REMOVAL OF IRON FROM WATER USING OXIDATION PROCESS

LIM LI PIN

A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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ABSTRACT

Ferrous iron is found naturally in groundwater. According to World Health Organisation (WHO), the maximum allowable concentration of iron in drinking water is 0.3 mg/L. However, groundwater in Malaysia especially Kelantan has elevated iron level. Groundwater with high iron content is not suitable to be consumed due to bad odour, unpleasant taste and the possibility of pipe clogging. Continuous intake of iron rich water can lead to health issue. Various technologies have been developed worldwide for remediation of iron contaminated groundwater. This work provides a review on the oxidation approach used to remove iron from groundwater, with emphasis on different types of oxidants (air, ozone, potassium permanganate (KMnO₄), sodium hypochlorite (NaOCl)) and effects of operating parameters (dosage of oxidant, pH of water, retention time). It was found that KMnO₄ has the highest iron removal efficiency up to 100 %. In addition, the evaluation indicates that the increase oxidant dosage to above stoichiometric amount can increase the iron removal efficiency. Next, it was discovered that oxidation of iron by air, ozone, NaOCl, KMnO₄ occur optimally in slightly alkaline condition. A retention time ranging from 5 to 30 minutes are sufficient to achieve desired iron removal efficiency. Other than conventional oxidation process, the recent improvement oxidation technologies (subterranean iron removal, Vyredox method) and catalytic filter materials (DMI-65, Birm, Pyrolox) to improve the conventional oxidation process for iron removal from groundwater were also evaluated. Lastly, a case study on the groundwater in Tanjung Mas, Kelantan was carried out in an attempt to identify the suitable oxidant to be used for iron removal. Thus, this study confirmed that oxidation process is applicable for iron removal in groundwater Malaysia.

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LIST OF SYMBOLS / ABBREVIATIONS

AKSB	Air Kelantan Sdn. Bhd
ANSI	American National Standards Institute
DO	Dissolved Oxygen
IWRM	Integrated Water Resources Management
GAC	Granular Activated Carbon
HOCl	Hypochlorous acid
KMnO ₄	Potassium permanganate
MLD	Mega Litres per Day
MOH	Ministry of Health Malaysia
NaOCl	Sodium hypochlorite
NGDWQ	National Guidelines for Drinking Water Quality
NSDWR	National Secondary Drinking Water Regulations
NSF	National Sanitation Foundation
OPAC	Online Public Access Catalog
TNB	Tenaga Nasional Berhad
WHO	World Health Organization
WTP	Water treatment Plant
WWF	World Wildlife Fund
UTP	University Technology PETRONAS

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Groundwater is being extensively used for potable water supply in some parts of Malaysia such as Kelantan, Perak and Terengganu (Razak, et al., 2015). While people have relied on groundwater as resource to meet the daily water demand, groundwater actually consists of some unwanted constituents and impurities. Iron naturally found in groundwater is a common issue, in which the groundwater may contain iron at concentrations up to 30 mg/L (Tawnie, et al., 2016). According to the Drinking Water Quality Standard established by World Health Organization (WHO), the maximum acceptable concentration of iron in drinking water is only 0.3 mg/L (WHO, 2004). Long term uptake of groundwater with iron concentration above the permissible limit can give negative impacts to human health and surroundings. Therefore, groundwater needs to be treated to reduce the iron concentration prior to consumption. Several iron removal technologies are available since the past few decades such as chemical precipitation, adsorption and ion exchange method (Sharma, 2001). However, these technologies have major disadvantages such as formation of extra sludge and fouling issue on ion exchange resin. Sludge handling is important in adsorption process as iron is not removed but accumulates in adsorbent phase, in which the spent adsorbent may turn out into another waste to handle (Sharma, 2001).

In recent years, oxidation process has displayed potential in iron removal from groundwater (El Azher, et al., 2008). Chemical oxidation is a treatment process which can oxidize the dissolved ferrous iron (Fe^{2+}) in water into ferric iron (Fe^{3+}) with the aid of oxidizing agents such as oxygen, ozone, potassium permanganate (KMnO₄) or sodium hypochlorite (NaOCl). The iron precipitate ($Fe(OH)_3$) produced is then filtered and removed out with simple filtration step. Chemical oxidation method is considered superior over other technologies due to its capability to remove iron from water effectively (Elsheikh, Guirguis and Fathy, 2018). In this study, treatment of iron by oxidation process with different types of oxidants will be investigated. The oxidants involved can be classified into gaseous oxidant, which are air and ozone, and liquid oxidant, which are NaOCl and KMnO₄. Different types of oxidants have their optimum efficiency at different operating parameters. To improve the feasibility of oxidants in iron removal process, an evaluation on the effect of operating parameters of oxidation process include dosage of oxidant, pH of water, and retention time for different types of oxidants will be studied. After finding out the optimum operating parameters for each oxidant, the most suitable oxidant will be selected to fit into the case study for Malaysia's groundwater condition.

1.2 Importance of the Study

The study will contribute to a better understanding on the oxidation process by comparing the efficiency of different types of oxidants to remove iron from groundwater. Also, this study will evaluate the optimum operating parameters for oxidation of iron by various oxidants to achieve high iron removal efficiency. Since groundwater is a major water supply for many rural areas in Malaysia and the maximum allowable iron concentration in water as recommended by WHO is only 0.3 mg/L, it is vital to improve the oxidation process to reduce high concentration of iron from groundwater efficiently. This can be beneficial to remote residential areas that rely on groundwater as major water supply for daily use.

1.3 Problem Statement

Lack of water supply in remote areas and increased surface water pollution problems have raised the concerns on the use of groundwater. Groundwater contamination has been a major issue in the areas where the groundwater supply is the dominant water source, such as Kelantan, the major groundwater user in Malaysia. Groundwater is highly contaminated with iron mineral as a result of natural occurrence in the aquifer. High concentration of iron in groundwater can lead to several issues such as pipe clogging and iron corrosion. Continuous intake of iron rich water can cause adverse health effects on human and damage the liver and heart especially for hemochromatosis patient. Other irritating impacts of using high iron water include itchy skin and brittle hair. Besides that, iron bacteria in water will cause undesirable metallic taste in water and make it unsuitable for drinking purpose. Therefore, various researches have been carried out to study different treatment technologies to remove iron from groundwater.

It is evidenced that oxidation is one of the reliable remediation technologies to remove iron from groundwater. Conventional oxidation process has utilized different types of oxidants and operating conditions for iron removal. Each of them has their advantages and disadvantages (Sharma, 2001). Therefore, the feasibility of different types of oxidant to remove iron from groundwater is studied. An evaluation on the optimum operating parameters for each oxidant is necessary to justify the efficiency of this technology.

1.4 Aim and Objectives

The aim of this study is to evaluate the performance of oxidation process in the removal of iron from water. The objectives of the study include:

- To evaluate the performance of different oxidants in the removal of iron from water using oxidation process.
- (ii) To evaluate the effect of operating parameters on the oxidation of iron in water treatment process.
- (iii) To evaluate the recent enhancement on the iron removal from water using oxidation process.
- (iv) To evaluate the suitability of oxidation process in large scale water treatment process in the removal of iron from water.

1.5 Scope and Limitation of the Study

Groundwater consists of various dissolved minerals include potassium, calcium, magnesium, iron, sulphate and sodium. Iron is the major concern in this project as water with high iron concentration is not safe to be consumed as drinking water. Various treatment technologies have been used around the world to remove iron from water. This research focuses on the use of oxidation method to remove iron from groundwater. Four types of oxidants are selected in this study, which are air, ozone, NaOCl, KMnO₄. The working scope of the current study is to evaluate the optimum operating conditions to improve the oxidation process. The effect of dosage of oxidant, pH and retention time are the main operating parameters that will be investigated in this research. The iron removal efficiency of oxidation process is calculated using Equation 1.1:

Iron removal efficiency (%) =
$$\frac{C_o - C_t}{C_o} \times 100$$
 (1.1)

Where

 C_0 = initial iron concentration, mg/L

 C_t = final iron concentration, mg/L

1.6 Contribution of Study

This study may contribute to convince the water treatment company that the oxidation process can be used for iron removal by providing a detailed comparison on the performance of different oxidants. Also, it may provide a basic for the optimum operating parameters in the designation of water treatment plant with large scale operation. Iron removal from groundwater is important to produce clean water for daily use.

1.7 Outline of the Report

This report consists of five chapters. Chapter 1 covers on the introduction of the study, which includes a brief introduction on groundwater in Malaysia, problem statement, objectives, scope and limitation and the contribution of the study. Chapter 2 discuss on the literature review, which includes sources of iron, iron concentration in groundwater Malaysia, and the available treatment technologies that have been investigated by other researchers. In Chapter 3, the methodology of the study is discussed to provide a better understanding on how review work is carried out. After collecting the data from different literature, Chapter 4 is used for result and discussion. The performance of oxidants, the effect of operating parameters, the recent enhancement technology and a case study will be discussed. Lastly, Chapter 5 will be the conclusion for the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is the most essential element to support the life of all living creatures in the world. According to Ritchie and Roser (2017), the global freshwater consumption surged dramatically from 500 billion m³ in the year 1901 to around 4000 billion m³ in the year 2014, and it is expected to reach a demand of 4350 billion m³ by 2040 (Tiseo, 2019). There are two main usable sources for freshwater, one is the visible surface water resources and another one is the invisible groundwater resources. Surface water exists on the land surface and can be obtained easily from lakes, ponds and rivers while groundwater is the water found under the Earth's surface. Owing to the rising water demand, groundwater has been paid substantial attention and becomes a key water source for municipal, industry and agriculture uses in many countries. Denmark is one of the countries that put continuous effort in groundwater management whereby more than 99 % of portable water in Denmark is extracted from groundwater (Jorgensen, et al., 2017). Groundwater is formed when a water table is drilled into the saturated zone of an aquifer. It is surrounded by rocks and soil and there is no air found in between the gaps. As a result, it consists of diverse dissolved minerals, organic constituents and unwanted contaminants. Among all, iron is the most common element found naturally in groundwater and the presence of iron in groundwater make it unable to be used directly as drinking water (Brown and Calas, 2011).

2.1.1 Iron

Iron or known as ferrum, is a chemical element that is symbolised as Fe. It is a transition metal that is located in the group 8 first transition metal period of the periodic table. Oxidation state determines the ability of elements to undergo oxidation and reduction. Iron can present in different oxidation states, which include the most common 0 charge (Fe), +2 charge (Fe²⁺), +3 charge (Fe³⁺) as well as the uncommon +4 charge (Fe⁴⁺) and +6 charge (Fe⁶⁺). Fe²⁺ is the reduced soluble divalent ion (ferrous ion) while Fe³⁺ is oxidized trivalent ion (ferric ion).

Solubility of iron is strongly dependent on the amount of dissolved oxygen and acidity in water. When the dissolved oxygen level is low, iron appears as ferrous ion, which is the most common form of iron found in water as it is highly soluble in water without any pH restrictions. Once the ferrous ion is exposed to oxygen, it tends to form ferric ion, which is the most stable form of iron in air. Ferric ion is soluble only in water at pH below 4.5. Beyond that, ferric ion will precipitate into ferric hydroxide (Fe(OH)₃) to form insoluble solid in water (Schloz, 2006).

2.1.2 Sources of Iron in Groundwater

Iron can be found easily in everywhere, as it is one of the most abundant elements on Earth's crust. In groundwater, the source of iron is natural occurring through weathering process. Weathering of iron bearing rocks and soils is a spontaneous process that will break down rocks and soils into bits and lead to the release of minerals in underground (Brown and Calas, 2011). Metasedimentary rocks that release pyrite minerals (FeS_2) is one of the major sources of iron (Sapari, Azie, and Jusoh, 2011b). Groundwater will actively pick up the iron mineral as water percolating through it. Therefore, underground water bounded by bedrocks is generally contaminated with iron. Moreover, the aquifer of groundwater is an oxygen-limited environment, in which the deeper the well aquifer, the lower the concentration of dissolved oxygen. Anaerobic condition in groundwater causes the surrounding iron from soils and rocks dissolves more readily in water. Hence, the concentration of iron is exceptionally high when the well is relatively deep. In addition, the slight acidic condition of groundwater due to the presence of carbon dioxide will further enhance the solubility of iron (Brown and Calas, 2011).

Other than natural occurring sources, there are other potential sources for iron contamination in groundwater. The runoff from agriculture land, the seeping of industry effluents into the ground as well as leaching of landfill chemicals will indirectly contaminate the groundwater and increase its iron concentration (Albright, et al., 2012).

2.1.3 Problems Associated with Iron

Since iron mineral is an important trace element which is required by human body for blood production, there is no direct impact on human or immediate health risk associated with consumption of low level of iron through drinking water. However, excessive intake of iron through drinking water for a long time may cause some negative impacts. Razak, et al. (2015) stated that the main reason for heavy metal poisoning is through ingestion of drinking water. Symptoms of iron overdose include stomach pain, nausea, diarrhea and vomiting. The condition is worsened when it comes to an individual who suffers from a rare genetic disorder known as hemochromatosis in which iron absorption of individual with hemochromatosis will abnormally high (Brazier, 2020). As a result, high iron concentration will accumulate in their tissues and all over the body, eventually lead to the damage of organs such as kidney, liver and heart. Consequently, individuals suffer from hemochromatosis disease will have greater risk of cancer once prolonged exposing to high dosage of iron via drinking water.

On top of human health consequences, there are other irritating effects associated with high concentration of iron in water. Utilization of high iron water for hair washing can cause fragile to hair and lead to itchy and dry scalp (Nelson, 2018). The increased of iron level in domestic water is found to be the culprit for damaged hair and hair discoloration (Pro Water Solution, 2018). While in term of skin perspective, iron can damage skin cell by clogging up the pores. Acne and eczema are the common skin infections resulted from high iron water especially for individual with allergic issue (Ewence, et al., 2011). Another hazardous issue of high iron water is the presence of iron bacteria. Iron bacteria is a type of microorganism that derives energy source from iron. It consumes iron in water and produce slime as metabolic by-product, leaving the water with reddish brown colour coupled with slimy deposits. According to Ityel (2011), drinking water with iron concentration exceeds 0.3 mg/L is noticeable by taste. Hence, water enriched with dissolved iron and iron bacteria will have a strong metallic taste and offensive odour. Metallic taste will affect food and beverage by making them less appealing.

Moreover, the problems associated with the presence of high concentration of iron become more significant when there is visible sign raised from the water supply for domestic use. When groundwater with high concentration of iron is pumped and exposed to atmosphere, dissolved iron will react quickly with oxygen and undergo oxidation process to form colloidal particle. Gad, Dahab and Ibrahim (2016) reported that iron concentration ranging from 2 mg/L to 10 mg/L tends to form rusty precipitate easily. These iron precipitates and sludges caused by iron bacteria will lead to accumulation of brown deposits in distribution system and clog the piping system. Household with pipe clogging may experience low water supply and slow draining. Consequently, regularly maintenance for piping system will be required and higher cost for distribution system will be incurred. Also, brownish iron water stains laundry, dishes and plumbing fixture (Jonathan, 2018). High iron water will cause reddish brown rust mark on fabric, clothes and sink as illustrated in Figure 2.1



Figure 2.1: Sink Stained by High Iron Water (Jonathan, 2018).

2.2 Groundwater in Malaysia

2.2.1 Production and Utilization

Hasty urbanization and rising population in Malaysia have led to drastic surge in the demand of fresh water. Sim and Murali (2020) reported that the average household consumption of water by Malaysian in 2019 was around 230 litres per person per day, which has far exceeded the minimum consumption needs of 100 litres per person per day as suggested by WHO. As the demand for water increases tremendously, clean water accessibility has become a challenge as the surface water in Malaysia is severely exploited and coupled with serious pollution issues (Mridha, et al., 2019). Therefore, water supply management in Malaysia becomes increasingly important to ensure sustainable supply of clean water. Instead of solely relying on surface water as major sources, Malaysia has implemented Integrated Water Resources Management (IWRM) to monitor the water resources as well as to emphasize on the potential of groundwater as a sustainable water resource (Suratman, 2013).

Due to the high accessibility to surface water, massive annual rainfall received, and lack of groundwater awareness, groundwater in Malaysia is still underutilized. According to a survey made by World Wildlife Fund (WWF) Malaysia (2020), utilization of groundwater in Malaysia is accounted for only 3 % while the remaining 97 % of water supply used in agriculture, household and industry are mainly obtained from surface water.

Groundwater is only used significantly in several locations in Malaysia. Kelantan, Terengganu, Perlis and Sabah are the few states that utilize groundwater as potable water supply to meet their daily demand (Razak, et al, 2015). Among all, Kelantan is reported to be the major groundwater user in Malaysia as shown in Figure 2.2:



Figure 2.2: Groundwater Usage by States from 2008 to 2017 (Jayakumar, 2019).

From Figure 2.2, it can be seen that the usage of groundwater in Kelantan had risen steadily from 2008 to 2017 (Jayakumar, 2019). According to Suratman (2013), 70 % of total water supply in Kelantan is contributed by groundwater due to the widespread of well location around the state. The main distribution area of well in Kelantan concentrates in the northern region, which include Kota

District	Existing Wellfield	Number of Wells in 1985
Kota Bharu	Kg. Puteh	18
Kota Bharu	Pintu Geng	6
Kota Bharu	Tanjong Mas	9
Kota Bharu	Kubang Krian	8
Kota Bharu	Pangkalan Chapa	11
Tumpat	Wakaf Baru	4
Pasir Mas	Rantau Panjang	3
Bachok	Kg. Chap	3
Bachok	Kg. Jelawat	1

Table 2.1: Distribution of Wells in Kelantan (Tan and Singh, 1989).

Groundwater in Kelantan is used in different sectors, which include domestic use, irrigation purpose, and industry application. Figure 2.3 illustrates the percentage of utilization of groundwater by different sectors. The pie chart in Figure 2.3 shows that 60 % of the groundwater in Malaysia in used for domestic area. Groundwater usage for industrial area accounts for 35 % while agriculture utilisation is only 5 %. Domestic usage is dominant as there are many remote villages in Kelantan solely depend on groundwater as their primary source for daily water supply due to inadequate public water supply system. Only a small minority of groundwater is used for agriculture.



Figure 2.3: Utilization of Groundwater in Different Sectors (Yaacob, 2014).

2.2.2 Groundwater Contamination Level

As more people rely on groundwater for potable use, the quality and safety of groundwater become a major concern. Groundwater contamination is accelerated by human activities such as discharging of industry effluent, spilling of underground oil, and leaking of landfill waste. The major heavy metals found in groundwater include mercury (Mg), arsenic (As), lead (Pb), manganese (Mn) and iron (Fe) (Isa, et al., 2014). Groundwater near to the radioactive waste landfill site and mining area will be highly contaminated with arsenic while groundwater near to municipal waste dumping and agriculture activity are probably high in iron and manganese content (Rizal, 2006).

In regard to this, monitoring well is generally constructed around to agriculture area, mining location, radioactive site, or landfill spot. There are 122 monitoring wells located in Peningsular Malaysia to monitor the quality of groundwater as well as to analyse the contamination level of groundwater in different potential contamination areas (Tawnie, et al., 2016). Based on the groundwater monitoring result prepared by Department of Environment Malaysia (2013), iron concentration in groundwater Malaysia is generally high and often beyond the acceptable level by 36 % to 75 %. Tan and Singh (1989) reported that iron level in shallow groundwater is mostly ranging from 0.85 mg/L to 10.95 mg/L. Table 2.2 shows the various iron concentration in different groundwater location in Malaysia.

	Average Iron	References	
Groundwater Sources	Concentration		
	(mg/L)		
UTP, Perak	2.66	Chaudhuri and Sapari, 2008	
Ampar Tenang, Selangor	1.83	Rahim, et al., 2010	
Beris Lalang, Bachok, Kelantan	0.226-14.09	Khan, et al., 2017	
Penang	5.25	Sapari, Azie and Jusoh, 2010a	
Melaka	2.39	Sapari, Azie and Jusoh. 2011b	
Kedah	2.39	Sapari, Azie and Jusoh, 2011b	

Table 2.2: Iron Concentration in Groundwater Malaysia.

Iron concentration in groundwater appears to be the highest in Kelantan. Air Kelantan Sdn. Bhd (AKSB) has further analysed on the water samples collected from groundwater located in Kg. Puteh, Kg. Chicha, Tanjung Mas and Kota Bharu. The results showed that the concentration of iron in these areas is rather high, which are ranging from 0.99 mg/L to 14.83 mg/L (A.K.S.B, 2010). In addition, Tawnie, et al. (2016) revealed that water sample collected from Tanjung Mas Water Works was once highly contaminated with iron with the iron concentration surged up to 30 mg/L in 1990. Therefore, it can be concluded that groundwater in Kelantan has always been facing a serious iron contamination issue.

2.2.3 Threshold level

Iron in water is a secondary contaminant that falls under National Secondary Drinking Water Regulations (NSDWRs) as it causes smaller effects compared to other major contaminates such as mercury and lead. According to the Drinking Water Quality Standard established by Ministry of Health Malaysia and WHO, the maximum acceptable concentration of iron in drinking water is 0.3 mg/L (MOH, 2020; WHO, 2004). The limit is made based on the taste and colour effects instead of health consideration. The concentration of iron as low as 0.3 mg/L is sufficient to turn colourless water into reddish brown and cause nuisance issues. As a result, the iron concentration above the permissible limit also not suitable for human consumption. While for aquatic life, the lethal dosage of iron is 1.0 mg/L (Kumar and Puri, 2012). Table 2.3 shows the percentage of exceedance National Guidelines for Drinking Water Quality (NGDWQ) for iron in Kelantan in the year 2017.

Groundwater Station in Kelantan	Percentage of Exceedance NGDWQ (%)		
Eastern Garment MFG no.1	75		
Panji no.1	75		
Panji no.2	75		
Pasir Mas	100		
Kampong Jembal	100		
Rantau Panjang no.1	75		
Kelab Golf & Desa no.1	100		
Kelab Golf Diraja Kubang Kerian no.1	100		
Kelab Golf Diraja Kubang Kerian no.2	100		
Bachock no.2	75		

Table 2.3: Percentage of Exceedance NGDWQ for Iron in Kelantan (Ministry of Environment and Water, 2019).

From Table 2.3, it can be seen that most of the iron concentration in Kelantan's groundwater has far exceeded the allowable threshold limit of 0.3 mg/L, which is set by MOH Malaysia. The exceedance percentage ranging from 80 to 100 % indicates that the iron concentration presents in groundwater is extremely high. High concentration of iron above 0.3 mg/L exists in groundwater can give rise to a series of issues. Since concentration of iron in groundwater Malaysia especially Kelantan has far exceeded this allowable limit, different techniques and technologies have been developed for iron removal from groundwater.

2.3 Available Treatment Technologies

Iron removal from groundwater is essential for portable water to achieve the world drinking water quality standards. Various approaches and methods have been implemented to remove iron from water in water treatment plant since the end of 19th century. These include chemical precipitation, ion exchange method, adsorption and oxidation. The mechanisms, operation process, advantages and disadvantages of these processes and operations are discussed in details.

2.3.1 Chemical Precipitation

Chemical precipitation is one of the most common technologies applied in water treatment plant to remove undesirable metallic ion constituents from water. It involved the alteration of physical state of a substance, from soluble ion in aqueous solution into an insoluble solid particle. Therefore, chemical precipitation process is usually followed by further physical water treatment operations such as sedimentation unit and filtration system to subsequently separate the unwanted solid particles from water (Hansen and Cheong, 2007). Chemical precipitation process is highly dependent on pH. The pH of the solution needs to be increased to a certain alkalinity level so that there is high enough concentration of hydroxide ion (OH⁻) available to promote the formation of metal hydroxide precipitate. In chemical precipitation process, precipitating reagent is introduced to the solution to interact with dissolved metal ions. Lime solution (Ca(OH)₂) and caustic soda (NaOH) are the common chemical agents used to precipitate dissolved metal ion to form metal hydroxides (Dahman, 2017).

Chemical precipitation is able to reduce high concentration of iron in groundwater by converting soluble ferrous ion in water into insoluble ferrous hydroxide precipitate. The ideal working pH for ion precipitation varies from case to case. Different types of dissolved metal ion precipitate into metal hydroxide particle optimally at different pHs. For iron precipitation, a study has been carried out to investigate the effect of pH on iron precipitates formed in ferrous solution (Hove, Hille and Lewis, 2008). The result shows that iron precipitates formed faster and more stable at pH 9.0 compared to a lower pH 6.0. This indicates that iron precipitation in water treatment is preferable at pH 9.0 and above. Therefore, in chemical precipitation process for iron removal,

hydrated lime or caustic soda is added to water to raise the pH to about 10.0. At this high base condition, ferrous ion, Fe^{2+} will precipitate into ferrous hydroxide, $Fe(OH)_2$. The reaction of iron removal through chemical precipitation is presented in Equation 2.1 (Barakat, 2011):

$$Fe^{2+} + 2(OH)^- \leftrightarrow Fe(OH)_2$$
 (2.1)

Original white colour of ferrous hydroxide will appear as a greenish blue precipitate when there is trace amount of oxygen. When oxygen is highly accessible, ferrous hydroxide will further oxidised to form ferric hydroxide, Fe(OH)₃, which is a reddish brown colour precipitate. These precipitations will undergo sedimentation and filtration process to separate out from water.

Iron removal through chemical precipitation is considered cost effective because the lime used is an inexpensive reagent (Barakat, 2011). Moreover, only little maintenance is needed for the process as the equipment is simple to operate and handle. However, there are several shortcomings for this technology. The treated water after chemical precipitation process is at high pH and highly corrosive due to the introduction of precipitating reagents. Therefore, additional recarbonation stage is required to adjust the pH of water back to neutral by bubbling through carbon dioxide into the water. On the other hand, chemical precipitation process causes extra sludge problem. Large amount of insoluble ferrous hydroxides that are formed after the chemical precipitation process need to be treated prior to disposal to reduce environment impact. As a result, large amount of chemicals will be required for iron-rich sludge treatment to reduce ferrous hydroxide to an acceptable level before discharging to the environment (Aziz, Adlan and Ariffin, 2008).

2.3.2 Adsorption Technology

Another common process used for iron removal in water treatment plant is adsorption, in which activated carbon is used as an adsorbent due to its highly porous characteristic. According to Cecen and Aktas (2011), granular activated carbon (GAC) has been introduced in water treatment since 1920s for the purpose of taste improving and odour removing. Nevertheless, Kouakou, et al. (2013) revealed that activated carbon used in adsorption technique has metalbinding capacity and high reliability to remove heavy metal ions especially iron and zinc from wastewater. Activated carbon traps particles and contaminants into the pores after surface adsorption. In adsorption technique, positively charged Fe²⁺ ion will be adsorbed and attached on the negatively charged surface of activated carbon (Jusoh, et al., 2005). The monolayer of Fe^{2+} ion will be oxidized in air and this reaction will be catalysed by the active carbon surface. Iron that has been oxidized will be precipitated and become hydrated iron oxide coated carbon. The adsorption capacity of iron from water is strongly dependent on the surface area, pore volume of the adsorbent and the adsorption temperature (Uchida, 2000). The higher the amount of activated carbon, the higher the iron removal efficiency can be achieved due to the increased sorption site of the adsorbent (Ismail, Harmuni and Rozainy, 2017). Besides that, adsorption technique is greatly affected by the pH of the solution as pH tends to control the solubility of metal ions and adsorption capacity of the adsorbent (Goher, et al., 2015). It was found that iron removal by adsorption with GAC occurred optimally under acidic condition around pH 5.0 (Ismail, Harmuni and Rozainy, 2017).

The major disadvantage of using adsorption technology is the formation of extra sludge (Chaturvedi, Dave, 2012). Iron is not removed but accumulated in absorbent phase. Spent adsorbent may turn into another waste to handle. Hence, the excessive sludge formed after adsorption process may require further treatment and the sludge disposal will give rise to anther environmental issue (Barakat, 2011). Activated carbon filter needs to be changed annually as its efficiency decreases over time due to the accumulation of contaminants.

2.3.3 Ion Exchange Technology

Ion exchange is another iron removal technology used in water treatment. Ion exchange process removes nitrate ions, heavy metals, as well as undesirable calcium and magnesium ions that are responsible for hardness of water. A study by Rao (2006) has found that ion exchange process which involved the application of resin, a polymer backbone where ionic functional groups are attached to it, has good selectivity towards metal ions. Resin is a cross-linked polymer that consists of well-dispersed ion-active exchange site throughout its structure. Fink (2013) stated that the conventional ion exchange resin made from

phenol, acrylates or polyamines could be further modified and designed accordingly to allow higher selectivity of specific active site towards certain metal ions. Polymeric resin will interact with the dissolved ion in the water by attracting the ion of opposite charge. The attractive force and bond strength between the attached ion and the functional group are relatively weak (Mazille, 2020). Therefore, ion exchange process occurs continuously through trapping of particular ion and releasing of another ion in water. This mechanism is illustrated in Figure 2.4.



Figure 2.4: Ion Exchange Process (Mazille, 2020).

Ion exchange process occurs when water with high concentration of iron flows through a column packed with sodium ion resin (Chaturvedi and Dave, 2012). Ferrous ion will displace the sodium ion that is originally attached to the resin and subsequently take up the empty site on the resin. Thus, sodium ion that has been displaced out will mitigate into water body. The ion exchange reaction is expressed in Equation 2.2 (Rohm and Haas, 2008):

$$2RNa + Fe^{2+} \rightarrow R_2Fe + 2Na^+ \tag{2.2}$$

Where R represents the cation resin. Sodium ion is commonly chosen for the ion exchange process as the dissolved sodium ions remain in the treated water is less harmful compared to iron. However, excessive amount of sodium ions in water also risky to individual with heart diseases (Proger, Ginsburg and Magendantz, 1942).

Ion exchange methods works optimally regardless of the pH of water (Chaturvedi and Dave, 2012). However, Kim, Zhang and Keana (2001) suggested that the water has to be maintained at pH value around 4.5 to 5.0 to ensure structural integrity of the resin so that it exhibits a high affinity for ion exchange. Ion exchange capacity depends on the sodium remaining on the resin. The higher the regeneration sodium dosage, the higher the working capacity. Therefore, regeneration process is essential when the resin bed is fully loaded with ions. Since ion exchange is a reversible process, regeneration is carried out by removing the attached ion from resin to allow resin to be reused. Iron is pushed out from the system during regeneration process. This can be done by passing through concentrated sodium chloride solution to the resin (Baipai, 2018).

The primary disadvantage of ion exchange process is that this method is only limited to water with ferrous iron concentration less than 5 mg/L (Sharma, 2001). This is because high iron concentration in water will cause accumulation and fouling issue. Ideally, dissolve ferrous iron is supposed to be removed with other cations from the ion exchange resin during proper discard operation and regeneration process. However, ferrous iron Fe²⁺ tends to undergo oxidation and form insoluble red precipitate upon exposing to air. The formation of iron precipitate will adhere and build up on the surface of ion exchange resin. As a result, ion exchanger bed will be contaminated with iron and this will affect the effectiveness for further ion exchange process. Therefore, backwash needs to be carried out frequently to strip off the iron precipitates stained on the surface of resin. In the case where the exchange medium is severely coated with iron precipitates and lead to fouling, additional chemical cleaning agent such as chelating agent may be required to clean the surface (Keller, 2004). Therefore, ion exchange process is not economically viable for groundwater iron removal due to its limitation as well as the expensive cleaning agent needed for cleaning purpose.

2.4 Oxidation

Other than chemical precipitation, ion exchange and adsorption process, oxidation is another conventional technology that has been widely adopted in water treatment plant for iron removal (Khatria, Tyagia and Rawtanib, 2017). Oxidation is a process that involves electron transferring (Shammas, et al., 2005). In water treatment plant, oxidation process is commonly coupled with a



Figure 2.5: Oxidation Process in Water Treatment Plant (Jafarinejad, 2017).

In oxidation reactor, any oxidisable substances that present in water will be oxidised to form insoluble solid (Shammas, et al., 2005). Among all, metal is the most readily element that tend to undergo oxidation as it is as an electron donor. Oxidation of metal will release electrons and it will become more positively charged. While oxidising agent is an electron acceptor, it will gain electron and lead to decrease in oxidation number. Oxidation of iron occurs readily when oxidant contacts with ferrous iron in water. Dissolved ferrous iron that is colourless in water will be oxidized into insoluble ferric iron in the presence of oxidant and further hydrolysed into ferric hydroxide precipitate according to the reaction described in Equation 2.3. Transformation of ferrous iron into ferric iron is an oxidation process that involves loss of electron. The reddish-brown ferric hydroxide precipitates produced will be screened out in a simple filtration step.

Ferrous iron + Oxidant + Water
$$\rightarrow$$
 Ferric Hydroxide Precipitate (2.3)

The main advantage of oxidation process is high iron removal efficiency as compared to other treatment technologies (Lundquist, 1999). Besides that, most of the chemical oxidants used for iron removal have powerful antibacterial effect and be able to act as strong disinfectant in water treatment plant (Villamena, 2017; Araby, Hawash, and Diwani, 2009). Hence, the dosage of disinfectant required to kill pathogenic bacteria can be reduced. The biggest drawback for oxidation process is related to its cost. The capital cost for the installation of oxidation column and filtration unit are considered high while the operating cost is highly dependent on the type of oxidant used. Since oxidation process involves introduction of oxidants, the process needs to be monitored and controlled carefully to prevent overdose of oxidants.

Oxidation of iron in water treatment plant can be carried out using liquid oxidants such as sodium hypochlorite, potassium permanganate, hydrogen peroxide or using dissolved gas such as oxygen, chlorine and ozone (El Azher, et al., 2008). The oxidants that will be focused in this study include air (oxygen), ozone, potassium permanganate (KMnO₄) and sodium hyprochlorite (NaOCl). The general advantages and disadvantages of these oxidants are tabulated in Table 2.4.

Oxidant	Advantages	Disadvantages	References
Air (Oxygen)	• Cost effective process as no chemical reagent is required.	Slow reaction and low iron removal efficiency.Lead to slime growth and sludge accumulation.	Theobald, 2014; Rozainy, Jamil and Adlan, 2015
Ozone, O3	 Does not produce persistent harmful residual. Can be used for disinfectant, odor removal and taste control. 	 High operating and facility cost. Difficulty in storage and transportation. Long term exposure can lead to breathing difficulties and respiratory diseases. 	Lunquist, 1999; Zhang, Wei and Fang, 2019
KMnO4	Highly efficient in iron removal.Complete reaction can be achieved and no by-product formed.	 Chemical cost is expensive. Monitoring of process is essential as overdosing will turn water into pinkish color and lead to health issue. 	Lunquist, 1999; Sharma, 2001
NaOCl	 NaOCl is not expensive and it is highly available in bleaching solution. Has strong disinfection property. 	 Formation of by products and carcinogenic compound like trihalomethanes (THM). Consists of offensive odor when high concentration is used. 	Lunquist, 1999; Clayton, Thorn and Reynolds, 2019

Table 2.4: Summary	for C	Dxidising	Agent A	Available	for Iron	n Removal.
			<i>G</i> · · ·			

2.5 Summary

High iron concentration in groundwater Malaysia especially Kelantan has always been a serious issue. Various remedies and technologies are essential to reduce the iron concentration. Table 2.5 summarizes the available technologies used in iron removal. Among all the iron removal technologies discussed, chemical oxidation is one of the most reliable technique used to remove iron from groundwater. There are various types of oxidants available for oxidation of iron and each of the oxidant has its own merits and demerits. Also, different oxidants have different iron removal efficiency under different operating conditions. Thus, an evaluation on the use of different oxidants to remove iron from groundwater and the effects of operating parameters were carried out.
Treatment Technologies	Effectiveness	Advantages	Disadvantages
Chemical Precipitation	Moderate	Cost effective.Simple operation.Low maintenance.	 Cause extra sludge problem and lead to the need of sludge treatment. The process is highly pH dependent.
Adsorption Technology	Moderate	Simple operation and low maintenance.No detrimental substance is added to the water.	Formation of extra sludge.Discharge of spent adsorbent cause pollution.
Ion Exchange	high	 Complete iron removal can be achieved. Iron exchange resin bed can be regenerated. Softening of iron can occur simultaneously. The effectiveness is not affected by pH of water. 	 Limited to water with low concentration of iron. Fouling issue and clogging tend to occur. Expensive cleaning agent is required.
Oxidation	High	Can effectively remove iron from water.Oxidants used have multifunction as disinfectant.	 High capital cost. Operation cost depends on the oxidizing agent used. Require constant monitoring on the process.

Table 2.5: Available Treatment Technologies.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Framework for Methodology of Literature Review

A literature framework is drawn as shown in Figure 3.1 to provide a comprehensive understanding on the structure and overview on the scope of study.



Figure 3.1: Literature Framework.

3.2 Sources of Literature

There are two main approaches to collect data, which are quantitative and qualitative research. In quantitative research, words are turned into numerical data and being analysed through statistical analysis. While in qualitative research, the data is collected through observation, interpretation or visual analysis (Pickell, 2019). In this study, both data collection methods were employed. For quantitative method, different graphs were generated to study the operating conditions of oxidation process. For qualitative research, document analysis was carried out to understand and explain on the background of the study, which includes groundwater in Malaysia, oxidation mechanism of iron, advantages and disadvantages of different methods. The data were reviewed and interpreted in order to create new ideas, opinions and discussions.

It is vital to select suitable literature sources during discussion. There are several types of literature sources, which can be divided into primary, secondary and tertiary resources. Primary source of literature refers to the first hand and original documents such as newspapers, manuscript and government publications. Neither modification nor amendment is being done on the primary sources. Hence, it can provide intact and reliable information to readers. In addition, primary sources act as supporting evidences to ensure the argument is convincing. However, solely depending on primary resources can be time consuming as the information is limited. Further exploration is needed to find out different perspectives of views on the topic. For secondary source of literature, it includes review papers, journals, textbooks or articles that have been interpreted or analysed by researchers (Dudovskiy, 2019). In secondary resources, researchers and experts will summarize the information together with their comments and opinions. As a result, a vast amount of information that cover different insights and perspectives can be obtained and collected from secondary resources. While for tertiary resource, it extracts the important information from primary and secondary data. Library catalogue, abstract and databases are the examples of tertiary resources and they appear as the summary and simple version for primary and secondary data (Streefkerk, 2018).

All of the sources were being used in this study. Primary sources were used as the references to support the discussions as they are closest to the original information. Secondary sources were used to analyse the literatures and the research materials in different standpoints. Abstract of relevant journals was read to have a quick overview on the literature.

3.2.1 Searching Platform and Strategy

After understanding the objectives, problem statement and scope of study, online resources were used to find the relevant data. UTAR library E-database was the main source used to find electronic materials such as journals, articles and e-book. In UTAR library OPAC, one can browse the relevant journals through title search, author search or keyword search. Among all, keyword search strategy was being used frequently. Keyword was entered into the database research box. A phrase of 2 to 4 words was used instead of a single word to avoid false match. At the same time, the synonyms of the specific terms were listed down to broaden the scope and ensure effective result search (Binghamton University Libraries, 2021). Table 3.1 shows the samples of keywords that were used to find the relevant paper based on the objective of the study.

Information				
To look for the distributions and usage of				
groundwater in Malaysia.				
To find out the contamination level of iron in				
groundwater.				
To look for the available treatment technologies for				
oxidation of iron.				
To look for the mechanisms of oxidation of iron in				
groundwater and the equation for the process.				
To look for the different types of oxidants with their				
advantages and disadvantages.				

Table 3.1: Keywords Used to Find Information.

Other than Utar library database, other searching platforms include Google Scholar, Wiley Online Library, Science Direct and Research Gate were also utilized to look for more relevant information.

3.3 Data Screening and Sorting

Initial abstract reading was carried out on the literatures and articles found. Once the data from the abstracts was found under the scope of the study, full text screening was further conducted to extract relevant data. The informative literatures were jotted down and grouped into a folder. Excel database was used to arrange and sort the relevant literatures to ensure tidiness of information. Different parameters that consisted of author, year of publication, type of oxidant used and iron removal efficiency were extracted from the literatures. Then, the information was recorded and filled in the column as shown in Figure 3.2. By having Excel database, the specific articles or journals were traced back easily without re-read again the journals. Also, the searches that have been performed were recorded down systematically to avoid repetitive work.

Author	Year of Publication -	Type of Oxidants Used -	Iron Removal Efficiency (%) -	Remarks/Findings	Link/Doi
Sanusi, et al.	2016	air (aeration-cascade aerator)	Not available	Iron removal efficiency is affeted by water flow rate.	http://dx.doi.org/10.4028/www.scientific.net/MSF.857.509.
Syazwan, Rozainy, and Jamil	2020	air (aeration-cascade aerator)	89.69	Higher dissolved oxygen level in water improve oxidation of iron.	10.1088/1757-899X/864/1/012006
Bordoloi, et al.	2013	$\rm KMnO_4$	98	KMnO ₄ is efficient oxidant in iron removal.	10.1016/j.jhazmat.2013.06.017
Araby, Hawash, and Diwani	2009	ozone	90	Increased dosage of ozone leads to higher iron removal efficiency.	10.1016/j.desal.2009.05.006
Reckhow, et al.	1991	ozone	Not available	Oxidation of iron by ozone occurred in a period of 5 minutes.	10.1080/01919512.1991.10555708

Figure 3.2: Excel Database for Data Organisation.

Next, Citavi referencing tool was used for references management. Online database was imported easily by typing in the specific identifier such as DOI or ISBN into the space provided as shown in Figure 3.3. The citation style could be efficiently adjusted accordingly. At the end of the write up, a list of references that was arranged alphabetically in the desired Harvard style was generated.

Retrieve reference by ID - Cloud pro	ject - Citavi				:
Retrieve references by ident Manual entry: Text from Clipboard Import file	ifier				Manual entry Type a single identifier (ISBN, DOI, or PubMed ID) and press Enter or click Add. Searching in: • The British Library
Add					Library of Congress
Identifier	Author or editor	Trite			Click here to select other catalogs.
			Add to project	Close	

Figure 3.3: Database Importing in Citavi Referencing Tool.

There were certain criteria and requirements to achieve in order to extract the useful information among various literature collected. The common criteria were listed as below:

- (i) Literature that has been published in the last 5 to 10 years (2011 2021) were prioritized.
- (ii) Literature must be written and published in English. Other languages were not considered during literature collection.
- (iii) Literature must relevant to the scope of study, which is oxidation of iron.
- (iv) Literature must have the list of authors, publication information and proper citation of the details in their content to ensure reliability of research.

3.4 Data Extraction and Analysis

Different literatures focus on different aspects of the study. Therefore, data extraction and analysis were essential to obtain the desired findings from various papers. Based on the first objective, which was to investigate the performance of oxidants in iron removal, four types of oxidants were studied. Hence, the literatures which included air, ozone, KMnO₄ and NaOCl as the oxidant were considered only. All kind of studies for the configuration of the process were taken into account, including lab scale study, pilot plant or column study. For the second objective that focused on the operating parameters of the

oxidants, the information from the literature which investigated the effect of dosage of oxidant, pH of water and retention time on the iron removal efficiency were extracted. For the third objective that studied on the recent enhancements for iron removal, Vyredox technology, subterranean iron removal method and catalyst enhancement were included.

3.5 Presentation of Literature Review

There are different approaches for presentation of review paper, such as grounded theory, narrative analysis, meta-ethnography, frequency analysis or meta-analysis (Haradhan, 2018). Narrative structure presentation was employed in the study to ensure the data obtained were described in an order of review paper for better understanding (Constant and Roberts, 2017).

Besides, there are different ways to arrange the outcomes of review paper, either by category, by section, by author or by timeline. In this study, the results obtained from various literatures were presented by category based on the objectives of the study. By writing in category, the flow of the study was linked smoothly and easier for reading.

CHAPTER 4

RESULTS AND DISCUSION

4.1 Types of Oxidants

Iron in groundwater can be removed through oxidation process with the aid of oxidant. Oxidant is a substance that has the ability to oxidize another reactant. It acts as an electron acceptor to receive electron from other substances and itself will undergo reduction process. Hence, the oxidation number of oxidants will reduce after the reaction. Generally, soluble ferrous iron in water will undergo oxidation to produce ferric iron. Ferric iron will be further hydrolysed to form insoluble ferric hydroxide that can be removed via filtration. Different types of oxidants can be used in iron removal process. Amongst the popular oxidants are such as gaseous oxidants (air and ozone) and non-gaseous chemical oxidants (KMnO₄ and NaOCI). The choice of oxidants in iron removal treatment process is greatly dependent on their oxidizing power and suitability.

4.1.1 Air (Oxygen)

Iron undergoes oxidation easily in the presence of atmospheric oxygen. Aeration is one of the oldest treatment methods used to remove iron from groundwater since 1874 in Germany. It makes use of the atmospheric air as the oxygen source to transfer oxygen into water and increase the dissolved oxygen level in the water to oxidise metals or other volatile organic compounds (Rozainy, Jamil and Adlan., 2015). Dissolved oxygen is essential to oxidise the soluble iron from ferrous state to insoluble ferric state. Since there is no additional chemical compound involved during the process aeration is classified as physical treatment technology. Aeration process is carried out by continuously pumping the air into an aeration tank that contains the iron rich groundwater (Krupinska, 2020). During the process, the water is aerated to oxidise ferrous iron into insoluble ferric iron to allow it to be filtered out from the water. The oxidation of ferrous iron together with the hydrolysis of ferric iron have been expressed by Kitaeva, et al. (2019) as shown in Equation 4.1:

$$4Fe^{2+} + O_2 + 10H_2O \to 4Fe(OH)_3 + 8H^+ \tag{4.1}$$

Based on the equation, the calculated stoichiometric amount of oxygen that is required to oxidize 1 mg/L of ferrous iron is 0.1433 mg/L.

Dissolved oxygen level in aeration treatment process is greatly affected by the water flow rate. When the water flow rate is too low, there will be insufficient of dissolved oxygen to oxidise the large amount of ferrous iron in the water. However, when the water flow rate is too high, the water will become saturated with dissolved oxygen. Water with high amount of dissolved oxygen will lead to corrosion of piping system (Jung, el al., 2009). As a result, constant monitoring is required to control the water flow through the process to allow optimum oxidation to occur for iron removal.

The main advantage of air as the oxidant in aeration treatment is that it is an inexpensive process as there is no involvement of chemical reagent. Since it is a natural process without chemical reagent to speed up the reaction, aeration can be slow compared to chemical oxidation of iron (Lundquist, 1999). The retention time for aeration process should be at least 30 minutes to allow the water to be adequately treated (WesTech Engineering, 2017). Besides that, aeration is not effective for the removal of iron that is complicated with organic or humic compounds as oxygen in air is not a powerful oxidant that able to break the complex molecule bonds (Chaturvedi and Dave, 2012). This implies that aeration alone is not able to oxidize ferrous iron completely. Thus, aeration is always recommended to serve as a pre-treatment process or combine with other chemical oxidation for water with iron concentration above 5 mg/L to save the cost for chemical oxidants (Azher, 2008). An aeration tank is needed to allow complete oxidation between iron and oxygen. The higher the concentration of iron in water, the larger the aeration tank is required (Minnesota Rural Water Association, 2020). Also, aeration method tends to promote the growth of slime and bacteria on the aeration tank (Theobald, 2014). The growth of microorganisms and pathogenic bacteria due to the presence of oxygen can cause offensive odour and taste to the water. Hence, strict inspection and maintenance should be carried out regularly to control the growth of the slime and microorganisms. Aeration tank and equipment should be cleaned periodically to prevent sludge accumulation as well as to remove the sticky layer of slime (Swistock, 2019).

4.1.2 Ozone

Ozone is a colourless gas that made up from three oxygen atom. However, it is a more powerful oxidizing agent compared to oxygen, with an oxidation potential of 2.07 V (Vercellotti, 1988). The most distinguishable characteristic between ozone and oxygen is the fishy smell found in ozone gas (Wei, et al., 2017). Ozone is formed when oxygen or air passes through a generator that consists of two electrodes. High voltage electricity from the electrodes will impose electron emission and the collision between electron and oxygen atom will lead to the formation of ozone as shown in Figure 4.1.



Figure 4.1: Formation of Ozone via Electrical Discharge (Putri, Oktiawan and Syakur, 2020).

Ozone is commonly used to improve water quality as it dissolves readily in water to perform instant reaction with any soluble compounds presented in the water (Bocci, 2011). Owing to its reliable antibacterial activity and outstanding oxidising potential, ozone is widely employed in water treatment plant as a disinfectant to kill waterborne pathogens and as an oxidising agent to oxidise heavy metal ions into insoluble solids (Araby, Hawash, and Diwani, 2009). In water treatment plant, ozone treatment system composes of an ozone generator, a contact chamber and a destructive unit as shown in Figure 4.2. Air or pure oxygen is passed into the ozone generator as the feed gas. High voltage ozone generator will impose electricity and energy to convert oxygen into ozone. Oxygen molecule will be split into single atom resulted from electrical discharge and the single oxygen atom will subsequently collide with another oxygen molecule to form ozone (Summerfelt, 2013). Ozone produced from generator will be transferred into a contact chamber to mix with untreated water for reaction to occur. Contact chamber is mechanically agitated to create turbulence and bubbles to ensure uniform mixing between ozone gas and water (U.S. Environmental Protection Agency, 1999). The greater the flow rate of untreated water enters into the contact chamber, the better the mixing between gaseous ozone and water. After the reaction, ozone residue or the off gas will be sent to destructive unit to destroy ozone molecules before releasing into environment. Treated water will be discharged and passed to subsequent filter facilities.



Figure 4.2: Schematic Diagram for Ozone Treatment Process (U.S. Environmental Protection Agency, 1999).

. Ozone is a highly reactive and unstable compound that tends to dissociate naturally in water in a very short period of time. Therefore, the oxidation of iron using ozone occurs rapidly in less than 5 minutes (Lundquist, 1999). The reaction mechanism between ferrous iron and ozone gas is represented in Equation 4.2 (Araby, Hawash, and Diwani, 2009):

$$2Fe^{2+} + O_3 + 5H_2O \to 2Fe(OH)_3 + O_2 + 4H^+$$
(4.2)

Based on Equation 4.2, 0.43 mg/L of ozone is required to oxidize 1 mg/L of ferrous iron.

Loegager, et al., (1992) have studied on the reaction mechanism between ferrous iron and ozone in acidic condition. Ferrous ion (Fe²⁺) reacts with ozone to produce ferryl ion intermediate (FeO²⁺). Excess ozone that presents in water will facilitate the ferryl ion intermediate to produce ferric ion (Fe³⁺). This is known as direct reaction, in which the oxidation occurs via ozone molecule due to its stability in acidic state. This mechanism can be explained by Equations 4.3 and 4.4:

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$$
 (4.3)

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH + OH^-$$
 (4.4)

In contrast, Galdeano, et al. (2018) have pointed out that indirect reaction tends to occur when water is in alkaline state. In indirect reaction, free hydroxyl radical (*OH) is the predominant reactive species that is responsible for oxidation to occur. Hydroxyl radical is a powerful oxidising agent formed when hydroxide ion in water reacts with ozone and initiates the chain propagation step for oxidation to occur (Glaze, et al., 1987). Thus, it is arguable that iron reacts directly with ozone or with the free hydroxyl radical.

Ozone is generally used for in situ chemical oxidation process and prepared onsite. The main advantage of ozone as oxidising agent is that no carcinogenic side product or residue will be produced (Lundquist, 1999). However, ozonation is not a cost-effective process due to high energy consumption of ozone generator and expensive facilities cost (Mundy, et al., 2018). In addition, due to the highly reactive characteristic of ozone, experienced operator is needed to handle complex treatment unit in water treatment plant. Regular checking and maintenance should be conducted by specialist to prevent ozone leakage. The effects associated with inhalation of ozone include coughing, breathing difficulties, throat irritation and other respiratory diseases (Zhang, Wei and Fang, 2019). In term of environment perspective, high amount of ozone presents in environment is undesirable as it is a harmful air pollutant that will affect the ecosystem and damage the vegetation. Therefore, decomposition stage for ozone residue is essential to break down the ozone molecule into its original state (Batakliev, 2014). Also, corrosive nature of ozone is another downside. Ozone tends to corrode piping system in water treatment plant. Hence, other than the cost for expensive ozone generator, facilities that deal with ozone have to opt for expensive ozoneresistant materials. Consequently, chemical oxidation with ozone is not economically viable as the operational and capital cost for ozone treatment unit are relatively high.

4.1.3 KMnO₄

Potassium permanganate, KMnO₄ or its IUPAC name potassium manganate (VII) is a chemical compound with a mixture of potassium hydroxide and manganese oxide. It is a strong chemical oxidizing agent which appears in bright purple colour. Owing to the powerful oxidising characteristic, KMnO₄ is widely used in medical field, environment application, and the most common water treatment industry. In drinking water treatment industry, chemical oxidation with KMnO₄ serves as a pre-treatment process prior to filtration process (Elsheikh, Guirguis and Fathy, 2018). KMnO₄ is intensively used to remove unpleasant smell in water such as nasty hydrogen sulphide odour, to control the growth of microorganisms and to reduce undesirable metal ion concentration especially iron and manganese (Cherry, 1962). In iron removal process, KMnO₄ will be injected to the water holding tank through a chemical feed pump. Injection can be performed either in continuous mode or discontinues way depending on several factors such as the dosage required, capacity of the tank, quality of water as well as the initial concentration of iron (Cherry, 1962). The tank is agitated to ensure uniform dispersion of KMnO₄ in the water body. Upon oxidation process, dissolved ferrous ion (Fe^{2+}) in water will be converted into ferric ion (Fe³⁺). Ferric ion in water will quickly react with hydroxyl group and precipitate into insoluble ferric hydroxide (Fe(OH)₃) (Phatai, et al., 2014). The suspended solid particles are then physically settled out through filtration

process. The reaction between ferrous iron and KMnO₄ is represented in Equation 4.5 (Vercellotti, 1988):

$$3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + 5H^+ + K^+ \quad (4.5)$$

Based on Equation 4.5, the stoichiometric dosage of KMnO₄ required to oxidize 1 mg/L of ferrous iron is 0.94 mg/L. Nevertheless, the study by Vercellotti (1988) has suggested that stoichiometric demand for KMnO₄ of 1.5 mg/L is favourable to oxidize 1 mg/L of ferrous iron as the excess KMnO₄ is needed for the regeneration purpose on the downstream greensand filter media.

A leading advantage of KMnO₄ is its high efficiency in iron removal. In a field study conducted by Bordoloi, et al. (2013) in Assam village India, the highest initial iron concentration of 5.0 mg/L in the area was successfully reduced to less than 0.1 mg/L by oxidation using KMnO₄ at pH range of 7.0 to 7.5. Superior result of 98 % iron removal efficiency was obtained without leaving harmful residue in the treated water. This implies that KMnO₄ is efficient and safe to be used. Although KMnO₄ can effectively remove iron from water and is more superior to other oxidants, there are some weaknesses need to be taken into consideration. Firstly, it is always a challenge for experts to determine the exact amount of KMnO₄ required (Khadse, Patni and Labhasetwar, 2015). The dosage of KMnO₄ required in water treatment process is dependent on the contamination level of raw water and the specific purpose of the treatment. The amount of KMnO₄ required to remove iron from groundwater will be greater than that from wastewater. In addition, odour removal may require higher dose of KMnO₄ compared to iron removal. As a result, it is essential to determine the appropriate dosage. Regular monitoring is important to control the dosage. Over dosing of KMnO₄ will turn water into pinkish colour. Pinkish colour water that enters the distribution system will stain on the surface of utensils and clothes (Sharma, 2001). Also, KMnO₄ is extremely poison and dangerous to human consumption. Ingestion of KMnO₄ can lead to gastrointestinal and respiratory distress (Willhite, et al., 2013). Therefore, it is compulsory to ensure that no residual of KMnO4 is left in the treated water after iron removal. Whenever KMnO4 is used in water treatment, a post water

treatment filter with sodium metabisulfite is suggested to neutralize the KMnO₄ in water before it can be used (Miller, 2017). Lastly, iron removal by KMnO₄ is not cost effective as KMnO₄ is an expensive chemical compound (Cherry, 1962). Utilization of KMnO₄ for groundwater iron removal may lead to high operational cost.

4.1.4 NaOCl

Sodium hypochlorite, NaOCl is a strong oxidant which is made up of sodium atom, oxygen atom and chlorine atom. It is a white powder compound that dissolves readily in water to form a pale-yellow solution with a strong, irritating smell. Alkaline sodium hypochlorite solution is prepared through electrolysis of sodium chloride solution (Brandt, 2017). Sodium hydroxide (NaOH) and chlorine gas (Cl₂) that co-produced during the electrolysis process will mix together and yield the main product sodium hypochlorite (NaOCl) and a byproduct sodium chloride (NaCl). The process is represented in Equation 4.6 (May, 2017):

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$
 (4.6)

NaOCl has a wide range of applications. It acts as a strong disinfectant that commonly used in sewage treatment, water purification and swimming pool sterilization (McKeen, 2012). In water treatment industry, NaOCl is primarily used in chlorination process to inhibit the growth of pathogenic microorganisms that cause waterborne diseases. Arias, et al. (2014) has evaluated on the microbial inactivation of NaOCl. When bacteria, viruses, mould and fungal spores are exposed to sufficient amount of NaOCl in water, NaOCl can effectively disrupt their DNA, break the chemical bond and degrade the organic molecules, leaving the microorganisms unable to perform vital cellular functions and settle out from water through filtration system. On the other hand, Lee (1988) claimed that NaOCl is capable to remove iron from groundwater. Similar to previous chemical oxidation process, NaOCl will react with iron in water by oxidizing the soluble ferrous ion into ferric ion. Ferric ion will then undergo hydrolysis to form insoluble ferric hydroxide precipitate and filter out

as usual. NaOCl dissociates easily in water to produce hypochlorous acid (HOCl) as shown in Equation 4.7 (Zinati and Shuai, 2005):

$$NaOCl + H_2O \leftrightarrow HOCl + NaOH \tag{4.7}$$

HOCl is responsible for the oxidation of iron (Zinati and Shuai, 2005). The decomposition of NaOCl and the concentration of HOCl are greatly dependent on the pH of water. The lower the pH of water (between pH 2.0 to pH 8.0), the higher the percentage of HOCl formed. However, oxidation of iron by NaOCl occur optimally at a pH of 6.5–7.5 (Khadse, Patni and Labhasetwar, 2015). This is because the lower the pH, the longer the time required for completion of the oxidation reaction. The optimum pH for iron removal should be maintained at near neutral so that NaOCl can effectively remove ferrous iron and pathogenic bacteria at the same time. The reaction between HOCl and ferrous iron in water is shown in Equation 4.8 and Equation 4.9 (Folkes, et al., 1995):

$$Fe^{2+} + HOCl \rightarrow Fe^{3+} + *OH + Cl^{-}$$

$$\tag{4.8}$$

$$Fe^{2+} + *OH \to Fe^{3+} + OH \tag{4.9}$$

Equation 4.8 and Equation 4.9 can be further expressed as the overall reaction between ferrous iron and NaOCl, which is shown in Equation 4.10 (Lee, 1988):

$$2Fe^{2+} + NaOCl \rightarrow 2Fe^{3+} + Cl^- + NaOH \tag{4.10}$$

Based on the above equation, the stoichiometric dosage of NaOCl required to oxidize 1 mg/L of ferrous iron is 0.66 mg/L.

The main advantage of using NaOCl to remove iron from water is low chemical cost (Lundquist, 1999). Besides that, NaOCl can act as a strong disinfectant. Villamena (2017) reported that HOCl is exceptionally effective in microbial inactivation. Neutral property of HOCl can penetrate into the negatively charged microorganisms and kill them easily. The drawbacks of NaOCl include the strong offensive odour and the formation of chlorine derivatives that might pose harm to human. Trihalomethanes (THM), which is carcinogenic in nature is one of the most unwanted by-products produced when free chlorine reacts with organic compound in water (Clayton, Thorn and Reynolds, 2019). Hence, additional de-chlorination step may be required after oxidation with NaOCl to ensure the water is safe to be consumed. Also, NaOCl is an unstable compound that decomposes easily in acidic condition or elevated temperature. Hence, extra care should be taken during transportation and storage of NaOCl.

4.1.5 Comparison for oxidants

Different oxidants have different characteristics. The comparison for oxidants can be done in a variety points of view. In this study, oxidants were compared in term of oxidizing potential, ability to deal with organic compounds and the effectiveness in iron removal.

4.1.5.1 Oxidising Potential

The oxidizing availability of an oxidant is related to the oxidation potential. The oxidation potential for the above-mentioned oxidants is summarized in Table 4.1. From the table, the effectiveness of oxidants based on the oxidation potential is following a sequence of air $< \text{KMnO}_4 < \text{NaOCl} < \text{ozone}.$

Oxidant	Oxidation potential (V)	pН	References
Air (oxygen)	0.82	7.0	Krupinska, 2020
Ozone	2.07	7.0	Koppenol, 1982
KMnO ₄	0.86	7.0	Krupinska, 2020
NaOCl	0.94	7.0	Biohydrox, 2016

Table 4.1: Oxidation Potential for Different Oxidants.

4.1.5.2 Ability to Oxidize Organic Compounds

The presence of organic substances in the groundwater will retard the ability of various oxidants in iron removal process as the organic substances tend to react with iron to form iron complex compound, which is harder to be oxidized as compared to ordinary ferrous iron. The effectiveness of oxidation of complex ferrous iron into ferric iron by oxygen, chlorine and ozone were greatly inhibited by the presence of organic compounds while KMnO₄ shows minimal interference (krupinska, 2020; Reckhow et al., 1991). This is further supported by the study of Knocke, Conley and Benschoten (1992), which proved that KMnO₄ has the ability to remove complex iron in water by breaking the carbon carbon double bonds and oxidizing functional group. However, higher dosage and longer retention time are required (Lundquist, 1999).

4.1.5.3 Effectiveness of Oxidants in Iron Removal

According to Lundquist (1999), ozone, KMnO₄ and NaOCl are effective and fast in the removal of iron from water while aeration is less effective and slow. In a lab scale aeration study conducted by Syazwan, Rozainy, and Jamil (2020), with 6.2 mg/L of initial iron concentration, the highest iron removal efficiency achieved by using cascade aerator alone without filtration treatment was ranging from 39.95 % to 45.20 %. However, a big contrast was observed in the study of Radzi, et al. (2020) and Sim, et al. (2001), where the iron removal efficiency by aeration can be as low as 7 % and as high as 99 %. In the study of Radzi, et al. (2020), aeration was carried out using Gravitational Aeration Tower System (GATS) and the results were obtained without any filtration involved. Hence, the iron removal efficiency was very low. While in the study of Sim, et al. (2001), the high iron removal efficiency obtained was because of the use of limestone packed column together with sedimentation unit. Thus, utilization of air as the oxidant can have a wide range of iron removal efficiencies depending on the configuration of the process.

For ozone, it is a more effective oxidant compared to oxygen due to its unstable molecular structure (Water quality Association, 2008). High iron removal efficiency up to 96.5 % was observed in the experiment conducted by Araby, Hawash and Diwani (2009) to remove iron by ozonation. In addition, KMnO₄ and NaOCl are highly effective oxidants, as stable iron removal efficiency of 100 % and 88 % were reported respectively (Elsheikh, Guirguis and Fathy 2018; Kan, et al., 2012). The reported performances for the oxidants are tabulated in Table 4.2.

Oxidant	On anoting Conditions	Iron Concentration (mg/L)		Maximum Iron Removal	Defenences
	Operating Conditions -	Initial Final		Efficiency (%)	Kelerences
Air	Cascade aerator	6.12	3.35	45	Syazwan, Rozainy, and Jamil,
(oxygen)	Oxidant dosage: Not available				2020
	рН: 6.5				
	GATS	4.90	4.56	7	Radzi, et al., 2020
	Oxidant dosage: 6.43 mg/L				
	pH: 6.79 to 7.01				
	Limestone packed column	40.0	< 0.3	≈99	Sim, et al., 2001
	Oxidant dosage: Not available				
	pH: 6.65 to 7.72				
Ozone	Oxidant dosage: 3 mg/L	2.60	0.10	96	Araby, Hawash and Diwani,
	pH: 8.0				2009
KMnO ₄	Oxidant dosage: 4 mg/L	1.50	0.00	100	Elsheikh, Guirguis and Fathy,
	pH: 7.0				2018
NaOCl	Oxidant dosage: > 3mg/L	0.65	0.08	88	Kan, et al., 2012
	pH: > 7.0				

Table 4.2: Performance of Different Types of Oxidants.

4.2 Configuration of Oxidation Process

The configuration of the treatment system for iron removal from groundwater is depending on the types of oxidants. In general, two types of configurations are available, which are for gaseous based oxidant (air, ozone) and liquid based oxidants (KMnO₄, NaOCl).

4.2.1 Configuration for Gaseous Based Oxidant

The general sequence of the treatment system using gaseous based oxidants, which are air and ozone is shown in Figure 4.3 (Sim, el al., 2001; Wei, el al., 2017). Incoming water with iron concentration normally less than 10 mg/L will enter the reaction unit for oxidation to occur. A blower or a packed column is mainly used as the reaction unit for gaseous based oxidant to ensure uniform gas liquid mixing between water and gaseous oxidants. It could be an aeration tank or a reactor that mix the contaminated water and the injected ozone. After the oxidation reaction, ferrous iron will be oxidized into insoluble ferric iron and form ferric hydroxide precipitate. The water will be passed to subsequent separation unit to separate out the iron precipitates. Sedimentation, filtration and adsorption are the commonly used techniques. Finally, the treated water with low iron concentration and free of solid precipitates will leave the separation unit is ready to be used.



Figure 4.3: General Sequence of Oxidation for Gaseous Based Oxidant.

Gas liquid contact between water and gaseous based oxidant is the most important parameter to ensure the effectiveness of the oxidation process. For aeration, it can be carried out using an aerator or a vessel to improve the mass transfer between air and water. The higher the oxygen level in water, the higher the rate of oxidation of iron. There are different types of aerators used in water treatment plant, which include gravity aerator, spray aerator and diffused aerator. In a recent study by Syazwan, Rozainy, and Jamil (2020), cascade aerator, which is an example of gravity aerator, was found to be useful in removing iron from groundwater. Cascade reactor has stepped spillway configuration as shown in Figure 4.4. In cascade aerator, water flows down steeply due to gravity. Air will be inducted naturally into the water to enhance the mass transfer as water falls down from step to step.



Figure 4.4: Cross Sectional Side View for Cascade Aerator (Azman, et al., 2018).

In addition, various studies have also been done on the effect of flow rate on the efficiency of cascade aerator. In an experiment conducted by Rathinakumar, Dhinakaran and Suribabu (2014), it was reported that when the flow rate of water was increased from 180 L/min to 1260 L/min, higher aeration efficiency was observed in the cascade aerator due to the increased shear force between gas and water. More bubbles will be created under the turbulence effect and hence increase the surface area for mass transfer of dissolve oxygen. The higher the aeration efficiency, the higher the rate of oxidation of iron. However, in the pilot study of Sanusi, et al. (2016) at the flow rate of 10 L/min, 25 L/min and 40 L/min using cascade aerator, it was found that the percentage of iron removal was optimum at the flow rate of 25 L/min instead of the highest flow rate of 40 L/min. This indicates that the efficiency of aeration tends to experience a downturn after reaching the maximum water flow rate. This phenomenon was explained by Syazwan, Rozainy, and Jamil (2020), which

stated that at an excessively high flow rate condition, coalescence of bubbles may occur. The bubbles will move upward and reduce the contact time for mass transfer. As a result, the level of dissolved oxygen in water reduces significantly.

Oxidation process by ozone in water treatment plant is commonly conducted in a bubbling reactor due to its simplicity and high interfacial area to enhance the mass transfer between ozone gas and incoming raw water (Wei, el al., 2017). Figure 4.5 shows the counter current flow of bubble column used in water treatment plant.



Figure 4.5: Schematic Configuration of Microbubble Ozone Reactor (Wei, el al., 2017).

Ozone gas produced from ozone generator is injected continuously to the bottom of reaction unit. Microbubble generator is used to break the bubbles into smaller size to increase the surface area for mass transfer. As the ozone gas slowly rises up and contacts with the incoming groundwater from the top of reactor, ozone gas dissolves in water and initiates the oxidation of ferrous iron into ferric iron in ozone reactor. After a 15 minutes of hydraulic retention time as suggested by Putri, Oktiawan and Syakur, (2020), the effluent will leave the column for off gas treatment.

4.2.2 Improvement Made for Gaseous Based Oxidant

To improve the gas liquid mixing between gaseous oxidants and water, a study by Azman, et al. (2018) showed that increased number of steps and height for cascade aerator will increase aeration efficiency. Sufficient height and slope of elevation are vital to facilitate in the movement of water. As water flows down from top of cascade, potential energy will change into kinetic energy. Hence, the higher the step of cascade, the greater the kinetic energy will be experienced by water. Consequently, the velocity of the water will increase dramatically and this will contribute to the turbulence flow and improve the aeration.

On the other hand, pilot study conducted by Sim, et al. (2001) found that limestone packed column in the reaction unit could improve aeration process as oxidation of iron occurs optimally at pH greater than 6.5. Limestone granules was used to maintain the high pH inside the column for oxidation of iron to occur efficiently. Limestone packed column was coupled with sedimentation and membrane filtration unit at downstage. Different mesh size of stainless-steel screens were used in the membrane filtration to filter out the insoluble ferric iron. It was found that the iron concentration in water was successfully reduced from 40 mg/L to the admissible limit of 0.3 mg/L in the conditions where 550 g/L of limestone was used with 2000 mesh size and 20 minute of hydraulic retention time. Figure 4.6 shows the schematic diagram of limestone packed column in the pilot plant study conducted by Sim, et al., (2001).



Figure 4.6: Schematic Diagram of Limestone Packed Column in Iron Removal (Sim, el al., 2001).

This was also supported by the work of Akbar, Aziz and Adlan, (2015), which proposed that the combination of ozonation and adsorption as shown in Figure 4.7 can lead to higher iron removal efficiency. This is because the limestone media packed inside adsorption column has the ability to remove metals in groundwater. It was observed that combination of ozonation and adsorption can yield as high as 99 % of iron removal efficiency while using ozone alone just able to reach approximately 85 % of iron removal efficiency.



Figure 4.7: Schematic Diagram of Combination of Ozonation and Adsorption (Akbar, Aziz and Adlan, 2015).

4.2.3 Configuration for Liquid Based Oxidant

Similar to gaseous based oxidant, the configuration process for liquid-based oxidant consists of a reaction unit and a separation unit. However, liquid based oxidant will be injected directly into the reaction unit to initiate the oxidation process. The general sequence of the system for liquid-based oxidant, which in this case are KMnO₄ and NaOCl is shown in Figure 4.8 (Elsheikh, Guirguis and Fathy, 2018; Tandon, 2015).



Figure 4.8: General Sequence of Oxidation for Liquid Based Oxidant.

Raw groundwater enriched with iron normally less than 10 mg/L is pumped and directed into the reaction unit. Then, the liquid-based oxidant (KMnO₄ and NaOCl) is injected directly to the reaction unit to mix with the incoming groundwater for oxidation of iron to occur. A mixing tank that consists of mixer will be used for liquid liquid mixing in order to disperse the liquid oxidant and homogenise the water and oxidants for effective oxidation reaction. After sufficient retention time in the mixing tank, the water will be transferred to a series of separation units to separate out the insoluble iron precipitates. Flocculation tank, sedimentation tank followed by filtration process are the common separation processes used after oxidation process in water treatment plant when liquid-based oxidant is used (Elsheikh, Guirguis and Fathy, 2018). The flocculation tank is normally designed with baffled channel to promote formation of larger aggregates and the settling of iron particles (Tandon, 2015). Successively, the water will flow to a sedimentation tank to remove the suspended particles. Lastly, sand filtration is generally employed to remove the large iron particles. Consequently, treated groundwater with low iron concentration will be obtained. Figure 4.9 illustrates a typical schematic diagram for iron removal by liquid-based oxidant followed by separation process in the pilot plant study conducted by Elsheikh, Guirguis and Fathy (2018).



Figure 4.9: Schematic Diagram for Pilot Plant Study for Iron Removal by KMnO₄ (Elsheikh, Guirguis and Fathy, 2018).

4.3 Effect of Operating Parameters on Oxidation of Iron

Other than introducing different configurations, it is reported that the operating parameters have crucial impact on the performance of oxidation in iron removal. In general, three important parameters were studied, which are oxidant dosage, pH of water and retention time.

4.3.1 Oxidant Dosage

The effect of oxidant dosage on the iron removal efficiency was summarized and evaluated. Figure 4.10 shows the effect of oxidant dosage on iron removal efficiency for different types of oxidants based on the data extracted from various researchers.



Figure 4.10: Effect Oxidant Dosage on Iron Removal Efficiency (Radzi, et al., 2020; Araby, Hawash and Diwani, 2009; Elsheikh, Guirguis, and Fathy, 2018; Kuberis and Gorbachov, 2014).

From Figure 4.10, it can be concluded that the higher the dosage of oxidant, the higher the iron removal efficiency from groundwater. This trend is observed in all types of the oxidants. Among the oxidants, air shows the least efficiency towards iron removal as compared to ozone, NaOCl and KMnO4. This could be due to the fact that air has limited amount of dissolved oxygen (DO) content, which is the main component in oxidation process. Consequently, air is not a strong oxidant compared to ozone, NaOCl and KMnO4. Nevertheless, it was found that the increase in DO will improve the iron oxidation. This was observed in the pilot plant study by Radzi, et al. (2020), whereby the DO level in water was increased from 6.19 mg/L to 6.43 mg/L, the initial iron concentration at 4.9 mg/L was reduced from 4.7 mg/L to 4.56 mg/L. Although the iron removal efficiency for aeration was still pretty low, the iron removal efficiency by air was still following the trend as other oxidants, in which the increase in oxidant dosage would result in the increase iron removal efficiency.

In comparison to air, the iron removal efficiency was more than 90 % when KMnO₄ and ozone were used as the oxidant, whereby the initial iron

concentration was less than 3 mg/L. As shown in Figure 4.10, the increase in KMnO₄ concentration from 1 mg/L to 2 mg/L improved the iron removal efficiency from 97% to 100% for a groundwater sample with 1.5 mg/L of initial iron concentration at pH 7, with a retention time of 10 minutes (Elsheikh, Guirguis, and Fathy, 2018). Similar trend is also observed in the work of Araby, Hawash and Diwani (2009) when ozone was applied as the oxidant. Figure 4.10 shows that the use of 1.25 mg/L was sufficient to reduce the iron concentration in the groundwater sample at 90% removal efficiency (iron concentration was reduced from 2.6 mg/L to 0.25 mg/L) at pH of 8.0 and 20 °C. This was also reported in the work of Reckhow, et al. (1991), which suggested that a 0.5:1 molar stoichiometry dosage of ozone to iron is ideal to oxidize 1 mg/L of iron in a synthetic water. A further increased in the iron removal efficiency to 96% was reported when the ozone dosage was increased to 3 mg/L. Further ozone dosage was not improving the removal efficiency. This is possibly caused by the presence of humic acid or fulvic material that inhibit the oxidation of iron by ozone.

Similar trend was also observed when NaOCl was used as the oxidant. However, it was reported that the requirement dosage of NaOCl to oxidize the iron has far exceeded the stoichiometric requirement. As shown in Figure 4.10, a high removal efficiency more than 95 % was only achieved when the NaOCl dosage was in the range of 100 mg/L to 150 mg/L, which is much higher than the initial required iron concentration in the study, which was 14.6 mg/L (Kuberis and Gorbachov, 2014). This is because the study area of Kuberis and Gorbachove (2014) was highly contaminated and polluted with various organic compounds, with 14.6 mg/L of iron, coupled with 2.2 mg/L of manganese, 4.5 mg/L of hydrogen sulphide, and high degree of colour and turbidity. When the dosage of NaOCl increased from 100 mg/L to 125 mg/L, iron concentration on the residue merely reduced from 0.58 mg/L to 0.38 mg/L, which was still above admissible limit of 0.3 mg/L. With further increasing the dosage of NaOCl to 190 mg/L, the residue iron content finally dropped to 0.28 mg/L. A higher dosage is required due to the competition of oxidant between iron and the organic compounds in the groundwater samples. This is further supported by a jar test study conducted by Lytle, Sorg and Snoeyink (2005), which reaffirm that the oxidant concentration must be greater than the theoretical stoichiometric amount in order to completely oxidize the ferrous iron.

In short, the co-existence of other compounds that have the tendency to undergo oxidation in water need to be taken into consideration while dosing the oxidants. Even though high oxidant dosage is desirable to achieve satisfactory iron removal efficiency, the dosage of oxidants need to be controlled carefully near to stoichiometric requirement to avoid high chemical cost and negative performance impact. For example, over dosage of ozone and KMnO₄ should be avoided to prevent over oxidation of manganese, which is also a common compound found in high level in the groundwater. Excessive ozone and KMnO₄ dosage will oxidize manganese from the oxidation state of Mn²⁺ to Mn⁷⁺ instead of required Mn⁴⁺. The presence of Mn⁷⁺ or known as permanganate will turn the water into pink solution (Araby, Hawash, and Diwani, 2009).

The initial concentration of iron, theoretical oxidant dosage required and the actual oxidant dosage used are summarized in Table 4.3. The stoichiometric or known as theoretical dosage of air, ozone, KMnO₄ and NaOCl required to oxidize 1 mg/L of ferrous iron were obtained from Equations 4.1, 4.2, 4.5 and 4.10 respectively. The ratio between the actual oxidant dosage used and the theoretical oxidant demand provides a clearer information on how many times the oxidants need to be increased to above stoichiometric amount. Small ratio value indicates that the actual oxidant dosage used to achieve high iron removal efficiency is near to the stoichiometric dosage.

Oxidant	A: Stoichiometry (mg Oxidant/mg Fe ²⁺)	B: Initial Iron Concentration (mg/L)	C: Stoichiometric Oxidant Demand (mg/L) (A× B)	D: Actual Oxidant Dosage Used to Achieve Optimum Iron Removal (mg/L)	E: Actual to Stoichiometric Ratio (D÷C)	References
Air (oxygen)	0.14	4.90	0.69	6.43	9.32	Radzi, et al., 2020
Ozone	0.43	2.60	1.12	3.0	2.68	Araby, Hawash and Diwani, 2009;
KMnO4	0.94	1.50	1.41	2.0	1.42	Elsheikh, Guirguis, and Fathy, 2018;
NaOCl	0.66	14.6	9.64	190	19.71	Kuberis and Gorbachov, 2014

Table 4.3: Comparison between Theoretical and Actual Oxidant Dosage.

4.3.2 pH of Water

Figure 4.11 shows the summary on the effect of pH of water on iron removal efficiency using different types oxidants based on the data extracted from various researchers. In general, it can be concluded that the use of oxidation process is only significant when the pH of water is in the range of 6.0 to 9.0. Based on the Figure 4.11, it can be further suggested the chemical oxidation is more effective under neutral to slight alkaline condition, in comparison to acidic condition.



Figure 4.11: Effect of pH of Water on Iron Removal Efficiency (Sim, et al., 2001; Araby, Hawash and Diwani, 2009; Elsheikh1, Guirguis and Fathy, 2018; Kan, et al., 2012).

Nevertheless, it is worth noting that the effect of pH of water is dependent on the types of oxidants used. In the lab scale aeration study by Sim, et al. (2001) using aerated limestone pack column, the initial iron concentration of highly polluted groundwater was 40 mg/L. When the average pH value of water increased from 6.65 to 7.82 by using higher amount of limestone, the final iron concentration decreased from 1.5 mg/L to less than 0.3 mg/L at the 6th hour operation. This indicates that aeration can oxidize ferrous iron effectively at the pH of water near neutral but higher iron removal efficiency can be achieved along with the increase in pH of water. Also, Sim, et al. (2001) found that

oxidation of iron by aeration occured slowly in the water with low pH. This is supported by the study conducted by Stumm and Lee (1961), which found that oxidation of iron via aeration occurred rapidly only when the pH of water is above 7.3. However, extremely alkaline condition is not favourable for aeration as chemical precipitation tends to take over. Khatria, Tyagia and Rawtanib (2017) claimed that the efficiency of aeration reduces significantly in alkaline and hard water.

For ozone, the lab scale experimental study by Araby, Hawash and Diwani, (2009) showed that when the pH of simulated groundwater increased from pH 5.0 to 10.0, iron removal efficiency improved vividly from 79 % to approximately 96.5 %. This is in agreement with an article published by Spartan Environmental Technologies (2021), which stated that oxidation of iron by ozone occurs optimally in a pH range from 6.0 to 9.0. This can be explained that high pH of water tends to stimulate the decomposition of ozone to produce hydroxyl radicals, which has higher oxidation power compared to ozone.

Knocke, et al. (1991) claimed that oxidation of iron by KMnO₄ takes place under all pH ranges of water. However, it is reported by other researchers that KMnO₄ works optimally and with faster result when water is at pH above 7.0 (Elsheikh, Guirguis and Fathy, 2018; Khadse, Patni, and Labhasetwar, 2015). In the work of Elsheikh, Guirguis and Fathy (2018) in treating 1.5 mg/L of iron contaminated groundwater, it was observed that oxidation of iron by KMnO₄ is drastically favourable when the pH of water is greater than 7.0, where a complete removal was reported, as shown in Figure 4.11. In addition, Stumm and Morgan (1995) also reported that the use of higher pH of water can lower the dosage of KMnO₄ required for the oxidation of iron. This can help to save the operating cost as KMnO₄ is an expensive oxidant.

Similar trend was observed for NaOCl. Figure 4.11 shows that the iron removal efficiency of NaOCl was increased from 70 % to 88 % as the pH of water increased from 6.0 to 9.0 when the groundwater with 0.65 mg/L of initial iron concentration was being treated (Kan, et al., 2012). This is supported by the claim made by Khadse, Patni, and Labhasetwar (2015), which revealed that oxidation of iron is the most effective at the pH around 6.5 to 7.5 when chlorine compound is used as the oxidant.

As a conclusion, it is suggested that high pH of water contributes to high iron removal efficiency for all of the oxidants. This is because the reaction of oxidation of iron is second order with respect to pH (Krupinska, 2020). Thus, the higher the pH of water, the higher the rate of oxidation of iron. High oxidation rate will lead to the higher iron removal efficiency. Nevertheless, optimum pH should always be selected instead of selecting the highest pH as high pH indicates higher cost for chemical consumption and process set up.

4.3.3 Retention Time

Retention time between oxidants and water will affect the effectiveness of oxidation process. (Lytle, Sorg and Snoeyink, 2005). Table 4.4 shows the effect of retention time on iron removal efficiency for different oxidants. From the table, it is proposed that the recommended retention time for oxidation is in range of a few seconds to 30 minutes. Among the oxidants, the retention time for ozone, KMnO₄ and NaOCl were shorter compared to air, in which high iron removal efficiency was achieved in less than 5 minutes. While for air, it required longest retention time as compared to other oxidants due to the fact that air is a weak oxidant. Sufficient contact time between dissolved oxygen and ferrous iron is needed to improve the oxidation process.

Oxidant	Retention Time	Iron Removal Efficiency	References
Air	20-30	99	Sim. et al., 2001
Ozone	0.5-5	≈100	Baruth, 2005; Reckhow, et al., 1991
KMnO4	1-5	≈100	Vercelotti, 1988; Elsheikh, Guirguis, and Fathy, 2018
NaOCl	0.5-20	≈100	Baruth, 2005; IFM Water Cycle Technology, 2018

Table 4.4: Effect of Retention Time on Iron Removal Efficiency.

Nevertheless, the retention time required for oxidation of iron is highly dependent on the groundwater condition such as alkalinity and the presence of foreign components. Vercelotti (1988) has studied on the oxidation of iron by KMnO₄ of the groundwater in Nelsonville. The groundwater was in pH 7.3 and containing of 1.3 mg/L of initial iron concentration. When 1.2 mg/L of KMnO₄ was added, the research showed that a time period of 60 seconds was sufficient for complete oxidation and precipitation of iron in the groundwater. However, in the pilot plant study conducted by Elsheikh, Guirguis, and Fathy (2018) with simulated groundwater, when 2.0 ppm of KMnO₄ was added into the water with pH 7.0 containing 1.5 mg/L of initial iron concentration, 5 minutes of retention was used to achieve complete oxidation of iron. The differences in the retention time could be due to the different in the water sample used. Natural sample used by Vercelotti (1988) might have high alkalinity and adsorptive capacity towards the precipitant formed compared to the synthetic sample used by Elsheikh, Guirguis, and Fathy (2018). Greater alkalinity in water contributed to larger buffer capacity and helped to neutralize hydrogen ions released during the oxidation reaction. Consequently, the pH inside the natural water sample was well maintained and hence required shorter retention time to achieve complete oxidation. Besides that, a wide range of retention time was observed in NaOCl. Baruth (2005) stated that the chemical oxidation process for NaOCl with iron is a rapid reaction. However, Raveendran, Ashworth and Chatelier (2001) revealed that the contact time of 3 minutes for NaOCl is ineffective as the kinetics of oxidation is slow. There is a study found that the adequate time for complete iron oxidation by NaOCl to take place is 20 minutes (IFM Water Cycle Technology, 2018).

In short, different oxidants have different retention time in the range of few seconds to 30 minutes. Among the oxidants, air requires the longest retention time. NaOCl shows the widest range of retention time as NaOCl may not a strong oxidant for iron removal. Moreover, oxidation of iron by NaOCl is greatly inhibited by the presence of organic compounds as mentioned earlier. Hence, it can be concluded that retention time is depending on two key things, which is the nature of oxidant and the conditions of groundwater. Treatment of groundwater that consists of organic compounds or humic acids will surely extend the retention time.

4.4 Recent Improvement on Iron Removal from Water via Oxidation Oxidation is an established technology that has been used in water treatment plant for years. In oxidation process for iron removal from groundwater, various oxidants are added to oxidize soluble ferrous iron in water into insoluble form of ferric iron and then precipitated out from water through filtration process. As time goes by, increasing water demand followed by the growing population has encouraged researchers to improve the conventional chemical oxidation process or look for effective alternatives that are affordable towards rural area in the world. In general, recent improvement done can be categorised into three sections, which are Vyredox technology, subterranean iron removal method and catalyst enhancement. Vyredox technology and subterranean iron removal are for the improvement of aeration process.

4.4.1 Vyredox Technology

Vyredox technology is an in-situ iron removal process based on the principle of subsurface iron removal and aeration, which has recognised to be a sustainable and low-cost technology in European countries to treat iron in groundwater for years (Ahmad, 2012; Hallberg and Martinell, 1967). Figure 4.12 shows the mechanisms of Vyredox technology. The technology consists of an aeration degassing equipment and a recharge well as illustrated in Figure 4.13. During the process, water will mix with atmospheric air to produce oxygen-enriched water. Degassing tank is needed to remove entrapped and non-dissolved oxygen. The aerated water with high oxygen level is injected periodically into an anoxic aquifer via a recharge well to create an oxygen rich zone around the well for oxidation to occur. The oxidized zone in the aquifer will promote oxidation of dissolved iron from ferrous into ferric state and subsequently producing ferric hydroxide. The insoluble ferric hydroxide that retains in the aquifer will become a new adsorption site for ferrous iron (Halem, et al., 2010). Consequently, the water that has passed through the highly oxidized zone will be free from soluble iron before pumping up via pumping well (Ahmad, 2012). The efficiency of

Vyredox technology is highly dependent on the efficiency ratio (Er), which is obtained by dividing the volume of water being pumped out, V_{out} with the volume of incoming aerated water, V_{in} (Ahmad, 2012).

Several advantages have been attributed to this technology. Firstly, there is no expensive chemical required by the process. Furthermore, no sludge is generated at the end of the treatment. Hence, it may help to shrink the operational and sludge handling cost. Only investment on the capital cost for the initial installation of facilities is needed before the treatment process. Also, no continuous supervision is needed as the process is easy and simple to control.



Figure 4.12: Vyredox Mechanism in Aquifer (Hallberg and Martinell, 1967).



Figure 4.13: Schematic Diagram of Vyredox Plant (Hallberg and Martinell, 1967).
Vyredox technology has been implemented in different countries to act as a pre-treatment technology to remove extremely high iron concentration before passing to typical conventional surface treatment for iron. The pilot study by American Water Works Association (1984) showed a positive result on the iron removal efficiency by Vyredox method. In their pilot plant study with volumetric flow rate of water at 0.132 m³/s, initial iron concentration of iron at 2.55 mg/L was successfully reduced to 0.30 mg/L after three recharge cycles, which was 88 % of iron removal efficiency.

In addition, a small-scale field study conducted by Halem, et al., (2010) in rural area of Bangladesh, also reported that an injection volume of aerated water less than 1 m³ was sufficient to reduce 1 mg/L of initial iron concentration in aquifer to below detectable limit. However, they recommended that groundwater should be aerated extensively to increase oxygen level in order to achieve complete oxidation of ferrous iron in real time operation.

4.4.2 Subterranean Iron Removal

Subterranean iron removal is another in-situ groundwater treatment technology that combines aeration and biological oxidation. This process is mainly applied for iron and arsenic removal. The process makes use of the microorganisms in the aquifer to carry out biological oxidation of water-soluble metal into water insoluble precipitate in subsurface. Figure 4.14 shows the schematic diagram for subterranean process. Groundwater is pumped up from shallow aquifer and is aerated by showerheads to increase the dissolved oxygen level in the groundwater. The oxygenated water will be stored in recharge tank and returned to the aquifer to create an oxygen rich area known as oxidation zone. This oxidation zone of aquifer act as a reactor and greatly encourage the growth of iron microbes that oxidize the soluble ferrous iron underground into insoluble ferric iron. After oxidation of iron, underground adsorption of ferric iron into soil matrix will take place. Unlike conventional iron removal processes that require periodic backwash for filter media to avoid clogging, the risk for subterranean technology to clog the aquifer is very small. This is because the adsorption volume occupied by the biologically produced precipitates is always

smaller than the pore volume available for the oxidation due to continuously expansion (Klinger, 2015).

Two pumping wells are usually installed and working alternatively to support continuous operation. Efficient aeration process is required to ensure the water is enriched with dissolved oxygen. First extraction well is used to pump up groundwater from aquifer for aeration purpose while second infiltration well is used to divert oxygenated water back to the aquifer. The cost and complexity of this technology can be further reduced by constructing only one well. In the case where only single well is installed, a storage tank will be needed to store the oxygenated water before recharging back to aquifer.



Figure 4.14: Simplified Diagram of Subterranean Technology (Rott and Kauffmann, 2008).

Subterranean method is simple and easy to operate as it only involves pump, piping and a degassing unit. No pre-treatment is needed on the groundwater as iron bacteria is generally able to survive under most of the conditions. The optimum pH for subterranean method is around neutral as high pH in groundwater will result in precipitation process (Sharma, Petrusevski and Schippers, 2005). The primary benefit of subterranean technology is the elimination of chemical reagent. There is no any chemical oxidant involved during the process. Hence, subterranean is a cost-effective option for iron removal due to lower operating and capital cost. Lastly, no sludge is produced after the remediation further add points to the method (Klinger, 2015).

The limitation of subterranean method is that spreading of oxygenated water is highly dependent on the flow of groundwater and porosity of aquifer. Since it involves biological oxidation, the process is relatively slow compared to physical and chemical oxidation methods. Subterranean iron removal may take up to several months for groundwater to achieve desired final concentration of iron. (Cañas, et al., 2020). Also, oxygen rich zone may encourage the excessive growth of undesired bacterial around the well.

Cañas, et al. (2020) has conducted a pilot scale plant investigation for subterranean technology in Mekong Delta, Vietnam. The result shows that initial iron concentration of 8.4 mg/L in groundwater was successfully reduced to below drinking water standard, 0.3 mg/L after eight months of operation. They concluded that subterranean technology has the potential be a sustainable and technically feasible alternative for iron and arsenic removal in Vietnam.

Subterranean iron removal method is relatively new in Malaysia and not being established yet. However, the potential for using this method to remove iron from groundwater in Malaysia is high as well. Subterranean with low operating cost is suitable to be adopted by rural areas in Malaysia especially Kelantan that depends on groundwater for domestic usage. A field study has been conducted by Syarikat Air Kelantan Sdn Bhd in Kampung Telok, Kelantan to solve the high iron issue in the groundwater. Subterranean method has resulted in a significant decrease in iron concentration from 9.78 mg/L to below 0.3 mg/L in a period of three months.

4.4.3 Catalyst Enhancement

Other than in situ oxidation, chemical oxidation can also be improved by using catalyst enhancement on the filter media. Silica sand is the common filtration media that are used in water treatment plant. By adopting catalytic filter media, the efficiency and rate of chemical oxidation can be improved significantly. Catalytic filter media works by providing extensive oxidation site on its surface to speed up the oxidation process. The catalytic filtration media that are popular for iron removal includes DMI-65, Pyrolox and Birm.

4.4.3.1 DMI-65

DMI-65 is a silica sand based catalytic filter media infused with manganese dioxide (MnO₂) and appeared as dark brown or black colour granular (Aremu, Lay and Gasglow, 2019). Application of infused technology in DMI-65 has increased the micro-porous catalytic surface area, as the active ingredients are homogenous with the media instead of forming a layer of coating on the media. Therefore, DMI-65 has resulted in high oxidation rate among other catalytic filtration media (Biela, Kucera and Pekny, 2017). This advanced catalytic filter media has been widely employed in United State for heavy metal removal especially iron and manganese in water treatment plant. Figure 4.14 shows the physical appearance of DMI-65 catalyst.



Figure 4.15: Physical Appearance of DMI-65 Catalyst (Quantum, 2020).

DMI-65 is introduced to improve chemical oxidation technology in iron removal as it has a good reputable to work as an effective catalyst to speed up the oxidation process. Pordage (2019) states that the linear filtration velocity of DMI-65 can up to twice that of the conventional method. This means that chemical oxidation with DMI-65 is expected to handle large throughput of water by achieving the same iron removal result compared to the conventional method. The most important feature of DMI-65 is its safeness in water treatment application. DMI-65 has been recognised by United States to be one of the safe components in drinking water applications by certifying it under American National Standards Institute (ANSI) and National Sanitation Foundation (NSF-61) (NSF International, 2016). Also, long life span is another encouraging characteristic for DMI-65 application. According to Pacific Water Technology (2019), attrition loss of DMI-65 per annum is only 1 to 5 %, which means that DMI-65 is not being consumed during the reaction. As a result, it can be continuously used in water treatment plant up to 5 to 10 years without the need to change it as long as it is maintained and operated optimally. Besides, no regeneration is required in DMI-65 filter media. However, activation of DMI-65 with NaOCl is important before the iron removal process (Quantum, 2020).

DMI-65 is believed to be able to reduce iron concentration in water to as low as 0.001 ppm due to the high iron capacity load (Quantum, 2020). During the operation, NaOCl will be used as the oxidising agent to initiate the oxidation of iron prior to DMI-65 catalytic filtration process. Dissolved iron presented in water will be adsorbed to the surface of the DMI-65 media. When the water contacts with catalytic media, the oxidation of iron is accelerated. Once chemical oxidation takes place, soluble iron, Fe^{2+} will turn into insoluble solid precipitate, $Fe(OH)_3$ and fill the gaps in DMI-65. The solid particles will be filtered out during backwash of the filtering bed on DMI-65. DMI-65 coupled with the use of NaOCl oxidant will keep the media free from bacteria.

The Cloudbreak iron ore mine site owned by Fortescue Metals Group, which is the global leader iron ore industry in Australia has adopted DMI-65 filter media in their groundwater management scheme since 2008 to reduce the elevated level of iron in the discharge water of iron ore site (Quantum Filtration Medium, 2010a). The iron level in water near to iron ore mining site normally in a range of 6.0 mg/L to 10.0 mg/L (Gleekia, 2016). It was reported that the iron concentration which was markedly high in the discharge water of Cloudbreak mining site was reduced intensely to ultra-low level (0.005 mg/L) after using DMI-65 filter media (Quantum Filtration Medium, 2010a).

In the case study conducted by George Municipal Water Works in South Africa, the water was highly contaminated with colour, manganese, iron and humic matter. The soluble iron in this type of water is barely possible to be oxidized by conventional chemical oxidation process and filtered out due to the formation of complex iron compounds. With the use of 550 metric tonnes of DMI-65, the final iron concentration in the water was reduced significantly up to 0.01 mg/L (Quantum Filtration Medium, 2014b). The result from this case

study has proven that DMI-65 is able to achieve satisfactory efficiency in removing complex iron compounds.

4.4.3.2 Pyrolox

Pyrolox is a granular filtration media made from high purity of manganese ore and it appears in black colour as presented in Figure 4.16.



Figure 4.16: Pyrolox Filtration Media (Clack Corporation, 2019a).

According to Clack Corporation (2019a), Pyrolox has been adopted in water treatment plant due to its high ability in removing a range of inorganic compounds from water which include iron, manganese and hydrogen sulphide. In chemical oxidation of iron, Pyrolox serves as a strong catalyst to accelerate the oxidation of iron. Water soluble iron will be oxidized to water insoluble iron precipitate when the water is in contact with the Pyrolox filter media. Once oxidation takes place, the precipitate will leave the media and the surface is again available for the next oxidation cycle. Similar to DMI-65, no regeneration with chemical is needed under normal condition. The operating pH for Pyrolox is ranging from 6.5 to 9.0. Nevertheless, water with higher pH is favourable to yield in higher efficiency. It is noteworthy that the use of oxidants like KMnO₄, chlorine or sodium hypochlorite prior to Pyrolox oxidation process is essential to activate the catalytic filter media, maintain the performance as well as to accelerate the oxidation rate especially when iron concentration is above 2 mg/L. (Lars, 2011).

The disadvantage for Pyrolox is the high backwash flow rate required. Daily backwash processes with up to 73 m^3/m^2 per hour of water is needed due

to the heavy characteristic of the media contributed by high bulk density (Lars, 2011). Furthermore, high backwash flow is also required to prevent fouling. This results in high water utility fees. Also, Pyrolox media is not applicable to treat complex iron (Munter, Overbeck and Sutt, 2008). Hence, the system is commonly designed to operate with aeration, ozonation or chlorination as a pre-treatment to decompose the complex iron before passing to Pyrolox filter media.

In a pilot plant testing conducted by Munter, Overbeck and Sutt (2008) to study the iron removal efficiency of catalytic filter media Pyrolox in groundwater of Kogalym, iron concentration in the raw water has reported to drop from 3.30 mg/L to 0.35 mg/L after passing through Pyrolox filter media.

4.4.3.3 Birm

Birm which is the short form for 'Burgess Iron Removal Method' is a black granular filter media coated with manganese dioxide (MnO₂) on its surface as shown in Figure 4.17. It acts as an effective catalyst in water treatment plant to iron and manganese. In iron removal, Birm enhance the reaction between iron and dissolve oxygen to oxidize iron from dissolve ferrous into insoluble ferric state.



Figure 4.17: Birm Filtration Media (Clack Corporation, 2019b).

Similar to most catalyst, Birm is not consumed during the oxidation reaction. It only needs periodic backwash to remove the precipitates and no regeneration with chemical is required. There are several conditions to follow as shown below to ensure optimum operation of the Birm filter media for iron removal as recommended by Clack Corporation (2019b):

- (i) The pH range of water should within 6.8 to 8.5 to avoid formation of colloidal iron that is hard to be filtered out during backwashing.
- (ii) The dissolved oxygen (DO) level of the water should be maintained at least 15 % of iron content for effective iron oxidation.
- (iii) The water must be free from oil, hydrogen sulphide and the amount of organic matter should not exceed 4 mg/L to prevent formation of complex compound that cannot be oxidized by Birm.
- (iv) The concentration of free chlorine presents in water should be less than 0.5 mg/L to avoid depletion of catalytic coating layer on the media (Raza, 2017).

Unlike Pyrolox and DMI-65 that work together with chemical oxidants, Birm is not used together with chemical oxidants as the presence of chemicals will disturb and inhibit the performance of iron removal (Raza, 2017). Once ferrous iron contacts with the Birm filter media in the presence of dissolved oxygen, oxidation of ferrous iron occurs immediately (Chaturvedi and Dave, 2012). Hence, it can be said that Birm is commonly used to improve aeration process. Clack Corporation (2019b) claimed that Birm has constantly achieve excellent iron removal efficiency. In Lars (2011) opinion, it was stated that Birm can only achieve high iron removal efficiency for iron level of below 3.0 mg/L while in the view of Raza (2017), the reduction capacity of Birm to deal with iron can be up to 8.0 mg/L, provided that there is only single contaminant found in water. In a research study conducted by Barloková and Ilavský (2009), it was observed that 0.46 mg/L of average concentration of iron in water was reduced to less than 0.1 mg/L after passing though Birm filter media

4.4.3.4 Comparison between DMI-65, Pyrolox and Birm

Table 4.5 shows the comparison between DMI-65, Pyrolox and Birm in different parameters. Each catalytic filter media has its own advantages and disadvantages depending on the condition of water. The range of operating pH

for three media are similar. No regeneration with chemical is required for these catalytic filter media can lead to cost saving as compared to conventional greensand filter media that requires regeneration with excess KMnO₄. Also, these filter media have a long life span up to 10 years due to low attrition loss. This can help to achieve cost saving as the downtime for service and maintenance is reduced significantly. Among the filter media, Birm and DMI-65 are lighter media as compared to Pyrolox. Hence, their backwash flow rate required is lower compared to Pyrolox.

Properties and Operating Parameter	DMI-65	Pyrolox	Birm
Bulk Density (g/cm ³)	1.46	2.00	0.58 - 0.61
Operating pH Range	5.8 - 8.6	6.5 - 9.0	6.8-9.0
Percentage of MnO ₂ (%)	Not available	75 - 85	<1.0
Service Flow Rate (m ³ /m ² /h)	5-30	12	8
Backwash Flow Rate (m ³ /m ² /hr)	25-40	61-73	24-29
Regeneration Requirement	No	No	No
Life Span	8 to 10 years	8 to 10 years	8 to 10 years
Common Oxidant Used	NaOCl	NaOCl, KMnO4	Air

Table 4.5: Comparison between DMI-65, Pyrolox and Birm (Quantum Fitration Medium, 2014b; Clack Corporation, 2019a; 2019b; Lars, 2011).

4.4.4 Summary for Recent Improvement

It can be concluded that Vyredox, subterranean iron removal and Birm filter media are more towards on the improvement of aeration process while catalyst enhancement of DMI-65 and Pyrolox are more towards on the improvement of chemical oxidation. Table 4.6 shows the comparison for the conventional iron removal method and the recent improvements.

Description	Conventional Iron Removal	Vyredox & Subterranean Iron	Catalyst Enhancement	
Description	Methods	Removal Technologies		
Sludge Formation	Sludge is produced.	No sludge is produced.	Sludge is produced.	
Data of Ovidation	Slow to moderate reaction	Clow montion	Fast reaction as catalyst can speed up	
	Slow to moderate reaction.	Slow reaction.	the rate of oxidation.	
Chemical Reagent	Chemical reagent is required	No chamical response is required	No regeneration with chemical is	
Requirement	except aeration.	No chemical leagent is lequiled.	needed.	
	More above ground facilities are	Lesser above ground facilities are	No alteration on the existing system is	
Facilities	needed compared to subterranean	needed. Only periodically injection	needed. Only replacement of the sand	
	and Vyredox technology.	of oxygenated water is required.	filtration with DMI-65.	
Filtration	Filtration step is needed to filter	No filter media is needed	Filtration is needed to filter out sludge.	
Requirement	out sludge.	No mer media is needed.		
Ex-Situ/In-Situ	Normally ex-situ except for	In citu	Ex citu	
Treatment	oxidant ozone.	III-Situ	Ex-situ	
Iron Removal	Moderate to high depending on	Low efficiency	Very high efficiency	
Efficiency	the types of oxidants.	Low enterency.	very high enterency.	

Table 4.6: Comparison between Conventional Iron Removal Methods and Recent Improvement Technologies.

From Table 4.5, it can be seen that the advantages of subterranean iron removal and Vyredox technology over the conventional iron removal method are the elimination of chemical cost and the absence of sludge formation. While for catalyst enhancement, the upside of using catalytic filter media in iron removal is its ability to improve the iron oxidation rate.

4.5 Case study: Iron Removal from Groundwater in Kelantan

4.5.1 Introduction

Kelantan is chosen to be the study area as the utilization of groundwater in Kelantan has started since 1935 and its utilization rate is the highest among other states. Kelantan is situated at the northeast of Peninsular Malaysia. About half of the population in Kelantan is greatly depending on groundwater as their daily drinking water supply due to the wide spread of wells distribution around the state and limited coverage of the treated surface water supplied by government (Awang, Abdullah and Latif, 2020). Owing to the natural weathering of iron bearing minerals, the dissolved iron concentration in Kelantan's groundwater is constantly exceeding the permissible limit set by the Ministry of Health Malaysia (MOH), which is 0.3 mg/L (Usman, et al., 2021). In order to meet the rising demands for safe drinking water associated with increasing population, removal of iron from groundwater becomes a major concern for water treatment plants (WTP) in Kelantan. The conventional approach of iron removal in WTP of Kelantan is aeration followed by filtration. The purpose of this case study is to compare the effectiveness of different oxidants available for oxidation process and the suitability of other treatment technologies to act as an alternative for iron removal from groundwater in Kelantan area.

4.5.2 Study Area Description

Kelantan has 10 districts and a total area of 17100 km². Kota Bharu, which is the capital of Kelantan is selected to be our main focus. Kota Bharu district is lying on the east of Kelantan river, which is located in northern of Kelantan as shown in Figure 4.18. There are a total of 79 monitoring wells in Kelantan area for monitoring the quality of groundwater (Tawnie, et al., 2016). Figure 4.19 shows several distribution of monitoring wells near Kota Bharu area.



Figure 4.18: Location of Kota Bharu, Kelantan (Tawnie, et al., 2016).



Figure 4.19: Distribution of Monitoring Well in Kota Bharu, Kelantan (Tawnie, et al., 2016).

The population in Kelantan has shown an increasing trend from 1.54 million (with 297000 in Kota Bharu) in year 2010 to 2.001 million (with 352000 in Kota Bharu) in year 2021 (Macrotrend, 2021). While for the climate in Kota

Bharu, the average annual rainfall received in Kota Bharu varies from 2500 mm to 2783 mm depending on monsoon rainfall. The average annual temperature of Kota Bharu is around 27.5 °C (Ebrahim, et al., 2020).

The initial iron concentration from the monitoring wells near Kota Bharu area in the frame of 2003 to 2013 was investigated by Akbar, Aziz and Adlan, (2015). The result was extracted and plotted in a graph as shown in Figure 4.20.



Figure 4.20: Iron Concentration from Monitoring Wells near Kota Bharu.

Figure 4.20 shows that groundwater in Kota Bharu were highly contaminated with iron, ranging from 0.9 mg/L to 12.64 mg/L, whereby the deeper the aquifer, the higher the iron concentration found. Since the iron concentration in Kota Bharu's groundwater has far exceeded the drinking water quality standard established by MOH and WHO, which is 0.3 mg/L, this study will focus on the groundwater in Kota Bharu Kelantan. Tanjung Mas, which is a small town in Kota Bahru was selected to be the study area. Groundwater in Tanjung Mas produces approximately 10 mega litres per day (MLD) water to serve approximately 352000 residents nearby. Table 4.7 shows the information and conditions of the groundwater sample collected from Tanjung Mas, Kota Bharu.

Parameter	Groundwater in Tanjung	WHO	Malaysia	
	Mas	Standard	Standard	
рН	6.80	6.50-8.50	6.50-8.50	
DO level (mg/L)	0.59	-	-	
Turbidity (NTU)	54	1	5	
Colour (Pt.Co)	20	15	15	
Iron Concentration (mg/L)	5.5	0.3	0.3	
Calcium Concentration, Ca ²⁺	2 70	200	_	
(mg/L)	2.70	200	-	
Sodium Concentration, Na ⁺	13 10	200	200	
(mg/L)	15.10	200	200	
Hardness (mg/L as CaCO ₃)	8.76	100-300	500	
TDS (mg/L)	111	600	1000	

Table 4.7: Characteristic of Groundwater in Tanjung Mas, Kota Bharu (Jusoh, 2013).

From the table, it can be observed that the groundwater in Tanjung Mas, Kota Bharu is not suitable to be used directly as drinking water based on its mineral content, turbidity and colour parameters. The iron concentration of groundwater sample collected from Tanjung Mas, is 5.5 mg/L, which has exceeded the allowable value recommended by WHO and Malaysia standards. Also, the turbidity of the groundwater in Tanjung Mas is extremely high up to 54 Nephelometric Turbidity Unit (NTU). Groundwater with high turbidity implies that the water is cloudy due to the presence of suspended solids such as clay, organic matter, plankton or algae. Besides, the water also contains slightly high level of the colour as measured by Platinum-Cobalt (Pt.Co) scale. While the turbidity may affect the selection of oxidants. Also, groundwater with high amount of colour is hygienically not acceptable. Hence, the purpose of the case study is to investigate the effect of different types of oxidants in the iron removal from the view of operating parameters and expected removal efficiency.

4.5.3 Selection of Oxidant

A suitable oxidant will be selected to treat the groundwater in Tanjung Mas. The selection of oxidant will be evaluated based on the performance on iron removal, dosage of oxidant and the retention time required.

4.5.3.1 Oxidant Dosage Estimation

The stoichiometric dosage of air, ozone, NaOCl and KMnO₄ required to oxidize 1 mg/L of ferrous iron were determined. In this study, the minimum oxygen demand based on the stoichiometric dosage was focused instead of the optimum oxidant dosage. This is because the information on the foreign components that may compete for the oxidation process are not available and the optimum dosage required is case dependant. Thus, the precise optimum oxidant demand for the groundwater in Tanjung Mas is hard to be estimated. Nevertheless, the actual oxidant demand is expected to be higher, as reported by other researches' works (Radzi, et al., 2020; Araby, Hawash and Diwani, 2009; Elsheikh, Guirguis, and Fathy, 2018; Kuberis and Gorbachov, 2014). The actual demand can be in a range of 1.42 to 19.71 times of minimum oxidant demands, as shown in Table 4.3, which is highly depending on the presence and concentration of foreign compounds in water. Detail calculations for the stoichiometric dosage are presented in Appendix A. The stoichiometric dosage and minimum demand for each of the oxidant are summarized in Table 4.8.

Oxidant	Stoichiometry (mg Oxidant/mg	Stoichiometric	Minimun Den	n Oxidant nand
	Fe ²⁺)	2004ge (111g/22)	(g/hr)	(kg/day)
Air (Oxygen)	0.14	0.77	320.83	7.70
Ozone	0.43	2.37	987.50	23.70
KMnO ₄	0.94	5.17	2154.17	51.50
NaOCl	0.66	3.63	1512.50	36.30

Table 4.8: Summary for the Minimum Oxidant Demand.

4.5.3.2 Cost Analysis for Oxidants

Cost analysis is carried based on the minimum oxidant demand, as discussed in Section 4.5.3.1. The cost analysis for gaseous oxidant (air and ozone) is based on the operating cost as there is no chemical cost involved for air and ozone production. The operating cost for air (aeration process) is the utility fee required to produce dissolved oxygen while the operating cost for ozone is the energy consumed by the ozone generator for the production of ozone. While for the cost analysis for liquid oxidant (KMnO₄ and NaOCl), it is calculated directly based on chemical cost purchased from the supplier.

For gaseous oxidants, the minimum oxygen demand to oxidize 5.5 mg/L of iron in the water with capacity of 10 MLD is 320.83 g/hr. The operation cost for aeration is calculated based on the electrical energy required to dissolve oxygen in water. Boon (1979) stated that the power required to produce dissolved oxygen in aeration equipment is between 600 to 1000 kWh per tonne of oxygen produced. In this case, the power of 1000 kWh per tonne of oxygen was assumed to calculate for the utility fee. On the other hand, the minimum ozone demand to oxidize 5.5 mg/L of iron in the water with capacity of 10 MLD is 987.50 g/hr. According to Mundy, et al. (2018), the energy consumption for ozone generation can range from 5.0 to 5.5 kWh per pound of ozone produced by taking into account the energy of ozone generator, ozone destructor, and pumps. By assuming 5.5 kWh/lb of energy consumption, the average daily energy cost for production of ozone can be calculated. Detail calculations for the energy consumptions for gaseous oxidants are presented in Appendix B. The approximation of utility cost for gaseous oxidants to remove iron from groundwater in Tanjung Mas are tabulated in Table 4.9.

Oxidant	Utility Cost (RM/annum)
Air	1069.45
Ozone	41708.55

Table 4.9: Estimated Utility Cost for Gaseous Oxidants.

For liquid oxidants, the mass order price per metric tonne for KMnO₄ and NaOCl were obtained from Alibaba platform. Detail calculations for the

chemical cost consumptions for liquid oxidants are presented in Appendix C. The approximated chemical costs for liquid oxidants to remove iron from groundwater in Tanjung Mas are summarized and tabulated in Table 4.10.

Oxidant _	Chemical Cost		
	(USD/annum)	(RM/annum)	
KMnO ₄	41522.40	172317.96	
NaOCl	5299.80	21994.17	

Table 4.10: Estimated Chemical Cost for Liquid Oxidants.

4.5.3.3 Summary for Cost Analysis

The calculation for cost analysis for each oxidant provides only the estimated cost to oxidize the 5.5 mg/L of iron in groundwater Tanjung Mas. Additional cost or adjustment may be needed to deal with system inefficiencies. The annual operating cost is lowest for aeration, followed by NaOCl, ozone and KMnO4. For gaseous oxidants, air show lower utility cost as compared to ozone. This is because ozone generator requires huge amount of voltage power supply to produce ozone from oxygen molecules. Moreover, ozone system and facilities costs are relatively high as compared to aeration equipment. Thus, air as the oxidant is an economical option as there is no chemical cost involved and the utility fee is lower. However, a longer retention time up to 30 minutes will be needed for aeration treatment process. Consequently, a huge retention tank is required to deal with high capacity of water. While for liquid oxidants, NaOCl is more cost effective as compared to KMnO4. KMnO4 is not suitable to be used in Tanjung Mas in a long term because of its extremely high chemical cost compared to NaOCl.

4.5.4 Operating Parameters and Expected Iron Removal Efficiency

For oxidant dosage, the minimum dosage required for air, ozone, NaOCl and KMnO₄ to oxidize 5.5 mg/L of iron is 7.70, 23.70, 51.50 and 36.30 kg/day respectively. Since the groundwater in Tanjung Mas has high turbidity which may due to the coexistence of organic and inorganic matters, higher oxidant dosage than the calculated requirement is recommended to achieve high iron

removal efficiency as the foreign organic compounds in water will compete with the ferrous iron for the oxidation process. However, the information about the foreign compounds present in Tanjung Mas's groundwater is limited. Therefore, the minimum dosage was being used to estimate the cost.

Next, iron removal through oxidation process depends on pH of water to achieve optimum result. The pH value of the groundwater in Tanjung Mas is 6.8, which is a safe pH for drinking water. Based on the result shown in Figure 4.11 for the effect of pH on iron removal, iron removal efficiency around this pH can be ranging from 73 to 100 %. At pH 6.8, KMnO₄ and air have excellent performance. KMnO₄ shows the highest removal efficiency at pH 7.0, which is up to 100 % followed by aeration, around 99 % efficiency. For ozone and NaOC1, high iron removal efficiency can only be achieved when the pH of water is in slightly alkaline condition. However, it should be noted that the results obtained in Figure 4.11 were varied from case to case. The high iron removal efficiency by aeration obtained in Figure 4.11 was due to fact that the process has passed through a sedimentation unit. Also, the flow rate of the incoming water in aeration process will affect its iron removal efficiency as water with high flow rate will contribute to well mixing between air and water.

For retention time, the estimated retention time for air is the longest, which is up to 30 minutes in order to achieve high iron removal efficiency. While for ozone, KMnO₄, and NaOCl, a retention time of 5 minutes is adequate for oxidation of iron in Tanjung Mas groundwater. Table 4.11 shows the estimated cost, retention time and the expected iron removal efficiency based on the groundwater condition in Tanjung Mas.

Oxidant	Estimated Cost (RM/Annum)	Retention Time (minutes)	Estimated Iron Removal Efficiency (%) (Based on pH 6.8)
Air	1069.45	30	≈ 99
Ozone	41708.55	5	≈ 82
KMnO ₄	172317.96	5	≈ 100
NaOCl	21994.17	5	≈ 75

Table 4.11: Estimated Cost, F	Retention Time and	d Efficiency for	Oxidants
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4.5.5 Summary for Case Study

In the view of cost analysis and iron removal efficiency, aeration is most suitable to be used in the groundwater of Tanjung Mas as Tanjung Mas is a rural area. KMnO₄ and ozone which have high operating cost are not recommended for this rural area. While for NaOCl, it is not recommended as the groundwater in Tanjung Mas has slightly high level of the colour. Organic compounds in coloured water will react with free chlorine and produce THMs (Chaturvedi and Dave, 2012). Thus, the recommended oxidant to treat groundwater in Tanjung Mas is aeration. The advantages of aeration include its ability to oxidize iron effectively at pH around neutral and the relatively low operating cost. However, high retention time up to 30 minutes is required. Also, iron removal efficiency by aeration is greatly depending on the quality of water as the presence of organic compound and complex iron in water will inhibit the aeration process significantly.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Removal of iron from groundwater by oxidation process with different types of oxidants was evaluated from the point of view of different types of oxidants and operating parameters. The oxidants involved can be classified into gaseous oxidants, which are air and ozone, and liquid oxidants, which are NaOCl and KMnO₄. The operating parameters investigated in oxidation process included dosage of oxidant, pH of water, and retention time. The results demonstrated that all of studied oxidants displayed ability to remove ferrous iron from groundwater, where the iron removal efficiency was in the range of 7 to 100 % depending on the types of oxidants, configuration of process and conditions of groundwater. For the comparison of oxidants based on the reported iron removal efficiency, the effectiveness of oxidants was following a sequence of air < NaOCl < ozone < KMnO₄.

The oxidation of ferrous iron was highly depending on the operating parameters. For oxidant dosage analysis, it was observed that increase in oxidant dosage above the stoichiometric requirement resulted in increase of iron removal efficiency for all types of oxidants as the presence of foreign compounds will compete with the oxidation process. For evaluation of the effect of pH on the oxidation process, the optimum operating pH for air, ozone, NaOCl and KMnO₄ oxidant were found to be ranging from 7.0 to 9.0. The higher the pH of water, the higher the iron removal efficiency due to high oxidation rate. More than 85 % of iron removal efficiency was observed for all oxidants when the water was in pH 9.0. This indicates that alkaline medium is favourable for oxidation of iron by most of the oxidants. Next, it was found that the retention time for ozone, NaOCl and KMnO₄ were relatively short, which were around 5 minutes. While for air, a retention time up to 30 minutes was required to achieve high iron removal efficiency. Adequate retention time is essential to allow sufficient contact between oxidant and ferrous iron in order to achieve higher removal efficiency.

Although conventional oxidation process shows excellent iron removal efficiency, there are several improvements can be made. Vyredox method and subterranean iron removal technology were studied. The main advantages of both methods are the elimination of chemical reagent and the absence of sludge formation. On the other hand, oxidation can be improved by catalyst enhancement. Catalytic filter media include DMI-65, Birm and pyrolox were investigated and it was found that all of the catalytic filter media were able to reduce iron concentration to below the maximum allowable limit, which is 0.3 mg/L.

A case study was conducted on the groundwater in Tanjung Mas, Kelantan, which had an elevated iron level up to 5.5 mg/L due to the natural occurring process. The pH of groundwater in Tanjung Mas was around 6.8. The estimated iron removal efficiencies for air, ozone, KMnO₄ and NaOCl based on the pH of groundwater were 99, 82, 100 and 75 % respectively. While all of the oxidants displayed an ability to remove the iron from water, air has an advantage over other oxidants in the view of cost. Therefore, it is suggested that aeration is suitable to be used for iron removal in Tanjung Mas, Kelantan.

5.2 **Recommendations**

Future research is suggested to focus on the improvement of oxidation process to remove complex iron compound via Vyredox method, subterranean iron removal method and catalytic filter media especially DMI-65. With these improvements, the oxidation technology can become an effective tool for the remediation of iron from groundwater. Combination of these improvements with the conventional oxidation process can lead to high iron removal efficiency.

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APPENDICES

APPENDIX A: Calculations for Stoichiometric Dosage of Oxidants

Sample Calculation for Stoichiometric Dosage for Air (Oxygen) The amount of oxygen required to oxidize 1 mg/L of iron is 0.14 mg/L as found in Equation 4.1.

Stoichiometric Dosage of Oxygen

$$= 5.5 \frac{mg \ of \ iron}{L} \times 0.14 \frac{mg \ of \ oxygen}{mg \ of \ iron}$$
$$= 0.77 \frac{mg}{L}$$

After that, the minimum oxygen demand in grams per hour (g/hr) required to oxidize 5.5 mg/L of iron in the groundwater that has the capacity of 10 MLD can be calculated.

Minimum Oxygen Demand

$$= 0.77 \frac{mg}{L} \times \frac{10 \times 10^6 L}{Day} \times \frac{1g}{1000 mg} \times \frac{1Day}{24 hr}$$
$$= 320.83 \frac{g}{hr}$$

APPENDIX B: Calculations for Cost Analysis for Gaseous Oxidants

The price of electricity in Malaysia is referring to the latest Tenaga Nasional Berhad (TNB)'s average base tariff rate. The pricing and tariff for industrial in Malaysia are listed in Table B-1.

Table B-1: Pricing and Tariff for Industrial (TNB, 2021).

Tariff	Cents/kWh
For the first 200 kWh	38.00
For the next kWh	44.10

Calculation for Air (Oxygen)

Energy Consumed =
$$1000 \frac{kWh}{tonne} \times \frac{1 \ tonne}{1 \times 10^6 g}$$

= $1 \times 10^{-3} \frac{kWh}{g}$

Assuming that the water treatment plant is operating 24 hours per day and 365 days per year. The total power per day required to produce 320.83 g/hr of dissolved oxygen is calculated:

Total Power =
$$1 \times 10^{-3} \frac{kWh}{g} \times 320.83 \frac{g}{hr} \times 24$$
 hours
= 7.70 kWh

Since the energy price for the first 200 kWh is 38.00 cents/kWh, the daily energy cost is calculated as shown below:

$$Daily Energy Cost = 7.70 \, kWh \times \frac{38.00 \, cents}{kWh}$$
$$= 292.60 \, cents/day$$
$$= RM2.93/day$$

To calculate for the energy cost per annum:

Annual Cost =
$$\frac{RM \ 2.93}{day} \times 365 \ days$$

= RM 1069.45/year

Thus, the total estimated electrical energy cost to dissolve oxygen for the oxidation of 5.5 mg/L of iron is RM 1069.45 per year.

Calculation for Ozone

Energy Consumption =
$$5.5 \frac{kWh}{lb} \times \frac{0.00220462 \, lb}{g}$$

= $0.0121 \frac{kWh}{g}$

Assuming that the water treatment plant is operating 24 hours per day and 365 days per year. The total power per day required to produce 987.50 g/hr of ozone is shown below:

$$Total Power = 0.0121 \frac{kWh}{g} \times 987.50 \frac{g}{hr} \times 24 hours$$
$$= 286.77 kWh$$

Since the energy price for the first 200 kWh is 38.00 cents/kWh while the following unit is 44.10 cents/kWh. The daily energy cost is calculated below:

$$Daily Energy Cost$$

$$= \left(200 \, kWh \times \frac{38.00 \, cents}{kWh}\right) + \left(86.77 \, kWh \times \frac{44.10 \, cents}{kWh}\right)$$

$$= 11426.56 \frac{cents}{day}$$

$$= RM \, 114.27/day$$

To calculate for the energy cost per annum:

Annual Cost =
$$\frac{RM \ 114.27}{day} \times 365 \ days$$

= $RM \ 41708.55/year$

Thus, the total estimated energy cost for ozone to deal with 5.5 mg/L of iron from 10 MLD of water capacity is RM 41708.55 per year.

APPENDIX C: Calculations for Cost Analysis for Liquid Oxidants

Table C-1 shows the mass order price per metric tonne for KMnO₄ and NaOCl obtained from Alibaba platform. For the price of NaOCl which is in a range, the highest price for the oxidants is taken into consideration to analyse the required cost.

Table C-1: Price of Oxidants KMnO₄ and NaOCl.

Oxidant	Purity (%)	Price (USD/tonne)	Reference
KMnO ₄	99.5	2200.00	Alibaba Group, 2021a
NaOCl	8 - 16	200.00 - 400.00	Alibaba Group, 2021b

Sample calculation for KMnO₄

To calculate for the price of oxidant required per hour:

$$Price = 2154.17 \frac{g}{hr} \times \frac{1 \, kg}{1000 \, g} \times \frac{2200.00 \, USD}{tonne} \times \frac{1 \, tonne}{1000 \, kg}$$
$$= 4.74 \frac{USD}{hr}$$

Assuming that the operation duration of water treatment plant is 24 hours per day and 365 days per year, the cost for the oxidant KMnO₄ required in a year is calculated:

$$Cost = 4.74 \frac{USD}{hr} \times 24 \frac{hrs}{day} \times 365 \frac{day}{year}$$
$$= USD \ 41522.40$$

The conversion between USD and Malaysian Ringgit is based on the currency on 31 March 2021, which is 1 USD equal to 4.15 Malaysian Ringgit:

$$Cost = USD \ 41522.40 \ \times \ \frac{RM \ 4.15}{1 \ USD}$$

= RM 172317.96