Effect of operating conditions on the efficiency of adsorption of Manganese (Mn) metals using Nano Zeolite adsorbents

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Abstract. Manganese (Mn) is one of the most abundant metal in the soil. The presence of this metal is essentially needed by living things for the formation of cartilage and bone as well as driving various enzymes. However, in excessive amounts, the metal can cause disruption of the central nervous system. In this study, the removal of Mn was carried out by the adsorption process using zeolite adsorbent. Effects of contact time, pH of sample (2, 3, 4, 5, 6, 7, 8, and 9) and dosage of adsorbent (1; 1.5; 2; 2.5; 3; 3.5; 4; 4.5 and 5 g) were evaluated. The optimal conditions were obtained under operating conditions of 100 minutes contact time, 7 and 9 pH of the sample, and 5 g dosage of adsorbent. The adsorption process was able to reduce Mn metal up to 79.52%. The initial concentration of Mn sample was 5 g/L and the concentration of effluent after the adsorption process reduced to 1.024 g/L. The adsorption process resulted in a significant reduction of Mn level. However, the final result of the process shows the level of Mn that still exceeds the limit permitted by KEPMENKES No. 907/MENKES/ SK/VII/2002 of 0.1 mg/L.

1. Introduction

Water is the natural resource most needed by all living things on earth. Water is needed by humans for daily use. The kind of water most used by humans is ground water. The problem in groundwater is the heavy metal content that is not expected to exist. One of the heavy metals contained in ground water is manganese (Mn) metal, that can be dangerous for health. Therefore, the government establish the maximum level of Mn in drinking water is 0.1 mg/L, which is regulated in Minister of Health Regulation No. 907/MENKES/ SK/VII/2002.

Research on the reduction of metal contained in groundwater has been widely carried out. In general, the method used is the adsorption using various adsorbents from biomass, including candlenut shells [1], crab shells [2], sawdust [3], nanosilica [4], and rice husks [5].

Natural zeolite is a potential adsorbent due to its high adsorption capacity and selectivity, long life, and abundant amount in Indonesia [6]. The adsorption process using natural zeolites has been studied by many researchers and provides results with a good metal ion removal efficiency, because zeolites have many pores and high cation exchange capacity that making it suitable for use as an excellent adsorbent [7]. The important factor in the adsorption process is the surface area [8], therefore in this

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study nano zeolites were used to increase the effectiveness of the adsorption of manganese metal. In this study also observed the effect of adsorption operating conditions including contact time, initial sample concentration, pH, and adsorbent dosage, in order to find out the best condition for removing Mn metal in ground water.

2. Experimental

2.1. Materials
The material used are Aceh's natural zeolite as an adsorbent and Potassium permanganate (KMnO$_4$) as an artificial solution. KMnO$_4$ was obtained from Sigma Aldrich and used without purification. While the tools used are magnetic stirrer, hot plate, pH meter, ball mill, shive shaker, and spectrophotometer.

2.2. Nano zeolite preparation
Natural zeolites were crushed by using a hammer to make small pebbles, then crushed using a ball mill to form powder. The powder is then filtered using a shive shaker with a filter size of 400 mesh (<37 µm). Nano zeolite was calcined in the furnace at 600°C for 2 hours to remove impurities in the pores of nano zeolite, and then was cooled to room temperature in a desiccator.

2.3. Adsorbent characterization
Nano zeolite has been characterized by using Fourier Transform InfraRed (FTIR) and X-Ray Diffraction (XRD). FTIR analysis was executed to investigate the spectrum of nano zeolites. The analysis was done by Shimadzu Prestige FT-IR 6400 and the spectrum was observed in the range of 2000 to 4000 cm$^{-1}$ wavenumber. The X-ray diffraction analysis was conducted to identify the components contained in nano zeolite. The analysis was performed at angle 20 within scan range of 10° to 40°, and measurement conditions of 40 kV and 30 mA.

2.4. Batch adsorption process
The adsorption process has been done by contacting nano zeolite adsorbents with KMnO$_4$ solution. The process was done at various contact time (25, 50, 75, 100, 125, and 150 min), concentration of KMnO$_4$ solution (5, 10, 15, and 20 mg/L), pH (3, 4, 5, 6, 7, 8 and 9), and the dosage of adsorbent (1; 1.5; 2; 2.5; 3; 3.5; 4; 4.5; and 5 g). The final concentration of KMnO$_4$ solution after adsorption was then analyzed using spectrophotometer every 25 min for 125 min. The removal efficiency of manganese (Mn) metal was calculated using equation 1.

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E = \frac{C_p}{C_f} \times 100\% 
\]

$E$: Mn metal removal efficiency (%)
$C_p$: final concentration of KMnO$_4$ solution (mg/L)
$C_f$: initial concentration of KMnO$_4$ mixture (mg/L)

3. Result and Discussion

3.1. Nano zeolite characterization
The results of XRD analysis can be seen in Figure 1. Three dominant diffraction peaks were observed. Diffraction peaks at 25.1° and 25.6° are quartz mineral characteristics (SiO$_2$), while the diffraction peak at 27.9° is the mineral calcite (CaCO$_3$). According to the previous research reported by Gultom [9], the natural nano zeolite peaks were between peaks of 25° to 29° which indicated the Si and Al compounds have been successfully synthesized and contained in natural nano zeolite.

3.2. Effect of contact time and initial concentration of the sample
The effect of contact time on the efficiency of Mn metal adsorption using nano zeolite is observed by making a metal solution with a various concentration of 5, 10, 15, and 20 mg/L into a beaker glass. Then stirring with a speed of 100 rpm, during the contact time of 25, 50, 75, 100, and 125 minutes. The effect of contact time on Mn metal removal efficiency can be seen in Figure 2.
Figure 1. XRD peaks of nano zeolite

Figure 2. Effect of contact time on the Mn metal removal efficiency

Figure 2 shows that the longer the contact time resulted in the increase in metal adsorption efficiency. There is a significant increase in adsorption efficiency during the first 25 min of contact time. This is caused by the availability of contact surfaces of many adsorbents that can adsorb Mn metals well. There is no reasonable increase in efficiency at the next interval of contact time, due to the slow diffusion of cations into the zeolite pores [10]. The optimum adsorption of Mn metal occurs at 100-minute interval with the efficiency of 79.52%. Based on the figure, it can also be stated that the higher the concentration of the sample solution, the smaller the adsorption efficiency. The decrease in adsorption efficiency is due to the amount of metal ions in the solution is not comparable with the amount of zeolite particles so that the surface of the zeolite reaches the saturation limit in absorbing Mn metal [11].

3.3. Effect of pH
The initial pH of the metal solution is an important factor that must be considered in the adsorption process by nano zeolites. It should be noted that ion exchange depends on the concentration and also the pH of the solution [12]. In this study, the effect of various pH of 2, 3, 4, 5, 6, 7, 8, and 9 with the initial
sample concentration of 5 mg/L and contact time absorption of 100 minutes was observed, and the results is presented in Figure 3.

![Figure 3. Effect of pH on Mn metal removal efficiency](image)

The figure shows that increasing the pH of the solution increases the adsorption efficiency of Mn metal. The amount of heavy metal ions adsorbed increase with an increase in the initial pH value of the solution. This is because the natural zeolite can adsorb H\(^+\) ions from the solution into heavy metals. Thus, in more acidic condition, the H\(^+\) ion can be adsorbed from the solution [10]. The adsorption efficiency of Mn metal reaches a maximum level at pH 9, that is 79.64%. This result is consistent with the theory that to eliminate Mn metal, the value of the solution is more than 8 [13].

![Figure 4. Effect of adsorbent dose on Mn metal removal efficiency](image)

3.4. Effects of Adsorbent Dosage
The adsorbent dosage is another important parameter that affect the level of metal adsorption efficiency [14-16]. This research studied the effect of various dosage of adsorbent of 1; 1.5; 2; 2.5; 3; 3.5; 4; 4.5;
and 5 g on Mn metal removal efficiency, with a condition of sample concentration of 5 mg/L, pH 7, contact time of 100 min and stirring speed of 100 rpm. The result is shown in Figure 4. The figure revealed that as the adsorbent dosage increase, the adsorption efficiency of Mn metal also increase. Significant increase in adsorption efficiency occurs in the range of adsorbent dosage of 1 to 3.5 g. This is due to the increasing number of particles and surface area available for the process. The maximum adsorption efficiency occurs at a 5-g adsorbent dosage of 79.51%.

4. Conclusions
Based on the above results, it can be concluded that:
1. The best condition for the removal of Mn metals using nano zeolite adsorbents was contact time of 100 min and concentration of solution of 5 mg/L, with the efficiency of 79.52%.
2. The maximum pH of the solutions was 9 with the removal efficiency of 79.664%.
3. The best dosage of adsorbent was 5 g with the percentage of Mn metals removal of 79.51%.
4. The adsorption process of Mn metal using nano zeolite with an initial solution concentration of 5 mg/L can reach a final concentration of 1.024 mg/L.

5. References
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