

**Removal of Iron from Groundwater by Filtration through
Carbonaceous Shale**

by

Abdul Fatah Bin Abdul Rahman

Dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
(Civil Engineering)

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Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL


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A Project dissertation submitted to the
Civil Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CIVIL ENGINEERING)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



AB. FATAH BIN AB. RAHMAN

ABSTRACT

The project covers a study on the topic entitled “Removal of Iron from Groundwater by Filtration through Carbonaceous Shale”. Generally speaking, Iron is commonly present in groundwater worldwide. The presence of iron in groundwater is not harmful to human health, however it is undesirable because of the associated aesthetic and operational problem, namely: bad taste, discoloration, stains on laundry and plumbing system and after-growth in the distribution system. Iron present in soluble ferrous form in groundwater oxidizes into insoluble ferric iron when exposed to the atmosphere. Iron removal from groundwater is, therefore, a major concern for water supply companies using groundwater. The objective of this study is to determine the effectiveness of carbonaceous shale in removing iron from groundwater by adsorption-oxidation mechanism and also the backwashing system for the filter. The scope of work consists of literature review, experimental design, laboratory set up, experiments and results analysis. The methods and procedures to achieve the objectives involve analyses of chemical parameters of groundwater used in the experiments including the properties of carbonaceous shale and also filtration performance of carbonaceous shale. Laboratory-scale column experiments were conducted using 31 mm diameter acrylic column pipes with 1.0 m depth of 1.0 mm mean size and having 70 cm depth of filter media. The filtration performance of the carbonaceous shale was compare with the sand that works like a ‘benchmark’ since it is been widely used in the conventional method for iron removal. Both filtration media that been used act as adsorbent of ferrous iron in filtration column. Results from the experiment shows that the concentration of total iron in the groundwater used in the experiment is 2.36 mg/L Fe and that the performance of carbonaceous shale filter is better than sand filter in the iron removal. Iron concentration in the effluent of carbonaceous shale filter is below standard for drinking water which is 0.3 mg/L.

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ABBREVIATIONS AND NOMECLATURES

AOC	- Antioxidant Capacity
AWWA	- American Water Works Association
BrO_3^-	- bromate ion
Ca^{2+}	- calcium ion
CaCO_3	- calcium carbonate
CH_4	- methane
Cl_2	- chlorine gas
Cl^-	- chloride ion
Co^{2+}	- cobalt ion
Cu^{2+}	- copper ion
DOE	- Department of Environment
EEA	- European Environmental Agency
Fe	- iron
Fe^{2+} , Iron (II)	- ferrous iron
Fe^{3+} , Iron (III)	- ferric iron
$\text{Fe}(\text{OH})_3$	- iron hydroxide
H^+	- hydrogen ion
H_2PO_4^-	- hydrogenphosphate ion
H_2S	- hydrogen sulphide
IWEM	- Institution of Water and Environment Management
KMnO_4	- potassium permanganate
MF/UF	- membrane filtration and ultra filtration
Mg^{2+}	- magnesium ion
Mn	- manganese
Mn^{2+}	- manganese ion
MnO_4^-	- permanganate ion
MOH	- Ministry of Health
MWA	- Malaysian Water Association

NF/RO	- nanofiltration and reverse osmosis
NH_4^+	- ammonium ion
O_2	- oxygen gas
OH^-	- hydroxide ion
THM	- Trihalomethane
SO_4^{2-}	- sulphate ion
TDS	- total dissolved solids
UNESCO	- United Nations Educational, Scientific and Cultural Organization
WHO	- World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Groundwater is water which percolates through the soil and accumulates in underground aquifers (Parsons and Jefferson, 2006). This water completely fills the pores spaces in sediment and rock in subsurface zone of saturation. The upper limit of this zone is called water table. The zone of aeration is above the water table where the soil, sediment and rock are not saturated (Lutgens and Tarbuck, 2003).

Since groundwater moves through rocks and subsurface soil, it has a lot of opportunity to dissolve substances as it moves. Even though the ground is an excellent mechanism for filtering out particulate matter, such as leaves, soil and bugs, dissolved chemicals and gases can still occur in large enough concentration in groundwater to cause problems (Spellman, 2001).

According to Oram (2003), iron is a metallic element found in the earth's crust. Water percolating through soil and rock can dissolve minerals containing iron and hold it in solution. According to the Guidelines for Drinking Water set by World Health Organization (WHO), the maximum permissible concentration of iron in potable water is 0.3 mg/L. Iron present in groundwater will cause a severe color condition when exposed to air, groundwater with dissolved iron turn to indissoluble and leave the water with brown-red color. The problems cause by iron is aesthetic problems, indirect health concerns and economic problems (Spellman, 2001)

Removal of iron from groundwater can be accomplished in several ways. The type of treatment largely depends on the quality of the raw water, financial resources available

and the philosophy of the water company (Sharma, 2001). Conventional treatment for iron removal from groundwater consists of oxidation and depth filtration. Oxygen or stronger oxidants, such as chlorine and potassium permanganate (KMnO_4), are generally used for Fe^{2+} oxidation. The solid products of oxidation ($\text{FeOO}\cdot\text{H}_2\text{O}$ and MnO) are then filtered through a granular bed, commonly green sand (Lessard *et al.*, 1999).

1.2 Problem Statement

Iron being the fourth most abundant element and second most abundant metal in the earth's crust (Silver, 1993; WHO, 1996) is a common constituent of groundwater. The presence of iron in groundwater is generally attributed to the dissolution of iron bearing rocks and minerals, chiefly oxides (hematite, magnetite, and limonite), sulphides (pyrite), carbonates (siderite) and silicates (pyroxene, amphiboles, biotites and olivines) under anaerobic conditions in the presence of reducing agents like organic matter and hydrogen sulphide (O'Connor, 1971; Hem, 1989)

According to Faust and Aly (1998), Iron usually exists in two oxidation states, reduced soluble divalent ferrous (Fe^{2+} or iron(II)) and oxidized trivalent ferric (Fe^{3+} or iron(III)). Iron may be present in groundwater in the following five forms: i) dissolved as iron(II), ii) inorganic complexes, iii) organic complexes, iv) colloidal and v) suspended. Water containing ferrous iron is clear and colorless because the iron is completely dissolved.

Iron present in groundwater will cause a severe color condition. When exposed to the atmosphere, groundwaters with dissolved iron turn to indissoluble and leave the water with brown-red color. This sediment is the oxidized or ferric form of iron that will not dissolve in water (Spellman, 2001)

Iron in water supplies, however, is undesirable, as it is a nuisance for domestic and industrial users and water suppliers causing various aesthetic and operational problems as listed below.

- Iron produces ugly and insoluble rusty oxide-red, yellow or brown stains and streaks on laundry and plumbing fixtures (O'Connor, 1971; Kothari, 1988). In extreme cases, iron interferes with the culinary using tea black and darkening the boiled vegetables (Hauer, 1950)
- Iron imparts color and typical bitter, astringent taste to the water. The taste threshold of iron in water is 0.04 mg/L (JMM 1985; WHO 1996). Turbidity and color may develop in piped systems at iron levels above 0.05-0.1 mg/L (WHO, 1996). Though harmless, these organoleptic characteristics give the impression that the water is somehow contaminated. Most importantly in the developing countries, the color and bitter taste caused by iron can result in well water being rejected. People then often return to the polluted surface water and so incidents of cholera and typhoid continue (Ahmed and Smith, 1987/1988; Chibi, 1991)
- The presence of iron is disastrous in some industrial wet processing operations. Water to be used in the textile, dyeing, beverage and white paper industries should contain less than 0.05 mg/L of iron or manganese (Cox, 1964). Additionally, the oxidation of iron-rich water applied to cultivated fields can lead to low-pH ferric hydroxide-rich soils that may severely damage agricultural productivity (Chapelle, 1993)
- Iron passing into the distribution system may promote the growth of microorganisms. Slime thicknesses of several centimeters have been observed in distribution pipes. These accumulations, consisting of hydrous iron and manganese oxides and bacteria, increase the friction loss and power consumption, require higher chlorine dosage, deplete dissolved oxygen, reduce the carrying capacity and may eventually clog the distribution pipes. Sloughing or re-suspension of this material by high flow causes high turbidities (O'Connor, 1971; Culp, 1986; Salvato, 1992; Vigneswaran and Visvanathan, 1995). Therefore, for the water supply companies the main concerns are minimizing the costs of operation and maintenance and reducing the "red water" incidents.

Iron removal from groundwater, therefore, a major concern for most water supply companies using groundwater as their source. To prevent the difficulties mentioned above, various regulatory agencies have put forward standards or guidelines to control iron concentrations in water supplies. An AWWA (1971) task group suggested limits of 0.05 mg/L for Iron and 0.01 mg/L for manganese for an “ideal quality water” for public use. Based on taste and nuisance considerations, the World Health Organization, WHO (1996) recommends that the iron concentration in drinking water should be less than 0.3 mg/L. In the Netherlands, the guideline level for iron in drinking water is ≤ 0.05 mg/L (VEMIN, 1993) and several water supply companies are aiming at level of ≤ 0.03 mg/L in order to minimize the distribution system maintenance costs.

Current groundwater treatment encounters many problems such as the continuous deposition of iron during the aeration processes in the air stripping system causing the efficiency of the system to reduce thus the maintenance to be done frequently (Nyer, 1992). Other methods also causing many difficulties, costly and incomplete iron removal are often encountered.

The idea of using carbonaceous shale as a filter media for iron removal from groundwater had been bring out after conducting an observation to the site that has an existence of carbonaceous shale. From the observation, the dark-grey color of carbonaceous shale seems to change to brown-red color after been exposed to rain water for certain period of time. These phenomena happen since there was iron oxide that has to be coated by adsorptive process to the surface of carbonaceous shale. Figure 1.1 shows the brown-red carbonaceous shale surface phenomenon at the site.



(a)



(b)

Figure 1-1. Brown-red carbonaceous shale surface phenomenon at the site

A study by Mohak (2007) has indicated the potential of carbonaceous shale as a filter media in the adsorption-oxidation removal of iron from groundwater. This project will involve a detailed study on the use of carbonaceous shale as filter media in removal of iron from groundwater. Study will be done on the mechanism of the removal process in filtration column and evaluation and observation on the performance of this media in removing the iron from groundwater.

1.3 Objectives of the study

The objectives of the study are listed as follows.

- To evaluate the potential and/ or performance of carbonaceous shale in iron removal from groundwater
- To study the adsorption-oxidation mechanisms of iron removal in filter
- To determine the potential and effectiveness of the backwashing in filter

1.4 Scope of the study

In order to achieve the objectives, this study has been divided into five major sections that are listed as follows.

- Literature Review
Study the properties of groundwater, carbonaceous shale, the potential of iron removal in groundwater by filtration through the carbonaceous shale as the filter media and also the process of the backwashing for the filter.
- Experimental Procedures Design
Design the experiment procedures and identify the apparatus and materials needed in the experiment
- Laboratory Set up
Prepare the materials and apparatus needed to carry out the experiment and checking the accuracy of the system.
- Experiments
Conduct the experiment according to the experimental procedures.
- Results Analysis
Results from series of experiment are analyzed and presented

CHAPTER 2 LITERATURE REVIEW

2.1 Groundwater source

According to UNESCO (1978), about 75% of the surface of the earth is covered by water, with the vast majority of this as oceans. Figure 2.1 illustrates the relative quantities and distribution of water. Fresh water accounts for about 2.5% of the total water in the world and less than 0.3% is on the surface in lakes and rivers. A much larger percentage of potentially available fresh water is stored in groundwater which is about 30%. The bulk of fresh water (69%) is locked in the polar ice caps and also not generally available for use. This means that although there is plenty of water on our planet, only a tiny fraction is potentially available for human use. Therefore, exploration of groundwater could solve the water shortage.

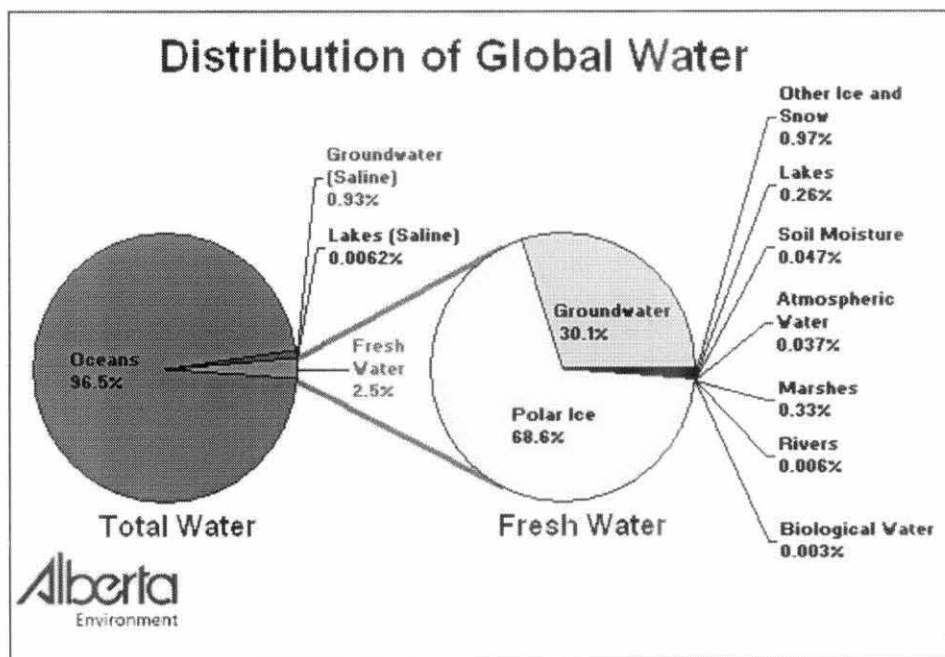


Figure 2-1. World Water Balance and Water Resources of the Earth, UNESCO, 1978

Groundwater is the major source of drinking water in many countries across the world. Table 2.1 summarizes the groundwater use as drinking water in different regions. Groundwater is extensively used as an important source of public water supply in Europe ranging from nearly 100% in Denmark, 72% in Germany, 56% in France and 27% in United Kingdom (EEA, 1999). More than 60% of cities and towns in the Russian Federation use groundwater sources as water supply (Zekster, 2000). Meanwhile in United States, over 96% of the rural population use groundwater as the primary potable water source (Biswas, 1997). In some Asian countries the usage of groundwater in drinking water supplies was as follows: India 80%, Maldives 80%, Philippine 60%, Thailand 50% and Nepal 60%.

Table 2-1. Groundwater as Share of Drinking Water by Region (Sampat, 2000)

Region	Share of Drinking Water From Groundwater (%)	People Served (millions)
Asia Pasific	32	1000 to 1200
Europe	75	200 to 500
Latin America	29	150
United State	51	135
Australia	15	3
World		1500 to 2000

According to Azuhan (1999), groundwater accounts for more than 90% of the freshwater resources in Malaysia. The total water available for use could be approximated as the sum of 10% of the surface runoff and the volume of groundwater recharge. Table 2.2 shows the summary of the water resources in Malaysia.

Table 2-2. Water Resources in Malaysia (Azuhan, 1999)

Water Resources	Quantity (billion m³)
Annual Rainfall	990
<i>Surface Runoff</i>	566
<i>Evapotranspiration</i>	360
<i>Groundwater Recharge</i>	120
Surface Artificial Storage	25
Groundwater Storage	5000

Minerals and Geo-Science Department of Malaysia has stated that, less than 2% of the present water use in Malaysia is developed from groundwater resources. The use of groundwater for domestic purposes is mainly confined to rural areas, where there is no piped water supply. However, groundwater is being significantly utilized for public water supply in Kelantan and Perlis. Other states that supplement the water supply systems with groundwater are Terengganu, Pahang, Sarawak and Sabah.

In Kelantan, groundwater plays very important role in the public water supply system. About 70% of the total water supply in the state is derived from groundwater, primarily in the Kota Bharu areas. Rural population depends very much on groundwater for their daily requirements by obtaining it from shallow dug wells. During the recent dry spell in the country, groundwater has provided relief for the people especially in Selangor and Sarawak.

Integration between the use of surface water and groundwater is needed to ensure sustainable utilization of both water resources. Groundwater is definitely capable of playing a bigger role in supplementing the water requirements in the country. Groundwater is generally a preferred source for water supplies because of its convenient availability close to where water is required, its constant and good natural quality. Which is frequently adequate for potable water supplies with minimal treatment, and relatively low capital cost of water supply system development

2.2 Groundwater Quality

Groundwater is naturally of very good microbiological quality and its chemical quality depends on hydro-geological conditions. Because these water have had prolonged exposure to calcium carbonate and sulphate they are typically hard and alkaline. The Total Suspended Solids (TSS), bacteriological and organic content of groundwater are filters out the microorganisms but also adsorbs the organics on which they feed. Treatment drivers from groundwater include inorganic that can leach from rocks such as iron, manganese and arsenic and often these water sources are impacted by surface water ingress leading to lowland source pollutants such as pesticides, nitrate and cryptosporidium entering groundwater.

According to AWWA (1999), Groundwater is characterized by a low temperature (7-10 °C) a low redox potential (absence of oxygen), a high carbon dioxide concentration, a high mineral content (high alkalinity and hardness) and very low suspended solid content. Iron and manganese, which are usually present in groundwater as divalent ions (Fe^{2+} and Mn^{2+}), are considered as contaminants mainly because of their organoleptic properties.

In Canada, the maximum recommended levels of Fe and Mn in drinking water are 0.3 mg/L and 0.05 mg/L, respectively (Government of Canada, 1996). Where as the International Standards are 0.3 mg/L for Fe and 0.1 mg/L for Mn (AWWA, 1999). Some form of treatment will be required for potable water supplies.

A high concentration of iron is by far the most common water quality problem associated with groundwater. World Health Organization (WHO) has prepared the guideline for drinking water quality for the protection of public health throughout the world (WHO, 1971). The quality of water depends on its physical, chemical, microbiological and radiochemical characteristics (MWA, 1994).

2.3 Iron Removal Methods

AWWA (1990) has pointed that the choice of a water treatment scheme depends on

- Water supply source quality
- Desired finished water quality
- Reliability of process equipment
- Operational requirements and personnel capabilities
- Flexibility in dealing with changing water quality and equipments malfunctions
- Availability space for construction of treatment facilities
- Waste disposal constraints
- Capital and operating costs

Faust and Aly (1998) has indicate that the current water treatment practice employs three (3) general methods for reducing iron contents to meet the minimum allowable concentration. The primary methods for reducing iron contents uses oxidation of the Fe^{2+} to Fe^{3+} , followed by sedimentation and filtration for the floc formation. Ion exchange is frequently employed where iron contents are less than 10 mg/L and where “low” volumes exist at municipal plants or for domestic purposes. The third method utilizes the stabilization of iron in a suspended state by dispersing agent, usually a polyphosphate or a silicate, to prevent deposition. This is not a removal method *per se* and limited to iron contents of 1.0 mg/L or less.

According to Sharma (2001), various methods are used to control iron in the water supply. Table 2-3 summarized the suitability, advantages and limitations of the most commonly used.

Table 2-3. Iron Removal Methods (Sharma, 2001)

Removal Method	Application	Advantage	Limitation
1. Oxidation, Precipitation and Filtration			
a) Oxidation by aeration	<ul style="list-style-type: none"> • Fe < 5 mg/L and little or no organic matter or other reducing agents • As pre-oxidation step to save chemical costs when Fe > 5 mg/L 	<ul style="list-style-type: none"> • No chemicals required • Simple in operation • Partly removes CO₂, H₂S and CH₄ present 	<ul style="list-style-type: none"> • Ineffective in case of low pH and high Fe and Mn concentration or when Fe is organically complexed • Initial cost is high
b) Oxidation with chlorine	<ul style="list-style-type: none"> • Beneficial to remove Fe and Mg in one step • Optimum pH 6.8-8.4 	<ul style="list-style-type: none"> • More rapid oxidation than aeration especially under conditions of organic matter interference • Less expensive and more effective than KMnO₄ • Can also be used for disinfection 	<ul style="list-style-type: none"> • Trihalomethane (THM) formation • Chloro-derivatives can cause taste odour problems • Require safe handling and storage of chlorine compounds
c) Oxidation with chlorine dioxide	<ul style="list-style-type: none"> • Effective when iron is organically complexed or ammonium concentration is high • Reacts more rapidly with Mn than chlorine 	<ul style="list-style-type: none"> • No Trihalomethane (THM) formation 	<ul style="list-style-type: none"> • Costlier than chlorine • Possible health effects of by products • Not used for iron removal only
d) Oxidation with potassium permanganate	<ul style="list-style-type: none"> • Fe < 5 mg/L • More efficient at pH > 7.5 	<ul style="list-style-type: none"> • Less equipment and capital investment compared to chlorine 	<ul style="list-style-type: none"> • Difficult to control • Overdose (≈0.05)

		<ul style="list-style-type: none"> • Efficient, rapid and complete reaction • Reacts with H₂S, cyanides, phenols and other taste and odour-producing compounds 	<p>mg/L) may produce a pink colour</p> <ul style="list-style-type: none"> • Ineffective for high iron concentrations • More expensive than chlorine and ozone
e) Oxidation with ozone	<ul style="list-style-type: none"> • Effective even when the iron is organically complexes 	<ul style="list-style-type: none"> • Powerful and effective oxidant • Multi-purpose applications of ozone e.g. disinfection, colour removal, taste and odour control • No THM formation 	<ul style="list-style-type: none"> • High Initial capital and operating costs • May oxidize Mn²⁺ to MnO₄⁻ resulting in a pink colour • Formation of unwanted by products e.g. BrO₃⁻
f) Hydrogen peroxide	<ul style="list-style-type: none"> • Very effective when the iron is organically complexes 	<ul style="list-style-type: none"> • Faster oxidation • Forms dense, easily settled solid • Cheaper than ozone • Leaves no residue 	<ul style="list-style-type: none"> • Formation of Antioxidant Capacity (AOC)
g) Biological iron removal	<ul style="list-style-type: none"> • Recommended for groundwater with acidic or neutral pH 	<ul style="list-style-type: none"> • Higher filtration rate • Longer filtration run • Reduced capital and operation and maintenance costs 	<ul style="list-style-type: none"> • Sensitive to process conditions (pH and temperature dependent) • Ineffective in presence of NH₄⁺ and H₂S
2. Ion Exchange (Zeolite softening)	<ul style="list-style-type: none"> • Suitable for individual water supply scheme with < 5 mg/L of Fe • Removes dissolved Fe and Mn together with hardness • Used as a polishing step 	<ul style="list-style-type: none"> • Softening occurs with exchange of Ca²⁺ and Mg²⁺ 	<ul style="list-style-type: none"> • Possibility of resin/ zeolite fouling or loss of exchange capacity in presence of O₂ due to iron precipitation • High capital cost • Requires skilled personnel

	in some plants/ household after municipal treatment		<ul style="list-style-type: none"> • Ineffective for colloidal or complexed iron
3. Stabilization or sequestering process (with polyphosphate-s and silicates)	<ul style="list-style-type: none"> • Fe should be < 1 mg/L • For distribution system corrosion and deposition inhibition • Practical in controlled use only 	<ul style="list-style-type: none"> • Complexes iron and holds it in solution and the consumers do not notice its presence • No sludge generation 	<ul style="list-style-type: none"> • More expensive than Cl₂ and KMnO₄ • Phosphate introduced may stimulate biological growth; may require chlorination to prevent bacterial growth • Cold water only (complex break down when heated) • Polyphosphate complexes may degrade after 48-72 hours
4. Lime softening/ Limestone bed filtration	<ul style="list-style-type: none"> • Pre-aerated water with pH>9.5 and sufficient alkalinity (>20 mg/L as CaCO₃) 	<ul style="list-style-type: none"> • Beneficial when a large amount of softened water is required 	<ul style="list-style-type: none"> • Not cost effective unless lime treatment is also required for hardness reduction • Increased sludge problems
5. Manganese greensand process	<ul style="list-style-type: none"> • Removes Fe and Mn by combination of sorption and oxidation • Maximum Fe and Mn < 10 mg/L • H₂S, < 2-5 mg/L • Optimum pH 6.2-8.0 	<ul style="list-style-type: none"> • H₂S can be removed together with Fe and Mn 	<ul style="list-style-type: none"> • Higher head loss, shorter run time • High Operation and maintenance costs (KMnO₄ regeneration) • Not suitable for larger water treatment plants
6. In-situ	<ul style="list-style-type: none"> • By infiltration 	<ul style="list-style-type: none"> • No chemicals 	<ul style="list-style-type: none"> • Potential for

oxidation (subsurface removal/ Vyredox method)	oxygen-rich water into the ground through a well	<ul style="list-style-type: none"> Abstraction- infiltration ratio of groundwater is high 	contamination of aquifer <ul style="list-style-type: none"> Clogging of the aquifer, corrosion of well screen Excessive bacterial may occur around the well
7. Membrane processes	<ul style="list-style-type: none"> NF/RO – to remove dissolved iron MF/UF – to remove iron flocs 	<ul style="list-style-type: none"> Can be combined with the removal of other constituents e.g. hardness and THM precursors 	<ul style="list-style-type: none"> High operation and maintenance costs MF/UF membranes require frequent cleaning

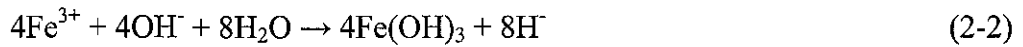
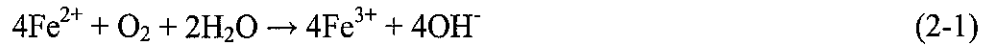
Other methods that have employed are calcined magnesite-diatomaceous earth filtration (O'Connor and Benson, 1970), sirofloc (activated magnetic) process (Gregory *et al.*, 1988) and catalytic or adsorptive filtration using patented filter media impregnated with various oxides of iron and/ or manganese like Birm, Pyrolox, anthrasand, Pyrolusite, AquaMandix, catalytic Carbon, etc. (Sommerfeld, 1999)

2.4 Oxidation of Iron

Oxidation-floc formation (floc filtration) is the conventional approach for iron removal from groundwater. In this method, soluble iron(II) present in anoxic groundwater is oxidized to insoluble iron(III) and after precipitation, iron hydroxides flocs are removed in the filters. The removal process consists of the following steps (Rotts, 1973).

1. Oxidation of Fe^{2+} to Fe^{3+} by aeration or by chemical oxidant
2. Hydrolysis of Fe^{3+} to iron hydroxides
3. Flocculation/ agglomeration of the hydroxide particles
4. Removal of flocs in filters

Iron oxidation and its removal are based on the transformation of the soluble ferrous form (Fe^{2+}) to an insoluble ferric form (Fe^{3+}). To understand the reaction, it can be simplified in notation below,



Equation 2-1 shows that about 0.14 mg of oxygen is required for the oxidation of 1 mg of iron(II). Therefore, the oxygen concentration in aerated water is theoretically sufficient for the complete oxidation of iron(II) normally present in natural groundwater. Iron hydroxides been formed after the oxidation of iron(II) take places.

2.5 Adsorption-Oxidation Removal of Iron

According to Parsons and Jefferson (2006), the process of adsorption involves separation of a substance, termed an adsorbate from liquid phase and the concentration at the surface of a material termed as adsorbent. The process follows four phases; initially the adsorbate must first travel from the bulk liquid phase to liquid film surrounding the adsorbent, typically a carbon particle. Then, the adsorbate must travel through the liquid film surrounding the carbon to the interstitial voids. Thirdly, the adsorbate must diffuse through the carbon voids in the carbon solid phase and finally adsorb onto the carbon.

The extent of adsorption depends on the specific nature of the carbon and of the molecules being adsorbed and is a function of the concentration, temperature and pH. Adsorption can be physical or chemical. In physical adsorption, the impurities are held on the surface of the carbon by weak Van der Waals forces and there is no significant redistribution of electron density in either the molecule or at the substrate surface. In

chemisorptions, a chemical bond involving substantial rearrangement of electron density is formed between the adsorbate and substrate. The nature of this bond may be anywhere between the extremes of virtually complete covalent character. If the reaction is reversible, molecules accumulate on the surface until the forward reaction (adsorption) equals the rate of the reverse reaction (desorption) (Parsons and Jefferson, 2006).

According to Appelo *et al.* (1999), In the adsorption-oxidation (adsorptive filtration) mechanism, the iron(II) present in anoxic groundwater is removed by adsorption onto the surface of the filter media. Subsequently, in the presence of oxygen, the adsorbed iron(II) is oxidized forming a new surface of adsorption. In this way the process continues. The method therefore relies on the iron(II) adsorption capacity of the filter media. In conventional filters, the iron entering the filter bed in iron(II) form is removed through the adsorption-oxidation mechanism. For the adsorption mechanism to dominate, pre-oxidation of iron(II) before filtration must be minimal. This can be achieved by reducing the oxidant concentration or the time available for the oxidation reaction. Adsorption-oxidation iron removal is only feasible for the removal of iron(II).

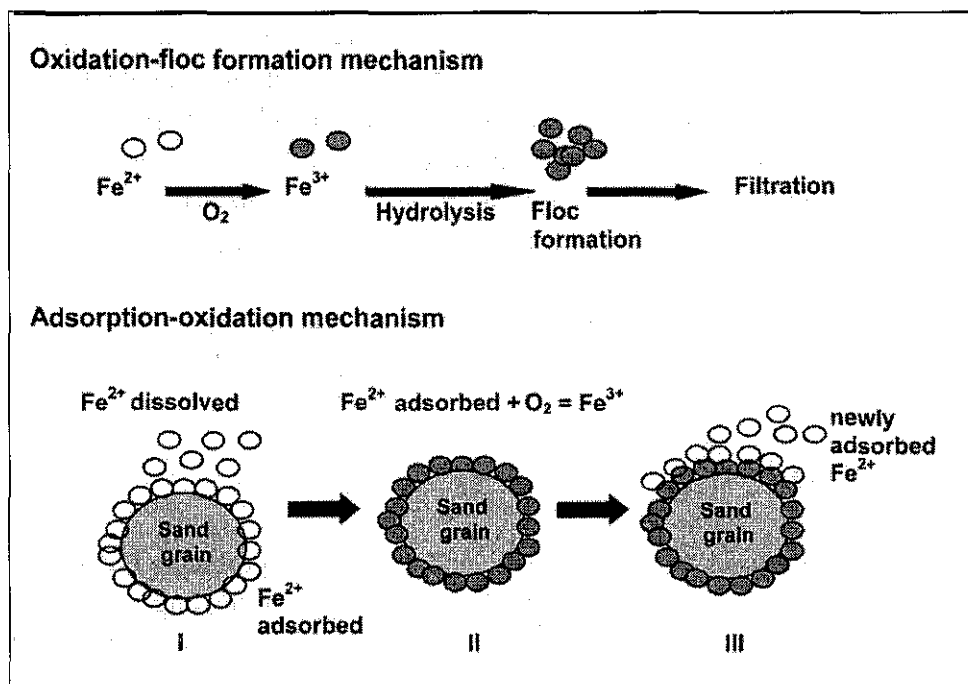


Figure 2-2. Physicochemical Iron Removal Mechanisms (Sharma, 2001)

To achieve principally adsorption-oxidation iron removal, filters can be operated in two modes as follows (Sharma, 2001)

- Filters are operated under anoxic conditions. Oxidation of Iron(II) is consequently suppressed by avoiding aeration. After the exhaustion of the Iron(II) adsorption capacity sites by oxidation of adsorbed Iron(II) by backwashing the filter with oxygen-rich water or a chemical oxidant like KMnO_4 .
- Filters are operated under aerobic conditions to allow continuous regeneration of the exhausted adsorption sites. A low concentration of oxygen and/ or a short pre-oxidation time is required to avoid the formation of iron hydroxide flocs. Some iron floc will be formed and backwashing is required when maximum head loss is reached

The Adsorption-oxidation mechanism of iron removal relies on the iron(II) adsorption capacity of the filter media and its subsequent regeneration. The iron(II) adsorption capacity may depend on characteristics of the filter media, water quality and process conditions applied. Furthermore, iron(II) adsorption capacity of the new media increases with the development of the iron oxide coating. In the presence of oxygen in the raw water, some iron hydroxide flocs are likely to be formed. The characteristics of these iron hydroxides also depend on water quality and process conditions applied (Misawa *et al.*, 1974; Robinson *et al.*, 1981; Carlson and Schwertmann, 1987; Cornell and Schwertmann, 1996). Iron hydroxides can absorb iron(II) and catalyze the iron oxidation (O'Connor, 1971; Tamura *et al.*, 1976), thereby enhancing the iron removal process. The adsorption capacity of iron hydroxides may also change with their ageing.

Advantages of adsorption-oxidation mechanisms are as follows

- The head loss is likely to be very low because the iron forms a coating on the filter media rather than a floc which blocks the filter pore
- Filter runs could be longer
- Backwashing cycles could be reduced
- The filter could be run at higher filtration rate

2.6 Carbonaceous shale

According to Mohak (2007), shale, one type sedimentary rock, is composed of tiny clay-sized sediment grains. Such sediment typically settles to the ocean floor where it is deposited in thin, well-defined layers. Settling to the ocean floor is organic matter (plant and animal detritus) that becomes mixed with the clay grains. Gradually, over a period of thousands of years, the clay and organic matter become compacted. The carbon from the organic matter is dark in color, so shale is often dark in color as well. Figure 2-3 show samples of carbonaceous shale at site.

Shale is a fine-grained sedimentary rock that contains organic matter is dark in color whose original constituents were clays or muds. It is characterized by thin laminae breaking with an irregular curving fracture, often splintery and usually parallel to the often-indistinguishable bedding plane. This property is called fissility (Mohak, 2007).

Bates (1980) has stated that shale has several potential uses. It may be finely ground and used as filter in paints, plastics, asphalt compounds, roofing cement, and some linoleum. Shale is often used in paved highway construction as sub-base fills material as it is readily available and less expensive to excavate than sandstone or limestone.



Figure 2-3. Samples of Carbonaceous shale at site

CHAPTER 3

METHODOLOGY

3.1 Research

At the beginning of the project, researches were more concentrated in acquiring information on the project background, scope of study, problems definitions and general literature review. Information regarding materials for this project was also gathered during this stage. Along with the progress of the project, more researches were conducted to continuously gather information on literature review and related matters. The information is obtained from the books, articles and journals provided in the UTP library and via internet with the scope given by the project supervisor.

3.2 Preparation of Carbonaceous Shale

Shale has to be crushed and sieved to a mean size of 1.0 mm. Equipments used are hammer, steel container, sieve pans and shaker. While carrying out this process, glove, goggle, apron and full covered shoes must be worn for safety precaution. After the shale has been ground and sized, it is cleaned with distilled water to remove the impurities and then were dried in the oven for 24 hours.

The experiment to obtain the characteristics of the material such as the specific gravity, Moh's hardness and porosity are determined. Specific gravity is obtained by dividing the weight of the material in air with the difference of weight in air and in water. The hardness of the material was obtained by using Moh's Hardness scale consisting of 10 known minerals by characterizing the scratch resistance of various minerals through the ability of a harder material through the ability of a harder material to scratch a softer

material. The porosity is obtained by dividing the volume of water occupied the pore spaces with the volume of the materials in the container.

3.3 Groundwater Analyses

The groundwater from the monitoring well should be pumped out a day before. This procedure is important so that the water that is going to be used for this experiment is fresh groundwater. Figure 3.1 illustrates the method to be used for groundwater sampling. The masterflex vacuum pump together with the equipments as shown in the figure 3.1 are going to be use to collect the water from the well. The groundwater taken must not be exposed to atmosphere otherwise the ferrous iron will be oxidized to ferric iron. Therefore, the groundwater should be pumped out in such a way that there is no or a very little contact with the atmosphere so that most of the iron concentration in the water is in ferrous state. When the pumping starts, water that was entering the container (1) will flow into the container (2) when it was full. The new water that entering the container (1) would has least contact with the oxygen.

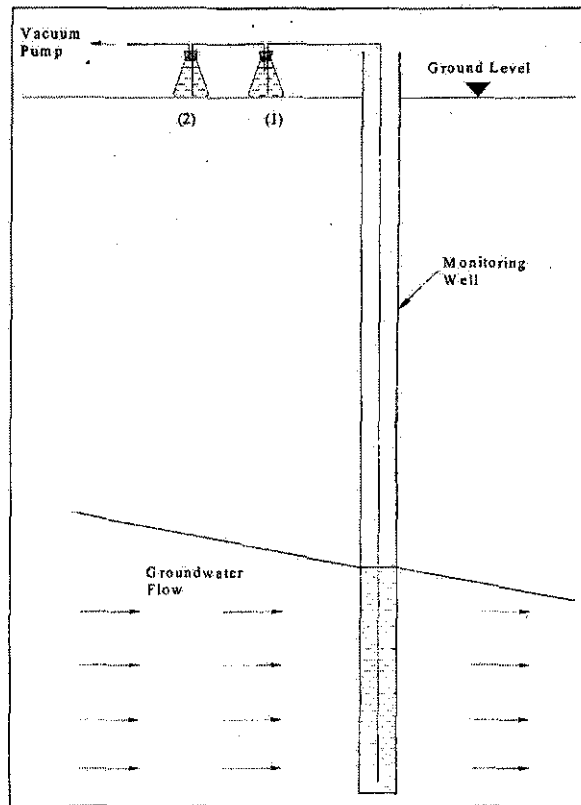


Figure 3-1. Groundwater Sampling

Iron contents should be greater than 0.3 mg/L. If the iron is not appreciable, appropriate quantities of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) will be added to give the desired iron concentrations. Types of experiments to analyze chemical parameters of groundwater are as follows:

Table 3-1. Experiments to Analyze Chemical Parameters for Groundwater (Standard Method)

Chemical Parameter	Method
• Ferrous (Hach Method 8146)	1,10 Phenanthroline Method
• Total Iron (Hach Method 8008)	FerroVer® Method
• Calcium and Magnesium Hardness	Atomic Absorption Spectrometer (AAS)
• Dissolved of oxygen, DO	Dissolved Oxygen meter
• pH	pH meter
• Alkalinity (bicarbonate) as CaCO_3	Titration Method

3.4 Adsorption and Catalytic Effect

An experiment was carried out to observe any reaction and differences for adsorption of ferrous iron and catalytic effect on oxidation ferrous iron. 2.0 g of sand and shale were filled with 200 ml of groundwater sample in the 250 ml volumetric flask. After the initial total iron and ferrous iron concentration had been tested, the flasks were shaken using rotary mechanical shaker at 150 rpm and 25°C. At every 15 minutes, the ferrous iron concentrations were measured.

3.4.1 Adsorption

In Adsorption experiment, purified nitrogen gas been filled up in the volumetric flask to maintain the anoxic conditions where the iron is kept in ferrous form. Consequently, the adsorbed ferrous iron could not be oxidized. This experiment was done for:

- Groundwater without contact with oxygen
- Groundwater with sand without contact with oxygen
- Groundwater with shale without contact with oxygen

3.4.2 Catalytic Effect

This experiment was conducted to observe the adsorption of ferrous iron onto filter media together with the oxidation of ferrous iron catalyzed by the sand and shale by oxygen, if any. This experiment was done for:

- Groundwater in the presence of oxygen
- Groundwater with sand in the presence of oxygen
- Groundwater with shale in the presence of oxygen

3.5 Direct Groundwater Filtration

Figure 3-3 shows the filtration set up for direct filtration of the groundwater from the well into the filtration column. This column experiment is carried out to observe the performance of shale compare to river sand in adsorption of ferrous iron in groundwater. Laboratory-scale column experiments were conducted using 31 mm internal diameter acrylic column (Perspex) with 1.0 m of length and 50 cm depth for the material (shale and river sand). Before starting the filtration run, the columns were brought to equilibrium by re-circulating the distilled water for about 15 minutes to make it saturated and fill up the pore spaces.

Automatic Centrifugal Pump was used to pump out the groundwater from the well into the tank (on 2.0 m stand height). There were three (3) pipe connection involved within the tank; 1) pipe connection from pump to the tank using 25 mm of PVC pipe about 50 m length, 2) pipe connection from the tank to the filter column using 6 mm of tube pipe, and 3) pipe connection from Nitrogen gas cylinder to the tank using 6 mm of tube pipe. The groundwater storage (tank) were sealed and connected to nitrogen gas supply to avoid oxidation of ferrous iron. A valve been installed within the pipe connection between the tank and the filter columns to adjust and maintain the filtration flow of ~10 m/hr.

The influent and effluent concentration of total iron and ferrous iron were measured for three (3) times per day until the measurements become constant. At this situation, backwashing must be performed. The adsorptive columns need to be backwashed with nine (9) times of filtration a flow which is ~90 m/hr. Figure 3-2 shows the set up for backwashing system for the filtration experiment.

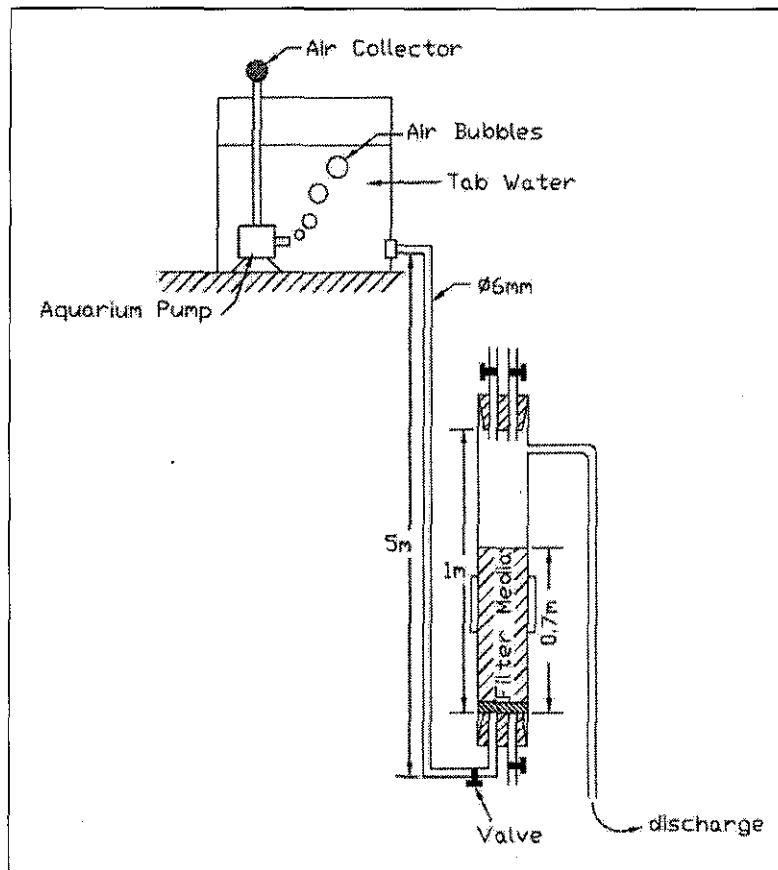


Figure 3-2. Experiment Set up for Backwashing System

Head losses along the filter columns (connection the tube pipe within the filters) were measured periodically using measuring tape.

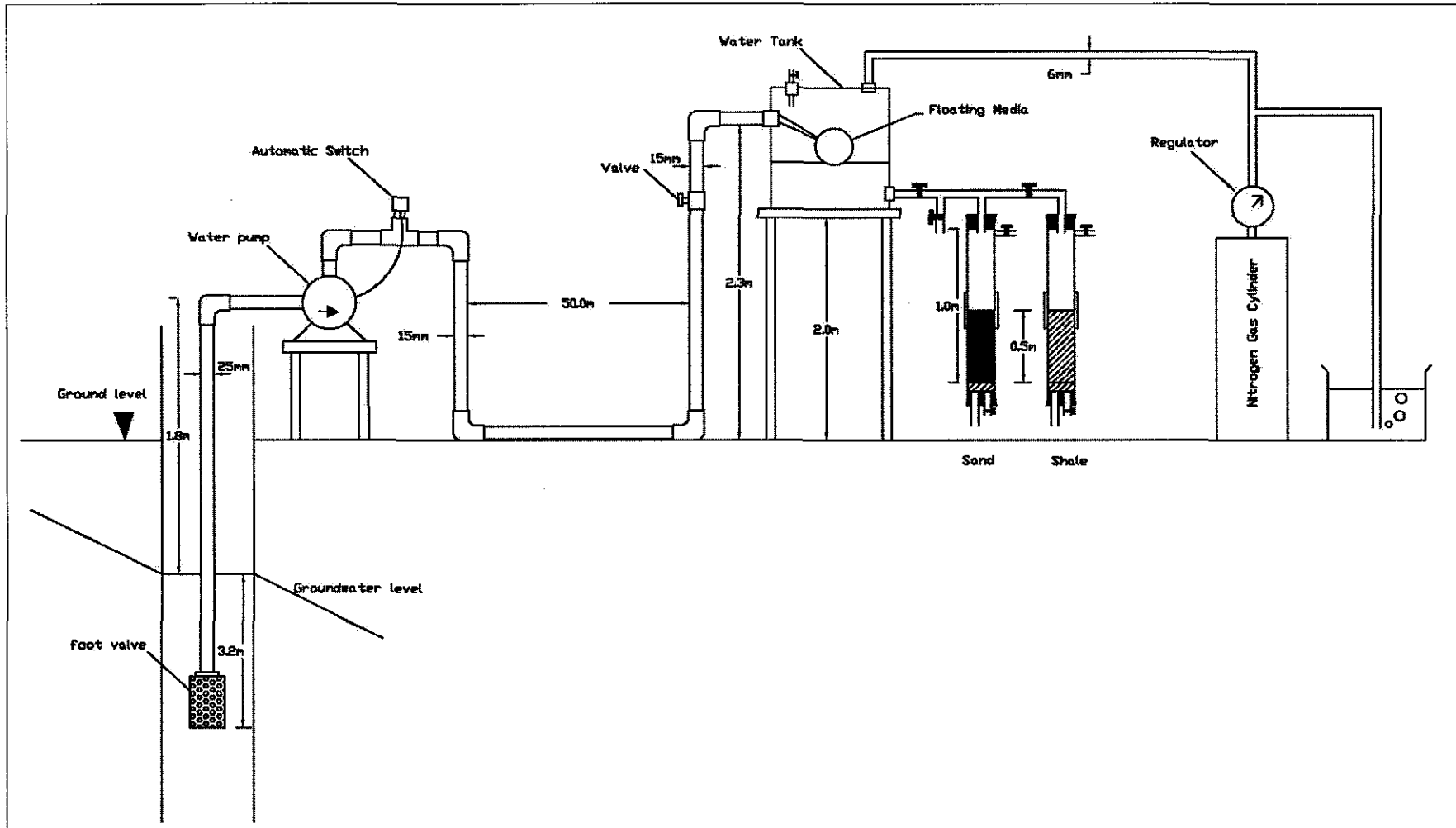


Figure 3-3. Experiment Set up for Direct Groundwater Filtration

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Properties of Carbonaceous shale

Table 4-1. Characteristics of Carbonaceous shale

Characteristics	Carbonaceous shale
Colour	Light grey
Mean size (mm)	1.0
Specific gravity (g/cm^3)	1.65
Moh's Hardness	3-4
Porosity (%)	50

Table shows the characteristics of carbonaceous shale. An experiment was conducted to check the hardness of the material. The hardness been obtained by using Moh's Hardness scale consisting of 10 known minerals by characterizing the scratch resistance of various minerals through the ability of a harder material through the ability of a harder material to scratch a softer material.

The experiment to check the porosity and the specific gravity of Carbonaceous shale also been conducted. The result is obtained by the formula in Appendix A.

(Please refer to Appendix A for detail results of the properties of carbonaceous shale)

4.2 Groundwater analyses

According to Mohak (2007), an experiment should be conducted to check the groundwater analyses. The experiment includes the groundwater alkalinity, total iron, dissolved oxygen for groundwater, pH, hardness; which is calcium hardness and magnesium hardness, the total dissolved solids and finally check the groundwater conductivity.

Table 4-2. Chemical analysis of Groundwater

Constituent	Measurement	
	pH value	Mg/L
pH	~ 7	
Total Iron		2.36
Ferrous Iron		1.98
Calcium Hardness as CaCO ₃ (ppm)		18.1124
Magnesium Hardness as CaCO ₃ (ppm)		3.4852
Total Hardness as CaCO ₃ (ppm)		21.1246
Dissolved Oxygen		0.42
Alkalinity as CaCO ₃		103

Table 4-3 shows the results obtained from the experiment. The pH obtained is nearly to 7.0 (6.918) under the temperature of approximately 25 °C. The total hardness as CaCO₃, calcium hardness as CaCO₃, magnesium hardness as CaCO₃, dissolved oxygen and alkalinity that have been obtained are 21.1246 mg/L, 18.1124 mg/L, 3.4852 mg/L, 0.42 mg/L and 103 mg/L respectively.

For total iron and ferrous iron measurement, the results obtained are 2.36 mg/L and 1.98 mg/L respectively. An orange color will form if iron is present when adding the specific powder pillow to the water sample during the testing. Iron contents should be greater than 0.3 mg/L. If the iron content is not appreciable, appropriate quantities of ferrous sulfate (FeSO₄.7H₂O) to give the desired iron concentrations. From the result obtained, the groundwater from the monitoring well can be used for the project without add in any ferrous sulfate.

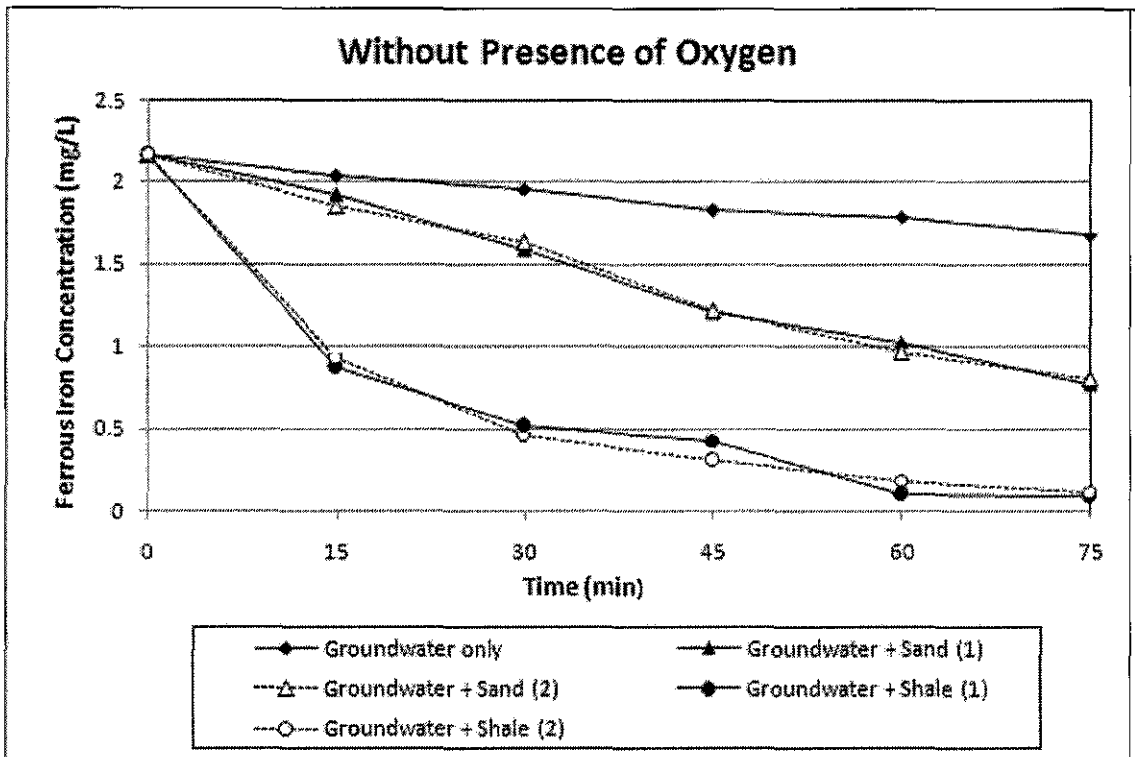
4.3 Performance of Carbonaceous Shale

4.3.1 Adsorption and Catalytic Effect

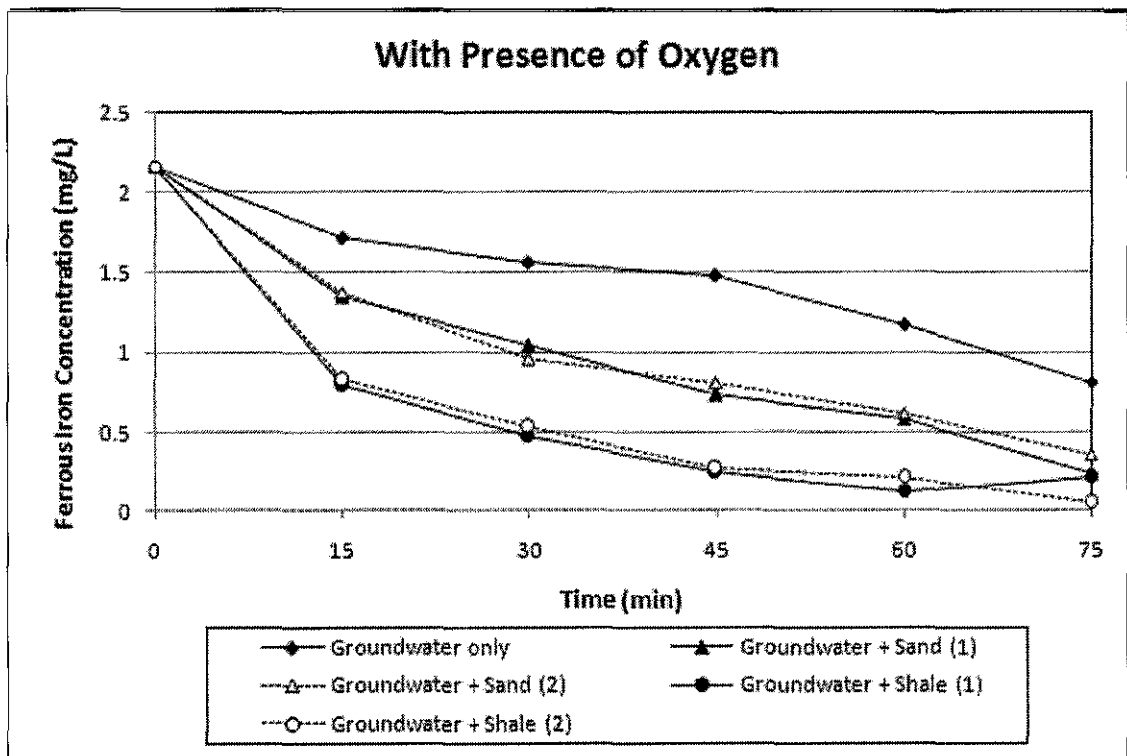
Ferrous iron would not be oxidized to ferric iron without the presence of oxygen. Since there is no oxidation occurs, ferrous ion in groundwater sample will undergo the adsorption reaction. In adsorption mechanism, ferrous iron being adsorb onto the surface of sand and carbonaceous shale. Due to little contact of oxygen in this experiment, ferrous iron in 'groundwater only' shows small decrease in the concentration. Figure 4-1 shows that shale adsorbs ferrous iron faster compared to sand.

Ferrous iron was oxidized to ferric iron because of the presence of oxygen. As shown in Figure 4.2, the adsorption and oxidation of ferrous iron catalyzed by sand and shale does not give much difference in remaining iron concentration as compared to adsorption of iron alone. Thus, the effect of coal and shale as the catalyst on the oxidation of ferrous iron is insignificant.

(Please refer to Appendix C for the datasheets of the results of the experiments)



**Figure 4-1. Adsorption and Catalytic Effect Experiment
(without oxygen contact)**



**Figure 4-2. Adsorption and Catalytic Effect Experiment
(with oxygen contact)**

4.3.2 Direct Groundwater Filtration

This experiment is a field experiment that was carried out by introducing direct filtration of the groundwater from the well to the filtration column. Iron entering the filter bed is in ferrous state. The results of the experiment are shown in Figure 4-3, Figure 4-4, Figure 4-5 and Figure 4-6.

The influent iron concentrations were monitored continuously. After certain period of time, the adsorption of ferrous iron by the filter media begins to fail. This is because the adsorption capacity of a solid adsorbent is generally proportional to the specific surface area. The surface characteristics of the media including surface charge with the development of iron oxide coated on surface media. So, to avoid this problem occur, a backwashing process should be conducted. The head loss in shale filter is larger than in sand filter with average depth of 153.4 cm in shale filter and 143.15 cm in sand filter.

Both two filters were operated at ~ 10 m/hr and having a same filter depth that is 1.0 m. Figure 4-3 shows of iron in influent and effluent of sand filter whereas Figure 4-5 shows the forms of iron in carbonaceous shale filter. Figure 4-4 and Figure 4-6 illustrates the head loss for both filter respectively.

(Please refer to Appendix C for the datasheets of the results of the experiments)

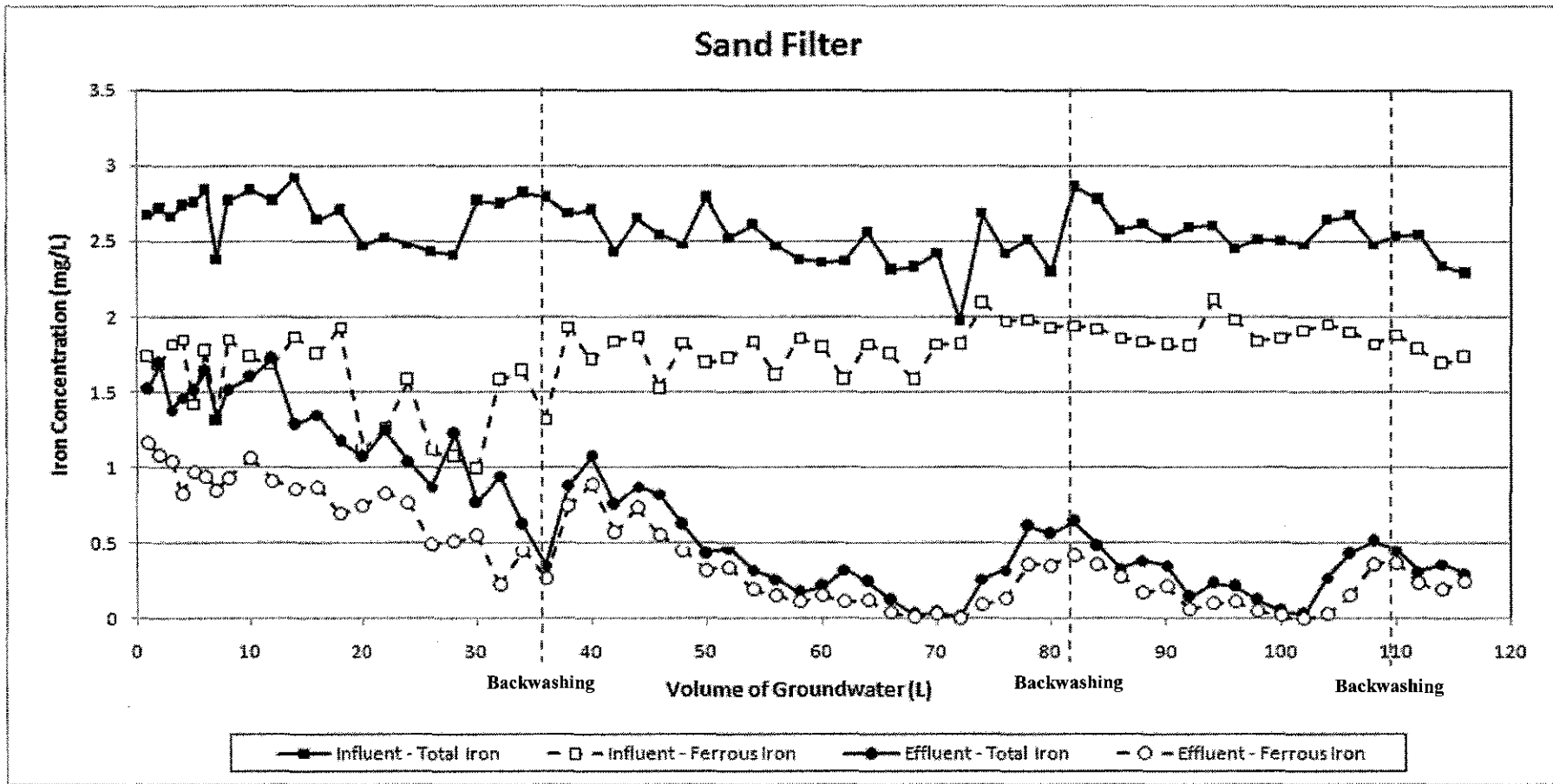


Figure 4-3. Forms of Iron in Influent and Effluent of Sand Filter

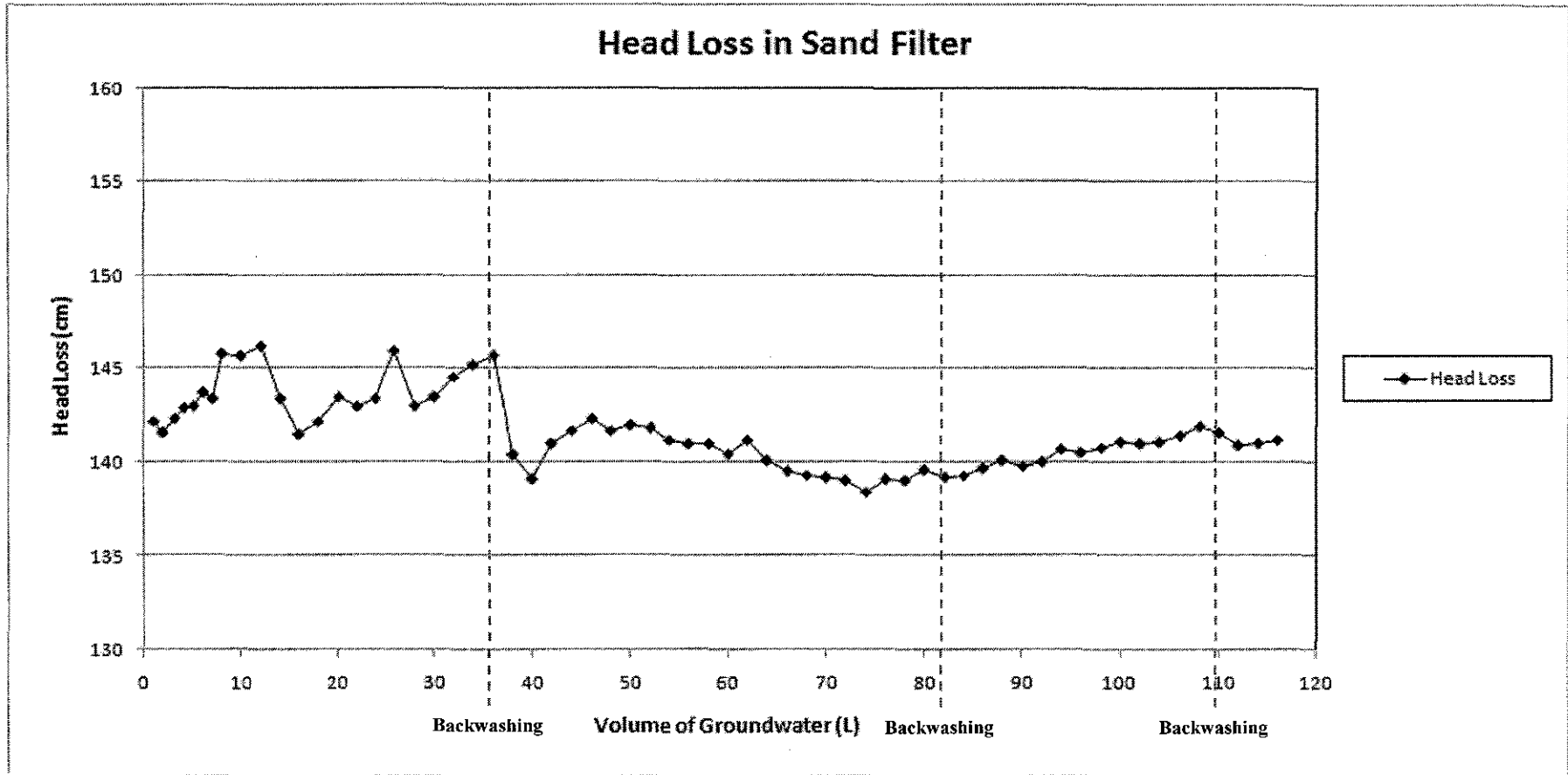


Figure 4-4. Head loss in Sand Filter

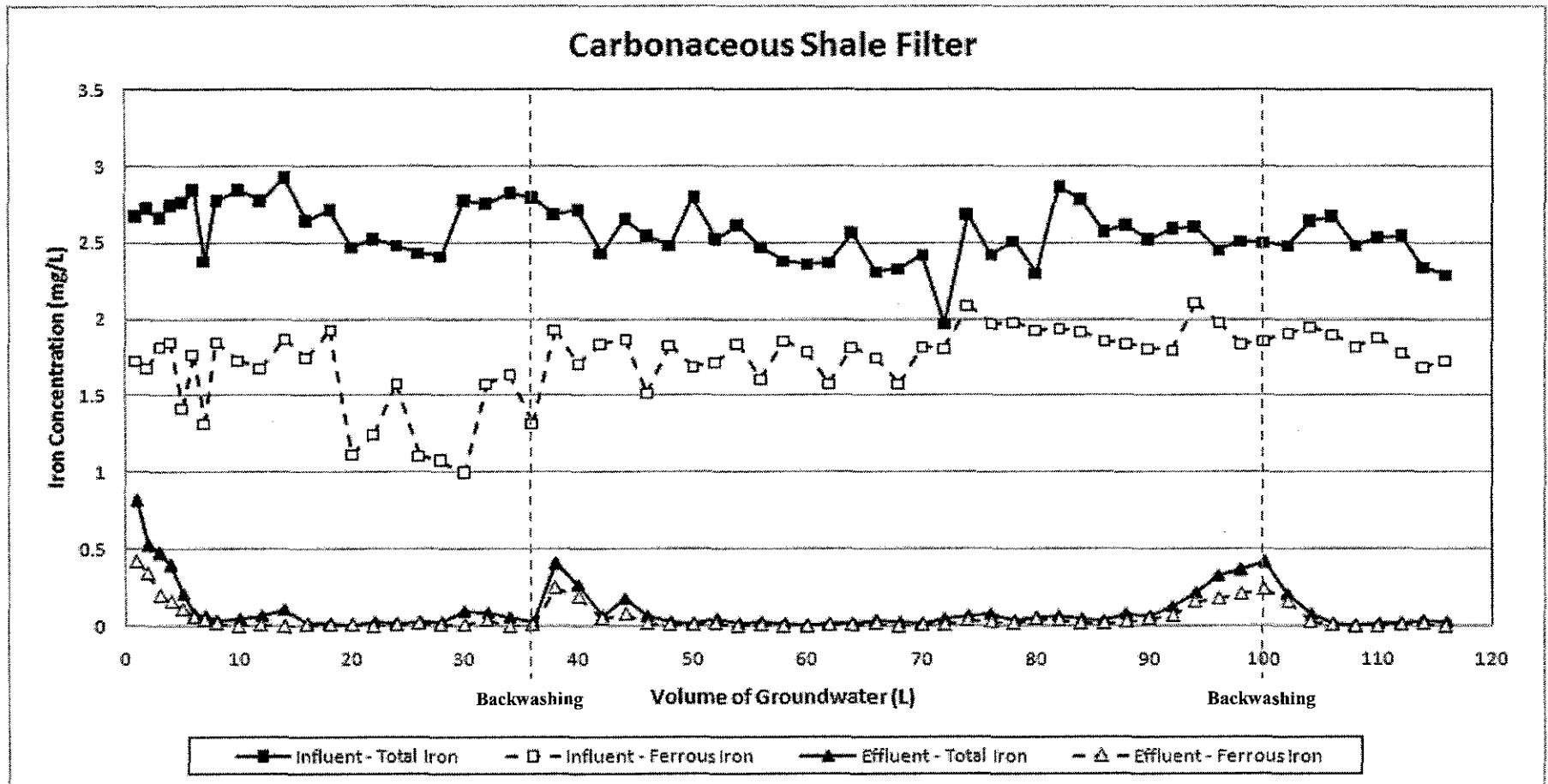


Figure 4-5. Forms of Iron in Influent and Effluent of Carbonaceous Shale Filter

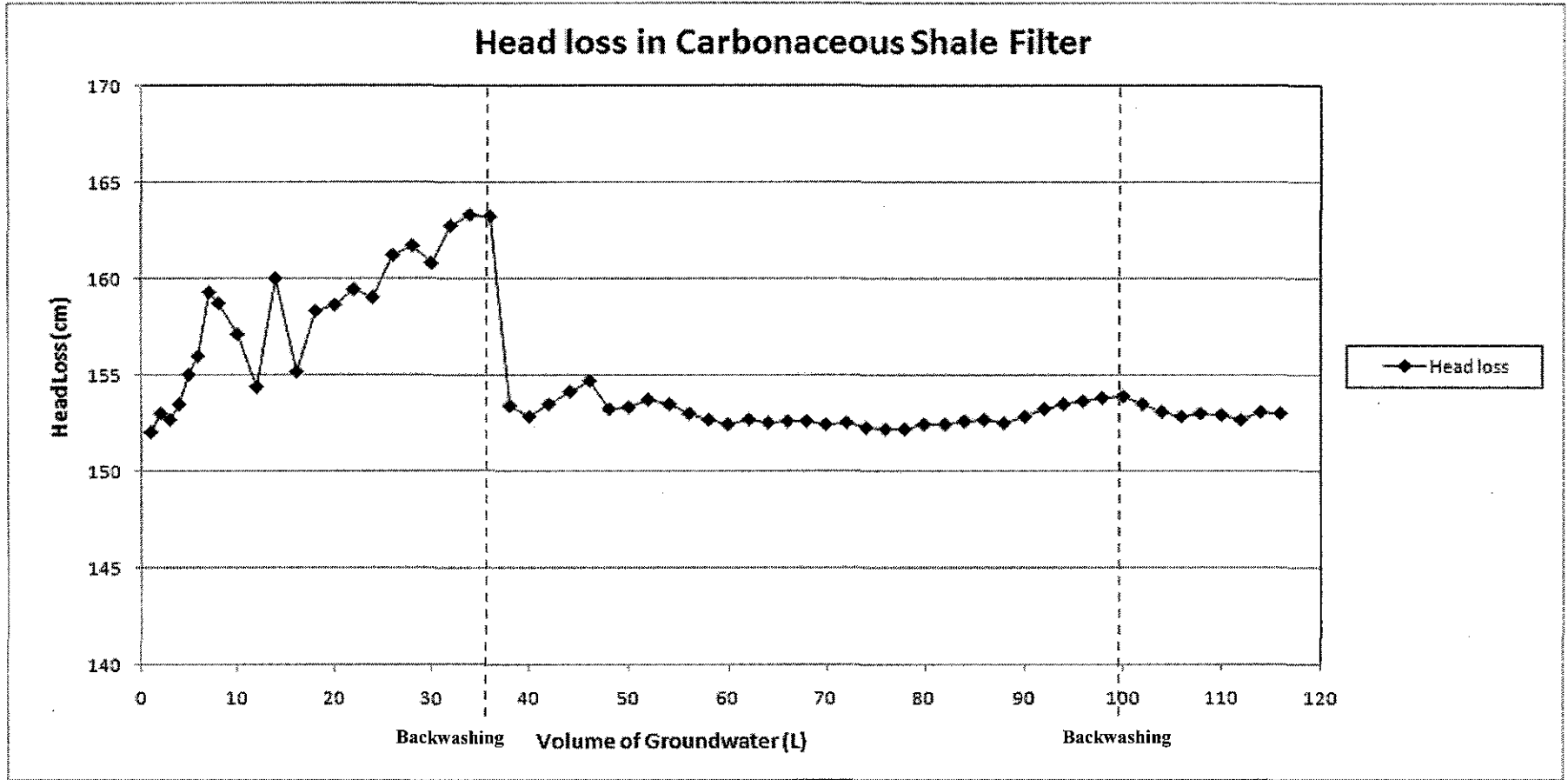


Figure 4-6. Head loss in Carbonaceous Shale Filter

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Total iron and ferrous iron content of the groundwater sample taken from the monitoring well near block 13 are 2.36 mg/L and 1.98 mg/L respectively. Hence, this water can be used in the experiment to examine removal of iron using adsorption-oxidation mechanism from groundwater by filtration through carbonaceous shale.

The data for the chemical analyses of the groundwater to be used in the experiment have been obtained for the calcium hardness as CaCO_3 , magnesium hardness as CaCO_3 , total hardness as CaCO_3 , dissolved oxygen and alkalinity as CaCO_3 . The values obtained are 18.1124 mg/L, 3.4852 mg/L, 21.1246 mg/L, 0.42 mg/L and 103 mg/L respectively.

The results from the experiments show that carbonaceous shale gives better performance compared to sand in adsorption of ferrous iron in filters. Carbonaceous shale gives longer run time and higher iron removal capacity than the sand. While for the head losses measured, the head loss in shale filter is higher than sand filter with average depth of 153.4 cm and 143.15 cm respectively.

Adsorptive iron removal process requires a long and continuous filtration run to be developed. The mechanism of iron removal relies on the iron(II) adsorption capacity of the filter media and its subsequent regeneration. The iron(II) is removed by adsorption onto the surface of the filter media. Subsequently, in the presence of oxygen, the absorbed iron(II) is oxidized forming a new surface for oxidation. The surface characteristics of the media including surface charge with the development of iron oxide coating on its surface. In conventional iron removal filters, the adsorption-oxidation

mechanism is expected to be responsible for the removal of an important part of iron entering the filter bed in iron(II) form.

The iron(II) adsorption capacity may depend on characteristics of the filter media, water quality and process conditions applied. Furthermore, iron(II) adsorption capacity of the new media increases with the development of the iron oxide coating. For efficient iron removal through the adsorption-oxidation mechanism, it is essential that coatings developed on the filter media have high iron(II) adsorption capacity. In addition, process conditions applied should be such that the pre-oxidation of iron before entering the filter is minimal.

5.2 Recommendations

These are the recommendation for future work related on this topic

- Adsorptive iron removal process requires a long and continuous filtration run to be developed. Further study should be done on the adsorption capacity of the shale until the material cannot be used any more.
- Filter media of adsorptive iron removal filters are expected to grow with time. The effect of water quality and process conditions on the rate of growth of filter media needs a further detailed investigation. Additionally, further studies should be conducted for different condition such as pH, temperature, hardness and etc.
- Iron and manganese are normally present together in groundwater. This study concentrated on adsorptive iron removal only. Hence, a detailed investigation should be conducted to check the effectiveness of the filter media for both iron and manganese removal process.
- The grain size for filter media in this study was limited to the specified size only. Further study should be conducted for different grain size to check the effectiveness for iron removal in groundwater by filtration process.

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APPENDIX A

PROPERTIES OF CARBONACEOUS SHALE

1) POROSITY (using volume/density method)

Table A-1. Porosity of Carbonaceous shale filter

Material	A	B	Pore Space (Porosity @ fraction)	Pore Space (Porosity) (%)
	Volume of material (cm ³)	Volume of water @ pore space (cm ³)		
Shale	150	75	0.5	50.0

$$\text{porosity} = \frac{A}{B} \times 100\%$$

2) SPECIFIC GRAVITY

Table A-2. Specific Gravity of Carbonaceous shale Filter

Sample	Sample weight in air (g)	Sample weight in water (g)	Sample density (g/cm ³)	Specific Gravity
Shale	51	20	1.65	1.65

$$\text{Density} = \frac{\text{weight}_{\text{air}}}{\text{weight}_{\text{air}} - \text{weight}_{\text{water}}}$$

$$\text{Specific gravity} = \frac{\text{Density of Substance}}{\text{Water Density}}$$

*Note

Water has a density of 1 g/cm³, thus it buoys up anything within it by 1 gram per cubic centimeter of displacement. Because of this, the weight in air minus the weight in water, is equal to the volume of the rock sample in cm³

APPENDIX B

GROUNDWATER ANALYSES

- 1) TOTAL IRON (using Hach Method 8008 - FerroVer® Method)

Table B-1. Results of Total Iron Experiment

SAMPLE	1	2	3	AVG
A	2.68	2.31	2.29	2.43
B	2.47	2.37	2.33	2.39
C	2.22	2.30	2.26	2.26

Total Iron = 2.36 mg/L Fe

- 2) FERROUS (using Hach Method 8146 – 1,10 Phenanthroline Method)

Table B-2. Results of Ferrous Iron Experiment

SAMPLE	1	2	3	AVG
A	1.97	2.02	1.89	1.96
B	2.12	1.92	2.07	2.04
C	1.85	2.04	1.93	1.94

Ferrous Iron = 1.98 mg/L

- 3) DISSOLVED OXYGEN (using D.O meter)

Table B-3. Results of Dissolved Oxygen Experiment

SAMPLE	A	B	C	AVG
Concentration (mg/L)	0.54	0.30	0.41	0.42

D.O = 0.42 mg/L

- 4) pH (using pH meter)

Table B-4. Results of pH Experiment

Temperature ~ 25 °C				
SAMPLE	1	2	3	AVG
A	6.885	6.923	6.850	6.886
B	6.896	6.931	6.903	6.910
C	6.972	6.963	6.942	6.959

pH = 6.918
 ~ 7 (Neutral)

5) HARDNESS (using Atomic Absorption Spectrometer, AAS)

5.1) Calcium hardness

Table B-5(a). Results of Calcium Hardness Experiment

SAMPLE	Ca Hardness as mgCaCO ₃ /L
A	18.4714
B	17.9810
C	17.8848
AVG	18.1124

5.2) Magnesium Hardness

Table B-5(b). Results of Magnesium Hardness Experiment

SAMPLE	Mg Hardness as mgCaCO ₃ /L
A	3.4988
B	3.4788
C	3.4779
AVG	3.4852

5.3) Total Hardness

$$\begin{aligned} \text{Total Hardness as mgCaCO}_3/\text{L} &= 18.1124 (\text{Ca}) + 3.4852 (\text{Mg}) \\ &= \mathbf{21.1246} \end{aligned}$$

6) ALKALINITY (using Titration method)

Table B-6. Results of Alkalinity Experiment

READING	SAMPLE A				SAMPLE B				SAMPLE C			
	INITIAL	FINAL	VOL	pH	INITIAL	FINAL	VOL	pH	INITIAL	FINAL	VOL	pH
1	6.6	11.8	5.2	3.18	21.6	26.8	5.2	3.07	37.4	42.4	5.0	2.39
2	11.8	16.8	5.0	3.18	26.8	32.4	5.6	2.81	42.4	47.0	4.6	2.38
3	16.8	21.6	4.8	3.19	32.4	37.4	5.0	2.41	47.0	52.8	5.8	2.23
AVG			5.0	3.18			5.3	2.76			5.1	2.33
Alkalinity	100				106				102			

AVG ALKALINITY= 103 mg/L

$$\text{Total Alkalinity, as MgCaCO}_3/\text{L} = \frac{(\text{Total mL H}_2\text{SO}_4 \text{ titrant used}) \times \text{Normality of H}_2\text{SO}_4 \times 50,000}{\text{mL sample}}$$

APPENDIX C

PERFORMANCE OF SAND AND CARBONACEOUS SHALE FILTERS

1) ADSORPTION AND CATALYTIC EFFECT

Groundwater sample = 200 mL

Material: Shale = 2.0 gram
Sand = 2.0 gram

Influent: Total Iron = 2.60 mg/L
Ferrous Iron = 2.16 mg/L

Table C-1. Adsorption and Catalytic Effect of Sand and Carbonaceous Shale on Ferrous iron

Without Oxygen					
Time (min)	15 min	30 min	45 min	60 min	75 min
Supernatant	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)
Groundwater	2.04	1.96	1.83	1.79	1.68
Sand 1	1.92	1.59	1.21	1.03	0.77
Sand 2	1.85	1.64	1.22	0.97	0.81
Shale 1	0.87	0.52	0.43	0.10	0.09
Shale 2	0.93	0.46	0.31	0.19	0.12
With Oxygen					
Time (min)	15 min	30 min	45 min	60 min	75 min
Supernatant	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ²⁺ (mg/L)
Groundwater	1.72	1.56	1.48	1.17	0.81
Sand 1	1.35	1.04	0.73	0.58	0.24
Sand 2	1.38	0.96	0.81	0.62	0.36
Shale 1	0.79	0.48	0.25	0.12	0.03
Shale 2	0.83	0.53	0.27	0.21	0.05

2) DIRECT GROUNDWATER FILTRATION

Table C-2(a). Direct Groundwater Filtration for Sand Filter

Volume (L)	Influent		Effluent		Head loss (cm)
	Total Iron (mg/L)	Ferrous Iron (mg/L)	Total Iron (mg/L)	Ferrous Iron (mg/L)	
1	2.67	1.73	1.52	1.16	142.2
2	2.72	1.68	1.69	1.08	141.6
3	2.66	1.82	1.38	1.04	142.3
4	2.74	1.85	1.46	0.83	142.9
* 5	2.76	1.42	1.51	0.97	143.0
6	2.84	1.77	1.64	0.94	143.7
7	2.38	1.32	1.32	0.85	143.4
8	2.77	1.85	1.51	0.93	145.8
10	2.84	1.73	1.60	1.06	145.7
12	2.77	1.68	1.72	0.91	146.2
14	2.92	1.87	1.28	0.86	143.4
16	2.64	1.75	1.35	0.87	141.5
18	2.71	1.93	1.17	0.69	142.2
* 20	2.47	1.12	1.07	0.74	143.5
* 22	2.52	1.25	1.24	0.83	143.0
* 24	2.48	1.58	1.03	0.77	143.4
26	2.43	1.11	0.87	0.49	146.0
28	2.41	1.07	1.22	0.51	143.0
30	2.77	0.99	0.76	0.55	143.5
* 32	2.75	1.58	0.94	0.22	144.6
* 34	2.82	1.64	0.62	0.45	145.2
* 36	2.79	1.32	0.35	0.27	145.7
Backwashing					
38	2.68	1.93	0.88	0.74	140.4
40	2.71	1.71	1.07	0.89	139.1
42	2.43	1.84	0.75	0.57	141.0
44	2.65	1.87	0.87	0.73	141.7
46	2.54	1.52	0.82	0.55	142.3
48	2.48	1.83	0.62	0.45	141.7
50	2.79	1.69	0.43	0.32	142.0
52	2.52	1.72	0.46	0.34	141.8
54	2.61	1.84	0.32	0.19	141.2

*- Test been conducted a day after the sampling

56	2.47	1.61	0.26	0.15	141.0
58	2.38	1.86	0.17	0.11	141.0
60	2.36	1.79	0.21	0.15	140.4
62	2.37	1.58	0.32	0.11	141.2
64	2.56	1.82	0.24	0.12	140.1
* 66	2.31	1.75	0.12	0.04	139.5
* 68	2.33	1.58	0.03	0.01	139.3
* 70	2.42	1.82	0.04	0.03	139.2
72	1.97	1.81	0.01	0.00	139.0
74	2.68	2.09	0.26	0.09	138.4
76	2.42	1.97	0.32	0.13	139.1
78	2.51	1.98	0.61	0.36	139.0
80	2.30	1.93	0.56	0.35	139.6
82	2.86	1.94	0.64	0.42	139.2
Backwashing					
84	2.78	1.92	0.48	0.36	139.3
86	2.57	1.86	0.33	0.28	139.7
88	2.61	1.84	0.38	0.17	140.1
90	2.52	1.81	0.35	0.21	139.8
92	2.59	1.80	0.14	0.06	140.0
94	2.6	2.11	0.23	0.10	140.7
96	2.45	1.98	0.21	0.11	140.5
98	2.51	1.84	0.12	0.05	140.8
100	2.50	1.86	0.05	0.02	141.1
102	2.48	1.91	0.03	0.00	141.0
104	2.64	1.95	0.27	0.03	141.1
106	2.67	1.90	0.43	0.15	141.4
108	2.48	1.82	0.51	0.36	141.9
* 110	2.53	1.88	0.45	0.37	141.6
Backwashing					
112	2.54	1.78	0.31	0.23	140.9
114	2.34	1.69	0.36	0.19	141.0
116	2.29	1.73	0.30	0.25	141.2

*- Test been conducted a day after the sampling

Table C-2(b). Direct Groundwater Filtration for Carbonaceous Shale Filter

Volume (L)	Influent		Effluent		Head loss (cm)
	Total Iron (mg/L)	Ferrous Iron (mg/L)	Total Iron (mg/L)	Ferrous Iron (mg/L)	
1	2.67	1.73	0.82	0.42	152.0
2	2.72	1.68	0.53	0.34	153.0
3	2.66	1.82	0.48	0.20	152.7
4	2.74	1.85	0.40	0.16	153.5
* 5	2.76	1.42	0.21	0.11	155.0
6	2.84	1.77	0.08	0.06	156.0
7	2.38	1.32	0.07	0.04	159.3
8	2.77	1.85	0.04	0.02	158.7
10	2.84	1.73	0.05	0.00	157.1
12	2.77	1.68	0.07	0.01	154.4
14	2.92	1.87	0.11	0.00	160.0
16	2.64	1.75	0.02	0.01	155.2
18	2.71	1.93	0.02	0.01	158.3
* 20	2.47	1.12	0.01	0.01	158.6
* 22	2.52	1.25	0.03	0.00	159.4
* 24	2.48	1.58	0.02	0.01	159.0
26	2.43	1.11	0.03	0.02	161.2
28	2.41	1.07	0.03	0.01	161.7
30	2.77	0.99	0.10	0.01	160.8
* 32	2.75	1.58	0.09	0.04	162.7
* 34	2.82	1.64	0.06	0.00	163.3
* 36	2.79	1.32	0.03	0.01	163.2
Backwashing					
38	2.68	1.93	0.41	0.25	153.4
40	2.71	1.71	0.27	0.19	152.8
42	2.43	1.84	0.07	0.05	153.5
44	2.65	1.87	0.18	0.08	154.1
46	2.54	1.52	0.07	0.02	154.7
48	2.48	1.83	0.03	0.01	153.2
50	2.79	1.69	0.02	0.01	153.3
52	2.52	1.72	0.05	0.02	153.7
54	2.61	1.84	0.02	0.00	153.5
56	2.47	1.61	0.03	0.01	153.0
58	2.38	1.86	0.02	0.00	152.7
60	2.36	1.79	0.01	0.00	152.4
62	2.37	1.58	0.02	0.01	152.7

* - Test been conducted a day after the sampling

64	2.56	1.82	0.02	0.01	152.5
* 66	2.31	1.75	0.04	0.02	152.6
* 68	2.33	1.58	0.03	0.00	152.6
* 70	2.42	1.82	0.02	0.01	152.4
72	1.97	1.81	0.05	0.01	152.5
74	2.68	2.09	0.07	0.04	152.3
76	2.42	1.97	0.08	0.03	152.2
78	2.51	1.98	0.04	0.02	152.2
80	2.30	1.93	0.06	0.05	152.4
82	2.86	1.94	0.07	0.04	152.4
84	2.78	1.92	0.05	0.02	152.6
86	2.57	1.86	0.04	0.02	152.7
88	2.61	1.84	0.08	0.03	152.5
90	2.52	1.81	0.07	0.05	152.8
92	2.59	1.80	0.13	0.07	153.2
94	2.60	2.11	0.22	0.16	153.5
96	2.45	1.98	0.33	0.18	153.6
98	2.51	1.84	0.37	0.21	153.8
100	2.50	1.86	0.42	0.24	153.9
Backwashing					
102	2.48	1.91	0.21	0.16	153.5
104	2.64	1.95	0.08	0.03	153.1
106	2.67	1.90	0.02	0.01	152.8
108	2.48	1.82	0.01	0.00	153.0
* 110	2.53	1.88	0.02	0.00	152.9
112	2.54	1.78	0.02	0.01	152.7
114	2.34	1.69	0.04	0.02	153.1
116	2.29	1.73	0.03	0.00	153.0

* - Test been conducted a day after the sampling

APPENDIX D

EXPERIMENT SET UP



(a)



(b)

Figure D-1. (a) Carbonaceous shale and (b) Weathering shale near Kellie's Castle, Batu Gajah, Perak, Malaysia



Figure D-2. Experiment Procedure in Adsorption and Catalytic Effect of Sand and Carbonaceous Shale of Ferrous Iron



Figure D-3. Automatic Centrifugal pump



Figure D-4. Set up for Direct Groundwater Filtration Experiment