a maximum value of 85.5%. Increasing pH to pH 7, the active surface of the adsorbent becomes negative causing Fe$^{2+}$ ions to be adsorbed more easily because of the electrostatic force between the surface of the adsorbent and the metal. In the pH range of 8-12, the efficiency of metal absorption decreases which is due to the precipitation of metal ions as hydroxide compounds.

4. Conclusion
Based on the results of this study, it is concluded that the use of bentonite as an adsorbent is capable to remove Fe metal in the water sample. The optimal operating conditions were obtained at 160 minutes of contact time with an adsorbent dose of 1 g/L and the pH of the sample was at a neutral condition. The best removal efficiency was obtained at 85.5%. The final concentration of Fe in the effluent is 2.82 mg/L. This condition has met the quality standard for sanitary water that is permitted to be used for community.

5. Acknowledgement
This study was funded by Thesis Magister 2020 research grant.

References
[1] Liu C, Bai R, San L Q. 2008 Wat. Res., 42 1511-1522.
[2] Ghaedi M, Mosallanejad N. 2013 J. Chem. Health Risks, 3 7-22.
[3] Ntwampe O I, Moothi K. 2018 Heavy Metals. 33.
[4] Akpomie K G, Dawodu F A. 2015 Beni-Suef Univ. J. Basic Appl. Sci., 4 1-13.
[5] El-Naggar H M. 2010 J. Egypt. Public Health Assoc., 85 169-88.
[6] Vasudevan S, Lakshmi J, Sozhan G. 2009 Clean–Soil, Air, Wat., 37 45-51.
[7] Al-Shahran S. 2013. Int. J. Technol., 13 1-12.
[8] Pascu D-E, Alina T G, Nechifor A C, Ralucu M A. 2016 J. Electrochem. Sci. Eng., 6 47-55.
[9] Sanusi M A, Adlan M N, Rozainy M R, Jamil R. 2016 Mater. Sci. Forum, 6 509-513.
[10] Bordoloi S, Nath S K, Gogoi S, Dutta R K. 2013 J. Hazard. Mate., r 260 618-626.
[11] Khadse G, Patni P, Labhasetwar P. 2015 Sustain. Wat. Resources Manage., 1 157-165.
[12] Tong M, Yuan S, Zhang P, Liao P, Alshawabkeh A N, Xie X, Wang Y. 2014 Env. Sci. Technol., 48 5145-53.
[13] Ujile A, Joel O. 2013 Int. J. Eng. Sci. Technol., 5 (6) 979-988
[14] Sadanand P. 2017 J. Mol. Liq., 241 1091-1113.
[15] Jalali M, Aboulghazi F. 2013 J. J. Mater. Cycles Waste Manag., 15 548-555.
[16] Heidari A, Younesi H, Mehraban Z, Heikkinen H. 2013 Int. J. Biol. Macromol., 61 251-263.
[17] Ozdes D, Duran C, Senturk H B. 2011 Environ. Manage., 92 3082-3090.