Removal of Iron and Manganese from Natural Groundwater by Continuous Reactor Using Activated and Natural Mordenite Mineral Adsorption

Y Zevi¹, S Dewita¹, A Aghasa¹,² and D Dwinandha¹

¹Department of Environmental Engineering, Faculty of Civil and Environmental Engineering, Bandung Institute of Technology (ITB), Jalan Ganesha 10, Bandung, West Java, Indonesia 40132
²Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro. Nam-Gu. Pohang. Gyeongbuk. Korea 37673
Email: yz59@cornell.edu

Abstract. Mordenite minerals derived from Sukabumi natural green stone founded in Indonesia was tested in order to remove iron and manganese from natural groundwater. This research used two types of adsorbents which were consisted of physically activated and natural mordenite. Physical activation of the mordenite was carried out by heating at 400-600°C for two hours. Batch system experiments was also conducted as a preliminary experiment. Batch system proved that both activated and natural mordenite minerals were capable of reducing iron and manganese concentration from natural groundwater. Then, continuous experiment was conducted using down-flow system with 45 ml/minute of constant flow rate. The iron & manganese removal efficiency using continuous reactor for physically activated and natural mordenite were 1.38-1.99%/minute & 0.8-1.49%/minute and 2.26%/minute & 1.37-2.26%/minute respectively. In addition, the regeneration treatment using NH₄Cl solution managed to improve the removal efficiency of iron & manganese to 1.98%/minute & 1.77-1.90%/minute and 2.25%/minute & 2.02-2.21%/minute on physically activated mordenite and natural mordenite respectively. Subsequently, the activation of the new mordenite was carried out by immersing mordenite in NH₄Cl solution. This chemical activation showed 2.42-2.75%/minute & 0.96 – 2.67 %/minute and 2.66 – 2.78 %/minute & 1.34 – 2.32 %/minute of iron & manganese removal efficiency per detention time for chemically activated and natural mordenite respectively.

1. Introduction
The utilization of groundwater as a source of clean water by urban areas in Indonesia is still conducted by urban communities who still have not got better access to clean water supply through piping system. Iron and manganese are found simultaneously in groundwater with manganese concentrations which typically lower than the concentration of iron. According to [1], Iron and manganese pollution is a problem often found in groundwater access in Indonesia caused by a soil layer in Indonesia which is formed as the result of volcanic rock sedimentation containing high concentration of iron and manganese.

Iron and manganese are found simultaneously in groundwater with manganese concentrations which typically lower than the concentration of iron. Iron and manganese in groundwater can be
removed effectively by using water treatment technique which could adapt to the form and concentration of iron and manganese contained in the water. In two previous studies conducted by [2] and [3] proved that the natural and activated mordenite were capable of removing iron and manganese ion content of artificial water sample. Meanwhile, this study was conducted to determine the ability of mordenite minerals to decreased iron and manganese in natural groundwater in accordance to the real condition on the field.

2. Materials and Methods

2.1. Preparation
A tubular shaped reactor made from acrylic was used in this research. The adsorbent was mordenite minerals derived from natural green stone of Sukabumi, West Java. Adsorbent was cleaned using clean water then was activated physically by heating at a temperature of 400-600°C for two hours. Chemical activation was also conducted by immersing mordenite in NH₄Cl solution for 24 hours. This research was conducted using groundwater from one of the residence wells in the settlement area around Bojongsoang, Bandung Regency, Indonesia.

2.2. Batch and Continuous Experiment
Variation of conducted experiments were shown in Table 1.

| Experiment       | System  | Adsorbent I          | Adsorbent II |
|------------------|---------|----------------------|--------------|
| I                | Batch   | Physical Activation | Natural      |
| II               | Continuous | Physical Activation | Natural      |
| III (Chemical Regeneration) | Continuous | Physical Activation | Natural      |
| IV               | Continuous | Chemical Activation | Natural      |

2.3. Groundwater Sample Preparation
This research was conducted using groundwater from one of the residence wells in the settlement area around Bojongsoang, Bandung Regency, Indonesia.

2.4. Measurement Parameters

2.4.1. Measurements of PH, Temperature and Turbidity. The type of tools used in this research for pH and temperature measurement were pH-meter and Orion® digital thermometer for measurement in the laboratory and also portable pH-meter CT-6022 for field measurement which can also measure temperature. Meanwhile, turbidity measurement was done by using Lovibond® turbidimeter.

2.4.2. Iron and Manganese Removal Efficiency. To determine the removal efficiency of iron and manganese removal, concentrations of iron and manganese in groundwater and treated groundwater were measured using Flame Atomic Spectroscopy Adsorbent (Flame AAS) and then calculated using standad removal efficiency equation.

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\text{Removal efficiency} = \frac{\text{Initial Concentration (ppm)} - \text{final concentration (ppm)}}{\text{initial concentration (ppm)}} \times 100\% \quad (1)
\]

3. Result and Discussion

3.1. Initial Characteristics of Adsorbent
Utilization of natural zeolite minerals for heavy metal adsorption can be done by using or without using treatment, such as physical and chemical activation which could enhance the adsorption capacity by producing a wider surface area through the formation of the porous structure and also eliminates polluting compounds. Physical activation was performed on mordenite by heating at a temperature of
400-600°C for two hours. Heating was used to reduce the water content and remove impurities inside zeolite pores. Mordenite has a stability to be heated up to 800°C in order to conduct physical activity in the form of heating without changing the structure of the zeolite and also avoiding the pore volume reduction. According to [3], heating of the zeolite at temperatures above 850°C could cause structural changes and also a decrease in surface area and zeolite pore volume. On the other hand, chemical activation was conducted by using NH₄Cl solution. According to [2], there is an exchange of NH₄⁺ with alkaline ion on mordenite. The exchange will reduce the mass percentage of some elements so that the selectivity of mordenite to iron and manganese were increases. Figure 1 shows the result of SEM analysis on mordenite.

![Figure 1 Mordenite before Adsorption](image)

3.2. Groundwater Initial Characteristics
Groundwater was collected from pipe directly connected to the wells. The results of groundwater characteristics analysis are shown in Table 2. It shows the high values of iron and manganese concentration which indicates that the groundwater must be treated before the usage while initial concentration of iron and manganese in groundwater used in the experiments are shown in Table 3.

| No | Parameter                | Unit       | Quality Standard | Methods        | Result  |
|----|--------------------------|------------|------------------|----------------|---------|
| 1  | Turbidity                | NTU        | 5                | SMEWW-2130-B   | 55.9    |
| 2  | Color                    | Pt.Co      | 15               | SMEWW-2120-B   | 125     |
| 3  | Conductivity             | uS/cm      | -                | SMEWW-2510     | 697     |
| 4  | Iron (Fe)                | mg/L       | 0.3              | SMEWW-3500-Fe-B| 36.4    |
| 5  | Fluoride (F)             | mg/L       | 1.5              | SMEWW-4500-F-D | 0.316   |
| 6  | Hardness (CaCO₃)         | mg/L CaCO₃| 500              | SMEWW-2340-C   | 252     |
| 7  | Chloride (Cl)            | mg/L       | 250              | SMEWW-4500-Cl  | 48.8    |
| 8  | Manganese (Mn)           | mg/L       | 0.4              | SMEWW-3500-Mn-B| 1.76    |
| 9  | Sulphate (SO₄)           | mg/L       | 250              | SMEWW-4500-SO₄-B| 1.13    |
| 10 | Total Bacteria Coliform  | Units per ml sample | 100 | J.P.T | 93     |
### Table 3 Initial characteristic of groundwater used in experiments

| Experiments | Source of Groundwater | Initial Concentration (mg/l) |
|-------------|-----------------------|-----------------------------|
|             |                       | Iron | Manganese       |
| I           | Water Storage         | 0.492 | 1.668          |
| II          | Water Storage         | 0.266 | 1.55           |
| III (regeneration) | Water Storage     | 0.177 | 1.689          |
| IV          | Water Storage         | 2.626 | 1.439          |

3.3. *Iron and Manganese Removal Efficiency*

Result of each experiments are shown in Figure 2. Iron and manganese removal efficiency from batch system in experiment I was fluctuated but tend to increase with the longer detention time. Iron removal was also higher than manganese same as in the previous study of [2] and [3]. According to [4], The presence of ions and other compounds in the solution may affect the adsorption of adsorbate while according to [5], heavy metal removal in batch adsorption process increases from the early stage until 60 minutes of detention time.

Continuous experiments were able to remove iron and manganese removal and were successful to meet the standard. Result of experiment II shows that there is no significant difference of iron and manganese removal efficiency between physically activated and natural mordenite. But chemical regeneration in experiment III was able to increase the efficiency after the adsorbent used for several days. Then it was continued to experiment IV that show significant difference of iron and manganese removal between chemically activated mordenite and natural mordenite. Different mechanism happened to affected the removal efficiency since activation could influenced the initial characteristic of the used mordenite. According to [2], chemical adsorption mechanism was slower than physical mechanism. Besides that, for the continuous process, the removal of iron and manganese were also influenced by the adsorbent characteristics which could be changed during the reactor operation. The iron and manganese removal in continuous reactor using down-flow system was not only involved in the mechanism of adsorption and ion exchange, but also involved in the filtration mechanism. According to [6], removal for heavy metals, such as Fe³⁺, Mn²⁺, Zn²⁺, and Cu²⁺ using zeolite adsorbents was not only involved in ion exchange mechanism, but also involved in the precipitation result of metal hydroxides from the solution. Figure 3 shows that the increase of particle accumulation on mordenite surfaces proved that adsorption had taken place during the experiments.
4. Conclusions
The removal of iron and manganese from natural groundwater by using mordenite derived from Sukabumi green stone through the conducted experiments showed that iron removal was better than manganese. Even though the physical activation was already given in the process, natural mordenite could still remove iron and manganese better than mordenite with physical activation. On the other hand, chemical activation which was given to the mordenite using NH$_4$Cl solution showed better iron and manganese removal than physical activation and natural mordenite. The maximum value of iron removal efficiency was obtained from natural mordenite which was 2.79 %/minute while manganese removal was 2.67 %/minute in chemically activated mordenite.

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