

Removal of Metal Iron from Groundwater Using Aceh Natural Zeolite and Membrane Filtration

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Abstract. The adsorption and the ultrafiltration processes were combined for removal of Fe^{2+} in water sample solution. Aceh natural zeolite used as an adsorbent, and three kind of ultrafiltration membranes (M10K, M30K, and MPVP) were used in this study. The concentration of Fe^{2+} in the product of adsorption and ultrafiltration is about 0.254 mg/L. This value is below the permissible limit of ferrous metal (0.3 mg/L) in drinking water. The combination of adsorption and ultrafiltration can be used as an alternative treatment of excess iron content in groundwater

1. Introduction

Iron is often present in groundwater worldwide. Its natural existence in the water could be in form of Ferro (Fe^{2+}) or Ferri (Fe^{3+}). The iron can also be obtained from the other sources such as mining and steel industry [1]. Iron is commonly encountered in natural water with a low level of oxygen, such as in groundwater and lake areas without air. Although iron is one of the essential elements for the human body, but its presence in water can lead to contamination. Iron content in ground water is varied, generally, the concentration is about 3-4 mg/L, but in some cases can reach up to 15 mg/L. Although at low concentration, the presence of iron in water could influence the taste and odor of the water. The appearing of iron ion in water could also affect to material corrosion due to oxidation by dissolved oxygen. At high concentration, iron ion in water can be toxic for human being and also causing infections such as neoplasia, cardiomyopathy, and arthropathy [2,3].

Several ways for removing iron ion from ground water include electrocoagulation [1], oxidation followed by filtration [4], ion exchange[5], bioremediation [6], aerated granular filter [2], and adsorption [7, 8]. Separation by adsorption and filtration methods have been performed by a number of researchers, but the results were not optimal. In this work, the combination of adsorption and ultrafiltration are designed for removal of Fe^{2+} from water sample solution. The adsorption process was done by using a local natural zeolite obtained from Aceh (Indonesia). Meanwhile the ultrafiltration was performed by using three kind of Polyethersulfone hollow fiber membranes (M10K, M30K, MPVP). In adsorption experiment, the effect of initial concentration and contact time between ferro solution and adsorbent was studied on the removal Fe^{2+} . Furthermore, adsorption isotherms were calculate based on the removal profile of ferro solution.



2. Experimental

2.1. Preparation and characterization of adsorbents

Natural zeolite used as an adsorbent in this study was obtained from the Ujung Pancu, Aceh (Indonesia). After pulverized in certain sizes, the zeolite was activated by physics and chemical methods. Physical activation was carried by calcination in a furnace at a temperature of 450°C for 4 hours. Granules of natural zeolite resulted from calcination were kept at room temperature. Chemical activation was conducted by soaking the zeolite in 0.1 N HCl with continuous stirring for 3 hours. Granules of natural zeolite were filtered and rinsed with distilled water. In the final step, the zeolite were dried in an oven at a temperature of 100-110°C for an hour. To investigate the chemical composition of adsorbent, the activated zeolite was analyzed by using X-ray Fluorescence (XRF).

2.2. Groundwater sample

The sample of groundwater containing Fe^{2+} ion was preparing by dissolving of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. In order to study the adsorption isotherms by Langmuir formula, the content of Fe^{2+} in feed water were set as several concentrations as 1.0; 1.25; 1.50; 1.75; and 2.0 mg/L.

2.3. Batch adsorption experiments

Batch adsorption experiment was conducted in a beaker containing 250 ml of Fe^{2+} solution. The adsorption process were carried out by adding 10 gr activated zeolite into solution. Particle size of activated zeolite were kept constant as 80 mesh for all experiment. To ensure the adsorption process of Fe^{2+} by the activated zeolite occur completely, the solutions were mixed by magnetic stirring at 100 rpm. The contact time between ferrous solution and adsorbent was set as 20; 40; 60; 80; 100 and 120 minutes. The concentration of Fe^{2+} in water sample before and after adsorption process were analyzed by a UV-VIS spectrophotometer.

2.4. Filtration process with membrane

A single cross-flow hollow fiber membrane module was performed to continue the removal process of ferrous solution resulted from adsorption experiment step. Three types of membrane fabricated from polyethersulfone (PES) were used at constant filtration condition. Solution sample of the adsorption process's effluent was passed through the membrane by a peristaltic pump at Trans Membrane Pressure (TMP) of 1 bar. The characterization of membranes are summarized in Table 1. The rejection of ferrous ion was calculated based on the equation (1).

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_f} \right) \times 100\% \quad (1)$$

Where: C_p and C_f indicated the concentration of ferrous in permeate and in feed solution, respectively.

Table 1. Membrane data information

Membrane	Material	Additive	Molecular weight cut-off	Inner Diameter (mm)
M10K	PES	-	10,000	0,75
M30K	PES	-	30,000	0,75
MPVP	PES	Polyvinylpyrrolidone	30,000	0,70

3. Results and Discussion

3.1. Chemical composition of Aceh natural zeolites

Alumina silicate is the main component of natural zeolites which is determine of porous structure the zeolite using as a cation exchanger, molecular sieving, catalyst and adsorbent [9]. The chemical

composition of Aceh natural zeolite are shown in Table 2. As shown in Table 2, the chemical composition of the Aceh natural zeolite consists of silica and alumina. Ratio of silica towards alumina represents the cation exchange capacity of these adsorbents. The ratio of silica to alumina is 2.7.

Table 2. Chemical analysis of Aceh Natural Zeolite

Elements in the form of oxide	Concentration (%)
SiO ₂	54.22
Al ₂ O ₃	20
Fe ₂ O ₃	11.05
CaO	5.65
MgO	3.51
SO ₃	0.04
K ₂ O	1.29
Na ₂ O	1.41
P ₂ O ₅	0.173
TiO ₂	1.045
Mn ₂ O ₃	0.162
CrO ₃	0.009
Loss on ignition	7.09%

3.2. The Effect of contact time on the removal of Fe²⁺

Contact time is one of the important parameters in the adsorption process [10]. The effect of contact time on Fe²⁺ removal is illustrated in Figure 1. It shows that the adsorption of Fe²⁺ increases with the increasing of contact time. Equilibrium conditions were recorded in the contact time of 100 minutes. From these results, it points out that the absorption of Fe²⁺ increases significantly at the beginning of the adsorption process. At the first 20 minutes of adsorption run, the removal rate was approximately 29%. The removal of Fe²⁺ kept increasing after 20 minutes of process, however it shows the rate of removal gradually decreases after 60 minutes. The increase of absorption rate in initial adsorption process is caused by the large surface area of the adsorbent, therefore, the contact between the Fe²⁺ in the solution and the adsorbent is still quite efficient.

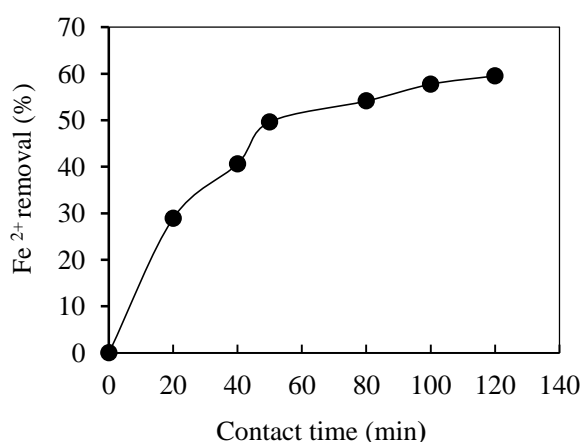


Figure 1. The Effect of contact time on the removal of Fe²⁺. The initial concentration of Fe²⁺ is 1.25 mg/L, and the stirrer speed is 100 rpm.

3.3. Effect of initial concentration on the removal of Fe^{2+}

The initial concentration of solution is also an important parameter in the adsorption process. The effect of initial Fe^{2+} concentration on the removal of metal (iron) is illustrated in Figure 2. It is shows that, the maximum removal of Fe^{2+} obtained at the lowest initial concentration of ferro solution. The initial concentration of the sample ions provides important driving force for the adsorption process. At the low concentration of metal ion in a sample solution, the adsorption rate is higher due to a good affinity between the adsorbent and the sample ions. This is caused by the contribution of adsorbent as an ion exchange which provided electrostatic interactions [11].

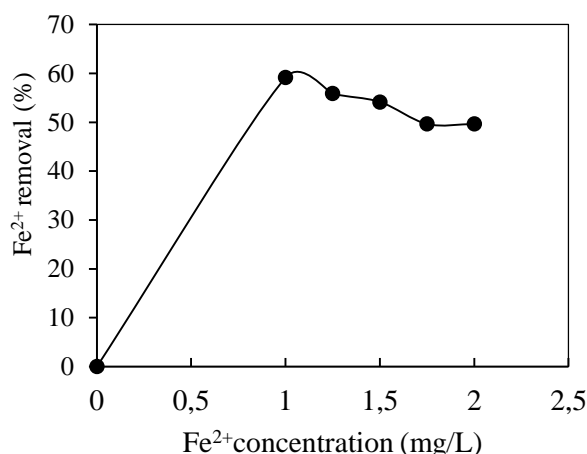


Figure 2. The Effect of initial concentration on the removal rate of of Fe^{2+} . Stirrer speed of 100 rpm, and the contact time of 100 minutes

3.4. Isothermal adsorption model

Isothermal adsorption is used to evaluate the adsorption capacity of an adsorbent, and to describe the interaction between the adsorbent against the metal ion [12]. This is very important in designing an adsorption-based process. Therefore, the application of isothermal adsorption model which is different to the data at equilibrium state is an important step to determine fitting model which is used for process design [13]. There are two types of general isothermal that are observed in this study, which are Langmuir and Freundlich isotherms. Langmuir isothermal model showed that uptake of metal ions occurs uniformly on the surface of a homogeneous single layer and the interaction between adsorbed molecules adsorbed is ignored [14]. Fe^{2+} were varied at 1; 1.25; 1.5; 1.75 and 2 mg/L.

Isotherm Langmuir and Freundlich are shown in Figure 3. Model isothermal Langmuir connected the metal concentration of Fe^{2+} in the sample solution at equilibrium (C_e) with the adsorption capacity at equilibrium (q_e). Correlation of these two components are plotted to observe the linear equation. The linear curve can be used to determine the Langmuir constant (n) and the maximum adsorption capacity of Fe^{2+} . Figure 3 showed that the coefficient of determination (R^2) for the Langmuir isotherm curve model is 0.9895. By using a linear equation of $y = 27.088 + 0.5314x$, it can be seen the maximum adsorption capability (Q) is 1.983 mg/g and constant Langmuir (b) is 0.0186. Langmuir isotherm model can be written as equation (2).

$$q_e = \frac{0,0369 C_e}{(1 + 0,0186 C_e)} \quad (2)$$

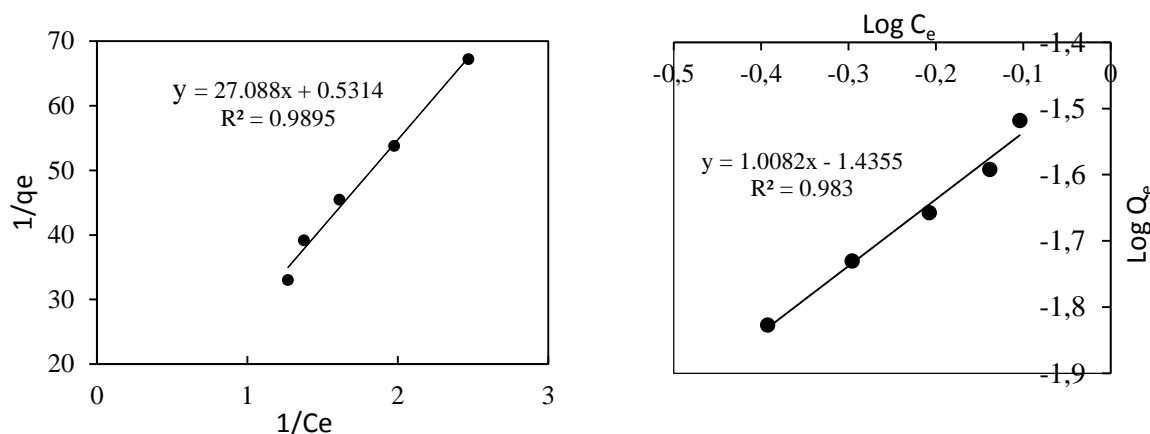


Figure 3. Langmuir (left) and Freundlich (right) isotherm of Fe^{2+} in batch system. Fe^{2+} concentration of 1-2 mg /L; the contact time is 120 minutes, stirring speed at 100 rpm.

Freundlich isotherm model linked the concentration of iron in the sample solution (C_e) with the amount of adsorbed adsorbate q_e . As can be seen in Figure 3, the coefficient of determination (R^2) is 0.9830 and the linear equation is $y = 1.0082x - 1.4355$. Regarding the data obtained from experiment and the linear equation from Figure 4, the Freundlich isotherm model can be written as:

$$q_e = 0,367 C_{1e}^{1,082} \quad (3)$$

Constant of isothermal obtained on the model of isothermal Langmuir and Freundlich is very useful in predicting the capacity of adsorption and to incorporate into the relationship of mass transfer which is used to design a batch reactor [11]. To determine the parameter model that occur in the process of adsorption can be used the value of the correlation coefficient (R^2). The high R^2 value indicates a high capability of isothermal models in describing the data at equilibrium [15]. From the data generated, it can be seen that the correlation coefficient (R^2) generated for Langmuir and Freundlich Isothermal models are 0.9948 and 0.9830, respectively. It indicates that the data fitting for Langmuir isotherm model against experimental data is better than the Freundlich model. The maximum adsorption capacity (q_{\max}) of Aceh natural zeolite is 1.983 mg/g. The absorption of iron in groundwater by Aceh natural zeolite occurred according to Langmuir adsorption isotherm model. Thus it can be concluded that the adsorption of Fe^{2+} with activated Aceh natural zeolite occurred chemically, irreversible and in a single layer (monolayer).

3.5. Ultrafiltration Process

The reduction of Fe^{2+} by Aceh natural zeolite was obtained as maximum as 58.50%. The concentration of Fe^{2+} after the adsorption treatment was 0.5188 mg/L. This concentration is over the drinking water standards for human body. The maximum level of Fe^{2+} concentration in drinking water is 0.3 mg/L. Therefore, the advance treatment of water samples are necessary. In this work, the effluent of batch adsorption step were followed with ultrafiltration process. In order to compare the removal performance of Fe^{2+} ion by adsorption and by membrane filtration, the experiment was run first by using Fe^{2+} of 1,5 mg/L directly without adsorption process.

Figure 4 shows the removal performance of Fe^{2+} ion filtrated by membrane. Membrane M30K has the greatest rejection capability than the others. The ferro concentration after filtrated by membrane M30K is 0.2417 mg/L. The coefficient rejection of the membrane M30K is 50.93%. The removal performance of Fe^{2+} ion separated by the combination of adsorption by Aceh natural zeolite and membrane filtrations

are shown in Figure 5. The efficiency of the combination process is calculated based on the combined results of adsorption and ultrafiltration.

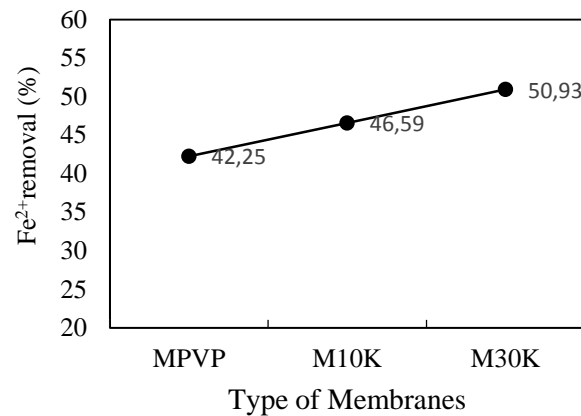


Figure 4. The efficiency of the process of ultrafiltration

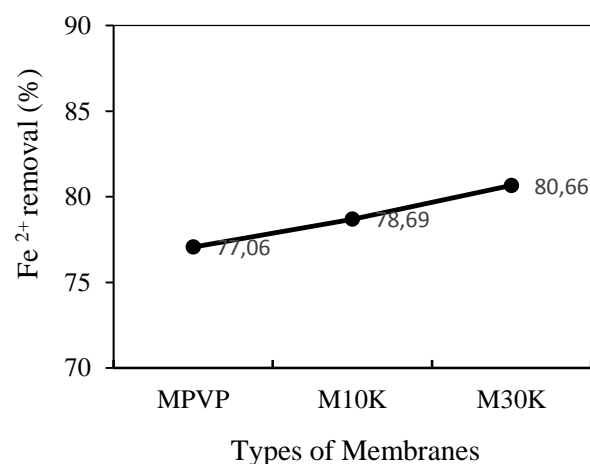


Figure 5. The efficiency of the combination process (adsorption-ultrafiltration)

As depicted in Figure 5, the removal of Fe (II) could be increase after filtrated by membrane. In all cases, the combinations of adsorption and ultrafiltration can be used as an alternative treatment of excess iron content in groundwater. The concentration of ferro in te product of adsorption and ultrafiltration is about 0.254 mg/L, and it's removal was about 80.66%.

4. Conclusion

The removal of iron metal in water solution using Aceh Natural Zeolite has been investigated in this study. Variation of iron removal with different parameters such as initial concentration of Fe²⁺ and contact time were studied. The removal are highly dependent on initial concentration of Fe²⁺ and contact time. The Langmuir isotherm model was best fitted to the isotherm data obtained. The concentration of ferro ion after the adsorption is still over the drinking water standards for human body. Therefore, the advance treatment of water samples are necessary. The combinations of adsorption and ultrafiltration can be used as an alternative treatment of excess iron content in groundwater. The concentration of ferro in the product of adsorption and ultrafiltration is about 0.254 mg/L. This value is below the permissible limit of iron metal (0.3 mg/L) in drinking water.

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