POTENTIAL USE OF OZONATION WITH LIMESTONE ADSORPTION PROCESS IN GROUNDWATER TREATMENT

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POTENTIAL USE OF OZONATION WITH LIMESTONE ADSORPTION PROCESS IN GROUNDWATER TREATMENT

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AKSB	Air Kelantan Sdn. Bhd.
ANOVA	Analysis of variance
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
DOC	Dissolved organic carbon
DOE	Department of Environment
DOM	Dissolved organic matter
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform-Infrared Spectroscopy
e.g.	for example
HRT	Hydraulic retention time
ICP-OES	Inductively-Coupled Plasma - Optimal Emission Spectroscopy
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JMG	Minerals and Geoscience Department
LOI	Loss on ignition
MnO_x	Oxide of manganese
MLD	Million litres per day
MOH	Ministry of Health
MPN	Most probable number
MTZ	Mass transfer zone
NAHRIM	National Hydraulic Research Institute of Malaysia

OH^-	hydroxyl radicals
rpm	Rotation per minute
SM	Standard Method
SUVA	Specific UV Absorbance
NOM	Natural organic matter
TDS	Total dissolved solid
wt	Weight
WTP	Water treatment plant
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

POTENSI PROSES OZONASI DAN PENJERAPAN BATU KAPUR DALAM RAWATAN AIR BUMI

ABSTRAK

Salah satu masalah utama yang berkaitan dengan air bumi ialah warna kemerahan disebabkan oleh kehadiran Fe dan Mn yang berpunca daripada proses semulajadi dan aktiviti manusia. Selain itu kandungan bahan organik semulajadi (NOM) yang tinggi mempengaruhi kualiti bau, rasa dan warna air selain berpotensi menghasilkan produk sampingan selepas pengklorinan yang dikenali sebagai (Disinfectant by-product) DBP. Oleh itu, kajian ini dilakukan bagi menguji keupayaan bahan penjerap yang berbeza (batu kapur dan antrasit) dalam menyingkirkan Fe, Mn, warna dan NOM dalam air bumi dari telaga USM dan telaga jejari Pintu Geng menggunakan proses pengozonan berbilang peringkat yang terdiri dari proses pengozonan tunggal, pengozonan-penjerapan batu kapur dan proses bersepadu pengozonan-penjerapan antrasit. Analisis kualiti air telaga USM menunjukkan ketidaksesuaiannya sebagai air minuman disebabkan kandungan bahan organik, Fe (1.23mg/L) dan Mn (0.56mg/L) yang tinggi. Data pemantauan kepekatan Fe di telaga jejari Pintu Geng di antara Disember 2013 sehinggan Ogos 2014 mecatat tahap kepekatan dari 0.16-2.05 mg/L melebihi had yang dibenarkan untuk air minuman. Batu kapur kaya dengan kumpulan berfungsi hidrofilik(O-H dan C=O) yang mempunyai keupayaan untuk menjerap Fe dan Mn. Permukaan antrasit terdiri daripada kumpulan berfungsi hidrofobik (C-C dan C-H) yang berkeupayaan untuk menjerap sebatian organik. Batu kapur menyingkirkan sebanyak 96.7% Fe, 87.6% Mn, 15.8% warna dan 32.4% UV_{254}. Penyingkiran Fe, Mn, warna dan UV_{254} oleh antrasit pula adalah masing-masing sebanyak 51.2%, 32.4%, 59.9% and 78.5%. Kajian isoterma mendapati penjerapan Fe dan Mn terhadap batu kapur mengikut model Langmuir sementara kajian kinetik mengikut Pseudo-tertib kedua yang dapat dikaitkan dengan penjerapan secara kimia. Penjerapan warna dan UV_{254} terhadap antrasit mengikut model Temkin dan Pseudo-tertib pertama yang dikaitkan dengan penjerapan fizikal. Penggunaan ozon sahaja hanya dapat menyingkirkan 72% dan 58% daripada Fe dan Mn. Efluen akhir selepas proses pengozonan masih melebihi had maksimum air minuman. Walau bagaimanapun, proses pengozonan sangat sesuai sebagai pembasmi kuman yang membunuh 100% jumlah koliform. Proses pengozonan tunggal juga berjaya menyingkirkan warna menepati piawai (<15 PtCo) dan menyingkirkan sebanyak 79% UV_{254}. Kajian turus tetap melalui proses bersepadu pengozonan-penjerapan batu kapur menunjukkan 99.5% dan 92% pengurangan dalam Fe dan Mn yang memenuhi piawaian air minuman. Proses bersepadu pengozonan-penjerapan antrasit menyingkirkan Fe sebanyak 92.2%. Walaubagaimanapun, sistem rawatan ini tidak berkesan dan hanya menyingkirkan 43.3% Mn. Oleh itu, proses bersepadu pengozonan-penjerapan batu kapur dicadangkan sebagai proses alternatif untuk merawat Fe dan Mn dalam air bumi.

POTENTIAL USE OF OZONATION WITH LIMESTONE ADSORPTION PROCESSES IN GROUNDWATER TREATMENT

ABSTRACT

One of the major problems related to groundwater is the presence of iron (Fe) and manganese (Mn) from natural processes and anthropogenic activities which causes groundwater to turn red-brown in colour. Besides, high natural organic matter (NOM) content influences the water organoleptic quality and potential to produce by-product after chlorination known as disinfectant by product (DBP). Therefore, this study was aimed at investigating the potential of different adsorbents (limestone and anthracite) in treating Fe and Mn, colour and NOM from groundwater at Universiti Sains Malaysia (USM) and Pintu Geng horizontal well by multiple stage ozonation process including single ozonation, ozonation-limestone and integrated ozonation-anthracite processes. Water quality analysis of USM well was not recommended to be used as drinking water due to high organic content, Fe (1.23mg/L) and Mn (0.56mg/L). The monitoring data for Fe concentration at Pintu Geng horizontal well between December 2013 and August 2014 recorded the level ranging from 0.16-2.05mg/L, which exceeded the permissible limit of drinking water. Limestone is rich of hydrophilic groups (O-H and C=O) and it has the capability to adsorb Fe and Mn. In comparison, the functional groups present on the anthracite surface are mostly of hydrophobic groups (C-C and C-H), which are beneficial for adsorbing organic compound. Limestone was found capable of removing 96.7%, 87.6%, 15.8% and 32.4% of Fe, Mn, colour and UV_{254}, respectively. On the other hand, the removals of Fe, Mn, colour and UV_{254} by anthracite were 51.2%, 32.4%, 59.9% and 78.5%, respectively. Analysis of isotherm showed that the adsorptions of Fe and Mn onto limestone fitted the Langmuir model and the Pseudo-second order kinetic in kinetic study which were associated with chemisorption. The adsorptions of colour and UV_{254} onto anthracite fitted the Temkin isotherm model and the Pseudo-first order kinetic which were associated with physisorption. The use of ozone alone only removed 72% and 58% of Fe and Mn, respectively. The final effluent after ozonation process still exceeded the maximum allowable limit for drinking. However, ozonation was useful as a disinfectant, which had destroyed 100% total coliform through this process. The ozonation process alone was capable of removing colour to below than the permissible limit (< 15 PtCo), as well as removing 79% of UV_{254}. The fixed-bed column using an integrated ozone-limestone adsorption exhibited 99.5% and 92% reduction in Fe and Mn respectively and complied with the drinking water standard. The integrated ozone-anthracite adsorption process had successfully removed 92.2% of Fe. However, the treatment system was found not effective to remove Mn with only 43.3% reduction. Therefore, the integrated treatment of ozonation with limestone adsorption was suggested as an alternative process to treat Fe and Mn in groundwater.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

The abundance of untapped groundwater may become a significant alternative of water source in Malaysia, which is expected to reduce the occurrence of water scarcity problems in this country. Currently, the use of groundwater is limited to some areas in Kelantan, Terengganu, Pahang, Perlis, Selangor, Labuan and Sarawak. However, the significant impact on its usage is the presence of Fe and Mn. It is also a common problem in other countries such as Northern Greece (Katsoyiannis et al., 2008), Bangladesh (Mondal et al., 2007), Netherlands (De Ridder et al., 2018), Yemen (Samsudin et al., 2009) and Vietnam (Le Luu, 2017).

According to the Ministry of Health Malaysia (MOH), the maximum acceptable limit of Fe and Mn for drinking water is 0.3 mg/L and 0.1 mg/L, respectively. Fe and Mn constitute significant contaminants, which can cause decolouration, metallic taste and staining laundry. The presence of dissolved Fe (Fe^{2+}) in groundwater can be divided into two types. The first type is from minerals such as magnetite, ilmenite, pyrite and siderite. The second type is from silicates such as pyroxene, biotite, amphiboles and clay minerals (Jusoh et al., 2011). This Fe^{2+} usually coexists with Mn^{2+} that occurs due to weathering of minerals and rocks. The source of Fe in groundwater is different compared to surface water where Fe^{2+} and Mn^{2+} for the latter occur due to human activities.

The presence of NOM in groundwater is related to the dissolution of organic matter bounded onto Fe and Mn oxyhydroxides and the production of soluble organic metabolites by reducing bacteria. However, in reductive condition, Fe alongside Mn are reduced to dissolved Fe^{2+} and Mn^{2+} and thus releasing organic matter. Elevated NOM in drinking water supplies also contributes to asthetic problems related to its colour, odour and taste. It also increases the cost of treatment operation due to the increasing chemical usage for treatment (Kornegay, 2000). NOM also plays a major role as a precursor in the formation of disinfection by-products (DBPs). Furthermore, NOM increases the coagulant demand and disinfectant, as well as enhances microbial growth in water distribution system by certain NOM fraction, which therefore contribute to corrosion problem. Thus, elevated concentrations of Fe and Mn in addition to high concentration of NOM cause adverse impact on drinking water which requires water treatment process.

There are several treatment methods for Fe, Mn and NOM in drinking water. Most water treatment plants are equipped with conventional treatment methods such as aeration, coagulation, sedimentation, filtration and disinfection. However, they do not remove Fe and Mn significantly. Several advanced water treatment technologies such as dissolved air floatation, actiflo clarification system, ultra-membrane filtration and ozone oxidation have been used in Malaysia’s water treatment plant (Razak et al., 2015). Among these methods, the advanced oxidation process by ozone has attracted recent attention due to its powerful oxidising and disinfecting agent leading to improve drinking water quality. A few studies conducted on integrated process of ozonation with adsorptions have been reported and most of the applications are for industrial wastewater (Lei et al., 2007 ; Konsowa et al., 2010), food processing secondary effluent (Alvarez et al., 2011), stabilised landfill leachate (Kurniawan et al., 2006) and other organic wastewater (Gu et al., 2008 ; Reungoat et al., 2012; Pratarn et al., 2011). It is more effective in treating toxic and non-biodegradable contaminants in water and wastewater (Badawy et al., 2006). In Malaysia, ozonation followed by post filtration method using anthracite has been applied at Pintu Geng Water Treatment Plant since 2013, which is the only system of its kind in Malaysia.

Ozone has the ability to oxidise Fe and Mn, convert ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) and Mn^{2+} to Mn^{4+}. As the pH value becomes higher, the decomposition of dissolved ozone becomes faster due to the increase in OH^- concentration. Furthermore, ozone is capable of oxidizing organic matter and it has been used for the disinfection of water (Upadhyay and Srivastava, 2005). Nevertheless, single ozonation process is less useful to remove pollutants from water and wastewater (Konsowa et al., 2010; Kurniawan et al., 2006).

Besides, advanced oxidation process by ozone is rarely documented in Malaysia due to its high operating cost and less performance removal compared to the integrated treatment (Garoma et al., 2008; Konsowa et al., 2010; Alvarez et al., 2011). Therefore, it needs some improvements to reduce the operating cost and increase the removal efficiency of Fe and Mn from groundwater.

Several types of filter media have been investigated for treating heavy metal contaminated groundwater. These include activated carbon, calcium carbonate based material and iron oxide minerals. Natural geo-mineral material including limestone (Aziz et al., 2008), siderite (Guo et al., 2007), magnetite, hematite, geothite and laterite (Aredes et al., 2013) as well as ferruginous manganese ore (Chakravarty et al., 2002) are cheaper and more effective for heavy metal groundwater treatment.

Limestone is an abundant and a widely available source especially in Malaysia. This low-cost media function in acid neutralisation, which increases the final pH of solution that cause metals to precipitate at alkaline condition and indirectly increases the removal percentage of heavy metals (Hussain et al., 2007). According to Wang et al., (2013) limestone contains calcium carbonate based material that has many applications as adsorbent material or permeable reactive barrier for in-situ groundwater remediation method. It is capable of removing heavy metals such as Cu, Zn, Cd, Ni, Cr, Fe and Mn through a batch process (Aziz et al., 2004). Aziz et al. (2008) used high quality limestone that contains 95.6 % of $CaCO_3$ with less amount of impurities such as $MgCO_3$ (2.39%) Fe_2O_3 (0.271%), Al_2O_3 (0.231%), SiO_3 (1.441%) and others (0.085%) in a filtration technique. Due to the high capability of limestone for the removal of heavy metals, this media offers a good alternative to replace anthracite in the integration of ozonation process for Fe and Mn removal in groundwater.

1.2 Problem Statement

One of the major problems related to groundwater is its reddish and blackish properties due to the high Fe and Mn contents in groundwater. Fe and Mn exist in groundwater originated from weathering process of natural minerals in the soil, sediment and bedrock. The presence of both metals that exceed the permissible limit resulted in the aesthetic problems such as metallic taste, discolouration, staining of laundry and turbidity (Chaturvedi and Dave, 2012).

For groundwater, it is used as drinking water in several states such as Kelantan, Terengganu, Pahang and Perlis, Sabah and Sarawak (Ong et al., 2007). Besides, 60% of the groundwater is exploited for domestic use, 35% for industrial use and 5% for agricultural use in peninsular Malaysia (Baharin and Ghazalli, 2009). In Malaysia, 75% of the population in Kelantan consume groundwater for domestic water supply, agriculture and human activities. However, the major portion of groundwater around Kelantan contains high concentration of Fe and Mn, which is above Malaysia Drinking Water Quality Standard (Malaysia Standard 2320, 2010). National Hydraulics

Research Institute of Malaysia (NAHRIM) conducted a preliminary study with the Department of Minerals and Geoscience (JMG) and found that majority monitoring wells in Kelantan producing a very high Fe concentration of groundwater. The groundwater well in USM Engineering Campus was also found contaminated with Fe and Mn. However, there is no long term characterisation study undertaken and reported to date. The analysis of the groundwater level in Malaysia has not been well presented until today.

To overcome the problems related to Fe and Mn, many treatment technologies such as precipitation (Bordoloi, 2011), adsorption and filtration (Jusoh et al., 2005; Esfandiar et al., 2014), ion exchange (Kim et al., 2001), oxidation with oxidising agent (El-Araby et al., 2009) and coagulation/ flocculation have been applied for Fe and Mn removal from drinking water.

Currently, ozone oxidation has attracted much attention in drinking water treatment.This is because ozone has a high oxidation potential (2.07V), which is capable of oxidising organic and inorganic pollutant that present in water. The ozone oxidation process is based on the effect of direct and indirect mechanisms, which are important in the disintegration of ozone in water into OH- radicals. Ozone is not only capable of oxidizing Fe and Mn, but also capable of oxidizing organic matters and acts as a disinfectant agent. Ozone is widely used in drinking water treatment to improve taste, colour, odour and biodegrability of impurities (Upadhyay and Srivastava, 2005). Ozone was found to not produce any secondary pollutant as compared to chlorine.

Chlorine has been widely used as a disinfectant due to its high efficiency and low-cost. However, the use of chlorine as disinfectant agent has the potential reaction with humic substance, forming halogenated disinfectant by–product (DBPs) such as THMs, HAAs, HANs and others. Elevated concentrations of DBPs have been found to be carcinogenic and mutagenic. Ozone is an alternative to replace chlorine, proven to be effective in minimizing the concentration of organic matter and thus reducing DBPs content in drinking water. The formation of DBPs is greatly dependent on the organic substances present in drinking water.

Although ozone possesses strong oxidizing properties, the application of single ozone is less effective and still limited in drinking water treatment since ozone tends to oxidize organic matter before removing Fe and Mn. Thus, ozonation coupled with the adsorption process is expected to improve the efficiency in removing contaminants from groundwater. For example, this treatment method has been applied at the Pintu Geng WTP, Kota Bharu Kelantan since 2013 to address the high Fe concentration in groundwater. This water treatment plant belongs to Air Kelantan Sdn Bhd (AKSB). Based on the continuous water quality monitoring data at the plant, the integrated process of ozone oxidation and filtration by anthracite produced excellent water quality compared to the conventional treatment method. The quality of water obtained from this treatment was satisfactory and complied with the MOH standard for drinking water. However, anthracite as filter media is rarely found in Malaysia and is currently imported from producing countries such as China, Korea and Russia. It costs about USD 200/ tonne. Although it is advantageous as an adsorbent media, the high cost of anthracite caused researchers to look for a cheaper alternative. Therefore, this study attempts to look for another media with lower cost.

Consequently, low-cost adsorbent media namely limestone (USD 20/ tonne) has been proposed as adsorptive filtration media in this study to overcome the problem. Previous studies found that limestone has a high potential to remove heavy metals in water and wastewater due to calcium carbonate content in the limestone that provides a buffer capacity to the water sample, which can enhance adsorption process (Aziz et al., 2001; Aziz et al., 2008; Aziz and Smith, 1992; Hussain et al., 2011).

To date, there is no study reported on the integrated treatment of ozonation followed by limestone adsorption to treat Fe and Mn from groundwater. A gap of knowledge in this treatment needs to be explored to provide a better alternative for groundwater treatment. Limestone was chosen as adsorptive filtration media to improve groundwater quality due to the presence of calcite structure (Gunasekaran and Anbalagan, 2007). Integrated treatment of ozonation followed by adsorption has shown an improvement in the Fe and Mn removals and enhance ozone utilisation efficiency while increasing the exhaustive time of limestone. Besides, ozone serves as a disinfectant agent in the groundwater. Therefore, the potential application of ozonation followed by adsorption processes using limestone for groundwater treatment was investigated in this study. The source of groundwater used was the well water from Pintu Geng water treatment plant and USM well, which were first characterised and compared.

1.3 Research Objectives

This study aims to examine and compare the performance of an integrated ozone-anthracite system with the integrated ozone-limestone system for groundwater treatment. The specific objectives are:

i. To determine, compare and analyse statistically the baseline data of groundwater selected area in Kelantan, USM tube well and to measure Pintu Geng WTP’s performance for removing Fe and Mn at different levels of treatment.

ii. To characterize the physical and chemical properties of selected adsorbents (limestone and anthracite) and determine their removal performances, isotherms and kinetic models for Fe and Mn adsorptions.

iii. To determine the removal performances of Fe and Mn by ozone alone with different ozone dosages, pHs and reaction time.

iv. To compare the removal performances of the ozone treatment, integrated ozone-limestone and integrated ozone-anthracite adsorption processes.

1.4 Scope of Study

The purpose of this study was to determine the potential of ozonation and adsorption processes in treating groundwater contaminants. Pintu Geng WTP was selected as a case study plant.

The scopes of this study are:

i. The sample was taken from USM tube well. Due to a long distance, a simulated raw groundwater well was used based on the quality of well at Pintu Geng WTP, Kelantan. For this, the USM tube well was chosen since its maximum level of Fe was less than 2.5 mg/L. When necessary, the groundwater sample taken from USM tube well was spiked using Fe and Mn standard solution and diluted by ultra-pure water (UPW) to maintain both metals' concentrations within the range as found at the Pintu Geng WTP. The sampling process and characterisation sample from USM tube well were carried out from February 2015 until Jan 2016. Meanwhile, the sample from Pintu Geng WTP was monitored from September 2014 until September 2016. Statistical analysis on Box and Whisker Plots was carried out from collecting the data (June 2005 until June 2012) of Fe and Mn concentrations representing shallow, intermediate and shallow aquifers at Northern Kelantan. There were four different sampling points (Raw groundwater, after ozonation, after filtration and final treated water) used at Pintu Geng WTP. Analysis on Spearman correlation coefficient was carried out for both USM tube well and Pintu Geng WTP samples to determine the correlation between each water quality parameter using Minitab 17 Statistical Software.

ii. The limestone and anthracite coal samples were characterised using X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Brunauer-Emmett-Teller (BET), Fourier Transform Infrared (FT-IR), and Field Emission Scanning Electron Microscope (FESEM) methods.

iii. The performance of limestone and anthracite media to remove Fe, Mn, UV_{254} and colour was investigated through batch adsorption study. The experimental works on the effects of adsorbent dosage, pH, shaking speed and contact time were carried out to determine the optimum removal of the pollutant without ozonation process. Analysis of the adsorption isotherms (Langmuir, Freundlich and Temkin) and kinetics (Pseudo-first order kinetic, pseudo-second order kinetic and intra-particle diffusion) models were investigated in this study.

iv. In the batch ozonation study, the effects of ozone dosage, pH and reaction time were focused to determine the optimum operating conditions. The maximum ozone dose produced from ozone generator was limited to 25 g/Nm^3 due to the maximum voltage supplied by transformer, which was only 180 V. The transformer was sparked and reduced to the half-life of ozone dose if the voltage was greater than 180 V.

v. The performance of integrated ozone-limestone and ozone-anthracite adsorption process were evaluated via column study. The pre-ozonated sample that passed through the column was simulated based on the preliminary performance of Fe and Mn removal using ozone alone. Analysis of the breakthrough curve model was done using Adam-Bohart, Thomas and Yoon-Nelson Models.

vi. The formation of disinfection by-products (DBPs) in drinking water ozonation processes is not focussed in this study.

1.5 Thesis Organization

This thesis consists of five chapters. This chapter discusses the problems arose on groundwater pollution and aimed at overcoming the problem by proposing a new integrated treatment of ozonation with limestone adsorption processes. The objectives of this study are presented in this chapter.

A comprehensive review of groundwater sources, issues and current treatment technologies are presented in Chapter Two. Integrated treatment using ozonation and adsorption processes is discussed detail. Besides, fundamental of adsorption process and mechanisms between adsorbent and adsorbate are explained through adsorption isotherm and kinetic study.

Chapter Three presents the flowchart of the steps in conducting laboratory works. A desktop study on collected data from monitoring well at the selected areas in Kelantan is discussed in this chapter. Groundwater characteristics and site sampling location are also explained in this chapter. The batch adsorption experiment was conducted to evaluate the performance of limestone and anthracite in removing Fe and Mn for groundwater. The performance removal of target pollutant using single ozone treatment was investigated through batch ozonation study. The experimental procedure in conducting batch ozonation and adsorption experiment is presented in this chapter. Meanwhile, detailed procedure on the integrated treatment of ozonation with limestone adsorption processes is described through fixed bed column study.

Chapter Four presents the results obtained from experimental works. It was divided into four subsections. Section 4.2-4.5 presents the result from characteristic analysis of USM tube well and Pintu Geng WTP. Statistical analysis of selected parameters was presented to obtain the correlation between parameters. Characteristics of limestone and anthracite coal adsorbents are discussed in Section 4.6. In Section 4.7- 4.8, the performance of both adsorbents to adsorb Fe, Mn, UV_{254} and colour is described through batch adsorption study. Further analysis on isotherm (Langmuir, Freundlich and Temkin models) and kinetics (Pseudo-first order, pseudo-second order and intra-particle diffusion models) were carried out in this study. A statistical goodness of fit measures was verified the theoretical and experimental data. The result of batch ozonation study is discussed in Section 4.9. The optimum ozone dose, pH and reaction time were obtained through this study. Section 4.9 discusses the result of batch ozonation study for varied ozone dosage, pH and reaction time. The optimum ozone dose, pH and reaction time were determined through batch ozonation study. The last section compares the performance of ozone treatment, integrated ozone-limestone and integrated ozone- anthracite through column study. Breakthrough curve modelling can be obtained from column study.

Chapter Five concludes the findings of the overall current study based on the objectives presented in chapter one followed by some recommendations for future studies presented in Section 5.2.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Currently, the water demand is increasing due to increasing population, rapid development as well as the growth of industrial and agricultural activities (Saimy and Yusof, 2013). Due to the anthropogenic activities, many countries including Malaysia are generally facing a problem to access clean and safe drinking water since many rivers have been contaminated and the cost of treatment is becoming more expensive over the years. Hence, the use of groundwater should be the main alternative.

2.2 Groundwater Resources

Groundwater has been identified as one of the alternative water sources for the use of future generation. It is an essential source of water for domestic, industries and agricultural activities. The world comprised one-third of all freshwater, which contributes to 36 % of domestic, 42% of agricultural and others for industrial purposes (Shrestha and Pandey, 2016). Based on the report from National Groundwater Association (2005), about 75%, 47%, 32%, 29% and 15% of the population in Europe, US, Asian- Pacific region, Latin America and Australia, respectively, depend on groundwater for their drinking water supply. Meanwhile, 26% of the population in Canada are using groundwater for their domestic needs. Significant portion of groundwater in Obama is used for domestic and commercial (15,300 m^3/d) while 4000 m^3/d of groundwater is utilised for melting snow during the winter season. In Thailand, groundwater is vital for water supply, which is estimated by 80% of the groundwater used for domestic water supply. The detail of water resources utilisation in some countries is listed in Table 2.1.

Table 2.1 Summary of water resources utilization in other countries

Country	**Purpose**	**Groundwater use / demand**	**Author**
Europe	Drinking water supply	75% of population	National Groundwater Association, (2005)
US		47% of population	
Asian-Pacific		32% of population	
Latin America		29% of population	
Australia		15% of population	
Canada		26% of population	
Groundwater in Obama	Domestic and commercial	15,300 m^3/d	Burnett et al., (2017)
	Melting snow (winter month)	4000 m^3/d	
Ljubljana, Slovenia	Drinking water supply	Supplying 300 000 people with drinking water.	Janza, (2017)
Thailand	Domestic water supply	80 % of domestic water supply is from groundwater source.	Buapeng, (2009)

Burnett et al., (2017) reported that the total annual groundwater in Obama city had increased gradually from 2004 until 2011 possibly due to increment in population. In north China Plain, both population and economic activity have rapidly increased 25 years ago and most of these developments were highly dependent on groundwater resources (Foster et al., 2004). Excessive population growth in Egypt also faced a problem of water scarcity and therefore used groundwater as an alternative of natural resource to increase the country’s economy (Nofal et al., 2018).

In Malaysia, the amount of groundwater available has been estimated at 10% surface runoff and total groundwater recharge (Razak and Karim, 2009). The summary of water resources in Malaysia is shown in Table 2.2.

Table 2.2 Summary of water resources in Malaysia (Azuhan, 1999)

Water resource	**Quantity (billion m^3)**
Annual rainfall	990
Surface runoff	566
Evapotranspiration	360
Groundwater recharge	164
Surface artificial storage	25
Groundwater storage	5000

Besides, there is about 99% of domestic water supply which are sourced from surface water, and the remaining 1% is from groundwater. In 2009, groundwater consumption is approximately 146 million per day (MLD) and increases by 2.5 % yearly (Sefie et al., 2015). Heng et al., (1989) reported groundwater demand in Northern Kelantan is expected to be increased from 12 MLD in 1985 to 211 MLD in the year 2010. Moreover, in Kota Bharu and Bachok, Kelantan, there is about 624,389 peoples relied on groundwater (Sefie et al., 2015).

In Shah Alam and Bukit Raja, Klang, groundwater utilization is mainly for industrial purposes. The rapid industrial growth in both areas causes increased in the water demand for factories operating such as for cleaning, washing and cooling process (Baharin and Ghazalli, 2009). In addition, groundwater is also being used by the Agricultural Commodities Centre in Rhu Tapai, Terengganu and aquaculture farm in Pekan, Pahang (Baharin and Ghazalli, 2009). The detail areas where groundwater is abstracted for domestic, agricultural and industrial purposes are listed in Table 2.3.

In Malaysia, water is placed under Federal government; however, water supply distribution is managed by different department state levels such as Public Work Department (Kedah, Perlis, Labuan,Sarawak), State Water Supply Department (Negeri Sembilan, Pahang, Sabah), State Water Supply Board (Melaka, Perak, Kuching, Sibu), Corporatised Company (Selangor, Terengganu) and Privatisation Company (Penang, Kelantan, Johor) (Saimy and Yusof, 2013).

Table 2.3 Area of groundwater abstracted in Malaysia

State	**Purpose**	**Groundwater demand**	**Author**
Kelantan	Domestic	100,000 m^3/d	
Kota Bharu		96,824 m^3/d	Narany et al., (2018)
Bachok		28,420 m^3/d	
Tumpat		22,516 m^3/d	
Kuala Terengganu, Terengganu		16,000 m^3/d	Jamaludin et al., (2013)
Arau, Perlis		6,000 m^3/d	Jamaludin et al., (2013)
Pahang			
Sg. Ular		5,000 m^3/d	Baharin and Ghazalli, (2009)
Rompin		2,000 m^3/d	
Selangor Shah Alam Bukit Raja,Klang	Industrial (cleaning, washing and cooling)	-	Baharin and Ghazalli, (2009)
Agricultural Commodities Centre, Rhu Tapai, Terengganu	Agricultural	-	Baharin and Ghazalli, (2009)
Pekan, Pahang.	Aquaculture	-	Baharin and Ghazalli, (2009)

Many water treatment plants use conventional treatment method to overcome contaminant problems that affect the quality of drinking water. However, a few water treatment plants have been recorded using advanced drinking water technologies such as ultra-membrane filtration, dissolved air floatation and ozone oxidation as listed in Table 2.4.

Table 2.4 Advanced water treatment technology in Malaysia (Razak et al., 2015)

Water treatment technology	**Water treatment plant**
Dissolved air floatation	Wangsa Maju, Selangor Sungai Kinta, Perak
Actiflo clarification system	Sungai Selangor
Ultra- membrane filtration	Wakaf Bunut & Perrala, Kelantan Sungai Rumput & Kepong, Selangor
Ozonation	Pintu Geng, Kelantan

2.3 Groundwater Problems and Issues

Rapid urbanisation and sophisticated industrialisation that led to an increase in population have a significant impact on water demand. Agricultural activities including cultivation plant have also attributed to high water demand. Groundwater may be utilised for these purposes to overcome water scarcity problem. However, human activities have led to groundwater contamination and contributed to the major issues that adversely affected drinking water.

High concentration of heavy metals is a major concern in addressing the problems of groundwater pollution. These metals enter groundwater during the weathering process of soils, sediments and minerals (Belkhiri et al., 2017). Minerals content in soil, sediment and rock such as Ca, Mg, Fe, and Mn may affect the quality of groundwater. Excessive Fe and Mn in groundwater can occur due to rain filtering process through soil, sediment, rocks and minerals. Fe in drinking water may also occur due to the corrosion of Fe pipes in water distribution system (Chaturvedi and Dave, 2012). The presence of high elevated Fe made the water to be unusable through metallic taste, discolouration and staining of laundry. The concentration of dissolved minerals in groundwater is proportional to the contact time (Wang et al., 2013). There are several factors that influence heavy metals concentration in groundwater, which include environmental reaction or soil condition such as oxidation and reduction, acidity and alkalinity, sorption or ion exchange (Hashim et al., 2011). According to MOH, the maximum permissible limits of Fe and Mn in drinking water are 0.3 mg/L and 0.1 mg/L, respectively. Most groundwater contains high level of heavy metals due to chemical degradation and redox condition in the change of oxidation states.

Groundwater can be contaminated by other contaminants that depend on its sources. Poor basic sanitation and sanitation facilities especially for those living in the rural areas contributed to high concentration of bacteria in the groundwater (Idrus et al., 2014). The presence of bacteria in groundwater may cause waterborne diseases. The effects of groundwater contaminated by several pollutants are listed in Table 2.5.

In Malaysia, the monitoring of groundwater quality is carried out by Department of Minerals and Geoscience (JMG), Department of Environment (DOE), water agencies and local councils. Some projects on groundwater monitoring are conducted by other workers to identify the causes of contamination, possibility of saltwater intrusion and concentration of contaminants in groundwater.

Table 2.5 The effect of groundwater contamination in the previous study

Pollutant	**Sampling**	**Sources**	**Impact**	**Reference**
Nitrate	Monitoring well, Bachok, Kelantan Monitoring well in agricultural area of Kuala Langat Selangor Shallow dug wells, Tanah Merah, Kelamtan	Nitrogeneous fertilizer (tobacco,rice agro system, cultivation of rubber) Pesticide, agricultural waste, domestic waste	Blue baby syndrome, methaemoglobinemia among infant gastrointestinal illness, multiple digestive tract impairment, indigestion and inflammation of the stomach, gastroenteritis, abdominal pain, diarrhea	Jamaludin et al., (2013) Suthar et al., (2009) Harun et al., (2019) Raj et al., (2018)
Turbidity		Fine sand, silt, and clay passing through well screen. Suspended particles of organic matter; precipitates forming in water.	Cloudy or gritty water; water pipes, filters, and water heater plugged	
Fe	Monitoring well, North Kelantan Aquifer	Soil, sediment and rock	Unpleasant-tasting water, red-stained clothing and plumbing fixture, hereditary chronic iron overload (hemochromatosis)	Hussin et al.,(2014)
Mn	Synthetic groundwater	-	discolouration of water, unpleasant metallic taste and odour, plumbing fixture	Kenari and Barbeau, (2014)
As	Bangladesh		Lead to lung, cardiovascular disease, kidney, liver and prostate cancer	Smith et al., (2006), Parvez et al., (2019)
Total Coliform & *E-Coli*	Rural Area, Kelantan	Poor sanitation and sanitation facilities	typhoid fever, hepatitis, ear infections	Idrus et al., (2014)

2.3.1 Groundwater pollution: Physical pollutant

Pollutants in groundwater can be divided into physical, chemical (organic and inorganic) and biological contaminants. Physical pollutant in groundwater is mainly assessed with turbidity and colour. Turbidity is caused by the presence of clay, algae and organic matter in groundwater. The water from the deep aquifer is ordinarily clear than shallow aquifer since the turbidity is filtered at the surface of the earth. Turbidity is not a crucial problem that affects the quality of groundwater. In Pakistan, turbidity has been found safe for drinking according to the standard by World Health Organisation (WHO). On the contrary, groundwater in Melaka contains a high concentration of turbidity in shallow and deep aquifer (Shirazi et al., 2015). The value of 5 NTU of turbidity is the allowable limit of drinking water by MOH.

2.3.2 Groundwater pollution: Inorganic pollutant

Inorganic pollutant in groundwater is classified into anion and cation. Cation includes iron (Fe), manganese (Mn), lead (Pb), cadmium (Cd) and other divalent ions while anion includes nitrate (NO_3), nitrite (NO_2), fluoride (F), sulphate (SO_4), phosphate (PO_4), chloride and fluoride. Fe and Mn are the major pollutants in most groundwater and the details of both Fe and Mn problems are discussed in the Section 2.4 and Section 2.5.

Besides heavy metal pollutants, groundwater also contains high level of anions such as nitrate (NO_3), nitrite (NO_2), fluoride (F), sulphate (SO_4) arsenite (AsO_3) and arsenate (AsO_4), which contribute to the groundwater issues. Nitrate is a potential groundwater contaminant. Nitrate in groundwater comes from septic tanks, application of nitrogen-rich fertilisers and agricultural activities. According to Jamaludin et al.,

(2013) the exposure of elevated nitrate in drinking well water was resulted from intensive agricultural activities in Bachok, Kelantan.

Utilisation of high volume of fertilisers poses adverse effect to human health for those consuming groundwater as drinking water. High exposure to drinking water containing nitrate can cause methemoglobinemia or blue baby syndrome among infants especially those younger than six months. Infants younger than six months are susceptible to nitrate poisoning as they depend on bacteria to digest food and the bacteria change from nitrate to nitrite, which can enter the baby blood, thus causing methaemoglobinemia (Mahler et al., 2007). The concentration of nitrate is influenced by rainfall, nitrate concentration entering the groundwater at the starting and throughout the rainy season (Jamaludin et al., 2013). The water table rises during heavy rainfall and nitrate is mobilised into groundwater and therefore increasing nitrate concentration in groundwater. According to MOH, the appearance of nitrate should be less than 10 mg/L to be considered acceptable to consumers. Besides, a concentration of nitrate in groundwater also depends on aquifer depth. Tawnie et al., (2011) conducted a study on groundwater contamination in Northern Kelantan and reported higher nitrate concentration appeared in shallow aquifer than that of deep aquifer. The excessive use of nitrate fertilisers on farmlands caused pollutants to quickly disperse in shallow aquifers (Narany et al., 2018). In the comparison, mobilisation of nitrate requires more extended time to move through impermeable clay layer before it reaches deep aquifer.

Besides, the long-term pattern of sulphate in Northern Kelantan's groundwater sample showed a high concentration of sulphate in the shallow aquifer. According to monitoring data, it was indicated that sulphate concentration has increased from 1989 to 2011. It was possibly due to bacteria oxidation of sulphur and sulphate-bearing fertilisers that occurred in shallow aquifer (Papatheodorou et al., 2006). Rahim et al., (2010) investigated the effect of leachate on groundwater quality in the Ampar Tenang open tiping site. They found that the groundwater contained phosphate (2.72 mg/L) associated with migrated leachate from landfill site. The concentrations of fluoride ion in groundwater from Al-Sahool, Mitm and Al-Sayyadah, Yemen were in the range of 0.4 - 2.44 mg/L, 0.38 - 0.9 mg/L and 0.34 - 0.7 mg/L, respectively (Samsudin et al., 2009). Raj et al., (2018) stated that high fluorine content in groundwater is due to the dissolution of fluoride- rich minerals (such as fluorite, mica, apatite, amphiboles and clay) from the bedrock. The inorganic pollutants found present in groundwater at different areas are listed in Table 2.6

Table 2.6 Inorganic parameters in groundwater at different areas of study

Groundwater sources	**Target pollutant**				**Author**
	NO_3 (mg/L)	**SO_4 (mg/L)**	**PO_4 (mg/L)**	**F^- (mg/L)**	
Yemen					
• Al-Sahool	7.1 – 20.3	20.5 – 57.7		0.4 – 2.44	Samsudin et al., (2009)
• Mitm	8.7 – 21.1	26.7 – 107	-	0.38 – 0.9	
• Al-Sayyadah	12.3 – 25.6	28.7 – 38.6		0.34 – 0.7	
Jilin City, Northern China	1.8 – 112.9	-	-	-	Huan et al., (2012)
Kelantan					
• Bachok	0.88 ± 0.88				Idrus et al., (2014)
• Gua Musang	0.23 ± 0.31				
• Kota Bharu	0.61 ± 1.03	-	-	-	
• Kuala Krai	0.18 ± 0.15				
• Machang	0.22 ± 0.16				
Borehole at Ampar Tenang Landfill site, Selangor (n=5)	7.45 – 12.67	67.5 – 78.6	1.2 – 2.1	0.06 – 0.1	Yusoff et al., (2013)
Monitoring well at Pulau Burung Landfill, Penang (n= 5)	1.8 – 7.9	0.7 – 18.7	0.3- 1.3	-	Aziz et al., (2010)
Tipping site in West Malaysia	10.4	4.75	2.72	0.35	Rahim et al., (2010)

2.3.3 Groundwater pollution: Organic pollutant

In groundwater, organic pollutants mainly come from the use of chemical fertilisers and insecticides in agricultural activities. A study conducted by Kong et al. (2016) focused on organic micro-pollutant contaminated at 27 groundwater sites in Beijing and Tianjin, North China. They found that high concentration of micro-pollutants appeared in groundwater due to intensive agricultural and industrial activities. In this study, a high level of pesticide was detected in a shallow well located near greenhouse vegetable cultivation area. Some pharmaceutical and personal care products (PPCPs) have been detected in groundwater with the concentration ranging from 0.05 – 0.17 µg/L as listed in Table 2.7.

Table 2.7 Organic pollutant in groundwater

Groundwater sources	**Target pollutant**	**Concentration (mg/L)**	**Author**
Beijing and Tianjin, North China.	PPCP	$(0.05 – 0.17)x10^{-3}$	Kong et al., (2016)
	benzyl alcohol	0.582	
	2-phenoxy-ethanol	0.129	
	Acetophenone	0.074	
	Pentamethylbenzene	0.051	
	Nitrobenzene	0.041	
	dimethyl phthalate	0.064	
Groundwater at Ampang Tenang Landfill, Selangor	PCBs	8.9	Yusoff et al.,(2013)
	COD	2685 - 2891	
	BOD	123-142	
Monitoring well at Pulau Burung Landfill, Penang	COD	19 - 160	Aziz et al.,(2010)
	BOD	116 – 655	

Organic pollutants such as pesticides can leach through the soil and contaminated groundwater. Toxicity of organic pollutant may cause an adverse effect on human and animals, which will cause cancer, congenital disability and other illnesses.

In Malaysia, most groundwater near to the landfill site has been contaminated with organic pollutants. High concentration of BOD and COD was found in five borehole samples located near to the Ampang Tenang landfill site, which were within the range of 123 to 142 mg/L and 2685 to 2891 mg/L, respectively (Yusoff et al., 2013). This indicates leachate migration into the wells especially during rainy days, which penetrated the ground and thus causing contaminated groundwater. In addition, Aziz et al. (2010) analysed five samples from different monitoring wells located near the Pulau Burung Landfill, Penang, and found that the average value of COD (19-160 mg/L) and BOD (116 – 655 mg/L) did not comply with the drinking water standard.

2.3.4 Groundwater pollution: Microbiological pollutant

The presence of coliform bacteria is important for the microbial characteristics of groundwater (Ojo et al., 2012). Coliform is an indicator in determining whether or not the water is of good quality and safe to drink. Poor sanitation and sanitation facilities that are too close to the wells can lead to problems of Faecal Coliform including *E-Coli* contamination in groundwater. High risk of waterborne disease occurred due to human and animal faecal wastes that infiltrate into groundwater. Human faecal sources include septic tank effluent and leakage of wastewater collection pipes, while animal source includes farm animals and pets (Atherholt et al., 2017). This is in agreement with Chin et al. (2010) who conducted a study at Pulau Tiga, Sabah. Similar studies to detect E-Coli at different wells have been conducted at Kemaman, Dungun, Marang, Kuala Terengganu, Hulu Terengganu, Setiu and Besut, Terengganu (Idrus et al., 2014). They concluded that *E-Coli* was a significant contaminant in the shallow well. According to the microbiological analysis of 454 groundwater samples in rural areas of Kelantan, it was reported that 49% of the samples (221 / 454) were found positive with Total Coliform while 14% of the samples

(65/454) contained *E-Coli*. Detailed result of microbiological parameters in nine districts in Kelantan's groundwater is recorded in Table 2.8.

Table 2.8 Microbiological parameters in groundwater sample at rural area, Kelantan (Idrus et al., 2014)

Groundwater source	**Total Coliform (MPN / 100 mL)**	**E-Coli (MPN / 100 mL)**
Bachok (n = 40)	215.73 ± 1082	0
Gua Musang (n = 21)	62.48 ±158.2	24.95 ± 104.37
Kota Bharu (n = 76)	1218.5 ± 4062.9	7.93 ±32.55
Kuala Krai (n = 22)	1.45 ± 4.15	0.09 ± 0.43
Machang (n = 20)	8.80 ± 22.85	4.05 ± 12.52
Pasir Mas (n = 55)	4.62 ±21.39	1.69 ± 9.67
Pasir Puteh (n = 80)	564.92 ± 2377	4.88 ± 30
Tanah Merah (n = 20)	2.45 ± 3.97	0.10 ± 0.477
Tumpat (n = 140)	10780 ± 33814	5.14 ± 19.55

Unfortunately, some people use untreated groundwater contributed to the high risk of infection and disease from a pathogen that gives adverse effect, causing illness (Hynds et al., 2012). Palamuleni and Akoth, (2015) reported the total coliform count that was found to be 1 to 579.4 cfu / 100 mL during spring and decreased to < 1 to 44 cfu /100 mL during winter in the United States due to the increase in temperature during spring, which affected the rate of proliferation of coliform bacteria.

The presence of coliform bacteria in groundwater may be affected by environmental and risk factors including well design and location, septic system location and maintenance, geological formation and climate events such as flooding (O'Dwyer et al., 2018; Hynds et al., 2012). The coliform bacteria can be transported from surface source to groundwater, thus increasing the concentration of coliform bacteria in groundwater.

One of the main factors influencing the concentration of coliform bacteria in groundwater is temperature. Palamuleni and Akoth (2015) stated that the total coliform is proportional to temperature. The rapid growth of coliform bacteria occurred in high water temperatures especially during the spring season. The high volume of rainfall