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IRON REMOVAL FROM GROUNDWATER THROUGH OXIDATION WITH DMI-65

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Abstract: Groundwater is one of the abundance waters resources in Malaysia. Malaysia groundwater comes with various of natural minerals and these minerals need to be processed before the water can be used as potable water. High Iron content is one of the major issues of processing ground water in Malaysia. To comply with Malaysian National Drinking Water Quality Standards, the Iron concentration must be controlled below 0.3 ppm. Chemical oxidation is one of the effective methods to reduce the Iron content of the groundwater. The iron oxidation process however has a low reaction rate, especially at low PH. Various catalysts have been developed to improve the efficiency of iron removal via the oxidation process. One such catalyst that is commercially available is DMI-65. In this paper, we investigated the efficiency and operating limits of DMI-65 in the removal of soluble iron from contaminated groundwater. Based on our results, DMI-65 is found to be very efficient in the removal of iron even at a very high level of iron contamination in the groundwater. This study found that groundwater at 7.4 ppm iron content can be oxidized to 0.126 ppm which is a 98.3% removal efficiency. A characterization of the catalyst was conducted to understand the surface characteristic of the catalyst. It was found that the catalysts shapes are non-uniform with average sizes of between 300 to 850 microns. The surface was found to exhibit various crevices that contribute a lot of additional surface areas for absorption of the iron. In addition to the above investigation, this study will also report on the proper preparation of DMI-65 prior to the introduction of the contaminated groundwater.

	Keywords: iron, catalyst, DMI-65, sodium hypochlorite, groundwater.
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1. Introduction

Groundwater is one of Malaysia's natural resources that has not been fully exploited. In the National Water Resources Study (2011), it was estimated that Malaysia has a storage potential for groundwater of 5000 billion cubic meters with estimated recharge of 63 billion cubic meter per year (Shahrizaila, 2016). Tapping into this vast resource will help in ensuring reliable and uninterrupted supply of clean and affordable water to the population. The large potential of the groundwater would be sufficient to support the requirement for household consumption and for economic sectors which was recorded at 3.8 billion cubic meters per year. In addition, the Malaysian Department of Statistics reported that only 92 million cubic meters of the national water usage came from groundwater in 2015 (Ho, 2018).

Earth soil naturally contains an abundance of organics and minerals. As the groundwater flows through these organically rich soils, the groundwater picks up the minerals, organic materials, and metal ions. These minerals will be collected and accumulated in the groundwater as it passes through layers of the organically rich soil. Subsequently the accumulated minerals will end up at the collection points where it they have to be removed from the groundwater if the groundwater is intended to be used other purposes such as domestic use, agricultural use, and industrial applications. The presence metal ions in the groundwater in particular creates some issues in the water treatment system. Presence of iron in the water supply system leads to precipitation that can cause severe esthetical and operational issues in water supply system and at the point of end use (Bordoloi et al., 2011).

Several options are available for removal of iron from groundwater such as ion exchange, sequestrations, biological treatment, membrane technology, and oxidation. Oxidation process is the most preferred method due to its simple operation, low cost and minimal impact to the environment (Khatri et al., 2017). The oxidation process is carried out by bringing the iron in the water into contact with a suitable oxidizing agent.

Even though this process is generally acceptable in term of removal efficiency, the reaction rate is often very low and if implemented on an industrial scale will translate into large reaction system because of the requirement of long reaction time. To help with the oxidation process, catalysts in various forms are introduced into the system.

Oxidation combined with filtration is a generally acceptable conventional method for the removal of heavy metals from groundwater (Ellis et al., 2000). Aeration, or exposing the contaminated water to strong oxidizing agents, can be used to achieve oxidation, or a combination of aeration and oxidizing agent injection. When the iron concentrations in groundwater exceed 10 mg/l, oxidation plus filtration treatment is preferred. In general, this method involves two steps: (1) the oxidation process, in which the divalent ions of iron are oxidized to form solids that are insoluble, and (2) the filtration process, in which the precipitated solids of the oxidized iron filtered using a suitable filter media. As an oxidation agent, strong oxidants such as oxygen, chlorine, or potassium permanganate are used in this method (Kouzour et al., 2017). The oxidants will oxidize the divalent ions of iron into solid

products that can be easily filtered and removed from the system using suitable filter media (Ellis et al., 2000).

Catalytical oxidation is the process of coating the filter media with metal oxides to increase the oxidation of soluble ions during the treatment processes. The filter media is coated with manganese oxides or iron oxides to increase oxidation rates in order to remove iron ions (Y. Cheng et al., 2020).

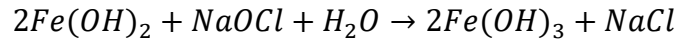
The use of metal oxides as a catalyst for the oxidation of iron and manganese in groundwater has received a lot of attention. To improve the removal efficiency of iron and magnesium from groundwater, some researchers have developed iron and manganese co-oxide filter mediums. These results were obtained by starting the oxidation-reduction process in the filters. The filter media were pumped with a solution of potassium permanganate, manganese chloride, and ferrous chloride. As the iron and manganese oxide products of the oxidation reduction reaction deposited on the filter media surface, an active film forms on the filter media surface (Y. Cheng et al., 2019).

Buamah et al. (2009) conducted research on the mechanism of metal oxide catalysis. The report suggested that the presence of metal oxides, specifically manganese oxides and iron oxides on the surface of filter media aids in the adsorption of the iron and manganese ions that are present in raw water (Buamah et al., 2009). According to another research, the catalytic oxidation process can be represented by the following steps: (1) formation of adsorbed metal ions on the surface, (2) formation of adsorbed hydroxides on the surface, (3) reaction between adsorbed hydroxide and metal ion to form a hydrolysis complex, and (4) formation of the hydrolysis complex to form a new active film (Guo et al., 2017). A recent study proposed that oxidation of metal ion on a manganese oxide coated filter media is governed by a two step mechanism called contact catalytic oxidation represented by physical autocatalytic adsorption followed by oxidation of the adsorbed metal ions (L. H. Cheng et al., 2020).

Several researchers have investigated some of the factors that can affect the performance or activity of the oxidation unit catalyst filter. The type of oxidants used, pH, and dissolved oxygen level of the contaminated water are among the factors investigated. Shafiquzzaman (2021) investigated a pre-filtration step to improve the iron and arsenic removal efficiency in household ceramic filters. The researcher attempted to represent a regular cylindrical shaped household ceramic filter in this study. This was accomplished by inserting a ceramic filter element into the bottom of a clay pot into which contaminated water is fed. The water will be filtered and collected in a bucket at the bottom of the clay pot. The pre-aeration was accomplished by alternately filling two buckets with fresh groundwater before feeding it into the clay pot. According to the findings of this study, the addition of a pre-aeration step in a household ceramic filter increases arsenic removal efficiency to 82 percent and iron removal efficiency to more than 99 percent. Furthermore, he concluded that the pre-aeration step significantly improved the removal efficiency (Shafiquzzaman, 2021).

The type of oxidant used in the oxidation process is also important in removing iron and manganese from groundwater effectively. Chlorination is a more common method for removing divalent iron. Because of its ability to deactivate microorganisms in water, chlorine has traditionally been the preferred agent for water disinfection (Cescon & Jiang, 2020). Chlorine deactivates microorganisms by damaging the cell wall and altering cell permeability, as well as inhibiting enzyme activity and cell production (Spellman, 2021). Chlorine can be

found in a variety of forms, including chlorine gas, solid calcium hypochlorite, and sodium hypochlorite solution. This study used sodium hypochlorite as the oxidizing agent due to its low cost, availability, and handling safety. The oxidation reactions when sodium hypochlorite is used as the oxidizing agent is shown below:



Even though the oxidation process is generally acceptable in term of removal efficiency, the reaction rate is often very low and if implemented on an industrial scale will translate into large reaction system because of the requirement of long reaction time. To help with the oxidation process, catalysts in various forms are introduced into the system. This research aims to study the efficiency of DMI-65 catalyst in the removal of iron from contaminated groundwater.

3. Methodology

3.1 Materials

To simulate the iron in the groundwater, a quantity of iron sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were added into distilled water which was kept at room temperature. Sodium hypochlorite (12% concentration) was used as oxidizing agent.

3.2 Experiment Setup

Treatment studies were conducted on a bench scale water treatment unit which was designed to model an actual groundwater treatment currently in use at a water treatment site in Malaysia. The complete Lab Scale Treatment Unit comprises various tanks in series, a mixing tank with oxidizing agent dosing mechanism, and a reaction tank. The Process and Instrumentation Diagram of the lab unit is as shown in the following diagram.

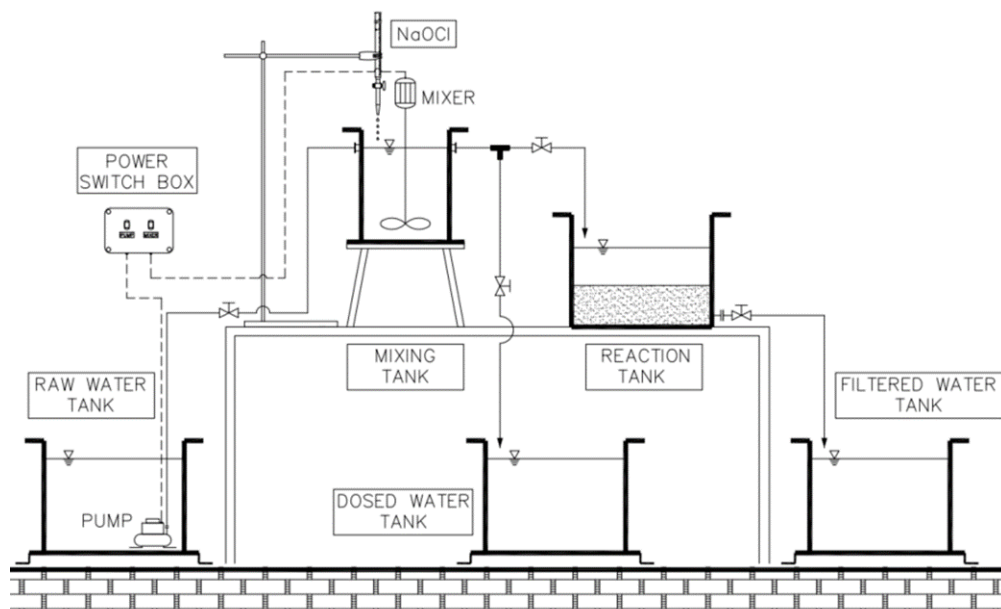


Figure 11: P&ID of Bench Scale Water Treatment Unit

The Raw Water Tank, Dosed Water Tank, and Filtered Water Tank are cylindrical containers with 300mm diameter and can accommodate around 21 liters of water. The maximum pump flowrate is 1 L/min. The Mixing Tank is a rectangular vertical tank with a volume of about 1.5 liters. With pump flowrate of 1 L/min, it will take about 1.5 minutes to fill up the mixing tank before the fluid overflows into the Reaction Tank which is sized to hold a maximum capacity of approximately 15 liters.

Flowrate of raw water into the mixing tank can be varied by adjusting the opening of the valve at the pump discharge and measuring the time to fill up the mixing tank.

The process study was conducted at three different service flowrates. The first round of investigation was conducted at service flowrate of 33.9, 8.8, and 3.8 m³/m²/hr. The manufacturer's recommended service flowrate is between 5-30 m³/m²/hr.

During the first round of the investigation samples were drawn at the raw water tank and at the outlet of the reaction tank to determine the iron concentrations. The raw water was prepared to have iron concentration that simulates an upset condition in a groundwater intake station in Malaysia. The service flowrate was fixed at 33.9 m³/m²/hr., while the sodium hypochlorite was varied from 0.0036 milliliters/second to 0.0053 milliliters/second. The iron content in the prepared groundwater was 12.8. At this iron concentration, the stoichiometric ppm sodium hypochlorite requirement is 0.0012 milliliters/second.

Sodium hypochlorite was injected directly into the mixing tank at the inlet point of the raw water. To ensure complete homogeneity of the mixture in the tank before it enters the reaction tank, a propeller mixer is provided to enhance the mixing of the raw water and sodium hypochlorite. The DMI-65 catalyst will be dumped manually into the Reaction Tank before activation process is initiated. The bed height of the catalyst will be varied during the process study to determine the optimum bed height required to achieve maximum iron and manganese removal at different concentration in the raw water.

In the second round of the process study, the iron concentration in the raw water was reduced to 7.4 ppm which is closer to the reported actual iron concentration in the groundwater at the water treatment site. The service flowrate was reduced to 3.8 m³/m²/hr. The sodium hypochlorite flowrate was varied from 0.0018 to 0.011 m³/m²/hr.

The third round of investigation involves fixing the service flowrate and the sodium hypochlorite dosage around the manufacturer's recommended range and varying the iron concentration in the raw water to find the limit at which the catalyst can remove the soluble iron from the groundwater. The service flowrate was fixed at 8.8 m³/m²/hr., while the sodium hypochlorite dosage was fixed at 0.028 milliliters/second.

3.1 Analysis and Characterization

The physical and chemical characteristics of the catalyst was studied using appropriate characterization techniques.

To understand the particle size distribution of DMI-65, the catalyst was sieved manually at 300 microns, 850 microns, 1mm, and 2 mm sieve sizes.

The surface topography and morphology of catalyst surface was observed using Hitachi S3400N with 15kV accelerating voltage at 1000x and 5000x magnifications. Ametek EDX machine coupled to the SEM machine was used to obtain the elemental composition of the sample surface.

FT-IR spectra were used to characterize the functional groups on the surface of DMI-65. The FT-IR spectrometer was performed with Thermo Scientific's Nicolet iS10 with 16 scans at a resolution of 4 cm^{-1} from 4000 cm^{-1} to 400 cm^{-1} wavelengths.

The concentration of iron in the raw water samples, dosed water samples, and treated water samples were analyzed using Perkin Elmer's Optima 7300 DV ICP-OES.

3.1.1 Catalyst Activation and Process Start-up

DMI-65 is a manganese oxide-based catalyst. The catalyst needs to be activated before it is ready to be used for iron removal investigations. The purpose of the activation process is to remove the excess manganese dioxides left over from the infusion process that have not cured onto the catalyst surface.

The first step in the activation process was filling of the raw water tank with clean water to about 75%. Simultaneously, the catalyst was charged into the reaction tank to a bed height of 150mm. This translates to a catalyst volume of 9.68 Liters. Using the pump, water from the raw water tank was transferred into the mixing tank which eventually overflowed into the reaction tank which has been charged with the catalyst. The feed pump was deenergized when about 50% of the freeboard in the reaction tank was submerged. This was followed by injection of sodium hypochlorite into the reaction tank. The injection volume was 10ml of 12.5% sodium hypochlorite to 1 Liter of catalyst.

The catalyst was soaked in the solution for 192 hours. After the completion of the soaking process, the catalysts were removed from the reaction tank and washed under flowing water for 2 hours. To prevent unnecessary attrition of the catalyst, a 100-micron filter cloth was used as the filter media during the washing process. The catalyst was loaded back into the reaction tank for the iron removal process. The final target for the activation process was to have a manganese residual concentration in the effluent of the reactor at below 0.3 ppm as per manufacturer's recommendations (Quantum, n.d.).

4. Results and Discussion

4.1 Characterization

To obtain the baseline data, the particle size distribution of the fresh catalyst was determined by sieving the material at different sieve sizes. The particle size distribution is listed in Table 1 below. From the analysis, it shows that more than 76% of the catalyst is made up particles with sizes smaller than 850 microns while particles of 2mm or higher contributes to slightly above 2%.

Table 1: Particle Size Distribution of DMI-65

Sieve size	Distribution
< 300 micron	1.50%
300 micron - 850 micron	76.30%
850 micron - 1 mm	14.80%
1 mm - 2 mm	5.20%
> 2mm	2.20%

SEM analysis was conducted to determine the shape, size, and surface morphological structure of the catalyst. The images from the SEM observations are shown in the following diagrams.

Figure 2 below shows the image at 50x magnification. Here it can be seen that the overall shapes of the catalyst particles are not uniform, and the size varies with particle size smaller than 2 mm make up much of the catalyst.

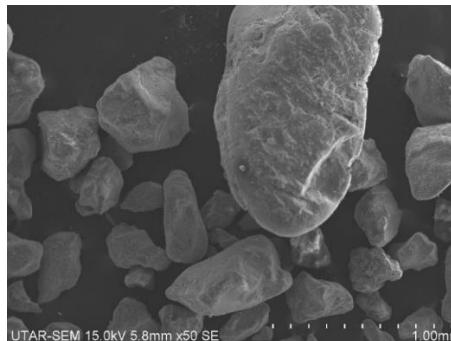


Figure 2: SEM Image of DMI-65 at 50x Magnification

This supports the investigations on the particle size distribution that shows particles larger than 2mm contribute only about 2.2% of the total mass. The high density of smaller size particles contributes to the high available surface area of the catalyst. Subsequent observations at 1000x and 5000x magnification are shown in Figure 3 and Figure 4.

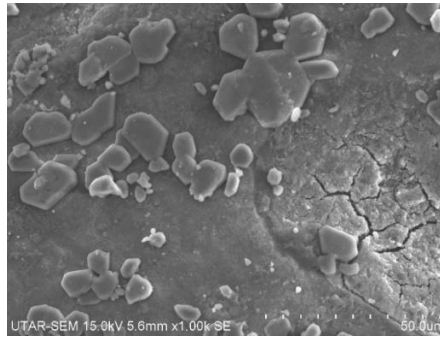


Figure 3: SEM Image of DMI-65 at 1000x Magnification

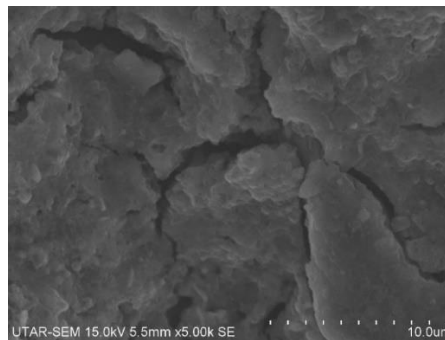


Figure 4: SEM Image of DMI-65 at 5000x Magnification

The above SEM images shows a detailed view of the catalyst surface. The surface of DMI-65 was observed to be dense with occasional flakes attached to the surface. Presence of cracks and crevices of non-uniform shape and dimension was also observed. These cracks and crevice may contribute to the enhance oxidation rate as the they provide some additional active area for the absorption of the ions onto the catalyst.

In addition to the above, EDAX analysis was also performed on the above samples and it was found that the catalyst surface is made up of 8.75% Carbon, 31.84% Oxygen, 21.87% Silica, and 37.53% Manganese by weight. This indicates that the DMI-65 catalyst is silica-based material which is infused with manganese oxides. Some of the Manganese in the catalyst are expected to leach out after the activation process during the initial treatment process. The analysis of Manganese in the treated groundwater is beyond the scope of this study.

4.2 Process Study

The results from the first round of the process study are as shown in Figure 5 below. There are two significant points that can be extracted from this. First, DMI-65 is efficient in removing iron from contaminated groundwater, even when the service flowrate is well above the manufacturer's recommended range. Second point is that the iron removal efficiency improves as the dosage of sodium hypochlorite is increased. In the above investigation, the removal efficiency improves from 97.6% at sodium hypochlorite dosage of 0.0036 milliliters/second to 98.3% when sodium hypochlorite dosage was increased to 0.0053 milliliters/second.

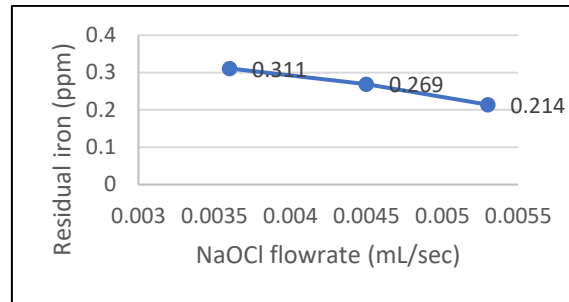


Figure 5: Iron Removal at 13.9 mL/s Feed, 12.8 ppm Fe

Similar to the first-round tests, during the second round of investigation, samples were also drawn from the raw water tank and at the outlet of the reaction tank. The results showed a similar trend to the first round of the investigation. This is depicted in the following graph.

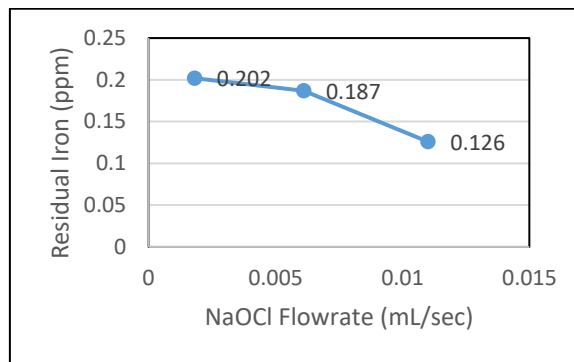


Figure 6: Iron Removal at 1.56 mL/s Feed, 7.4 ppm Fe

In the third-round investigation, samples were drawn from the raw water tank, at the outlet of the mixing tank, and at the outlet of the reaction tank. The results from the third-round investigation are tabulated in Table 2.

Table 2: Iron Removal at Various Feed Concentration

Raw Water	Pre-Reaction Tank		After Reaction Tank	
Iron (ppm)	Iron (ppm)	Removal (%)	Iron (ppm)	Removal (%)
490	463	5.5%	12.4	97.3%
871	788	9.5%	34.7	95.6%
1225	854.18	30.3%	20.58	94.5%
3672	1313.53	64.2%	25.60	98.0%

Table 2 shows that the catalyst can remove soluble iron from groundwater even at very high inlet concentrations. As clear from the table, at 490 ppm iron concentration, iron residual of below 12.4 ppm which is translated to a 97.3% removable is still achievable in the process. However, this result also shows that at this incoming iron concentration the catalyst is already overloaded as the residual iron is above the allowable concentration of 0.3 ppm. One thing to note is that, at elevated iron concentration in raw water, the uncatalyzed oxidation of the iron ion increases significantly with the increase of iron content in the raw water. As shown in Table 2, the removal efficiency increases from 5.5% to 64.2% as the iron content in the raw water was increased to 3672 ppm.

5. Conclusion

The study has shown that DMI-65 is undoubtedly capable of efficiently removing iron from contaminated groundwater in a lab environment. The study can be extended to other types of metal contaminants to determine the range of applications that are appropriate for DMI-65. Suitable techniques can then be employed to scale up the process so that it can suit industrial scale iron removal requirements.

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