EFFICIENCY OF MARBLE FILTER SYSTEM FOR GROUNDWATER TREATMENT

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UNIVERSITI SAINS MALAYSIA

2019

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by

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Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

November 2019

ACKNOWLEDGEMENT

There are many people that I would like to thank for helping me throughout this whole research. So many have made my journey towards finishing my thesis to be easier despite the obstacles and predicaments that I have to face towards the end. Alhamdulillah, praise to Allah S.W.T for His blessings and forgiveness, for without His willing, it will be almost impossible to complete my thesis. First, I would like to thank my supervisor Dr Noor Aida Saad for her guidance, encouragement and patience over these two years of hardship. Thank you so much for forcing me, for giving me endless support and advices. Without her support, I would not have enough perseverance and motivation to continue this difficult task, which I almost feel like quitting so many times. Therefore, I thank you again for never giving up on me. I would like to express my deepest appreciations to my co-supervisor Professor Dr Nor Azazi Zakaria, who in the meantime held the position of the Director of River Engineering and Urban Drainage Research Center (REDAC) and Director of Engineering Campus USM. Much of my experimental work would not have been completed without his assistance and support. All I could say is he is much like a father to us who is always giving advice and guidance to his staffs and students for a better life in the future. I would also like to extend my thanks to Associate Professor Dr Mohamad Hekarl Uzir (School of Chemical Engineering, USM), Professor Dr. Zulkifli Ahmad (School of Material Engineering, USM) and Dr. Goh Hui Weng (REDAC, USM) for providing a ton of valuable opinions, information and supports on different aspects to open my mind to break the hardship during the progress of this research's experiment.

I love to express my indebtedness to my beloved parents, Mohd Akhir Ahmad and Ramlah Awang; my gorgeous wife, Dyg Farah Hanim Abu Bakar; and my brother, Muhammad Hafiz Mohd Akhir for their love and indispensable support throughout my life. Big thanks to my REDAC family, which is my second family who always cheer me up and help each other in any work.

Great deals appreciated to REDAC staff i.e. Mr. Rahim Rhazali, Mr. Zakariaansori Rahman, Mr. Shahrizor Salim, Mr. Khairul Nizam Abu, Mr. Sufian Osman, Mr. Mubarak Mat Zin, Mr. Suhaizar Sulaiman and Mr. Norzaide Baharudin who were giving a hand in my data collection and preparation of experiment. A special thanks to the technician who was in charge in helping me during handling the ICP-OES machine (Mr. Azrul Zainol Abidin), Crusher and Sieve machine (Mr. Junaidi Ramli), XRD machine (Mr. Zaini Saari), XRF machine (Mr. Kemuridan Md. Desa), SEM-EDX machine (Mr. Khairi Khalid), TGA-DSC machine (Mr. Mokhtar Mohamad), and furnace (Mr. Shahrul Ami Zainal) from School of Material and Mineral Resources Engineering, USM. Not to forget Mr. Nizam Kamal from School of Civil Engineering, USM who has generously lent me the required equipment whenever I am in need.

Last but not least, thanks to all my friends and my assistants including the undergraduate students who had undergone this journey together. The sweet and sour moments with all of you will be always be in my mind and will be an encouragement for me to further my study in the future.

Muhammad Fitri Mohd Akhir
November 2019

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Unit Symbols

Θ	Angle
^{o}C	Celsius
cm	Centimeter
€	Euro
g	Gram
h	Hour
^{o}K	Kelvin
k	Kilo
kW_{el}	Kilowatt Electric
>	Less than
l	Litre
l /s	Litre per second
m	Meter
mA	Milliampere
mg	Milligram
mm	Millimeter
mV	Millivolt
min	Minute
<	More or greater than
ppm	Parts per million
ppt	Parts per thousand
%	Percentage

lbs	Pound
s	Second
t	Time
$	US dollar
W	Watt

Chemical Symbols

Al_2O_3	Aluminium oxide
Al	Aluminum
Al^{3+}	Aluminum (III) ion
$Al_2(SO_4)_3$	Aluminum sulphate
NH_3N	Ammoniacal nitrogen
NH_4OH	Ammonium hydroxide
$[FeO_4]^-$	Anionic iron (VIII) oxide
$As(III)$	Arsenic (III) ion / Arsenite
As^{5+}	Arsenic (V) ion
$As(V)$	Arsenic (V) ion / Arsenate
Ba	Barium
B	Boron
$Mn^{2+}Mn^{3+}{}_6[O_8\|SiO_4]$	Braunite
Cd	Cadmium
Ca	Calcium
Ca^{2+}	Calcium (II) ion
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$CaSO_4$	Calcium sulfate/

CO_2	Carbon dioxide
Cl^-	Chloride
Cl	Chlorine
$FeCrO_4$	Chromite
Cr	Chromium
Cr^{4+}	Chromium (VI) ion
Co	Cobalt
Cu	Copper
Cu^{2+}	Copper (II) ion
CuO	Copper oxide
$CuSO_4$	Copper sulfate
ρ	Density
$Cu_2CO_3(OH)_2$	Dicopper carbonate hydroxide,
$FeCl_3$	Ferric chloride
$Fe(OH)_3$	Ferric hydroxide
Fe^{3+}	Ferric ion
$Fe(OH)_2$	Ferrous hydroxide
Fe^{2+}	Ferrous ion
F^-	Fluoride ion
α-$FeOOH$	Goethite
Fe_3S_4	Greigite
$(CaSO_4.2H_2O)$	Gypsum
Fe_2O_3,Fe_2O_3-hydrate	Hematite
H	Hydrogen
H^+	Hydrogen ion

H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
$FeTiO_3$	Ilmenite
IrO_2	Iridium(IV) oxide
Fe	Iron
$FeCO_3$	Iron Carbonate
Fe_2O_3	Iron oxide
Pb^{2+}	Lead (II) ion
γ-$FeOOH$	Lepidocrocite
Li	Lithium
$Fe_{(x+1)}S$	Mackinawite
Mg	Magnesium
Mg^{2+}	Magnesium (II) iron
$MgCl_2$	Magnesium dichloride
MgO	Magnesium Oxide
$MgSO_4$	Magnesium sulfate
Fe_3O_4	Magnetite
Mn^{7+}	Manganate (VII) ion/ Permanganate
Mn	Manganese
$MnCO_3$	Manganese (II) carbonate/ Rhodochrosite
$MnCl_2$	Manganese (II) chloride
Mn^{2+}	Manganese (II) ion
MnO	Manganese (II) oxide
$MnSO_4$	Manganese (II) sulfate
Mn^{4+}	Manganese (IV) ion

$MnCO_3$	Manganese carbonate
Mn_2O_7	Manganese heptoxide
MnO	Manganese oxide
M	Molar
Mo	Molybdenum
Ni	Nickel
Ni^{2+}	Nickel (II) ion
NiO	Nickel oxide
NO_3^-	Nitrate
HNO_3	Nitric acid
N	Nitrogen
$(Mg, Fe)_2 SiO_4$	Olivine
O^{2+}	Oxygen (II) ion
O_2	Oxygen gas
P_2O_5	Phosphorus pentoxide
K	Potassium
K^+	Potassium ion
K_2O	Potassium oxide
$KMnO_4$	Potassium permanganate
$[Ba, H_2O]_2Mn_5O_{10}$	Psilomelane
FeS_2	Pyrite
MnO_2	Pyrolusite
$Fe_{(1-x)}S$	Pyrrhotite
Eh	Redox reaction
Sc	Scandium

Se	Selenium
SiO_3	Silica
Na	Sodium
Na^{2+}	Sodium (II) ion
$NaOCl$	Sodium hypochlorite
$FePO_4.2H_2O$	Strengite
Sr	Strontium
SrO	Strontium oxide
SO_4^{2-}	Sulfate ion
S^{2-}	Sulfide
SO^{2-}_3	Sulfite
S	Sulfur
Ta_2O_5	Tantalum pentoxide
Ti	Titanium
FeS	Troilite
$Fe_3(PO_4)_2.8H_2O$	Vivianite
H_2O	Water
Fe^0	Zero valent iron
Zn	Zinc

LIST OF ABBREVIATIONS

AMD	Acid mine drainage
BES	Bio-electrochemical system
BOD	Biological oxygen demand
ρ_m	Bulk density of the marble
CEB	Chemical enhanced backwashing
COD	Chemical oxygen demand
ρ_w	Density of water
DOE	Department of Environment
D_{well}	Depth of the well
DAF	Dissolved air flotation
DO	Dissolved oxygen
DSARO	Draw solution assisted reverse osmosis
EPA	Environmental Protection Agency
f_{valve}	Filtration flowrate taken at the valve
DO_f	Final result of dissolved oxygen
f_w	Final weight of the filter
f_p	Flowrate of the pump (l/s)
FO	Forward Osmosis
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
DO_i	Initial result of dissolved oxygen
i_w	Initial weight of the filter
LOI	Loss on ignition

M_a	Mass of crucible + sample
M_b	Mass of crucible + sample after ignition
M_s	Mass of sample
MBR	Membrane bioreactor
MD	Membrane distillation
ME	Microbial electrolysis
MF	Microfiltration
nZVI	Nano zero valent iron
NF	Nanofiltration
NAHRIM	National Hydraulic Research Institute of Malaysia
NWQS	National Water Quality Standard
SPAN	National Water Services Commission
PVC	Polyvinyl chloride
PAC	Powder activated carbon
RSD	Relative standard deviation
t_R	Retention time
RO	Reverse osmosis
SP	Sampling point
SEM-EDX	Scanning Electron Microscopic-Energy Dispersive X-ray
SPS	Seberang Perai Selatan
SBR	Sequence batch reactor
SI	Sub index
SRB	Sulfate reducing bacteria
G_m	The specific gravity of marble
TGA-DSC	Thermogravimetry-Differential Scanning Calorimeter

E-coli	Total coliform organisms
Fe_T	Total concentration of iron
S_T	Total concentration of sulfur
V_T	Total of filter media's volume
TSS	Total suspended solid
UF	Ultrafiltration
V_V	Void's volume of filter media
VOC	Volatile organic compound
V_b	Volume of the bottle
V_m	Volume of the marble in the column
V_{pg}	Volume of the pumped groundwater
V_s	Volume of the sample
V_{well}	Volume of the well
WQI	Water quality index
M_m	Weight of the marble
XRF	X-ray fluorescence
XRD	X-ray Powder Diffraction
YSI	Yellow springs instruments

KECEKAPAN SISTEM PENAPIS MARMAR UNTUK RAWATAN AIR BAWAH TANAH

ABSTRAK

Baru-baru ini, fenomena gelombang panas El Nino telah menyerang negara Malaysia dan akibatnya, paras air tiga empangan di Malaysia telah jatuh di bawah tahap kritikal. Bagi menyelesaikan krisis kekurangan air ini, air bawah tanah sememangnya sumber air yang terbaik untuk manusia kerana sifatnya yang terletak di bawah permukaan bumi yang terlindung daripada gelombang panas, oleh itu, air bawah tanah tidak akan kering cepat berbanding air permukaan. Walau bagaimanapun, pencemaran air bawah tanah tidak dapat dielakkan dan tidak terkawal, namun ia masih boleh dirawat secara ekonomi. Dalam kes ini, telaga tiub 55.6 m yang terletak di dalam Kampus Kejuruteraan Universiti Sains Malaysia digunakan sebagai sampel air bawah tanah dalam kajian ini. Didapati bahawa air bawah tanah sangat tercemar oleh sumber semula jadi dan aktiviti manusia. Pada asalnya, warna air bawah tanah berwarna hijau kekuningan dan mengeluarkan gas H_2S, tetapi akibat tindak balas pengoksidaan, air tersebut segera berubah warna menjadi hitam iaitu mendakan FeS dalam masa 40 saat selepas terdedah kepada udara. Kepekatan saliniti yang tinggi (5.1 ± 0.1 ppt), kepekatan NH_3N yang tinggi, dan pelbagai unsur juga telah dikesan dalam sampel air bawah tanah. Oleh hal yang demikian, air bawah tanah dikelaskan sebagai kelas IV berdasarkan kualiti indeks air Malaysia dan dianggap berbahaya kepada manusia. Untuk mengatasi masalah ini, satu penyelidikan telah dijalankan untuk mencari jalan bagi menjadikan air bawah tanah menjadi sumber air yang selamat kepada manusia dan telah terbukti bahawa marmar merupakan salah satu media penapis terbaik untuk sumber air bawah tanah. Sifat-sifat marmar yang terdiri daripada

97% $CaCO_3$ telah berjaya meningkatkan reaksi redoks pencemar, kemudian meningkatkan kadar pemendakannya dan memudahkan proses penapisan. Dari segi saiz media penapis, telah didapati bahawa saiz pasir jauh lebih baik daripada saiz kerikil untuk menghilangkan pencemaran air bawah tanah. Saiz pasir marmar dapat menghilangkan sebahagian besar bahan pencemar air bawah tanah dengan peratusan di atas 90% dan manakala beberapa unsur lain seperti Al, Ba, dan Ca dapat dibuang hanya melebihi 70%. Walau bagaimanapun, kepekatan unsur-unsur ini selepas penapisan masih di bawah had ambang standard air minuman berdasarkan NWQS Malaysia, EPA, dan WHO. Hasil daripada penyingkiran bahan pencemar air bawah tanah, ia telah mencapai hasil kualiti air kelas I dan kelas II. Sebaliknya, marmar dalam saiz kerikil menghasilkan kualiti air di kelas III.

EFFICIENCY OF MARBLE FILTER SYSTEM FOR GROUNDWATER TREATMENT

ABSTRACT

Recently, El Nino heatwave phenomena has attacked Malaysia and consequently, the water level of three dams in Malaysia have fallen below the critical level. In order to solve this water shortage crisis, groundwater is indeed the best source of water for human beings as its nature of being located deep down beneath the earth has protected it from the exposure to the heatwave, thus would not be dried up as fast as compared to the surface water. However, the contamination of groundwater is inevitable and uncontrollable, yet it can still be treated economically. In this case, a 55.6m tube well located inside the Engineering Campus of Universiti Sains Malaysia was used as a groundwater sample in this research. It is found that the groundwater is highly contaminated by natural sources and human activities. Originally, the colour of the groundwater is yellowish green and emits H_2S gas, but due to the oxidation reaction, it immediately changes its colour to black which is FeS precipitate in 40 seconds after being exposed to the air. A high concentration of salinity (5.1 ± 0.1 ppt), high concentration of NH_3N, and various elements have also been detected in the groundwater sample. Due to this condition, groundwater is classified as class IV based on the water quality index Malaysia standards and considered to be harmful to human. To overcome this issue, a research has been carried out to find a way to make the groundwater to become a safe water resource to human beings and it has been proven that marble is one of the best filter media for groundwater resources. The properties of marbles which consist of 97% of $CaCO_3$ have successfully enhanced the redox reaction of the contaminants, subsequently increase its precipitation rate and ease the filtration

process. In term of the filter media size, it has found that the sand size is much better than the pebble size in removing the groundwater contaminants. The sand size of marble able to remove most of the groundwater contaminants with a percentage of above 90% and whereas some other elements such as Al, Ba, and Ca could be removed only above 70%. Nonetheless, the concentration of these elements after filtration are still below the threshold limit of the drinking water standard based on NWQS Malaysia, EPA, and WHO. As a result of the high removal efficiency of groundwaters' contaminants, it has achieved a water quality result of class I and class II. On the other hand, marble in pebble size produce a water quality in class III.

CHAPTER 1

INTRODUCTION

1.1 Groundwater Resources

Water is the main source of all beings in the world to survive. For human, water is used not only for drinking but also being utilized for daily activities such as washing clothes, industrial production, transportation, cooking and so on. Two of the main sources of water that are commonly used for human daily activities are surface water and groundwater resources. Based on the water cycle theory, surface water source naturally occurs by the evaporation of water from the surface of the earth to the atmosphere. Subsequently, it cools down and condensed to become snow and rain in the clouds and finally fall back to the ground. On the other hand, groundwater resources happen in such a way that the water moves slowly from the surface to the earth's underneath thanks to the existence of gravity as illustrated in Figure 1.1. For instance, water from a river will pass through a small fraction of unsaturated zone, which we call as a confined aquifer to a saturated zone below the water table.

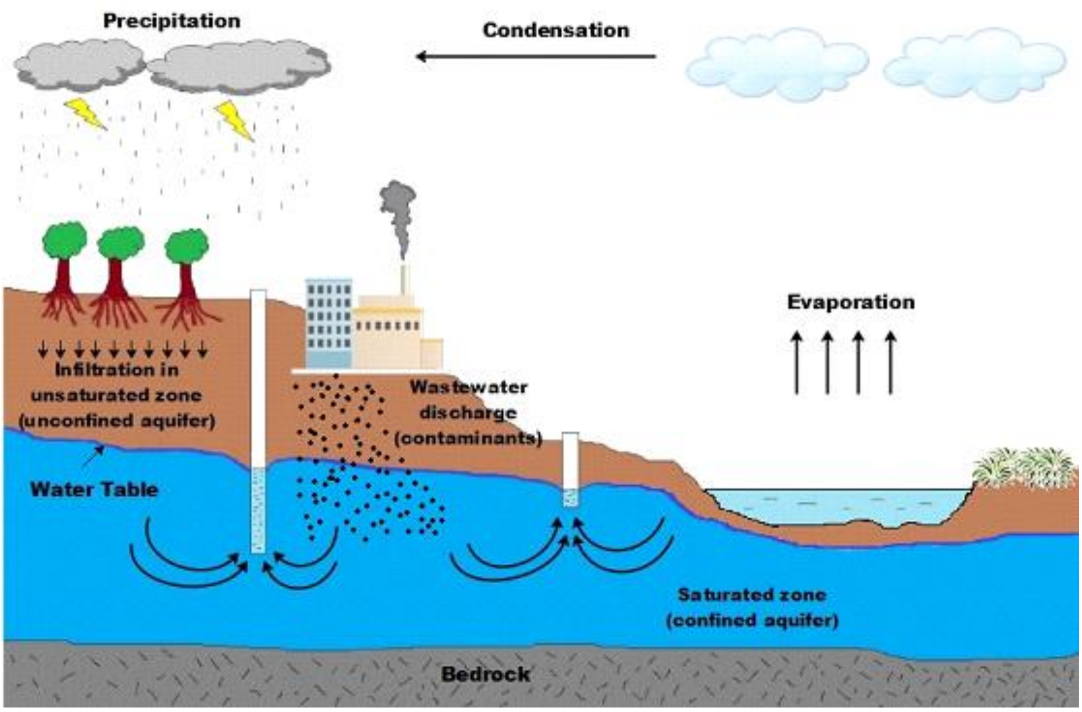

Figure 1.1 The occurrence of contaminants in groundwater via natural phenomena and human induced.

There are 4 types of region which has the potential to become groundwater resources i.e. alluvial, hard rock, fractured sandstone and fractured igneous rock (Tawnie et al., 2016). Alluvial aquifer is composed of sand, silt, clay and gravel deposited in river channels. Generally, it is shallower than fractured sandstone and fractured igneous rock aquifer. It can also discharge and recharge rapidly hence it is critically important for human habitation and agriculture.

Groundwater resource (Figure 1.2) is one of the major sources of drinking water and cleaning agents around the world. In European countries, such as Denmark, Austria, and Iceland have been using more than 95% of their water supply originate from groundwater reservoirs since 2008 (Gudmund & Reitan, 2008). In the United States, groundwater is used to supply potable water more than 96% of its population in rural areas (Sharma, 2001). In Asia, ground water is also widely used for their water supplies for example 80% in the interior of India, 80% in the Maldives and more than 60% of water supply in the Philippines and Nepal comes from groundwater resources (Sharma, 2001).

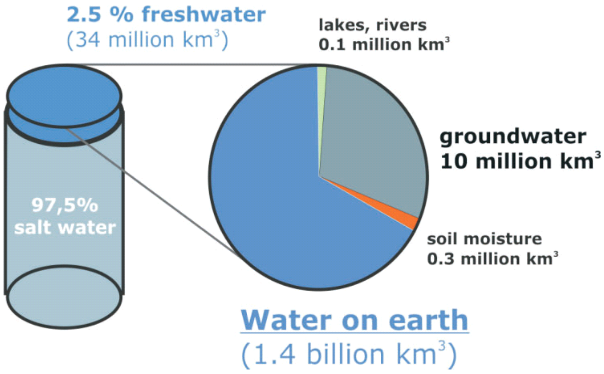

Figure 1.2 Source of world freshwater (after BGR, 2008).

On the other hand, groundwater in Malaysia accounts for over 90% of the country's water resources and is spatially distributed all over the country (Kura et al., 2018). Kura et al. (2018) reported that over the last three decades, there has been an increase in freshwater demand due to the huge economic and infrastructure development in Malaysia. Accordingly, Manap et al., (2013) estimated that the groundwater demand in Malaysia has been estimated to rise by 63% from 2000 to 2050 particularly as an alternative water source in the urban areas.

1.2 Groundwater Pollution

Despite the fact that groundwater plays a crucial role for human's survival, it is unfortunately easily susceptible to pollutants. The pollution of groundwater can be either natural or human-induced. For instance, water is a solvent that can dissolve minerals from rocks where it makes a contact. The transition of water from the surface to the saturated zone cause mixing of elements during the transportation of water through the rocks as shown in Figure 1.1. The transportation of contaminants makes the aquifers become more polluted and accumulate with the soil, hence worsening the contamination of the groundwater. The most daunting circumstance is when there is a contamination of heavy metal elements in the water as it can cause detrimental effects to the human beings.

Toxicity of heavy metal elements is very harmful to human and the environment even at a lower dose of exposure. In general, the localities issue of groundwater contamination with a high concentration of iron and manganese are inevitable. Although we cannot deny that the insufficiency of iron (Fe), cobalt (Co), zinc (Zn), nickel (Ni), chromium (Cr), Manganese (Mn), magnesium (Mg), copper (Cu), selenium (Se) and Molybdenum (Mo) could results in a variety of deficiency diseases and syndromes (Edzwald, 2011). However, excessive intake of some minerals can trigger and upset homeostatic balance and cause toxic side effects (Soetan et al., 2010).

Nevertheless, the extensive use of groundwater has been successfully developing due to its easy access to the resource, better protection from the sources of pollutants, higher water quality compared to surface water (Hallberg & Martinell, 1988), less subject to seasonal and perennial changes, the nature itself where it can spread uniformly in large areas (Zekster & Everett, 2004), and the lower capital cost production (Sharma, 2001). Thus, these advantages that seems to be beneficial to human beings lead to its widespread use at a large scale globally.

Unfortunately, this continuous process will cause the utilization of excessive groundwater that could cause several troublesome impacts which includes the change in the groundwater content. Excessive use of groundwater in many crop-producing areas will push the water table downwards. Subsequently, the change in groundwater flow will carry the pollutants into other non-contaminated areas (Sinisi, 2003). This groundwater pollution substantially occurs due to human activities in industry, agriculture and urbanization. These activities make groundwater vulnerable to sewage discharge, thus making it unsafe and unfit for human use.

1.3 Differences of Shallow and Deep Well in Terms of Pollution

The depth of well is not measured by the well's length, but it is measured on how far its casing extend below the water table. There are two types of well according to the difference of its depth which are shallow well and deep well. Shallow well is measured less than 30m from the water table. Commonly, water from a shallow well is more susceptible to contaminants due to the local activities and usually from the land consumption of less than two years. The contaminants in a shallow well are quite sensitive and easily changed due to the surface pollution because the water source is relatively close to the ground surface. However, the water quality of shallow well may be altered in different seasons. For instance, in certain occasion where the area has not been manipulated for any industry or agriculture for quite some time, it can be safely used as a source for drinking water.

As for deep well, it is defined as the depth of well above 30m from the water table. Contamination of deep well usually occurred from a long-term impact of local activities. Generally, the water quality in a deep well changes much slower than the shallow well. This happens because the contamination of deep well is affected by the land use of more than 10 years and influenced by weathering of rock through the aquifer (Mechenich & Shaw, 2011). In this case, the water will move slowly in the aquifer which could take many years before it could reach above the depth of 30m; approximately a foot or a mile per day based on the type of soil and rock.

1.4 Research Area Geomorphology

The site is located at Mukim 9, district of Seberang Perai Selatan (SPS), Penang Peninsular of Malaysia. This region is a type of lowland and flat area close to the Kerian River flood plain. This area was used to be a palm oil estate. Currently, the area has been developed as a university campus named Universiti Sains Malaysia Engineering Campus since 2001. Oil palm trees can still be seen inside the campus and are well cultivated. Based on the bore hole study by Hassan (1989), this area is a quaternary alluvial marine deposit.

In the campus, there is a tube well with a diameter of 6 inches and 60-meter depth which is used for geomorphology and groundwater study. According to the water table in this study area, it is ±1.76m from the surface area and the depth of the tube well is 58.24m. Therefore, in this case, this study will be focusing on the deep well where the contaminants may consist of several minerals that dissolve in water and anaerobic microorganisms. Based on Figure 1.3, coastline distance is about 8km away from the study area. Regarding to Tawnie et al. (2016) report, the saline can extend over 10 km from the coastline even in groundwater. This will affect the invasion of salt into river and groundwater.

Figure 1.3 This picture was taken from google map shows that the study area is close to the Kerian river. The Kerian river is connected to sea water and swamps which can be seen along the river. Most of these areas are cultivated with oil palm plantations (Google Earth, 2019).

1.5 Groundwater Treatment

There are three types of groundwater treatment which include conventional, biological and membrane. Primarily, conventional methods consist of coagulation, flocculation, clarification and filtration. Conventional treatment always begins with pre-oxidation and pre-sedimentation. Generally, aeration oxidation is used to oxidize dissolved metals such as Fe, Mn, and heavy metals. However, there are certain requirements that need to be fulfilled in order to enable the oxidization process to take place. Usually, strong oxidizing agents are used to oxidize iron and manganese rapidly and at the same time, it could also oxidize or destroy organic matter such as chlorine, ozone, chlorine dioxide, or potassium permanganate. Furthermore, catalytic action is also effective in oxidizing metal elements. However, it is important to note that the oxidized metal or solidified metal will sediment due to its high density thus it will be separated with the clean water.

In different circumstances, biological methods make use of the microorganisms specifically for the organic biodegradable materials in the water. Owing to this fact, this treatment relies on microorganisms such as bacteria, protozoa, nematodes and other microbes to break down organic matter by using cellular process. The biological process consists of aerobic and anaerobic digestion. An example of aerobic treatment is activated sludge. Aeration provides oxygen to bacteria and other organisms to decompose the organic matter. In addition, the aeration also helps to reduce the unpleasant smell of the treated water as well. Alternatively, anaerobic treatment or in other words known as anaerobic digestion will degrade the food, chemical effluent and agriculture waste by the absence of oxygen. This treatment also produces biogas which provides more benefits to the industry.

On the other hand, high technology membrane is also one of the useful methods in the water treatment process. The membrane type is classified based on the porosity of the membrane. For instance, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and osmosis are sorted by increasing order of its pore diameter. Osmosis is divided into two types i.e. reverse osmosis (RO) and forward osmosis (FO). Recently, osmosis is used for desalination treatment which is rapidly growing nowadays. Many researchers have tried to develop the membrane technology due to its ability to remove nanoparticle contaminants. Nevertheless, these three types of water treatments are different as each of them has its own pros and cons, therefore should be evaluated comprehensively according to the water demand and also economic concern. In certain circumstances, some procedures might require the combination of different methods of groundwater treatment in order to improve the efficiency of contaminants removal.

1.6 Problem Statement

Malaysia is a tropical country where its climate is categorized as equatorial, or in other words being near to the equator, causing it to have a warm and humid environment throughout the year. Recently in April 2019, the water level at three dams in Johor have been reported to be drying up faster due to the dry and hot weather. One of the dams involved is the Sungai Lebam Dam in Johor which has been recorded by the National Water Services Commission (SPAN) to have a water level is of about 15.9% . According to Ahmad (2019) as report in The Star Online, the water level at the three dams fall below the critical level. In view of this worsening condition, three tube wells have been built to ensure enough water supply can be attained by means of reaching the groundwater. This is because groundwater is a very important water resource that can replace surface water despite easily being exposed to the natural and human activities. However, the awareness of using the groundwater as a water resource instead of surface water is still lacking in Malaysia. Compared to European and United Stated countries, the groundwater is widely used as their main water resources for water supply especially for domestic use (Petersen-Perlman, 2018). Since groundwater has various contaminants affected by the surrounding condition, it is beneficial to do a deeper study of groundwater based on the condition of the surrounding affecting the source and the different types of the water treatment that can be done.

From our preliminary study, the colour of groundwater generally could be seen as rusty and blackish due to its high content of iron, manganese and sulfur. Although element like iron and manganese elements generally not considered as threats to human's health, it is however not suitable for domestic consumption when the level exceeded ($Fe > 0.3$ mg/l) and ($Mn > 0.1$ mg/l) (Gorchev & Ozolins, 2011; Standard

United States, 2018). Furthermore, the existence of other contaminants such as microbes, salinity and ammoniacal nitrogen (NH_3N) are very hazardous for human being. However, since the groundwater has been proven to provide more advantages rather than disadvantages for human being, one should consider developing this method as an important alternative supply for domestic use with a lower groundwater filtration cost. Therefore, one should consider chemical exclusion as one of the ways to reduce the unnecessary cost for the water treatment.

The methods involved for the water treatment process includes electrocoagulation, ion exchange, dissolved air flotation (DAF), adsorption, membrane filtration and coagulation-flocculation, all of these indeed required high capitals and operating costs to a very great degree. For example, the coagulation-flocculation process usually will generate sludge, which requires additional operating costs for sludge disposal as well as the need for expertise in sludge management. Due to the risk of fouling and rapid clogging, ion exchange is not recommended for removing large concentrations of iron and manganese. Considering this fact, the membrane filtration method should not be recommended to be put forward as a water treatment process due to its complicated operation, low permeability flux and the membrane that is prone to fouling.

This study was focused on a physical treatment rather than a chemical treatment as a way to prevent additional and avoidable costs. In this case, variables such as flow rate, pH, removal efficiency, adsorption capacity, temperature and contact time are some of the parameters that were observed in this filtration studies. As a matter of fact, calcium carbonate ($CaCO_3$) has been shown to be effective in removing metals, turbidity, suspended solids, and total coliform organisms (E-coli) from groundwater and wastewater, where the removal was up to 96% (Adlan, Aziz & Maung, 2008). Furthermore, heavy metal such as copper can also be removed from the solutions using $CaCO_3$ (Aziz *et al.*, 2001). However, there are certain circumstances where the water can become difficult to be treated and required another way to handle this problem. For example, manganese oxidation usually is more difficult than iron oxidation due to the slower reaction rate and only can be effectively oxidized at higher pH above 8 (Chaturvedi & Dave, 2012). In 2016, Mohd Sanusi et al., (2016) faced the same difficulty which the highest removal of manganese of the same groundwater source as this research area was only 0.2 mg/l using the limestone as the filter media. Yet, the manganese concentration has not reached Malaysia's water quality standard of 0.1 mg/l. The removal efficiency was 82%.

As the purer of the calcium carbonate increases the performance of filtration, instead of limestone, marble is easier to get a high purity of calcium carbonate. This is because, if the limestone is nearly pure (very few of impurities) and subjected to the heat and pressure of metamorphism, a white marble is formed (Hobart M. King, 2019). The impurities are accumulated and separated from the calcium carbonate thanks to the metamorphism process. This is much easier to separate the impurities and picking a high purity of calcium carbonate. Even though the limestone is twice cheaper than marble (limestone = US$39-US$50 and marble = US$65-US$95) where the current price was referred on Alibaba website which had been accessed on 3th March 2019, however, the impurities in the limestone are spread and this will increase the operation cost for separating the impurities.

Besides that, the presence of liquids substantially reduced the strength of the calcium carbonate rocks and yet, marble has higher uniaxial compress strength (UCS) than limestone. The Mohs hardness scale of a marble is stronger than a limestone (marble = 3-4 > limestone = 3). So that this will reduce the solubility of marble and abrasion with a liquid during filtration. Marble is fair in resisting acid and fair in abiding alkali, whereas, limestone is poor to maintain its state in acid and alkali condition. In the section. In spite of that, the performance of the filtration was influenced by the different climates and temperature. For instance, the removal of salinity tends to be less efficient during the cold period (Ahmed *et al.*, 2004).

1.7 Objective of Study

The main goal of this research is to find a better way to understand the mechanism of two different sizes of marble filter media in removing contaminants found in groundwater. In addition, this study will assist in developing filtration technology in a more economic and eco-friendly way.

Therefore, to achieve this goal, the objectives of this study have been defined as follows:

1. To characterize and identify contaminants that exist in the groundwater of the research area.
2. To measure and compare the performance of marble filter media (pebble and sand size) based on Water Quality Index (WQI) data.
3. To provide the groundwater quality after the treatment including the removal efficiency of contaminants.

1.8 Scope of Study

The main focus of this study was the design of the marble filter in term of particle size (pebble and sand size), the high purity of marble, flowrate of filtration, temperature and the cascade theory that have potential to treat the groundwater efficiently using a physical treatment. The groundwater treatment was also focused on the deep well cause of the groundwater quality in a deep well changes much slower than the shallow well. In order to achieve the main objective of this study, characterization of the groundwater at the study area was determined to measure the performance of the marble filter in removing the groundwater contaminants based on the WQI data and the removal efficiency of contaminants. As a matter of the facts, this study will give a contribution for groundwater treatment especially groundwater that contaminated due to seawater intrusion.

1.9 Outline of Thesis

In the introduction section **Chapter One**, how the groundwater exists and how it is easily exposed to the contaminants was emphasized clearly. Some contaminants could cause detrimental effects to human's health. USM Engineering, Pulau Pinang, Malaysia is a great choice for the location of this study in view of oil palm plantations are still being cultivated around this place, thus making it a suitable place for this study owing to the impact of agricultural activities on this land. In this chapter 1, I also briefly explain three objectives that needed to be achieved in this research.

Chapter Two covered literature review on groundwater quality study. Based on the main topic of this study which discuss about marble filter, this chapter revealed the gap in knowledge among previous study in $CaCO_3$ physical filtration. Other methods were also described to support the benefit of using this marble filter.

Chapter Three describes the overall methodology of the experiment, starting from the preliminary study of groundwater quality to the data preparation. This chapter also emphasized the method associated with EPA standard to conduct water quality study. Filter media was prepared in two types of particle sizes which are pebble and sand size. The jaw crusher and cone crusher were used to produce the required size while the Gilson sieve was used to separate the size after crushing. Characterization and identification of groundwater content were carried out via Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). To identify high $CaCO_3$ in marble, X-ray Powder Diffraction (XRD) was used to analyse elements in powder form. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), ammoniacal nitrogen (NH_3N), total suspended solid (TSS) and pH test were carried out in order to test the groundwater quality in accordance to Malaysian standards.

Chapter Four explains the results of using marble filter in removing contaminants. The water quality index (WQI) was calculated from the results of groundwater quality tests to investigate the influence of marble size on the removal efficiency. This study also yielded information on optimum flow rate and adsorption capacity of marble filter in removing metal elements and microbes. According to the result obtained, this chapter answered the three objectives that previously mentioned in chapter one.

Finally, **Chapter Five** summarized all the results and limitations that have been established in this study. Recommendations also provided for practical use and improvement in the further study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Groundwater contaminants have various of organic compounds and inorganic elements which influenced by places and seasons. Every different level of depth in the ground shows distinct contaminants in the groundwater. In order to plan for an efficacious treatment of groundwater, a thorough research regarding the historical area, current development and previous treatment is essential to impart a great deal of proposition to treat groundwater in a highly efficient and economical way.

2.2 Research Area Background

Malaysia is a country located in southeast Asia with a population of about 32. 4 million persons in 2018 based on a report from (Malaysia Department of Statistics, 2019). This country is separated by the South China Sea into two regions, namely Peninsular Malaysia and Borneo. About 3 over 4 of Malaysia is surrounded by the sea and the climate is tropical. According to the annual rainfall data which was taken from (Malaysia Department of Statistics, 2018), the highest and lowest was recorded at Labuan station (4,938.9mm) and Kuala Kangsar (1,955.4mm).

Before 1960s, Nibong Tebal was an estate. However, about a decade afterwards, this region has been transformed into an oil palm plantation. Since oil palm is highly beneficial in the food industry and it has an advantage of being highly resistant to oxidation which causes it to have a long shelf life, oil palm has always been on high demand until these modern eras. Consequently, this long-established 78 years of palm oil plantation has contaminated the ground for decades, and this explains why the contaminants can reach above 30m depth beneath the water level.

2.3 Groundwater Quality

Just because there is a plenty of water in a well does not mean it is drinkable. It is because water is such a great solvent that may contain a lot of dissolved chemicals. As it is passing through rocks and subsurface soil, it will often have more dissolved substances than surface water will. Even though the ground itself is a mechanism for filtering particulate matter and yet, it is still contaminated with various dissolved chemical and microorganisms. Therefore, it is highly prominent to verify the quality of groundwater before using it either as a permanent or temporary use.

Groundwater quality describes the properties and the characteristics of water beneath the Earth. As mention before in subsection 1.2 which emphasized about groundwater pollution, groundwater is highly influence to the geological area and urbanization (Haque & Roslan, 2017). One of examples based on the elevation of ground, there is a large difference between higher and lower area in terms of salinity in the subsurface area (Naus et al., 2019). The higher lying area such as the hilly areas has very low salinity intrusion caused by density-driven salinization and direct rainwater infiltration (Islam et al., 2017; Naus et al., 2019). Thus, based on the example given, it has been giving a clear picture that geological study and consideration of urbanization is important to predict the groundwater quality of an area.

In Malaysia, water quality index (WQI) in National Water Quality Standard Malaysia and Malaysia Department of Environment has been widely used for river quality assessment. It is effectively used in monitoring pollution and hazard by classifying the quality of water as stated in Table 2.1 based on the calculation of 6 parameters which are chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved oxygen (DO), ammoniacal nitrogen (NH_3N), pH and total suspended solid (TSS). The calculation of WQI will be discussed in section 3.8.7 for further details.

Table 2.1 DOE Water Quality Index Malaysia Classification (Malaysia Department of Environment, 2017).

Parameters	**Units**	**Classes**				
		I	**II**	**III**	**IV**	**V**
NH_3N	mg/l	< 0.1	0.1 – 0.3	0.3 – 0.9	0.9 – 2.7	> 2.7
BOD	mg/l	< 1	1 – 3	3 – 6	6 – 12	> 12
COD	mg/l	< 10	10 – 25	25 – 50	50 – 100	> 100
DO	mg/l	> 7	5 – 7	3 – 5	1 – 3	< 1
pH	-	> 7	6 – 7	5 – 6	< 5	< 5
TSS	mg/l	< 25	25 – 50	50 – 150	150 – 300	> 300
WQI	mg/l	> 92.7	76.5 – 92.7	51.9 – 76.5	31.0 – 51.9	< 31.0

Application of water quality index in groundwater quality assessment is not well applied in Malaysia since surface water source i.e. river and dam are the main sources of water supply. Malaysia too depends on river and dam as water resources and it makes groundwater as an optional for water supply. Since the tragedy of water shortage at Selangor in 1997 due to high water demand and El Nino phenomena, many industries have taken an initiative to use groundwater as their water supply.

The recent Minister of Water, Land and Natural Resources (Malaysia), Dr. Xavier Jayakumar Arulanandam said in National Groundwater Conference at Shah Alam that Malaysia has 5 trillion m^3 groundwater resource but only 3% has been used since 2013 (Zulkifli, 2019). This is shown that the usage of groundwater in Malaysia is still low due to lack of knowledge about the potential of groundwater instead of surface water as a daily water supply. This has been clarified by Dr. Azuhan Mohamed, Ex-Director General National Research Institute of Malaysia (NAHRIM) that groundwater is cleaner than surface water and the treatment cost is much cheaper cause groundwater is not easily exposed to pollution compared to surface water (Lisut, 2017).

Considering the potential of groundwater as an alternative source for surface water, Department of Environment (DOE) had put an effort to explore and determine the groundwater quality status through the National Groundwater Monitoring Programme. Since the groundwater quality standard is still not established yet, DOE had monitored 110 of tube wells from some specific land uses such as agricultural, urban and sub-urban, industrial sites, solid waste landfills, golf courses, rural areas, ex-mining area (gold mine), municipal water supply, animal burial areas, aquaculture farms, radioactive landfill, and resort. Proceeding from the monitoring result, DOE has issued a benchmark of groundwater quality standards by following the National Water Quality Standard (NWQS) Malaysia. On the other hand, DOE water quality index is a simplification of the 72 parameters of NWQS to 6 parameters (i.e. BOD, COD, NH_3N, pH, DO and TSS) and it eases to make a legislative decision for the quality of water by looking the index range as shown in Table 2.2. The result of the WQI calculation will be in the range of 0 to 100 and it is divided into 5 classes with different colour codes. Class I is classified as very clean meanwhile Class V stands for very polluted water.

Table 2.2 DOE water quality index classes and colour codes (Malaysia Department of Environment, 2017; Naga et al., 2018).

Aptitude Class	Colour	Description
Class I (> 92.7)	Blue	Very Clean
Class II (76.5 – 92.7)	Green	Clean
Class III (51.9 – 76.5)	Yellow	Slightly Polluted
Class IV (31.0 – 51.9)	Orange	Polluted
Class V (< 31.0)	Red	Very Polluted

2.4 Advantages and Disadvantages of Previous Groundwater Treatment

Most groundwaters contain free ion heavy metal due to the under pressure and high temperature condition. Thus, groundwater treatment is a process to treat contaminated groundwater by removing the contaminants or converting them into harmless compound. The contaminants indeed are the major contents of the surface pollution which have been carried away into the groundwater. 25% of population around the world take their groundwater from limestone sediment area which also makes one of the most productive aquifer in the world (Muhammad et al., 2018).

Generally, groundwater treatment is almost similar to wastewater treatment where it uses the same concept, yet it has a different method and it depends on the type and number of contaminants. Based on the compilation of groundwater treatment in Table 2.5, treatment of groundwater where the contaminants exist such as iron, manganese, sulfur, NH_3N and salinity, are the most crucial to establish an appropriate treatment (Vidović et al., 2014). Owing to this, there are many water treatment technologies which include conventional, biological and membrane technologies have been combined and developed in order to treat those contaminants efficiently, yet they still have a lot of disadvantages especially when it comes to its high priced and uneconomical technologies.

Conventional treatment such as coagulation-flocculation, flotation, oxidation/precipitation, $CaCO_3$ based media filter, sand filter, ion exchange, electrochemical and adsorption are commonly combined with biological and membrane technologies to treat those contaminants. Conventional methods are usually applied during the initial treatment process to reduce the massive amount of contaminants' concentration and larger particle size. The remaining particles will then be removed using biological treatment and membrane filtration.

An example of powder activated carbon membrane bioreactor (PAC-MBR) is a combination of activated carbon adsorption and membrane filter. As a result of the adsorption capability of PAC, the experiment that was conducted by Du et al. (2017) has found that about >90% removal of Fe, Mn and NH_3N can be achieved via this method. Unfortunately, the inevitable membrane fouling that was caused by the continuous growth of iron and manganese bacteria had almost failed the experiment. The consequence of this problem is that it will eventually increase the maintenance and the operational cost. The monetary cost has been discussed in desalination part.

Fundamentally, application of simple filtration such as $CaCO_3$ filter is the most economical way compared to the other water treatment method. Based on the name itself, it does not need chemical use or energy consumption during filtration, and this makes it undemanding and easy to be used. In the monetary aspect, this treatment is also low cost and affordable. In some cases, the treatment might need a longer period to treat the contaminants depends on the filter capacity, adsorption capacity and total amount of contaminants. For instance, a treatment conducted by Y. Wang et al. (2016) required 50 days of filter treatment to achieve a perfect removal of contaminants. This might be harder for iron, where the concentration was 30 mg/l and it certainly required a large scale of filter capacity to treat the groundwater.

Zeolite is a micro porous resin type that consists of natural and synthetic type. It has been used as an adsorbent in the ion exchange process. Zeolite was classified by Kasmuri et al. (2018) as a sterling ion exchange material in the contact solution. The effectiveness of zeolite is because of its three-dimensional structure that consists of monovalent and divalent cations which can remove anion contaminants effectively such as NH_3N (H. Huang et al., 2015). As shown in Table 2.3, Kasmuri et al. (2018) found zeolite with particle size of 0.5mm-1mm has a NH_3N removal efficiency of 93% without additional aeration, whereas when it is composed with aeration, the removal efficiency had increased to 95%.

Nevertheless, it has shown a difficulty when it comes to remove a large quantity of coloured ions such as Mn^{2+} and Fe^{2+}. These ions will form manganese and iron zeolite which could become troublesome during regeneration of zeolite (Shiva, 2014). Furthermore, high turbidity will also inactivate the cation adsorption function due to the clogged zeolite's pore (Shavandi et al., 2012). The pore is sensitive to the acidic water (Mohd Akhir et al., 2017; Shiva, 2014). Acidic water can destroy or decrease the pore volume and reduce the surface area of the zeolite.

Denitrification of groundwater using electrolysis is less efficient compared to electrochemical via biological process. The difference between the electrolysis and electrochemical is that the electrolysis uses electric current to generate chemical reaction. Whereas, the electrochemical uses microorganism to produce chemical reaction and convert it into electric current. According to F. Liu et al. (2018)'s research, they have found that an optimum current density at 30 mA/cm^2 was enough to reach 91.7% of removal efficiency after 90 min. An addition of salt, NaCl has been proven to improve the treatment and can reach a 100% of removal efficiency. This occurs when the chloride ion lead to the ion exchange process and thus forming an oxidizing compound that can oxidize the nitrate.

In contrast to the process without the existence of microorganisms, Rajic et al. (2018) found that 120 mA/cm^2 is the optimum current density that should be applied in order to reach 53.2% of nitrate removal efficiency. Since the microorganisms create the chemical reaction and generate current intensity, F. Liu et al. (2018)'s experiment did not use much current density to oxidize the nitrate. Concurrently, it will reduce the operational cost from electrical energy consume. Higher current intensity can promote vigorous hydrogen bubbles production and form N-H bond and thus reduces the N-N bond. This circumstance will create a competition between nitrate hydrogenation and nitrate, hence, minimizes the sorption of nitrate ions on the cathode. In spite of that, in practical usually a suitable amount of current density will be selected according to the conditions that affect the treatment itself.

The use of electrode is a contributor to the increase of operational and maintenance cost. As a result of oxidation process, the electrodes could be dissolved during the water treatment process, hence they usually will need a regular replacement. A cost study about water electrolysis had been reviewed by Schmidt et al. (2017) to reveal the economical way for this treatment. They have found that the lowest capital cost for the common water electrolysis using aqueous potassium hydroxide oxidation method was in between 1000-1200 $€_{2016}/kW_{el}$ and the lifetime of the system was 60000-90000h or approximately after 10 years of the usage.

Nowadays, the NF technology is one of the technologies that is capable to replace the RO filtration for the groundwater treatment especially for brackish water. Considering the membrane fouling problem that RO has been going through in desalination, NF pore size is larger than RO. Hence, it could reduce the complication of membrane fouling effortlessly. The size of pore membrane of NF is still in range in which it can remove the dissolved salt. Therefore, Ramdani et al. (2018) had carried out an experiment of NF to reduce salinity in groundwater where it is located in South-Algeria. The NF was named as NF90 during that time. Based on the result in Table 2.3, fluoride (F^-), Cl^-, SO_4^{2-}, Na^+, mg^{2+} and Ca^{2+} have been removed with the efficiency of 90%, 84%, 100%, 80%, 90% and 90% at with a pressure of 8.8 bar.

As a result of that, the salinity reading has been reduced from 3000 ppm (3 ppt) to 270 ppm (0.27 ppt) with removal efficiency of 91%. As a conclusion, NF90 enables to partially demineralized brackish water and avoids remineralization which makes the process cost effectively. In addition, it can retain more than 90% of salinity removal at pH 7.85 despite with the presence of other ions. It is undoubtable to admit that NF90 can deal with high concentration of the contaminants. However, membrane fouling occurrence is still inevitable and needs a pre-treatment to handle the problem.