

**STUDY ON THE IRON AND MANGANESE
REMOVAL FROM GROUNDWATER AT
NAHRIM COMPLEX,
SERI KEMBANGAN, SELANGOR**

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**Utilisation of ozone in the study on the iron and manganese removal
from groundwater at NAHRIM Complex, Seri Kembangan,
Selangor**

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Abstract

The aim of this study is to examine the removal of Fe^{2+} and Mn^{2+} from groundwater utilising ozone as one of the oxidizing agents. The pilot-scale experiments were executed in mini water treatment plant at NAHRIM Complex, Seri Kembangan, Selangor. The methods applied were aeration by internal circulation, ozonation and nanofiltration. The removal effects of iron and manganese under the different conditions were investigated. The raw water containing iron and manganese ions were firstly oxidized in raw water tank by internal circulation through mechanical action followed by ozonation and nanofiltration process. All the groundwater samples were filtered with 0.45 μm filter paper except groundwater sample passing through the nanofiltration. Ozone as a powerful oxidizing agent, which was used in this study to oxidize iron and manganese converting ferrous ions (Fe^{2+}) iron to ferric state (Fe^{3+}) and Mn^{2+} to Mn^{4+} state. The Fe^{2+} and Mn^{2+} concentration were gradually decreased from raw water of 3.9 to 0.03 mg/L after completing the treated cycles. By increasing contact time of raw water during aeration, the concentration of Fe^{2+} and Mn^{2+} were reduced tremendously, however the accumulated sludge of Fe and Mn oxide would also increase. The accumulated sludge of Fe and Mn due to aeration was removed by sand filtration. The remaining Fe^{2+} and Mn^{2+} in groundwater were significantly reduced after passing through the ozonation injection. After going through ozonation and nanofiltration process, the iron and manganese concentrations came down from 0.08 to 0.03 mg/L and 0.30 to 0.17 mg/L respectively. For optimum removal of iron and manganese ions, the ozone dose has been noted as 3 mg/L or (30% of maximum ozone output) at an optimum temperature of 28°C which improved removal of Fe^{2+} and Mn^{2+} to more than 50% and 43% respectively. Therefore, this study could concluded that ozone application was effective agent in improving groundwater quality to meet the water quality standards without using any chemicals.

1. Introduction

Groundwater is an important source of drinking water used in Malaysia as a complimentary resources against shortages of surface water particularly during dry period. Although the use of groundwater in Malaysia is small compared to surface water, but it is of quite a significant usage for industrial activities and private domestic needs, mostly people living in rural areas. Iron and manganese are common metallic elements found in the earth's crust (Oram, 1995). Water percolating through soil and rock can dissolve minerals containing iron and manganese, and hold them in solution (Jusoh et al, 2005).

However, iron and manganese are the two naturally occurring contaminants found in tropical region, which are usually present in groundwater as divalent ions (Fe^{2+} and Mn^{2+}). They are considered as contaminants mainly because of their organoleptic properties (Ellis et al., 2000). The concentration of iron sometimes goes up to tens of mg/L where laterisation is dominant mechanism of chemical weathering. Groundwater containing iron and manganese is usually anoxic. Iron and manganese often occur together in groundwater but manganese usually occurs in much lower concentration than iron. Both iron and manganese are readily apparent in drinking water supplies (Colter & Mahler, 2006). The iron and manganese concentrations in excess, the water becomes red-brown, and endues the scaling problems in pipeline system.

The maximum recommended levels of Fe^{2+} and Mn^{2+} in drinking water are 0.3 mg/L and 0.1 mg/L, respectively (Department of Standards Malaysia, 2010) and (WHO, 2008), but these are not health related and not enforceable. Conventional treatment for iron and manganese removal from groundwater consists of oxidation and sand filtration. Strong oxidants such as chlorine and potassium permanganate (KMnO_4) are generally used for Fe^{2+} and Mn^{2+} oxidation. An aeration step may precede oxidation for oxygenation and removal of carbon dioxide (pH increase), sulphur and other volatile substances. The conventional process works fairly well if Fe^{2+} and Mn^{2+} concentration were below 5 mg/L and in the absence of dissolved organic matter. However, for higher concentrations, excessive amounts of solids tend to shorten filtration cycles and render the overall process unprofitable. The selection of various oxidants depends on which kinds of pollutants in water and their effects on the water quality.

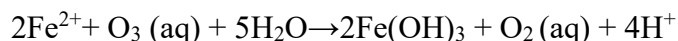
Ozone is the most powerful oxidizer available that can be safely used in water treatment. It is used to treat drinking water, bottled water, swimming pool water, waste water, food and beverage processing water, and in many other applications. Ozone is effective in performing the following:

- i. Disinfection – bacterial disinfection, inactivation of viruses and cysts.
- ii. Oxidation of inorganics – precipitates, iron, manganese, sulfides nitrides and organically bound heavy metals.

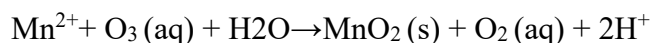
- iii. Oxidation of organics – including organics causing colour, taste and odour problems. Some detergents and pesticides, phenols, VOCs, turbidity control, and micro-floccuity control and micro-flocculation of soluble organics.

In recent years, ozonation has received more attention as a method for treating numerous water quality problems (Piper, 2008). Scientists have found that chlorine can have a tendency to create carcinogenic compounds as it breaks down into other byproducts (Cheremisinoff, 1990). To this end, there is increasing pressure to reduce chlorine as a primary disinfectant in our drinking water supplies. Unlike other chemical purifying processes (International Ozone Association, 1999) ozone leaves no environmentally harmful residues.

Removal of iron and manganese consists of transforming the soluble form to insoluble that can be filtered out of the water; the ferrous iron is, therefore, easily oxidized by ozone according to the following reaction:



As for oxidation of manganese but conversion of Mn^{2+} into MnO_2 requires more oxidizing power than the conversion of Fe^{2+} into $\text{Fe}(\text{OH})_3$ because it needs more energy (Dore, 1989). The oxidation reaction of manganese by ozone takes the following form:



The objectives of this study is to examine the efficiency of ozone as an oxidant in removal of iron and manganese in groundwater.

2. Materials and Methods

2.1 Pilot water treatment plant site description

The NAHRIM Complex is located in Seri Kembangan, Selangor about 25 km south of the city centre of Kuala Lumpur within latitudes of 2° 59' N and 3° 0.1' N, and longitudes 101° 41' E and 101° 46' E. It covers an area of about 47 acres. It is bounded on the north and east by private palm oil plantation, west by MAJU Expressway and south by Universiti Putra Malaysia (UPM). The climate of the area is tropical characterised by uniform temperature and high rainfall with mean annual temperature varying from 24.2 - 32.3 °C and mean annual rainfall varying from 2137-2667 mm.

The study area lies entirely within the Kenny Hill Formation (Yin, 1961) believed to be deposited during the upper Palaeozoic. Lithologically, it consists of interbedded sandstones, shales and mudstones which are thought to have been deposited in a moderately deep marine environment near a large supply of reworked sediments (Yeap, 1969). The formation is characterised by fracturing and foliation which facilitate groundwater movement

The raw groundwater of this experimental was supplied from a deep well which was drilled into metasedimentary rock aquifer with 100 m depth. The total iron and manganese concentration of raw water were 3.9-6.0 mg/L and 0.6-1.0 mg/L respectively, and the water appeared to be light brown in colour. The pilot plant comprise of the following: raw water tank with circulation aeration, filtration columns with different media (gravel, sand, charcoal), ozone and nanofiltration. Groundwater is pumped to the aeration tank to increase dissolved oxygen and iron and manganese are oxidised by mechanical circulation. After the oxidation process, the Fe and Mn oxides are then removed through the sand filter.

The filtration column is 1625 mm high with a 600 mm outer diameter and maximum capacity of 5000 L/h. The filter has a layer made up of rough siliceous sand granules with the diameter of about 100 mm at the bottom. Above this layer was a filter medium with a diameter of 1–3 mm. The layer was 150 mm thick and the filter layer was 800 mm thick.

ClearWater Tech CD10 ozone equipment was used to generate the ozone. The ozone is generated by exposing oxygen molecules (O_2) in an air stream to a controlled, high energy electrical field. As the air stream passes through the electrical field produced inside the ozone generator, some oxygen molecules are split, forming single oxygen atoms (O_1). These oxygen atoms then recombine with other oxygen molecules in the air stream, forming ozone (O_3) as shown in Figure 1.

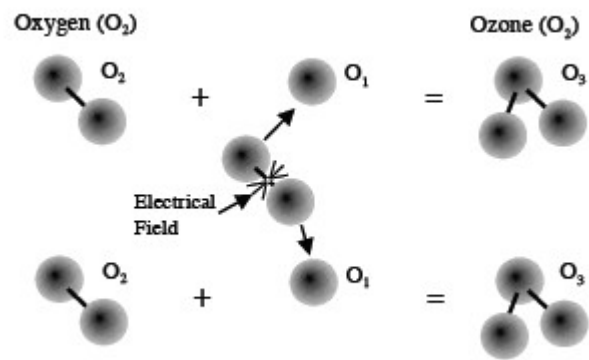


Figure 1: Ozone generation

2.2 Sampling and analytical methods

To measure the efficiency of Fe and Mn removal, five sampling points were used; S1 (raw water), S2 (after aeration), S3 (after sand filtration), S4 (after ozonation), S5 (after nanofiltration) were evaluated. The concentrations of Fe and Mn ions at all sampling point were determined by Hach DR 2800 Portable Spectrophotometer and the groundwater treatment schematic diagram is showed in Figure 2.

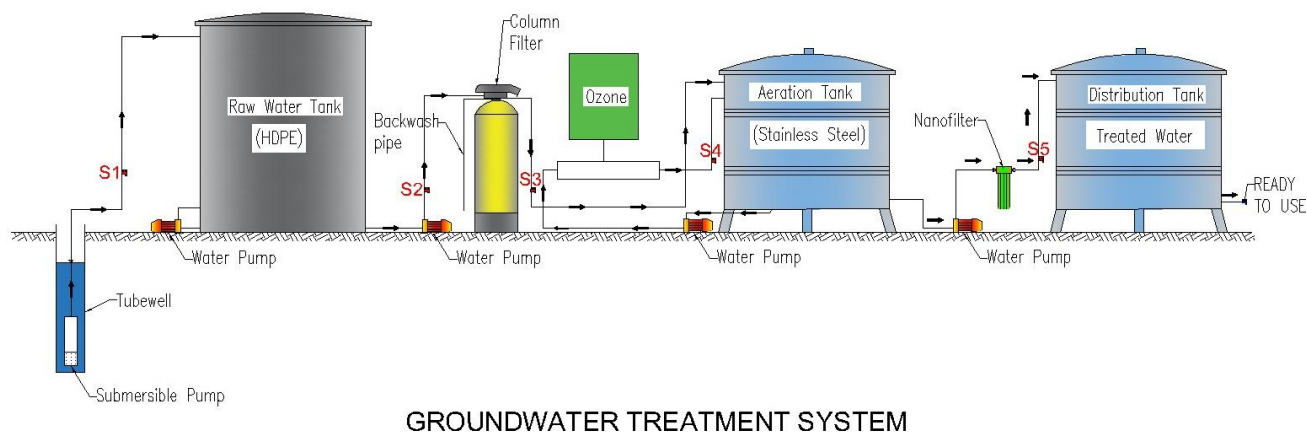


Figure 2: The schematic diagram of the groundwater treatment

3. Results and Discussion

3.1 Oxidation (aeration) time

The reaction time (5-120 min) of Fe^{2+} oxidation and pH were investigated. The experiments were executed by aeration at different contact time. During the aeration, the Fe^{2+} concentration was reduced tremendously from 3.6 mg/L to 0.6 mg/L at 5 minute. However, the Fe^{2+} remained

constant after 10 minute as well as at 120 minute at concentration of 0.58 mg/L. Therefore, the contact time of 5 minute is sufficient to oxidise the Fe^{2+} in groundwater and form particles that was larger than the pore size of the nanofiltration membrane. The removal efficiency of iron under mentioned conditions is shown in Table 1 and Figure 3.

Table 1: The removal efficiency of Fe^{2+} concentration in raw water at different contact time

Time (minutes)	Fe^{2+} (mg/L)	DO	pH
0	3.90	5.90	6.80
5	0.62	6.38	7.08
10	0.58	6.53	7.10
15	0.59	6.79	7.11
20	0.60	6.95	7.11
25	0.59	7.06	7.13
30	0.58	7.18	7.15
40	0.60	7.35	7.18
50	0.59	7.38	7.20
60	0.59	7.60	7.21
75	0.57	7.64	7.25
90	0.57	7.79	7.28
105	0.58	7.86	7.29
120	0.58	7.88	7.35

Notes: DO - Dissolved oxygen

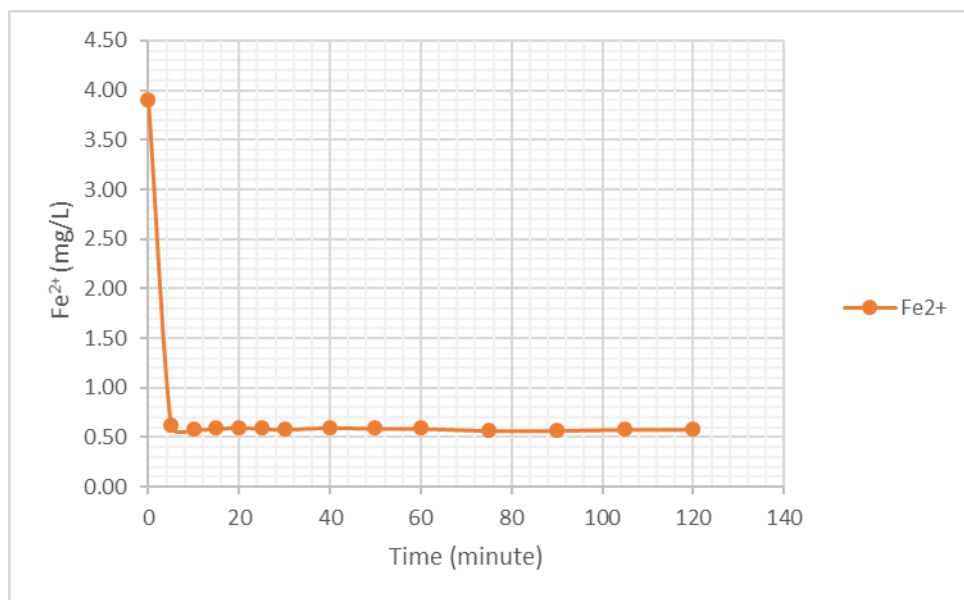


Figure 3: The Fe²⁺ concentration at different period of aeration

3.2 Fe²⁺ and Mn²⁺ removal

In this study, the Fe²⁺ and Mn²⁺ concentration in raw water generally range from 3.9 - 6.0 mg/L and 0.6 - 1.0 mg/L, respectively. After the aeration, Fe²⁺ and Mn²⁺ were easily oxidized and converted into particles. The Fe²⁺ concentration was dramatically dropped from 3.90 to 0.08 mg/L after aeration and filtration which is much lower than the water quality standard of 0.3 mg/L (WHO, 2008). However, the Mn²⁺ concentration was reduced from 0.60 to 0.32 mg/L but still above the drinking water standard of 0.1 mg/L. Previous study has illustrated that the Mn²⁺ oxidation by air was only about 70% efficient even at high pH of 11 at the initial Mn²⁺ concentration 0.5 mg/L (Kaya et al, 2005). Hence, an oxidant (ozone reaction) is required to complete the removal of Mn²⁺. The Fe²⁺ and Mn²⁺ removal at different sampling point is shown in Table 2.

Table 2: The Fe²⁺ and Mn²⁺ removal at different sampling point.

Sampling point	pH	Fe ²⁺ (mg/L)	Mn ²⁺ (mg/L)
S1 (raw water)	5.01	3.90	0.60
S2 (aeration)	5.43	0.08	0.32
S3 (sand filtration)	5.45	0.08	0.30
S4 (ozone)	6.12	0.04	0.17
S5 (nanofiltration)	5.82	0.03	0.15

4. Conclusions

In this study, the removal of Fe^{2+} and Mn^{2+} in groundwater by aeration, sand filtration, ozone and nanofiltration was very encouraging. The result showed that Fe^{2+} was 0.08 mg/L and below the drinking water quality standards of 0.3 mg/L by aeration and sand filtration, while Mn concentration (0.32 mg/L) still remained higher than drinking water quality standard of 0.1 mg/L. After going through ozonation and nanofiltration process, the iron and manganese concentrations came down from 0.08 to 0.03 mg/L and 0.30 to 0.15 mg/L respectively. For optimum removal of Fe^{2+} and Mn^{2+} , the ozone dose has been noted as 3 mg/L or (30% of maximum ozone output) at an optimum temperature of 28°C which improved removal of Fe^{2+} and Mn^{2+} to more than 50% and 43% respectively. The iron and manganese type and concentration, and pH of water helps determine the best procedure and treatment system to be used. Ozone is not only increase the pH and oxidise the remaining Fe^{2+} (after aeration and sand filtration) but also remove unpleasant odours. Therefore, it can be concluded that ozone application is one of the best method for iron and manganese removal in groundwater to meet water quality standards without using any chemicals.

5.0 Recommendations

It is recommended that future research is required in order to comprehensively understand the Mn^{2+} behavior and to lower the Mn^{2+} concentration further to drinking standard of 0.1 mg/L.

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