SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

MANGANESE REMOVAL IN GROUNDWATER TREATMENT USING HIGH GRADE LIMESTONE

By

AINUL AFEEQAH ATHIRAH BT ABDUL RAHIM

Supervisor: Dr. Nor Aida bt Saad

Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours (Mineral Resources Engineering)

Universiti Sains Malaysia

MAY 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Manganese Removal in Groundwater Treatment using High Grade Limestone**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any examining body or University.

Name of student: Ainul Afeeqah Athirah bt Abdul Rahim   Signature:

Date : 25^{th} May 2018

Witness by

Supervisor : Dr. Nor Aida bt Saad   Signature:

Date : 25^{th} May 2018

ACKNOWLEDGEMENTS

Principally, I would like to uphold my greatest appreciation towards my supervisor, Dr. Nor Aida bt Saad for her continuous support, encouragement and guidance throughout my experimental studies. It is without doubt that her presence has positively driven me to complete my work.

I would also like to convey my sincere gratitude to the postgraduate student, Fitri that continuously aid in my study and put aside his own research to help me complete mine. Not only that, I would also like to thank all the staffs and technicians of School of Materials and Mineral Resources Engineering for lending me a helping hand and for their warmest cooperation.

My sincerest gratitude also to all my colleagues that relentlessly guide and help me throughout my research as well as for their valuable knowledge and input in various fields.

Last but not least to all that have aided me directly or indirectly either during my experimental works or report writing. All your contributions in terms of ideas, skills, knowledge and expertise are very much appreciated. Thank you very much.

TABLE OF CONTENTS

CONTENTS **PAGE**

LIST OF FIGURES

PAGE

LIST OF TABLES

PENYINGKIRAN MANGAN DALAM RAWATAN AIR BAWAH TANAH MENGGUNAKAN BATU KAPUR BERGRED TINGGI

ABSTRAK

Mangan ialah salah satu elemen yang sukar disingkirkan dari air bawah tanah kerana sifat kelarutannya yang tinggi dalam keadaan berasid mahupun neutral. Walau bagaimanapun, batu kapur sangat berkesan dalam menyingkirkan Mangan sekiranya wujud dalam kepekatan yang rendah. Kajian ini adalah untuk merawat air bawah tanah menggunakan batu kapur bergred tinggi untuk menyingkirkan Mangan. Pencirian terhadap batu kapur yang diperoleh dari Ipoh telah dilakukan dalam kajian ini. Batu kapur yang digunakan mengandungi CaCO3 sebanyak 97.26%. Sampel air bawah tanah diperoleh dari USM Kampus Kejuruteraan di mana Mangan mempunyai kepekatan sebanyak 0.5 ppm dan melebihi paras piawai yang ditetapkan pada 0.1 ppm. Penapisan air bawah tanah dilakukan dengan menggunakan batu kapur bersaiz kerikil (14 mm, 10 mm, 6 mm, 4mm, 2mm) dan pasir (1mm, 0.6 mm, 0.4 mm, 0.3 mm) serta menggunakan kadar aliran yang berbeza (0.007 L/s, 0.008 L/s, 0.011 L/s, 0.017 L/s) bagi setiap percubaan. Untuk kolum batu kapur bersaiz kerikil, peratusan tertinggi penyingkiran Manganese adalah 58.15% di mana kadar aliran ialah 0.007L/s Di samping itu, untuk kolum batu kapur bersaiz pasir, peratusan tertinggi penyingkiran adalah 97.26% dengan kadar aliran 0.017L/s. Partikel batu kapur bersaiz halus menunjukkan kadar keberkesanan yang tinggi dalam menyingkirkan Manganese berbanding batu kapur bersaiz kasar. Ini disebabkan luas kawasan permukaan yang besar oleh partikel bersaiz halus. Kadar aliran pula tidak menunjukkan trend yang ketara terhadap penyingkiran Mangan.

MANGANESE REMOVAL IN GROUNDWATER TREATMENT USING HIGH GRADE LIMESTONE

ABSTRACT

Manganese is one of difficult elements to remove in groundwater due to its high solubility in both acid and neutral condition. However, limestone is effective in removing Manganese if the Manganese is in low concentration. This study investigate the groundwater treatment using high purity limestone in removing Manganese. In this research, the characterization of limestone sample obtained from Ipoh was done. The limestone sample contain CaCO3 in majority at 97.3%. Groundwater sample obtained from USM's Engineering Campus also characterized and the concentration of Manganese is approximately 0.5 ppm exceeding the Raw Water Quality Standard at 0.1 ppm. Filtration of groundwater using pebble size limestone and sand size limestone column filter was done with different flowrate. For pebble size limestone column filter, the highest percentage removal is 58.15% where the flowrate is 0.007 L/s. On the other hand, for sand size limestone column filter, the highest percentage removal is 97.26% where the flowrate is 0.017 L/s. Fine size limestone particle shows an efficient Manganese removal in groundwater compared to coarser size particle. This was most probably due to the high surface area of smaller particle. The flow rate did not shows any significant trend in removing Manganese.

CHAPTER 1

INTRODUCTION

1.1 Groundwater

Groundwater is the world's largest accessible freshwater and an important resource for human daily uses. Groundwater can be used as drinking water supply, irrigation, industrial uses and many other uses. Approximately one-third of the world's population depend on groundwater for drinking purpose (UNEP, 1999). In fact, there are several states that use groundwater as their primary freshwater in Malaysia source such as Kelantan, Perak and Sabah (The Star, 2014). As for Kelantan, groundwater is being significantly used for fresh water supply and is the largest groundwater operator in Malaysia. Traditionally people in Kelantan have used groundwater resource as the potable use since early civilization, before fully developed into industrial potable use in 1935 (W Ismail 2009).

However, the groundwater cannot be readily use without prior treatment. The groundwater can be contaminated with both organic and inorganic materials which result it to be unsafe and unfit for human use. Many technologies are established to treat groundwater and the cost for water treatment is biggest concern for the design and implementation of a groundwater treatment system.

In conventional water treatment plant, a high capital cost is spent on reverse osmosis (RO) filtration system treatment to decrease dissolved minerals besides removing taste, colour and odour-producing organic compounds in the water. The water treated by RO filtration system is suitable for household use as RO membrane can remove virtually all microorganism in water. Besides RO filtration system, AC could be a potential material used in water treatment system to remove contaminants just like the RO membranes yet the capital cost is estimated to be much lowered.

Several trace metals can be found naturally in the groundwater such as Manganese, Iron. However, industrial activities such as mining and metallurgy, solid waste disposal, can lead to severe groundwater pollution with elevated concentrations of toxic metals including lead, cadmium and chromium (Jaishankar et al., 2014).

Groundwater contamination occur when man-made products and chemical seeps through the soil and get into the groundwater (Groundwater Foundation, 2018). Human activities such as agriculture, industrial and residential are among the causes of the groundwater contamination.

Contamination of groundwater can result in poor drinking water quality, loss of water supply, degraded surface water systems, high clean-up costs, high costs for alternative water supplies, and/or potential health problems. Drinking water containing bacteria and viruses can result in illnesses such as hepatitis, cholera, or giardiasis (EPA, 2015).

Manganese is commonly found in groundwater because of the weathering and leaching of manganese-bearing minerals and rocks into the aquifers; concentrations can vary by several orders of magnitude (Groschen et al., 2009).

Manganese is an essential nutrient needed for human body, but in excess it can lead to neurotoxicity; dysfunctional of the nervous system (Riojas-Rodríguez et al., 2010; Zoni et al., 2007). Health-based guidelines for the maximum level of manganese in drinking water are set at 300 μg/L by the U.S. Environmental Protection Agency (EPA) (2004) and at 400 μg/L by the World Health Organization (WHO) (2008). Neurobehavioral deficits in human have been shown to correspond with manganese exposure (Chang et al., 2009). Despite of the negative effects on human health, Manganese is an important substance in the industry. Manganese is primarily used in manufacture of steels, alloys, and as an ingredient in various products; batteries and fireworks (IPCS, 1999; ATSDR, 2000).

1.1.1 Limestone in water treatment

Most methods, such as ion exchange, coagulation flocculation, distillation require high capital and operating costs. The coagulation-flocculation generates sludge, which require extra operational cost for sludge disposal. For ion exchange, due to high concentration of iron and manganese, there is a high risk of fouling and rapid clogging. Therefore ion exchange is not recommended in treating water with high concentration of iron and manganese.

Calcium carbonate has been proven effective in removing metals, turbidity, suspended solids and total coliform from water, where the removal was up to 96% (Adlan, Aziz and Maung, 2008).

Limestone is used widely in acid mine drainage (AMD) treatment to increase pH of AMD, also used to neutralize acidity in industrial wastewater. There are few physicochemical factors which control the effectiveness of water treatment using limestone such as co-precipitation of metal ions or adsorption, redox processes, pH fluctuation and dilution of groundwater by mixing with limestone (Mandadi, 2012). In this study, different sizes of marble are used as filter media in a column filter which could determine the efficiency of Manganese removal using different sizes of limestone.

Physical adsorption is a common method adapted to remove metal contaminants in raw water. The common media for physical adsorption includes activated carbon, sand and some other rock adsorbents such as limestone.

In this research work, application of high purity limestone taken from Zantat Sdn. Bhd. in Simpang Pulai, Perak based on different sizes and also different water flow rate will be used to study the removal of Manganese.

1.2 Problem statement

Groundwater is one of the primary sources for freshwater in Malaysia. Groundwater can be a substitute to surface water and become a primary freshwater source because contain less contaminants. This project is significant because the Director of USM Engineering Campus need to see the potential of using groundwater as primary source of fresh water in our campus.

However, it is not 100% free from contaminants and must undergo certain treatments to remove the contaminants such as microorganisms, nitrates and heavy metals. Heavy metals often found in groundwater are Fe, Mn, Cu, Cr, Pb, Zn and Ni. The highest content of heavy metal found in groundwater are Fe and Mn (Magesh, Chandrasekar and Elango, 2017).

The presence of heavy metals in groundwater can be removed through many methods such as ion exchange, carbon adsorption and removal by limestone.

Removal heavy mineral from groundwater using limestone is known as one of effective methods of water treatment. Limestone is effective in controlling the water pH and also removing heavy minerals in the water (Aziz et al., 2001). Although there are other methods available, limestone is still widely chosen in treating water mainly because it is cost-effective and a simple process.

1.3 Research Objective

The purpose of this research are to remove Manganese in groundwater using high grade limestone as filter media.

The main objectives are as follows:

i) To study groundwater treatment using high grade pebble and sand size limestone.

ii) To measure the removal of Manganese in groundwater using pebble and sand size limestone column filter.

iii) To study the flow rate which has the highest percentage removal of Manganese from groundwater

1.4 Scope of Study

In this work, limestone is used as a filtration media to remove Manganese from the groundwater. The limestone is prepared physically via crushing, grinding and sieving to allow particle of different sizes. The limestone is then undergo XRF process to determine the elemental composition of the limestone. As for the groundwater sample, the groundwater is taken from the well using a pump. The groundwater sample is then tested using ICP-OES to detect the percentage of trace and chemical elements present. To ensure the precision of the sample for each experiment run, the experiment is carried out the same day as the groundwater sampling. By doing so, the percentage of trace elements present in the sample will be similar at the beginning of each experiment run. The groundwater sample is then treated using limestone of different sizes in each tank. The process is continuous from the first tank (coarser particle size) until the third tank (finer particle size). After each filtration process, the sample is tested using ICP-OES again to know the percentage of Manganese present after the treatment.

1.5 Thesis Outline

This thesis contains five chapters. Chapter 1 includes the introduction of the research background and also provide the objectives and problem statements related to the project.

Chapter 2 reviews the literature and studies on groundwater, limestone and Manganese removal from groundwater.

Chapter 3 explains the materials and experimental methods used in this research work. This include raw material selection, sample preparation and experimental setup.

Chapter 4 discussed the data analysis and interpretation. The data were obtained through XRF, ICP-OES, SEM analysis and other corresponding methods.

Finally, Chapter 5 is about the overall finding of the project and recommendation for improvement in future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Groundwater

2.1.1 Background

Freshwater found underneath Earth's surface in the soil or rock fractures is what we called as groundwater. Groundwater is contained in water-bearing permeable layer called aquifers. An aquifer is a geological formation that made of permeable materials such as gravel, sandstone, sand or fractured rock such as limestone. Groundwater is not a still water body, it can seep and flow through cracks and pores solely by gravity.

There are two main aquifer systems (Saim, 1997):

i. shallow aquifer - mostly unconfined but occasionally semiconfined, thickness normally 2-3 m and may reach up to 17.5 m. It is usually referred to as first aquifer.

ii. deep aquifer - mainly confined, thickness usually more than 15 m. This deep aquifer comprises three different layers, separated from each other by semipermeable strata of silt, normally referred to as the second, third and fourth aquifer.

The flow rate will be slower upon reaching the aquifer. Physical characteristics of the aquifer will determine how fast the groundwater flows. Groundwater will continue to move until it reaches another aquifer or water body like a river, lake or an ocean.

The Groundwater Quality Standards for Malaysia is still not established, but considering potential of groundwater as an alternative source for surface water, DOE had started the National Groundwater Monitoring Programme to determine the groundwater quality status (WEPA).

Since the Groundwater Quality Standards is still not established, the groundwater quality status was determined based on the National Guidelines for Raw Water Quality as the benchmark. Table below is national guidelines for Raw Water Quality in Malaysia

Table 2. 1 National Guidelines for Raw Drinking Water Quality

(Revised December 2000)

Parameter	Symbol	Benchmark
Sulphate	SO4	250 mg/l
Hardness	CaCO3SO	500 mg/l
Nitrate	NO3SO	10 mg/l
Coliform	-	Must not be detected in any 100 ml sample
Manganese	Mn	0.1 mg/l
Chromium	Cr	0.05 mg/l
Zinc	Zn	3 mg/l
Arsenic	As	0.01 mg/l
Selenium	Se	0.01 mg/l
Chloride	Cl	250 mg/l
Phenolics	-	0.002 mg/l
TDS	-	1000 mg/l
Iron	Fe	0.3 mg/l
Copper	Cu	1.0 mg/l

Lead	Pb	0.01 mg/l
Cadmium	Cd	0.003 mg/l

2.1.2 Groundwater Resources

Groundwater in Malaysia is the secondary source of freshwater since decades ago which covered less than 10% of public water supply in the nation (Abd-Razak Y, 2009) and the demand of groundwater supply might rise as major source of freshwater in certain states which included Kelantan, Pahang, Terengganu, Sabah and Sarawak (Nampak, Pradhan and Manap, 2014). The reliance on groundwater varies among different countries, and it is estimated as freshwater supply to one third of the world population for their daily activities (Hiscock, 2011).

Malaysia is a tropical country which has plenty of rainfall which contributed to abundance of groundwater resource from the annual rainfall and the estimated groundwater storage resource is 5000 BCM (Azuhan, 1990). Table below shows water resources in Malaysia. Groundwater in Malaysia is underutilized as the current usage is only at 197 Ml/d (Malaysia Water Guide, 2009).

Table 2. 2 Water Resources in Malaysia

HYDROLOGY PARAMETER	TOTAL ANNUAL VOLUME (BCM)
Annual Rainfall (3000 mm)	990
Eco-transpiration	360

Effective Rainfall	630
Surface Runoff	566
Groundwater Recharge	64
Surface Artificial Storage	25
Groundwater storage	5000

In Malaysia, the largest usage of groundwater is in Kelantan. Almost all part of Kelantan state use groundwater as water source whether as primary or secondary back up source. Groundwater provides 40% of potable water supply in Kelantan (NAHRIM, 2015).

The reliance on groundwater varies among different countries, and it is estimated as freshwater supply to one third of the world population for their daily activities (Hiscock, 2011). Malaysia is not depending on groundwater as primary water sources but the usage of groundwater is estimated to increase in 2020 from 13,200 Million Liters per Day (MLD) to 16,500 MLD (JMG, 2010).

Malaysia is expecting to seek potential of using groundwater as backup water sources in order to ensure long term water availability. For example, during climate change, drought, prolonged dry seasons where there is no rainfall, groundwater can be a backup water supply.

Thus, it is compulsory to have more study and research on groundwater to maximise utilization of groundwater resources in Malaysia. More study on groundwater treatment and management needed for general improvement of groundwater quality and providing low cost treatment system in order to make groundwater as a dependable and sustainable sources.

2.1.3 Groundwater Contamination

Groundwater contamination occur when man-made products and chemical seeps through the soil and get into the groundwater (Groundwater Foundation, 2018). Human activities such as agriculture, industrial and residential are among the causes of the groundwater contamination.

Contamination of groundwater can result in poor drinking water quality, loss of water supply, degraded surface water systems, high clean-up costs, high costs for alternative water supplies, and/or potential health problems. Drinking water containing bacteria and viruses can result in illnesses such as hepatitis, cholera, or giardiasis (EPA, 2015).

The contaminants in water could be classified as inorganic, organic and microbiological contaminants.

The inorganic contaminants are metals, nitrates like aluminium, arsenic, chloride, cyanide, mercury, dissolved solids, iron, lead etc. Heavy metals often found in groundwater are Fe, Mn, Cu, Cr, Pb, Zn and Ni. The highest content of heavy metal found in groundwater are Fe and Mn (Magesh, Chandrasekar and Elango, 2017). Iron and Manganese occur naturally in groundwater (Tredoux et al., 2004).

The organic contaminants are volatile organic compounds, pesticides, phenols and dioxin. Microbiological contaminants in groundwater such as bacteria, E-Coli and microorganisms.

EPA has categorized the drinking water contaminants into four general categories as listed in Table 2.3 together with examples of the contaminants. A list of Contaminant Candidate List (CCL) is establish by EPA to serve as first level of evaluation for unregulated water contaminants that require investigation and research of potential health effect.

Table 2.3 Types of Drinking Water Contaminants and Examples

Type of Contaminant	Examples of Contaminant
Physical	Sediment, organic material suspended in water which came from erosion.
Chemical	Nitrogen, bleach, salts, pesticides. Metals, toxins from bacteria, and human or animal drugs.
Biological	Microbes (bacteria, viruses, protozoan, and parasites)
Radiological	Elements which can emit ionizing radiation (caesium, plutonium and uranium)

2.2 Water treatment process

Groundwater treatment, also called as groundwater remediation can be categorized into three classes: i. Chemical Treatment Technologies, ii. Biological Treatment Technologies, iii. Physicochemical Treatment Technologies (Hashim *et al.*, 2011). Most groundwater treatment system utilize a combination of technologies. The most widely used groundwater remediation is Pump and Treat, a physical treatment where the groundwater is pumped to the surface and couple with either biological or chemical treatment to remove contaminants.

2.2.1 Filtration

Filtration process is a physical process which use a filter media in order to separate two different phases which is solid and liquid. It is a process where solid particle is removed from a liquid. There are many types of filter media such as, semi permeable membrane, activated carbon, limestone and porous material. Water will flow through the filter media and the solid particle will be remained on the filter media. The filter media can be re-used by backwashing the filtration system.

2.2.2 Distillation

Distillation is a physical water treatment method which incorporating the mechanism of evaporation and condensation to separate ingredients in the water. This process uses heat energy rather than chemicals to purify water. Distillation can remove nearly all impurities in water including sodium, calcium, magnesium, iron, manganese, and even microorganisms. Boiling process will inactivate all the microorganisms but if the distiller is idle for an extended period, the microorganisms can be reactivate and may contaminate the water.

Distiller use heat to boil water and produced steam. The heat will inactivate microorganisms and bacteria. The steam is then enter condensing coil and cools, condenses and changes back to liquid form. The water then flows into a storage container.

Distillation units generally consist of a boiling chamber, where the water is heated, condensing coils, where the water is cooled and storage tank where the distilled water is kept. Figure below shows the typical assemble and process of a distiller.

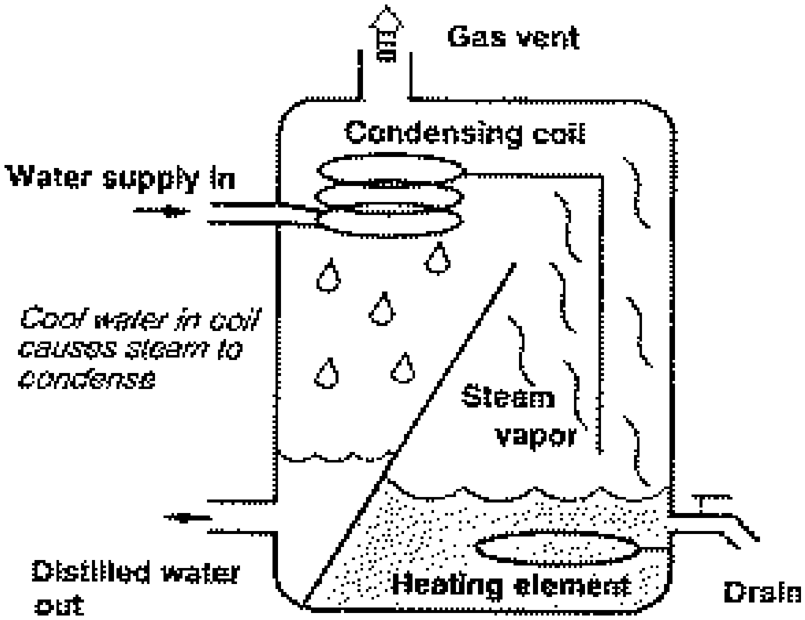


Figure 2. 1 Distillation process in distiller (McGraw-Hill Dictionary of Scientific & Technical Terms, 6E., 2003)

Limitation of this process is that water containing volatile organic contaminants cannot be used. This is because when heated, the volatile material which have lower melting point that water will vaporize alongside with water. So, the compounds will not completely removed unless another designated process is used before condensation.

Operation costs for distillation can be among the highest for water treatment systems (Dvorak, 2013). Distillation system cost approximately $1000 including the installation and operational cost primarily for electric energy would cost about $15 per month (DOE, 2011).

2.2.3 Disinfection

Surface waters have been the focal point of water disinfection regulations since their inception, as groundwater (like wells) have been historically considered to be free of microbiological contamination. Current data indicates this to not be true. Amendments to the Safe Drinking Water Act in 1996 mandate the development of regulations to require disinfection of groundwater "as necessary".

Water disinfection means the removal, deactivation or killing of pathogenic microorganisms. Microorganisms are destroyed or deactivated, resulting in termination of growth and reproduction. Disinfection can be attained by means of physical or chemical disinfectants.

The agents also remove organic contaminants from water, which serve as nutrients or shelters for microorganisms. Disinfectants should not only kill microorganisms. Disinfectants must also have a residual effect, which means that they remain active in the water after disinfection.

Disinfection process if the final process after combination of water treatment processes including filtration, distillation, flocculation, coagulation and sedimentation. The process is not an independent process.

Disinfections only can remove and kill bacteria, viruses and microorganisms. This process cannot be incorporated in removing inorganic contaminants.

As an individual pathogenic organism can be difficult to detect in a large volume of water or wastewater, disinfection efficacy is most often measured using "indicator organisms" that coexist in high quantities where pathogens are present.

The most common indicator organism used in the evaluation of drinking water is Total Coliform (TC) (Water Environment Federation, 2001).

Table below shows 2 different types of disinfectants, chemical and physical disinfectants.

Table 2.4 List of chemical and Physical Disinfectants

Chemical disinfectants	Physical disinfectants
Chlorine (Cl_2) Chlorine dioxide (ClO_2) Hypo chlorite (OCl^-) Ozone (O_3) Halogens: bromine (Br_2), iodine (I) Bromine chloride (BrCl) Metals: copper (Cu^{2+}), silver (Ag^+) Potassium Permanganate ($KMnO_4$) Phenols Alcohols Soaps and detergents Hydrogen peroxide	Ultraviolet light (UV) Electronic radiation Gamma rays Sounds Heat

2.3 Removal of Manganese

Apart from potential health problems, Manganese is typically removed in order to preserve water quality and also to prevent operational problems. Manganese deposits are also known to cause problems in drinking water systems, stemming from increased tuberculation in pipes and coating development in concrete tanks (Tobiason, Bazilio, Goodwill, et al., 2016).

Manganese gives greyish-black colour to the water and this will arise many problems such as staining to any surfaces and also induce doubt in consumer towards the water quality.

Manganese is an important nutrient but it is toxic at high concentration. A toxicological profile for Manganese was published by the Agency for Toxic Substances and Disease Registry (ATSDR), which includes a recommendation that Manganese intake not exceed 5 mg/day (Tobiason, Bazilio, Goodwill, et al., 2016).

Removal of Manganese in water can be done by various physical, chemical and biological processes. Characterisation of Manganese present (particulate or dissolved) and also other parameters are crucial step in determining suitable treatment process.

Recent publications from the Water Research Foundation (Brandhuber, Clark, Knocke and Tobiason, 2013) and the American Water Works Association (Civardi, Tompeck, 2015) provide useful guidance in order to select appropriate treatment process for Manganese removal. Range of available treatment choices is shown in a simplified manner in figure below.

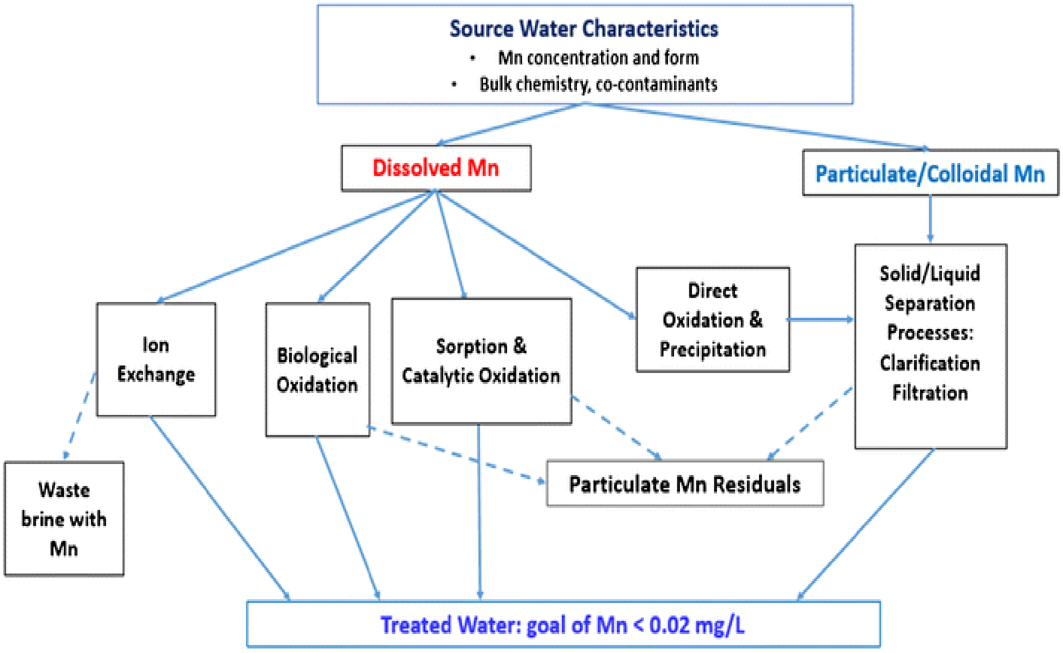


Figure 2. 2 Schematic diagram of Manganese removal treatments

2.3.1 Chemical process of Manganese removal

Manganese can be remove through chemical processes such as direct oxidation and ion exchange. Oxidation process is where Mn2+ is oxidise into Mn4+ which exists in particulate form. After this, the solid formed can be physically removed from water by filtration process.

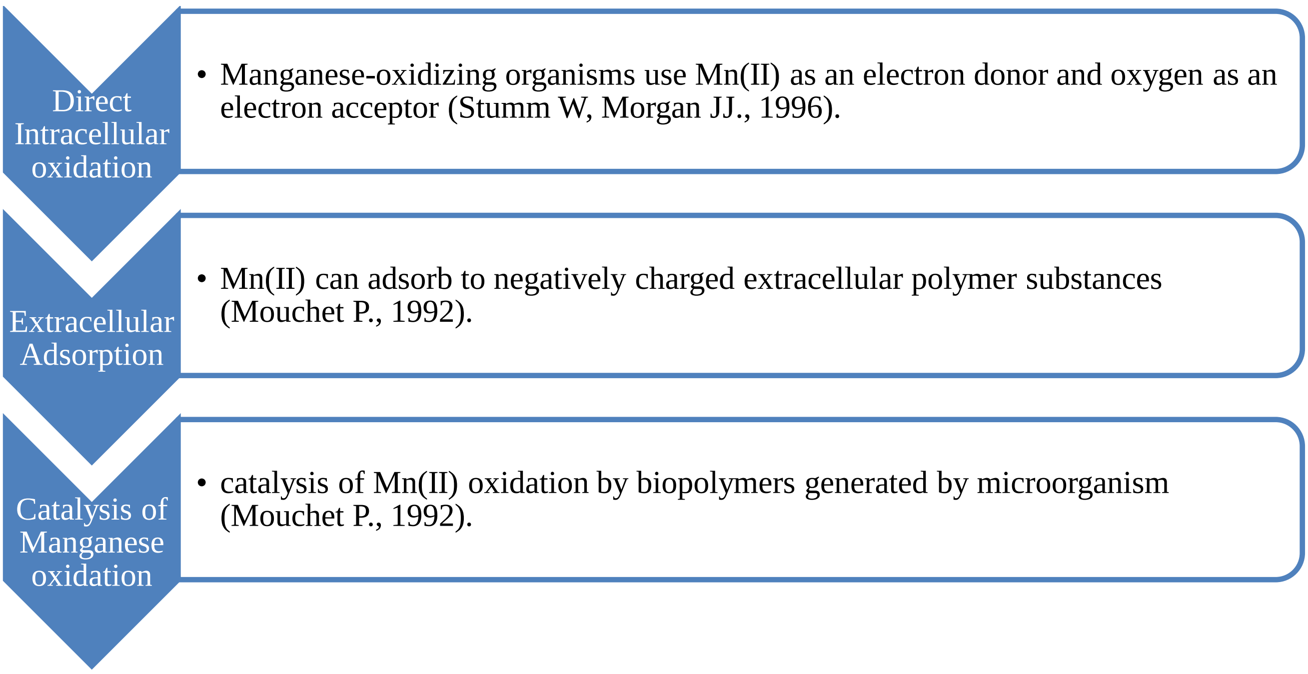
The kinetics of oxidation of Mn(II) by oxygen (O_2) or free chlorine (Cl_2, present in water as HOCl and OCl^-, depending on pH) are very slow relative to the hydraulic retention times typically encountered in drinking water treatment systems when pH < 9, with the estimated half-life of Mn(II) in the presence of O_2 and Cl_2 on the order of years and hours, respectively, for these conditions (Pankow, Morgan, 1981). Therefore, strong oxidants such as chlorine dioxide (ClO_2), permanganate (MnO_4^-), and ozone (O_3) are required (Knocke, Van Benschoten, Kearney, Soborski, Reckhow, 1991).

There are various oxidizing agent that can be used in oxidation of dissolved Manganese ion such as:

1) Chlorine Dioxide
2) Ozone
3) Permanganate

2.3.2 Biological process of Manganese removal

Biological process in removing Manganese from water using biofiltration media and does not require addition of any chemical. There are three steps in order for microorganism remove Manganese from the water.



2.4 Limestone and marble

2.4.1 Mineralogy

Limestone is a sedimentary rock consists of calcium carbonates as its major constituents. Limestone is a versatile rock which have many uses such as, aggregate for road base, components in cement production and also as acid-neutralizing agent. Common colour for limestone is white, yellowish and greyish depending on impurities present.

Marble is a type of metamorphic rock which is altered from limestone under high temperature and pressure. The impurities in limestone such as sand, clay, iron oxides and sometimes organic matters will affect the colour of marble after metamorphism. It is common to have white, pink and black marble. The hardness of marble on Mohs Hardness Scale vary from 3-4. The major uses of marble such as building stone, dimension stone, and also as pigment in paint and paper.

2.4.2 Limestone in groundwater treatment

Marble chips are studied for its uses in water treatment since it has alkali properties to act as pH regulator in acidic water just as limestone. Besides hardness, marble has similar chemical properties like limestone. It is common to find limestone used by industry in water treatment process such as acid mine drainage treatment and neutralizing industrial wastewater.

Different kind of limestones such as pure limestones, brecciated limestones and carbonaceous limestone carry different degree of effectiveness in heavy metal removal (Yao

Zhigang, 2009). Limestone is also applied in an AMD treatment located at Gangneung, Korea since 1999 and it successfully maintain effective long-term treatment where physicochemical process of co-precipitation/adsorption with iron hydroxide in the AMD stream is a main control variable of the process (Shim *et al.*, 2015).

Hence, limestone has a strong potential in treating heavy metals from water. The selection of limestone type in a treatment is depending on the purpose of the water treatment.

CHAPTER 3

MATERIALS AND RESEARCH METHODOLOGY

3.1 Introduction

This chapter described the steps that has been taken for manganese removal in groundwater treatment using limestone.

3.2 Raw Material

In this study, high grade limestone is used as raw material supplied by Zantat Sdn. Bhd. from their limestone quarry in Simpang Pulai, Perak. The size of sample as received, ranging from Groundwater sample is taken from USM's well and sulphuric acid is used to preserve the sample. Table 3.1 shows the list of chemicals and material used throughout the experiment.

Table 3.1 List of materials used in the experiment

Material	Purity	Supplier
Groundwater	-	USM's tube well
Limestone	>98%	Zantat Sdn. Bhd.
Nitric acid		

3.3 Equipment

Various equipment were used throughout the project to achieve the objectives. The equipment were used in several processes such as crushing, sizing, heating, filtering and analysing.

Jaw crusher, cone crusher and sieve shaker were used to prepare the limestone to the desired sizes (14 mm, 10 mm, 6 mm, 4 mm, 2 mm, 1 mm, 06 mm, 0.4 mm, 0.3 mm) and separate them accordingly while water pump was used to extract the groundwater from the tube well.

The list of equipment and its general use is tabulate in Table 3.2 below.

Table 3.2 List of equipment used in the experiment

Equipment	**Purpose**
Water pump	Pump groundwater to surface
Crusher (Jaw, Cone)	Reduce limestone size
Sieve shaker	Separate limestone accordingly to size
Pulverizer	To crush limestone sample into fine powder for XRF

3.4 Research work flowchart

The overall experimental activities were carried out as presented below.

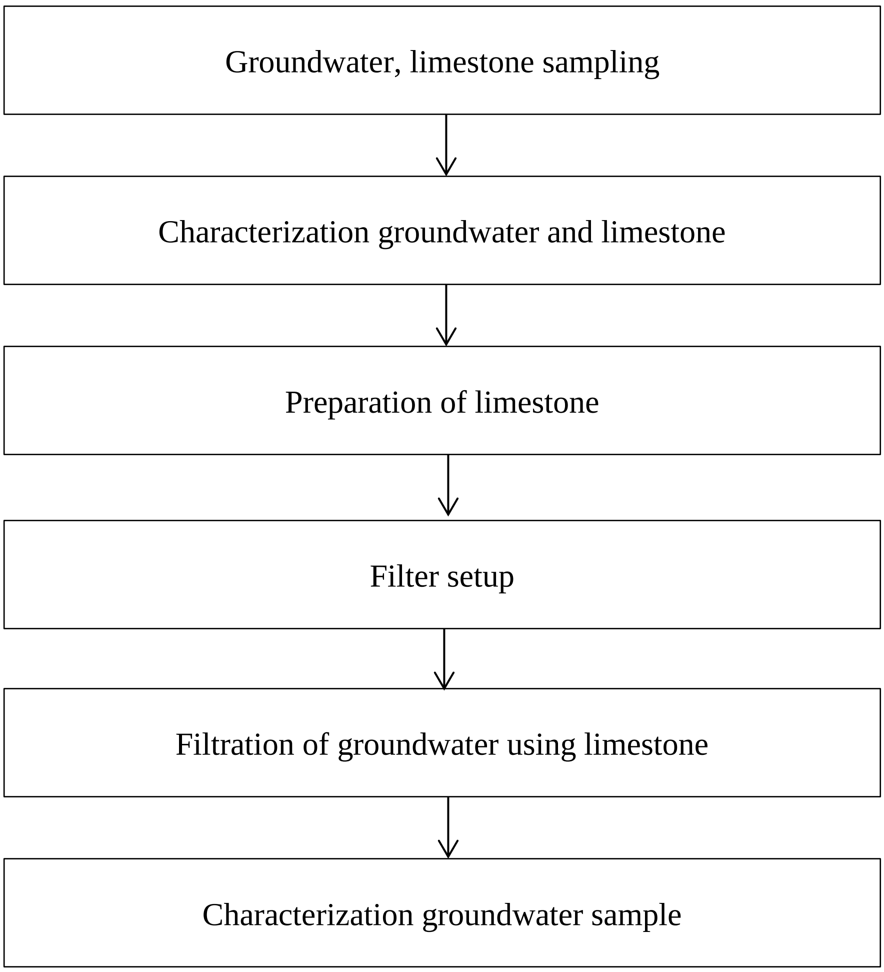


Figure 3. 1 Schematic Flow Diagram of Experimental Procedure