ADSORPTION STUDY OF HEAVY METALS AND NATURAL ORGANIC MATTERS (NOM) IN GROUNDWATER USING METAKAOLIN

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by

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LIST OF ABBREVIATION

AAS	Atomic absorption spectrophotometer
ANOVA	Analysis of variance
BBD	Box-Behnken Design
BET	Brunauer–Emmet-Teller
BOD	Biological oxygen demand
CCD	Central composite design
CDOM	Chromophoric dissolved organic matter
DBPs	Disinfection by-products
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EDX	Energy dispersive x-ray
FAAS	Flame atomic absorption spectrophotometer
FEEM	Fluorescence excitation-emission matrix
F value	Fisher value
FTIR	Fourier transform infra-red
GFAAS	Graphite furnace atomic absorption spectrophotometer
HAAs	Haloacetic acids
HPI	Hydrophilic fraction
HPO	Hydrophobic fraction
ICP-OES	Inductive couple plasma optical emission spectrometry
ICP-MS	Inductive couple plasma mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LOAEL	Lowest-observed adverse effect level
NOM	Natural organic matters
NTU	Nephelometric Turbidity Unit

NDWQS	National drinking water quality standard
OFAT	One factor at a time
PI	Permanganate Index
POM	Particulate organic matter
ppb	Part per billion
ppm	Part per million
ppt	Part per thousand
rpm	Rotation per minute
RSM	Response surface methodology
R^2	Correlation coefficient
r	Pearson's correlation coefficient
r_s	Spearman's correlation coefficient
SEM	Scanning electron microscope
SPE	Solid phase extraction
SUVA	Specific UV absorbance
TDS	Total dissolved solid
THMs	Tetrahalomethanes
TSS	Total suspended solid
UV_{254}	Ultra violet ray absorbance at 254 wavelength
WHO	World Health Organization
XRF	X-ray fluorescent
XRD	X-ray diffraction

KAJIAN PENJERAPAN LOGAM BERAT DAN BAHAN ORGANIK SEMULAJADI DI DALAM AIR BUMI MENGGUNAKAN METAKAOLIN

ABSTRAK

Kepentingan air bawah tanah semakin disedari dengan berkurangnya bekalan air dari sumber air permukaan. Pengurangan ini disebabkan oleh dua faktor iaitu faktor cuaca yang tidak menentu dan penurunan kualiti air permukaan. Walaubagaimanapun, adalah penting untuk mengetahui kualiti air bawah tanah sebelum digunakan kerana ia berbeza mengikut kawasan. Kepekatan logam berat terlarut yang tinggi di dalam air bawah tanah adalah biasa terjadi disebabkan tahap kepekatan oksigen yang rendah dan keadaan air yang reduktif. Kepekatan bahan organik (NOM) semulajadi juga merendahkan nilai estetik air, lebih membimbangkan tindakbalas antara bahan organik semulajadi (NOM) dan pembasmi kuman menghasilkan produk sampingan yang membahayakan kesihatan. Oleh itu, objektif kajian ini termasuklah; 1) kajian kualiti air bawah tanah diukur terutamanya kepekatan logam terlarut seperti besi, mangan, nikel dan bahan organik semulajadi; 2) mengkaji kemampuan metakaolin digunakan untuk mengurangkan kepekatan bahan pencemar tersebut dan 3) Mencari model isotherm dan kinetic yang sesuai untuk setiap bahan pencemar. Kepekatan purata bagi besi (615.4 µg/L), mangan (444.0 µg/L), nikel (174.6 µg/L) dan NOM (diukur dengan parameter UV_{254})(1.23 cm^{-1}). Tetapan (dos, kadar agitasi dan tempoh tindakbalas) untuk penjerapan optima dijalankan dengan menggunakan teknik tidakbalas permukaan (RSM) dengan kadar pengurangan kepekatan bagi besi, mangan, nikel dan NOM adalah 82%, 38%, 39% dan 22%. Kekuatan ionik dan persaingan dalam penjerapan dikenalpasti sebagai faktor penghad. Penjerapan bahan pencemar di atas permukaan

metakaolin mengikut model Freundlich (kajian isoterma) kerana nilai $1/n > 1$ yang menunjukkan adanya tindakbalas antara bahan pencemar dan permukaan bahan penjerap. Model Langmuir tidak sepadan dengan data eksperimen disebabkan oleh nilai q_m, K_L dan R_L yang tidak menunjukkan kesesuaian. Manakala berdasarkan kajian kinetik, data eksperimen selaras dengan *pseudo-second-order* disebabkan oleh nilai peratusan Δq_e yang lebih rendah dari *pseudo-first-order*. Nilai Δq_e untuk logam besi adalah 95% (*pseudo-first-order*) dan 1% untuk *pseudo-second-order*. Manakala Δq_e untuk *pseudo-first-order* bagi logam mangan, nikel dan NOM, masing-masing dengan nilai 97%, 98% dan 96%. Peratusan Δq_euntuk *pseudo-second-order* pula masing-masing bernilai 28%, 16% dan 18%. Keputusan-keputusan yang didapati dari kajian isotherm dan kinetik membuktikan wujudnya tindakbalas permukaan iaitu penjerapan fizikal.

ADSORPTION STUDY OF HEAVY METALS AND NATURAL ORGANIC MATTERS (NOM) IN GROUNDWATER USING METAKAOLIN

ABSTRACT

Groundwater is an increasingly important source of water due to lack of surface water supply that caused by climates vagaries and declined surface water quality. However, prior to consumption, it is very essential to recognize the quality of groundwater to avoid adverse effect to health as the quality differs based on location. Elevated heavy metals concentrations in groundwater are one of the common issues due to the anoxic and reductive condition in groundwater. In addition, high natural organic matter (NOM) content in groundwater decrease the water aesthetic value and develop disinfection by-product when reacted with disinfectant. Therefore, the objectives of this study are; 1) To study the quality of groundwater sampled; 2) to explore capability of metakaolin in order to reduce the contaminant (iron, manganese, nickel and NOM) concentration in groundwater and the factors (dosage, agitation rate & contact time) optimization using RSM; and 3) to determine the suitable isotherm and kinetics behavior for each contaminant. . In average, the concentration of the contaminant is high with iron (615.4 μg/L), manganese (444.0 μg/L), nickel (174.6 μg/L) and NOM (as measured in UV_{254})(1.23 cm^{-1}). The optimum setting (dosage, agitation rate and contact time) was assessed using RSM where the removal of iron, manganese, nickel and NOM was 82%, 38%, 39% and 22% respectively. High ionic strength and competitive adsorption in a multi-solute system have been recognized as limiting factors. Isotherm study signified that the adsorption of all contaminants onto metakaolin fits with the Freundlich model as the values of $1/n > 1$ denotes that there is cooperative

adsorption. Langmuir models per contra, does not fit with experimental data due to unfavorable value of q_m, K_L and R_L. While in kinetic study fits Pseudo-second-order as a results of lower % Δq_e value compare with Pseudo-first-order. The percentage of Δq_e (*pseudo-first-order)* for iron, manganese, nickel and NOM are 95%, 97%, 98% and 96% accordingly. While the value of Δq_e for *pseudo-second-order* for each metal are 1% (iron), 28% (manganese), 16% (nickel) and 18% (NOM). These findings suggesting that there is a surface interaction between contaminants and adsorbent's surface which is physisorption.

CHAPTER ONE

INTRODUCTION

1.1 Background of study

Malaysia is blessed with abundant of water supply from fresh surface water approximately 150 river systems (Chan et al., 2007) and recharged by high rate of rainfall estimated exceeding 2000 mm throughout the year which is greater than global average (Abidin et al., 2017) . Nonetheless, water supply is still not sufficient in dry season, due to the demand that keep increasing and the source that gradually depleted. Many had studied to harvest other resource such as rain (Autixier et al., 2014; Belmeziti et al., 2014; Kim et al., 2016; Malassa et al., 2014) and groundwater (Flindt Jørgensen et al., 2016; Hoque et al., 2016; Tiwari et al., 2017) that may be suitable to be one of the alternative source. Rapid urbanization and industrialization cause even higher pressure to overall water supply system with increasing demand from high population area and manufacturing industries that requires high volume of treated water (Chan et al., 2007; Siwar and Ahmed, 2014).

Despite the importance of surface water, humans seem to pay less attention to manage their water source. Rivers are always neglected, abused and mismanaged as a cheapest and easiest way to toss away human waste either domestic, industrial or agricultural origins (Weng, 2005). These disrespectful acts are actually hitting humans back where the depleted and polluted water source is poisoning and deteriorating the surrounding nature thus endangering organism including people who depend on it. In Malaysia as instance, a total of 43 rivers were categorized as polluted, 189 others are slightly polluted and another 244 rivers are considered as clean by Natural Resources and Environment Department (Bernama, 2016). Polluted water source not only incurred higher cost of treatment, it will also lessen the capability to supply water for human consumption. Thus alternatives such as groundwater should be aggressively explored to ensure continuity of water supply.

Groundwater generally known as the water that fill in the void or gap between rocks, gravel, sands or limestones. The water may originate from rainfalls, rivers or lakes where the water seeps through the crack or gap (Ojo et al., 2012). The dependency on groundwater is different between countries. Swaziland, Saudi Arabia, Iceland, Mongolia, Russia and Libya are examples that relied on groundwater for fresh water supply and its estimated that globally, almost $900km^3$ groundwater pumped out annually (Kura et al., 2018).

Contamination in groundwater systems derived mostly from anthropogenic activity particularly as natural-derived contaminant normally comparatively very small (Abdulrafiu et al., 2016; Babarinde and Onyiaocha, 2016; Gleeson et al., 2015; Li et al., 2015). While untreated effluent drained to water bodies can be clearly witnessed, the pollutions infiltrated into groundwater streams however are hardly noticed. Certain countries suffering from high heavy metals content in their groundwater such as arsenic (As) (Das et al., 2016; Maizel et al., 2016; Saha, 2009), iron (Fe) (Batabyal and Gupta, 2017; Shakoor et al., 2016), manganese (Mn) (Gillispie et al., 2016; Samantara et al., 2017; Ying et al., 2017; Zhang et al., 2018) and nickel (Ni) (Heikkinen et al., 2002; Mehta et al., 2017; Verma et al., 2016). Iron and manganese for instance, are affecting the aesthetic values of water such as taste and color, contrarily nickel and arsenic have less significant effect on appearance at the concentration rated as fatal, 70 µg/L and 10 µg/L accordingly.

In Malaysia, groundwater normally utilized in rural area for domestic purpose where there is no piped water supply. Considered as secondary source, this hidden system remains untouched as people failed to recognize the vast potential of this huge invisible water source. Total usage of groundwater in Malaysia was estimated only 2% mostly used in Kelantan and Perlis (Issa et al., 2012; Suratman, 2004). Malaysia’s groundwater also suffers from elevated concentration of heavy metals (Fe, Mn and Ni) reported by researchers (Akbar et al., 2015b; Ambu et al., 2014; Halwani, 2012; Ibrahim et al., 2015; Lin et al., 2012; Zawawi et al., 2017)

NOM is a complex mixture contains high diversity of organic chemical compound that may vary depend of source and level of degradation, might be derived from terrestrial, aquatic life or anthropogenic source. Various origin of NOM signifies the mixture complexity of chemical compositions that leads to sizes, molecular weights, charge, hydrophobicity, aromaticity and polarity dissimilarity. These variations are giving challenges to water treatment operations and made NOM characterization even more complicated (Erhayem and Sohn, 2014; Lee et al., 2016; Philippe and Schaumann, 2014a). Although NOM generally is not harmful to human, the formation of disinfection by-products (DBPs) can be reduced by eliminating NOM content in water. The existence of NOM also affects aesthetic value of water such as color, taste and odor thus demands higher dosage of coagulant (Bhatnagar and Sillanpaa, 2017; Shutova et al., 2014).

Clays has been studied as an adsorbent in water and wastewater treatment to remove heavy metals and NOM as it is found abundantly and considered as cheap (Alkan et al., 2008; Gautam et al., 2015; Khatri et al., 2017; Kounou et al., 2015; Lakherwal, 2014; Uddin, 2017a). In 2008 to 2012, Malaysia produced more than four hundred thousand metric tonnes of kaolin annually (Reichl et al., 2014). Theoretically kaolinite structure exist with no substitution of Si^{4+} with Al^{3+} in its tetrahedral layer and no substitution of Al^{3+} with other ion (Mg^{2+}, Fe^{2+}, Zn^{2+} or others) in the octahedral layers hence resulted net layer charge for kaolin is zero (Al-essa and Khalili, 2018). In actual condition somehow, it has small net negative charge on the clay crystal due to deprotonation in aqueous solution where this characteristic is responsible to prevent the surface from being completely inert (Al-essa and Khalili, 2018). However, kaolin naturally has a relatively low adsorption capacity and small small surface area. This characteristic leads many researchers to enhance the adsorption capacity by chemical or physical treatment (Al-essa and Khalili, 2018).

This study will help in decision making in terms of the water usability. The correlation result will aid to recognize which metal content contributes to bulk parameter. This information is useful in order to find the best solution for treatment purposes. The assessment on capability of metakaolin as an adsorbent in multi solute system and brackish water will be an added knowledge in water treatment generally. All the data obtained will also useful for further improvement on the adsorbent capability with additional treatment.

1.2 Problem statement

Water scarcity has been one of major issue globally where climates and the decreasing of water supply sources have been identified as a few factors that contributed to the issue. The vagaries of climatic condition affects water supply in the occurrence of event of low precipitation that lead to drought. The annual precipitation rate has been recorded by Malaysian Meteorological Department, (2016) shows that the average of rainfall may vary from approximately 2400 mm to 3800 mm annually. During the event of low precipitation, surface water recharge rate reduced and then followed by drought as recorded in 1992, 1998 and 2014 (Abdullah et al., 2014). Surface water is the main water supply for the country where in 2014 and 2015, approximately 98% of water supply is from surface water and less than 1.5% of water supply is from groundwater (Suruhanjaya Perkhidmatan Air Negara, 2015). Moreover, Huang et al., (2015) reported that the number of rivers that rated as clean reduced from 338 to 278 rivers due to human activity from agriculture, land clearing, untreated sewage and industrial waste thus, exploration of alternative source such as groundwater is essential.

It has been estimated by Manap et al., (2013) that the groundwater storage in Malaysia is about 64 billion cubic meters. In general, states like Kelantan, Pahang, Terengganu and northern part of Malaysia rely on the groundwater as one of freshwater supply and the dependency to groundwater is even higher in the small islands (Kura et al., 2018). Despite of its massive availability, recognizing groundwater quality is crucial prior to its consumption as there tendency for groundwater to be consumed without any treatment (Ambu et al., 2014; Nshimiyimana et al., 2016; Saana et al., 2016)

High content of heavy metal such as Fe, Mn and Ni in groundwater affects the usability of the groundwater. High heavy metals content in groundwater has been reported throughout Malaysia especially where the groundwater abstracted as a fresh water supply. Fe has been detected in excessive value of concentration in Pulau Pinang (Akbar et al., 2016), Perak (Ibrahim et al., 2015; Zawawi et al., 2017), Kelantan (Hussin et al., 2016; Sefie et al., 2018; Yap et al., 2017) , Selangor (Shamsuddin et al., 2014) and Terengganu ((Hamzah et al., 2017). As for Mn, elevated concentration has been measured in Sabah (Kato et al., 2010; Lin et al., 2012), Selangor (Ambu et al., 2014; Shamsuddin et al., 2014), Terengganu (Hamzah et al., 2017), Johor (Musa et al., 2015) and Kelantan (Hussin et al., 2016; Sefie et al., 2018; Yap et al., 2017). While for Ni, fewer researchers include this metal in their study due to rare occasion of high concentration in groundwater. However, Zawawi et al., (2017) and Akbar et al., (2016) identified elevated concentration in Perak and Pulau Pinang respectively.

The importance of disinfection process in groundwater is to minimize waterborne diseases outbreak such as cholera, gastroenteritis, typhoid fever and dysentery, thus chlorine has been used for disinfectant widely (Coulliette et al., 2013; Liu et al., 2016; Mandal et al., 2011; Saana et al., 2016). Chlorine has been considered as predominant disinfectant globally due to its effectiveness, relatively low cost, capability to stay in distribution system as residual to halt microorganism growth (Gil et al., 2015; Liu et al., 2016). Although chlorine's supremacy is hardly competed, it has huge undesirable drawback. Chlorine reacts with natural organic matters (NOM) producing carcinogenic, harmful, toxic disinfection by-products (DBPs) namely trihalomethanes (THMs), haloacetic acids (HAAs) and others (Bridgeman et al., 2014; Heeb et al., 2017; Ye et al., 2014). Additionally, NOM is also another contributor to the reduction of water's aesthetic value where elevated concentration of NOM caused unwanted yellowish to brownish colour of water.

Alternative adsorbent especially natural-sourced adsorbent such as clays has been extensively studied in order to find versatile adsorbent that stable in various operation condition, abundance, non-expensive material and high capacity of adsoption. Additionally, thermal treatment or calcination of kaolin clay produces metakaolin that exhibits higher surface area for adsorption site and researchers had proven in their studies that metakaolin has better capability in heavy metals removal (Anagho et al., 2013; Essomba et al., 2014; Kounou et al., 2015). Formation of metakaolin also develops a hydrophobic surface that can be an adsorption site for hydrophobic interaction for NOM. Moreover, Malaysia is one of kaolin producer thus, the mineral can be found in abundant locally.

Therefore, removal of these contaminants (heavy metals and NOM) is essential to ensure safe consumption of groundwater. In this study, the application of metakaolin was explored as adsorbent material to reduce the concentration iron, manganese, nickel and NOM in groundwater abstracted.

1.3 Objective of studies

The core objective for this research is to study the treatability of groundwater concerned to remove certain contaminates namely heavy metals and NOM as well as to further understand about relationship between parameters that has been measured for groundwater sampled and the capability of adsorbent namely metakaolin to adsorb NOM. Subsequently, this research targets the following objectives:

a) To characterize groundwater, for specific duration on contaminants concentrations (iron, manganese, nickel & NOM) and the correlation between parameters.
b) To optimize setting (dosage, rotation speed and contact time) for iron, manganese, nickel and NOM removal using metakaolin as adsorbent via RSM as platform and develop a mathematical model for each response.
c) To determine the suitable isotherm and kinetics behavior for each parameter (Fe, Mn, Ni and NOM (as is UV_{254})).

1.4 Scope of study

The scope of this study is to test the adsorption capability of metakaolin to immobilize heavy metals specifically iron (Fe), manganese (Mn) and nickel (Ni) as as well as natural organic matter (NOM) from groundwater located in Universiti Sains Malaysia, Engineering Campus located in Nibong Tebal, Pulau Pinang (5° 08' 50.5"N, 100° 29' 34.7"E). These heavy metals content were selected as parameters of interest due to the elevated concentration in the groundwater studied. Another reason that influences the selection of these metals in this study is due to their consistency in groundwater sample.

Three parameters were evaluated which is dosage, speed of the rotary shaker and contact time. These treatment parameters were optimized by response surface methodology (RSM). The efficiency of the treatment was assessed by percentage removal of stated parameters. The performance of the adsorbent used in this study (metakaolin) was evaluated based on isotherms and kinetics. Prior to adsorption study, groundwater characterization and the correlations between parameter will be performed.

1.5 Structure of thesis

Chapter One consists of a brief introduction of the research work, problem statement and objectives of research.

Chapter Two contains a comprehensive review of literature related to the water treatment generally, the background and definition of the parameters studied together with groundwater composition. This chapter also reviews on the theory of the process, isotherm and kinetics together with the involvement of RSM for parameters optimization.

Chapter Three lists all the methodologies associated with this study. This chapter provides the sites and sampling routines; technics and methods of samples/adsorbent preparations, characterizations and preservations; details of each process setting; programming used and all the equipment utilized.

Chapter Four appointed for results and discussions which presents the purging duration result for groundwater, characterization's qualities as in concentrations of concerned attributes, the correlation between parameter measured, removal efficiency for each response affected by different variables, optimization results via RSM utilization, isotherms and kinetics findings discussed in details.

Chapter Five states the conclusions and recommendations based on the results and discussions transcribed in chapter four. This chapter includes the potentials and possibilities for future assessments as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Water supply adequacy is an essential factor for human to live and plays a huge role in producing foods, practicing hygiene as well as supporting the operation in industries. Siwar and Ahmed, (2014) highlighted three elements of water security which are the accessibility, affordability and safety. These elements emphasize that each individual in a community have a right have access to adequate water supply with affordable cost and the water must pose such quality that no significant health risk arises from its use.

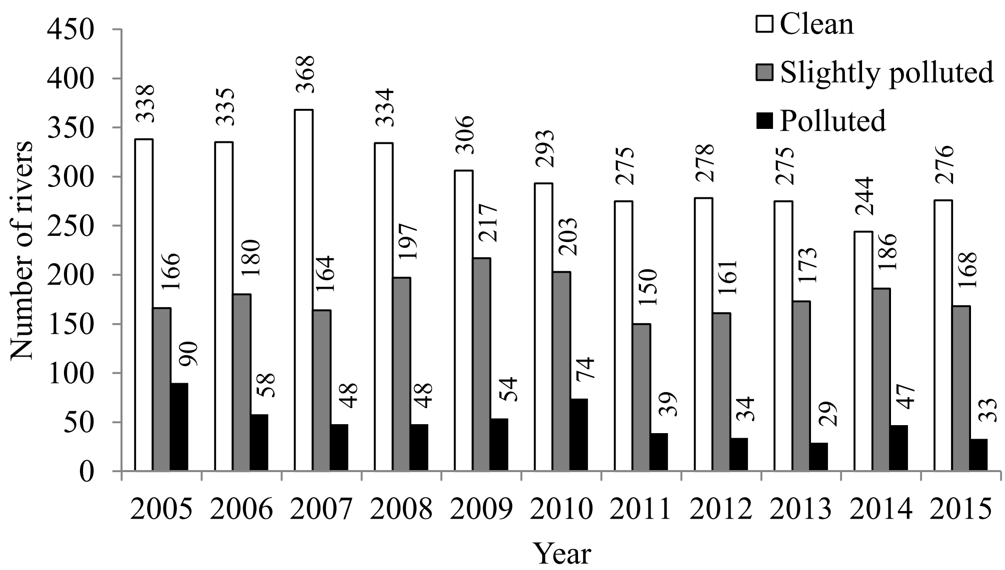

Figure 2.1 : Quantity river with clean, slightly polluted and polluted status (Huang et al., 2015b; Ibrahim, 2018)

Although Malaysia is rich with the source of surface water and recharged by a high volume of rainfall annually, the vast increment of the population with the rapid growth of industrial and agriculture imposes huge pressure on current water supply. Climate change and clean water source scarcity put even tremendous pressure on the water supply. Figure 2.1 shows the status of river quality in Malaysia from 2005 to 2015 and it can be seen that the total quantity of clean river is declining. In 2015, only 276 rivers declared as clean which is less than 60% of the total count of rivers in the entire country.

In the current situation the dependency on surface water is very high. Suruhanjaya Perkhidmatan Air Negara, (2015) reported that almost 98% of raw water was abstracted from surface water. The usage of groundwater is still very low compared to surface water as depicted in Figure 2.2 where only 1.5% of total raw water is abstracted from groundwater. Groundwater however, is subject to treatment prior to usage in daily activity.

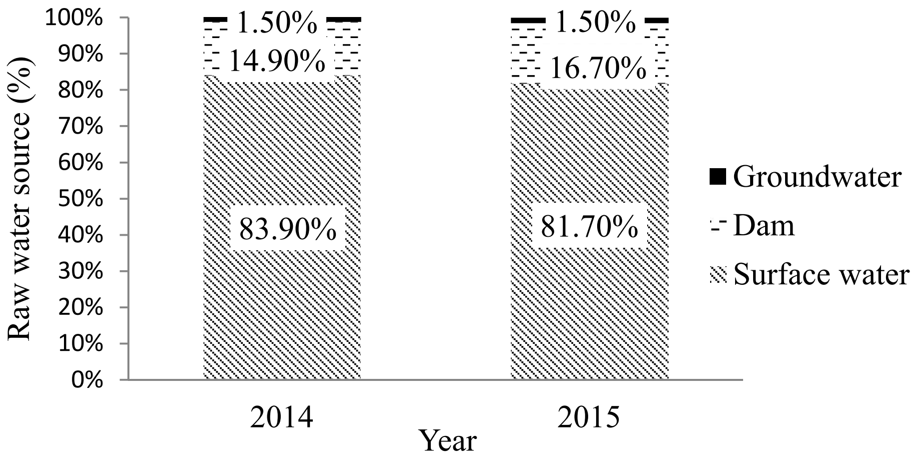

Figure 2.2 : Raw water source in Malaysia for 2014 and 2015 (Suruhanjaya Perkhidmatan Air Negara 2015)

2.2 Raw and drinking water

World Health Organization (2017a) divided water contaminant into 3 major groups which are microbial aspects, chemical aspects and acceptability aspects. Chemical aspects as in heavy metals affect the aesthetic value of the water and how safe the water to be consumed. Table 2.1 shows heavy metals permissible limit comparison between raw water, drinking water quality standard that established in Malaysia and the World Health Organization (WHO) that related to this study.

Table 2.1 : Heavy metals maximum permissible content in drinking water standard related to this study (Ministry of Health Malaysia 2010; WHO 2017c; WHO 2017b)

Parameter	**Raw Water Quality Standard (Malaysia)**	**Drinking Water Quality Standard (Malaysia)**	**Drinking Water Quality Standard (WHO)**
Iron (Fe)	1000	300 µg/L	300 µg/L
Manganese (Mn)	200	100 µg/L	100 µg/L
Nickel (Ni)	-	20 µg/L	70 µg/L

In Malaysia, the maximum permissible limit for raw water for iron and manganese are controlled at 1000 µg/L and 200 µg/L respectively. Whereas for nickel, there is no specific permissible limit established for raw water. The heavy metals permissible concentration for drinking water however were established for iron, manganese and nickel and a brief comparison between standard established in Malaysia and the World Health Organization (WHO) is reviewed.

There is no difference between both standards in iron content for drinking water. However, WHO (2017d) stated in details that the established concentration for guideline value is based on acceptability aspect. It means that the value established in the guideline is the value where the concentration of iron affects the aesthetic value (odour, taste or appearance) of water and no health-based established due to not of health concern at levels found in drinking water. Personal maximum tolerable daily intake for iron is 8 mg/kg body weight where 10% is allocated for drinking water giving 2 mg/L as a concentration maximum for drinking water which is above the range of normal iron concentration found in natural water. Below 300 µg/L iron content seldom gives any obvious taste but there might be a noticeable colour and turbidity. At higher than 300 µg/L, iron has the ability to stain laundry and develop layers of deposit in water delivery system that might clog the system in long term.

Similar to iron, the guideline of manganese concentration has been established based on the acceptability aspect and not of health concern at the level that affects acceptability issue. WHO (2017c) in chemical fact sheet (chapter 12) mentioned that as the health-based guideline value which is 0.4 mg/L is much higher than acceptability level, thus it is not vital to derive the health-based standard. Compare to iron, only 100 µg/L manganese concentrations may influence the beverage taste and stains laundry where higher concentration may lead to black layer deposits in a distribution system.

While Mn and Fe have similar maximum acceptable value for both standards, maximum acceptable concentration of Ni for National drinking water quality standard (NDWQS) is lower than WHO's standard. Malaysia is one of the 72 countries that established a lower value than WHO guideline from total 82 countries that has set a regulatory value (WHO, 2018). Only 7 countries followed the guideline proposed by WHO while the balance set higher maximum acceptable value compared with WHO. Based on a study reported by World Health Organization, (2005b), lowest-observed adverse effect level (LOAEL) for Ni is 130 µg/L. This value however is not sufficiently protective for individual that sensitized to Ni, thus another value established after further experimental work which is 70 µg/L (WHO, 2017c). On the other hand, this value is still consider close to LOAEL, thus certain country further reduce the maximum acceptable concentration to 20 µg/L for safety precaution for nickel-sensitive individual. It is also acknowledged that nickel is not included as the chemical that influences the aesthetic value of water in WHO (2017b).

Microbial aspects are directly related to the waterborne disease such as cholera, gastroenteritis, dysentery, typhoid etc. Epidemics such as cholera generally occurred in a place where limited access to well-treated water available, unsatisfactory management of drinking water supplies, poor sanitation implementation and inefficient hygiene practices (Lin et al., 2010; Mandal et al., 2011). However, waterborne outbreaks reduced tremendously after the introduction of chemical disinfection which was introduced in the early twentieth century particularly by chlorine (Lazaridis and Colbeck, 2010). Table 2.2 summarized comparisons of parameters related to microbial aspects between Malaysia's standard and WHO.

Table 2.2 : Drinking water standard established by Malaysia and WHO (Ministry of Health Malaysia 2010; World Health Organization 2017b)

Parameter	**Drinking Water Standard (Malaysia)**	**Drinking Water Standard (WHO)**
Total Coliform	0 in 100 ml	0 in 100 ml
E.Coli	0 in 100 ml	0 in 100 ml
Clostridium perfringens (including spores)	Absent	-

The aesthetic value of water is judged by 3 main factors which are appearance (colour and turbidity), odour and taste. As per discussed previously, these organoleptic qualities are included as major evaluation factors for potable water. *Guidelines of drinking water quality* (WHO, 2017b) listed 2 keys of water aesthetic quality reduction includes biological and chemically derived. Certain organisms may not have a direct significant effect on human health but may produce chemicals that give unwanted organoleptic quality to water bodies. Algae, fungi, cyanobacteria and iron bacteria are examples of organisms that influence drinking water acceptability. Chemicals such as aluminium as example start to alter water appearance at 0.1 mg/l to 0.2 mg/l with the existence of aluminium hydroxide flocs. Hydrogen sulfide for an instance, gives noticeably rotten egg-like smell to water at 0.l mg/l that normally spotted in groundwater or stagnant water due to depletion of oxygen. All the listed aesthetic value of water should be controlled with acceptable range as they can lead to the consumption of water that aesthetically more acceptable, but potentially less safe.

2.2.1 Surface water as drinking water

Surface water is the main water source in most of the country including Malaysia. Accessibility is one of the biggest reasons that make surface water as the main source, while other sources like groundwater need to be dug to make it available for consumption. Surface water is recharged by many sources namely rainfall, groundwater and even snow meltdown. In a country that is blessed with huge precipitation rate, surface waters are recharged throughout the year, made the water source seems limitless.

Accessibility however is also one of the major factor that leads to its pollution. Rivers as an example have been the place to dump discharges from domestic, commercial, agriculture and industrial effluent causing pollution (Weng, 2005). Table 2.3 summarized a number of studies executed within Malaysia on physiochemical and physical water quality. Referring to Table 2.3, it can be summarized that most of parameters are well within the permissible limits except for COD for Sungai Sembrong, Langat River Basin and Sungai Juru; Ammonical nitrogen for Langat River Basin and Sungai Juru; BOD for Langat River Basin and Sungai Juru.

Table 2.3 : Studies on water quality for surface water in Malaysia compared with Malaysia's standard for raw water

Name of surface water	Parameter	Value	Malaysia Standard (Raw water)	Reference
Sembrong Dam	DO (mg/l)	2.25 – 4.95	N/A	(Awang et al., 2015)
	TSS (mg)	5 - 59	N/A	
	NH_3-N (mg/l)	0.08 – 0.30	1.5	
	BOD (mg/l)	1.3 – 14.2	6	
	Total Coliform (cfu)	28 - 175	5000	
Sungai Johor	DO (mg/l)	5.61 – 7.32	N/A	(Zulhafizal et al., 2015)
	TDS (g/L)	21.9 – 26.1	1500	
	Turbidity (NTU)	6.4 – 23.4	1000	
	Cond (mS/cm)	36.0 – 42.8	-	
	Salinity (ppt)	22.7 – 27.5	N/A	
Sungai Sembrong	DO (mg/l)	6.95 – 7.30	N/A	(Zaidi et al., 2017)
	SS (mg/l)	850 – 800	N/A	
	NH_3-N (mg/l)	1.18 – 1.32	1.5	
	BOD (mg/l)	3.84 – 3.90	6	
	COD (mg/l)	47 - 71	10	
Selangor River	DO (mg/l)	0.54 – 3.35	N/A	(Daniel and Kawasaki, 2016)
	NH_3-N (mg/l)	0.010 – 0.810	1.5	
	Cond (µS/cm)	0.019 – 42.68	-	
	Salinity (ppt)	0.01 – 24.31	N/A	
Langat River Basin	DO (mg/l)	3.15 – 7.37	N/A	(Sakai et al., 2016)
	SS (mg/l)	1 - 265	N/A	
	NH_3-N (mg/l)	0.34 – 5.92	1.5	
	BOD (mg/l)	0.6 – 15.9	6	
	COD (mg/l)	2.1 – 14.1	10	
Sungai Juru	DO (mg/l)	2.64 – 2.75	N/A	(Zin et al., 2017)
	SS (mg/l)	44.67 – 61.73	N/A	
	NH_3-N (mg/l)	3.63 – 4.76	1.5	
	BOD (mg/l)	10.47 – 11.57	6	
	COD (mg/l)	37.05 – 38.18	10	
Sungai Kerian	DO (mg/l)	5.22	N/A	(Ibrahim et al., 2015)
	TDS (mg/l)	34.7	1500	
	Cond (µS/cm)	56.1	-	
	Salinity (ppt)	0.02	N/A	

2.2.2 Rainwater as a source of water

Rainwater has been one of the main supplies to the water cycle where it is a natural way to return the evaporated water to land. In early age, rainwater was collected and stored into a ground level man-made jar, communal tanks and surface water ponds before consumption until lately, a better system developed together with simple filtration to enhance the quality of harvested rainwater (Hoque et al., 2016; Nasir et al., 2009). As rainwater harvesting serves its main purpose to fulfill human's demand for water, more than that it is assisting to give a suspension for surface run-off which is beneficial to prevent the occurrence of flash floods (Ayob and Rahmat, 2017).

Data collected by Mohammed et al. (2007) in the urban area shows the turbidity, BOD and TDS are well below the raw water specification given Ministry of Health Malaysia (Ministry of Health Malaysia, 2010) (refer to Table 2.4). Most of the data collected in the Table 2.4 are well below the acceptable value for raw water that intended for drinking water purpose except for ammonical nitrogen as reported by Farreny et al., (2011) and E.Coli in a study by Mohammed et al., (2007) and Lee et al., (2010).

Table 2.4: Studies on rainwater quality compared with Malaysia standard for drinking water (raw water)

Location	Parameter	Value	Malaysia standard for raw water	Reference
Universiti Putra Malaysia, Selangor	Turbidity (NTU)	3.97	1000	(Mohammed et al., 2007)
	BOD (mg/l)	1.20	6	
	TSS (mg/l)	10	N/A	
	TDS (mg/l)	12	1500	
	E. Coli	1	0	
Hebron, Palestine	DO (mg/L)	8.3 – 9.15	N/A	(Malassa et al., 2014)
	Cond (µS/cm)	240 -1700	-	
	pH	7.1 – 8.2	5.5 – 9.0	
	TDS (mg/L)	136.7 – 1139.0	1500	
Barcelona, Spain	pH	6.54 – 8.85	5.5 – 9.0	(Farreny et al., 2011)
	Cond (µS/cm)	15.4 - 456	-	
	TSS (mg/L)	0 – 38.5	N/A	
	TOC (mg/L)	0.65 – 53.6	-	
	NH_3-N (mg/L)	0.04 – 2.42	1.5	
Gangneung, Korea	pH	4.3 - 6	5.5 – 9.0	(Lee et al., 2010)
	Cond (µS/cm)	6 - 82	-	
	TDS (mg/L)	3.4 – 52.1	1500	
	NH_3-N (mg/L)	0.0 – 0.05	1.5	
	E.Coli (CFU/100ml)	0 - 60	0	
Tanjung Malim, Perak, Malaysia	pH	7.07 – 7.37	5.5 – 9.0	(Ngah et al., 2014)
	Turbidity (NTU)	0.81 – 3.5	1000	
	DO (mg/L)	4.82 – 5.10	N/A	
	TSS (mg/L)	9 - 53	N/A	

2.2.3 Groundwater as a source of drinking water

Groundwater is widely recognized as water that sips through the unsaturated zone to the water table and resides for a long duration until it is released to some water body. It is recharged by precipitation, melted ice and surface water so it is considered as a renewable resource. Basically, water underneath the soil surface exists in two zones which are unsaturated zone and saturated zone. Unsaturated zone is where the water and air mixed filled between rock fractures and soil. Water in this zone however, is unable to be extracted or pumped. Contrarily, the water in the saturated zone can be pumped as the gaps utterly filled with water. The surface of the saturated zone is known as water table and the water in the saturated zone is termed as groundwater. Groundwater has been an alternative source for locations which treated water supply is limited or unavailable (Ambu et al., 2014).

The volume and recharge rate is due to many factors which include climates, physiography and hydrogeology (Ayob and Rahmat, 2017). In a certain place that the recharge is slow compared to usage rate, the volume of groundwater may decrease and lead to seawater intrusion in the aquifer (Salem et al., 2016). Groundwater extracted by drilling wells where shallow wells are normally hand-dug with the depth generally less than 15 meters and deep wells are classified with the depth greater than 50 meters (Ojo et al., 2012).

Groundwater generally contains higher contents of minerals, organic matters and major ions due to leaching process from the aquifers component and soils they seep through (Zhang et al., 2012). Contrarily, common groundwater only required little pre-treatment before chemical disinfection (Lazaridis and Colbeck, 2010). Table 2.5 and Table 2.6 shows the characterization results in previous studies performed in Malaysia and other countries.

It is shown in the tables some basic parameter for groundwater characterization such as pH, electrical conductivity, dissolved oxygen, turbidity, total dissolved solids and ammoniacal nitrogen. All the parameter is wide in range because of many factors such as the recharge source of groundwater, type of sand that the source seeped through, the pH of the source and humans activity together with their waste such as agriculture, industry and domestic.

Most of the data in these studies summarized in Table 2.5 were collected from more than one well except for the study by Akbar et al., (2015). Studies of groundwater quality in Pulau Kapas, Malaysia reported TDS value higher than acceptable value for raw water which is 1500 mg/L. The highest value of TDS was 8213 mg/L as for conductivity the highest value recorded was 14085 µS/cm and these elevated values were attributed by seawater intrusion (Kura et al., 2013, 2014).

Compared to surface water and rainwater, sampling for groundwater however requires different approach to ensure the validity and accuracy of a sample. It is important so that the characterization presents the actual properties in the aquifer with minimum interference. In groundwater sampling, purging is necessary to ensure there is no disturbance from stagnant water that filled the tube.

Table 2.5 : Groundwater characterization from previous works in Malaysia

Reference	**Location**	**Parameter**					
		pH	EC (µS/cm)	DO (mg/L)	Turbidity (NTU)	TDS (mg/L)	NH_3-N (mg/L)
(Lin et al., 2010)	Pulau Tiga, Sabah	6.84 – 7.33	330 - 1005	1.1 – 6.0	-	165 – 502	-
(Isa et al., 2012)	Kapas Island, Terengganu	6.7 – 7.6	410 - 910	0.6 – 8.5	-	204.0-455.0	-
(Lin et al., 2012)	Pulau Manukan, Sabah	6.86 – 7.89	460-3400	-	-	-	-
(Kura et al., 2013)	Pulau Manukan, Sabah	4.5 – 7.7	139-14085	2.3 – 9.7	0.9-1297	70.3 – 8213	-
(Shamsuddin et al., 2014)	Langat Basin, Selangor	5.6 – 8.1	4 - 211	-	14 - 306	22 – 120	-
(Ambu et al., 2014)	Kg. Sg. Buloh, Selangor	5.44 – 6.62	-	-	0.57 - 2.56	-	0.09–7.30
(Isa et al., 2014)	Kapas Island, Terengganu	7.04 – 7.41	320 - 680	1.2 – 11		158.8–342.0	-
(Kura et al., 2014)	Kapas Island, Terengganu	7.1 – 7.7	399.5 - 7800	2.3 – 8.4	0.9 – 135.2	205.9-4462	-
(Idris et al., 2014)	Tioman Island, Pahang	6.2 – 8.3	79 – 510	-	-	72 – 282	-
(Akbar et al., 2015)	Nibong Tebal, P. Pinang	6.2 – 6.7	8897–13258	-	3.1 – 37.9	6153 – 8021	-
(Nazri et al., 2016)	Kerian, Perak	5.36 – 7.50	129 - 732	-	-	30 - 122	-
(Izzah et al., 2017)	Kuala Nerang, Kedah	6.23	-	9.50	98.23	208	-
(Hamzah et al., 2017)	Terengganu	4.11 – 9.86	10 – 685	-	0.5 – 55.0	100 – 400	-
Drinking water limit		6.5 – 9.0	-	N/A	5	1000	1.5
Raw water limit		5.5 – 9.0	-	N/A	1000	1500	1.5

*Drinking and raw water permissible limit is based in Malaysia's standard.

Table 2.6 : Groundwater characterization from previous works in other country

Reference	**Location**	**Parameter**					
		pH	EC (μS/cm)	DO (mg/L)	Turbidity (NTU)	TDS (mg/L)	NH_3-N (mg/L)
(Zhang et al., 2012)	Songnen Plain, China	6.72 – 8.80	97 – 2680	-	-	-	-
(Wongsasuluk et al., 2014)	Ubon, Thailand	3.69 – 7.90	58.9 – 1162.3	-	-	-	-
(Singh et al., 2014)	Rupnagar, India	7.06 – 8.29	355 - 1295	-	-	150 - 440	-
(Kumar et al.,2015)	Andhra Pradesh, India	6.56 – 7.90	526 - 3541	3.36–7.94	0.14 – 6.04	44 -2860	-
(Li et al., 2015)	North China Plain	6.23 – 8.94	200 - 253			230- 1950	
(Abdurabu et al., 2016)	Juban, Yemen	7.57 – 9.09	300 - 1580	-	-	347 - 1533	-
(Nshimiyimana et al., 2016)	Arjaat, Morocco	6.89 – 8.27	533 - 2880	-	-	-	-
(Salem et al., 2016)	Nile Delta, Egypt	8.5 – 10.8	4100 - 12300	-	-	2020 - 6150	-
(Saana et al., 2016)	Ghana	6.14 – 7.50	131 – 873		0.13 – 105	80 – 524	0 – 0.08
(Tiwari et al., 2017)	Rajashtan, India	8.26 – 8.87	-	-	-	704 - 3585	-
(Batabyal and Gupta, 2017)	West Bengal, India	6.67– 9.98	198 - 577	-	-	140 - 415	-
(Samantara et al., 2017)	Tamil Nadu, India	6.1 – 8.2	117 - 2510	-	0.1 – 18.8	77-1657	-
Drinking water limit		6.5 – 9.0	-	N/A	5	1000	1.5
Raw water limit		5.5 – 9.0	-	N/A	1000	1500	1.5

*Drinking and raw water permissible limit is based in Malaysia's standard.

2.2.3 (a) Sampling and Purging

It is generally acknowledged that the water that has been stagnant in a well is not representing the water collected within aquifer and purging is essential prior to groundwater water sample collection (Barcelona et al., 2005). Thus, one of the major challenges in groundwater sampling is on how to optimize sampling method so samples obtained will be representative of the actual condition of groundwater studied. Purging is important to minimize properties change that affected by the stagnant condition. The presence of the air at the top of water causing gradient dissolved oxygen difference with depth and volatiles loss at the upper of the water column. Materials used in well's casing and filter pack may release or adsorb certain chemicals hence affecting the water properties. Other than that, surface infiltration such as dried leaves, insect and other may lead to additional impurities (Puls and Barcelona, 1995). Two most widely applied methods are low-flow method and well-volume method.

Low-flow method listed a few in situ parameters such as pH, temperature, turbidity, dissolved oxygen (DO), conductivity, total suspended solids (TSS) and oxidation-reduction potential (ORP) to determine adequate purging duration when three consecutive readings are stable, then the water being purged is considered representative of aquifer water (Qi et al., 2017). This method normally allows the pumping flow rate between 0.1 – 1.0 $Lmin^{-1}$ to minimize the disturbance of stagnant water but a study by Barcelona et al. (2005) proven that even in the occasion of significance drawdown especially for low-permeability aquifer, sampling after the stabilization of well's drawdown and monitored parameter as per previously listed will still help in obtaining representative groundwater samples and results.

Another purging technique is known as the well-volume method. This method required purging multiple volumes of well approximately two to five as suggested by Barcelona et al. (2005). In contrast, Vail (2013) and Van Driezum et al. (2017) suggested that it is not necessary to purge three volumes of well to meet the adequacy level of purging, it depends on when the parameters (pH, conductivity and dissolved oxygen) stabilized in three consecutive measurements. Thayalakumaran et al., (2015) however stated the adequacy of purging can be decided by both methods either three volume purging or referring to in situ data stability (pH, conductivity and DO).

Table 2.7 : Stabilization criteria during purging (Vail, 2013).

Parameter	Stabilization criteria
pH	Within 0.1 standard units
Conductivity μS/cm	Variation less than 5%
Dissolved Oxygen (DO), mg/L	<0.2 mg/L

The temperature of groundwater is influenced by the depth of the aquifer, ambient temperature and the source of groundwater which charged the aquifer (Calvache et al., 2011). Temperature mainly affects the microorganism growth in groundwater that will have the odour and taste affected, however the existence of microorganism is rarely found in groundwater (Ojo et al., 2012). The ambient temperature exhibits a gradient effect towards groundwater depth. The influence is maximum at the surface of the well and reduced when the water table is deeper due to the air contact with the stagnant water surface. The temperature however, will remain constant even with the ambient temperature change after the depth of 15m to 45 m and will increase due to the geothermal effect after 100 m depth (Calvache et al., 2011). The soil between the atmosphere and the aquifer plays important parts in minimizing the influence of ambient temperature. Space that filled with various kind