

CHAPTER 1

INTRODUCTION

1.1 Introduction

Groundwater has the potential to be the source of potable water to supplement the freshwater demand of the increasing population and industries in Malaysia [1]. It constitutes the underground part of the 'water cycle' and represents 40% of the usage of fresh water in the world [2]. Groundwater can be used to solve water shortages especially in areas with limited surface water resources [3]. In Malaysia, surface water is used as water resource, thus groundwater is neglected due to the availability of surface water such as rivers, lakes and ponds. However, the increasing water demand with limited supply of surface water has attracted the attention of people towards groundwater. Groundwater abstraction points are mostly drawing water from coastal alluvial aquifers and only about 10% from hard rock aquifers [4].

Although groundwater practically can be found anywhere in Malaysia, high volume of production for water supply can only be done in areas where sand aquifers are present such as in Kelantan [5] and Selangor [6]. In other areas, groundwater can be found in fractured rocks such as granite and sedimentary formations [6].

1.2 Overview of groundwater potential and usage in Malaysia

In Malaysia, the total annual water usage is estimated to be about 15.2 billion m³/year, of which only 1.7 billion m³ is from groundwater [7]. Industrial use of groundwater is yet to be documented. The most beneficial use is in industries where potable water quality is not required. In 2011, the Department of Environment [8] reported that about 44% of the industries in Malaysia were using groundwater as an additional source of water supply [9]. The quality of groundwater in Malaysia is

monitored by the Department of Environment, Malaysia. According to the Malaysia Environmental Quality Report of 2011, 109 monitoring wells were established at 79 sites in Peninsular Malaysia and 15 each in Sarawak and Sabah [10]. The selection and categorization of these sites were determined by the surrounding land uses which include agricultural, solid waste landfills, urban/suburban, rural, industrial areas, golf courses, radioactive landfill, animal burial areas, municipal water supply and ex-mining areas (gold mine). Table 1.1 shows the distribution of groundwater monitoring wells in Malaysia.

Table 1.1: Distribution of Groundwater Wells in Malaysia, 2011 [9]

Category	Number of Wells	Category	Number of Wells
Agricultural Areas	12	Ex-mining Area (Gold Mine)	3
Urban/Suburban Areas	11	Municipal Water Supply	9
Industrial Sites	18	Animal Burial Areas	14
Solid Waste Landfills	24	Aquaculture Farms	6
Golf Courses	7	Resorts	1
Radioactive Landfill	3	Rural Area	1

The computerized databank of the Geological Survey Department of Malaysia indicates that more than 2,466 wells were drilled throughout peninsular by various sectors. The total yield of these operations was about 552,000 m³/day comprising of Kelantan (216,000 m³/day), Selangor (68,000 m³/day), Pahang (57,000 m³/day), Negeri Sembilan (48,000 m³/day) and other states producing 16,000 m³/day [11]. This amount of groundwater production is only about 10% of the present water supply in Peninsular Malaysia [11]. However, the usage of groundwater in Malaysia (10%) is less as compared to other countries such as Thailand (80%), Austria (98%), Denmark (100%) and China (78%) which use groundwater as water supply [12].

Groundwater contains dissolved mineral ions, which can affect its use for various purposes. Some of the dissolved minerals are essential for good health while others can cause problems such as odor and stain at high concentration [13]. Additionally, the presence of low concentrations of iron in drinking water is beneficial because it can increase the energy and human metabolism, enhance the immune system and can help in transporting the oxygen to body's cell [14]. However, at higher levels, the human body can be affected and can hamper child development and growth with a resultant anaemia [15]. For this reason, it is important to know the quality of groundwater before it can be

used either for domestic, industrial, agricultural or livestock activities. The quality of groundwater is often described by its mineral contents, hardness, turbidity, color, taste and odor. Groundwater is generally less affected by pollution because it is protected by the soil that acts as a filter [16]. However, it may contain minerals such as iron and manganese in excessive levels that render the water unsuitable to be used directly as drinking water supply [17]. These minerals are influenced by its parent materials in the rock which can affect the concentrations of parameters in the water such as iron, sulfide, fluoride, hardness, and total dissolved solids. Therefore, several treatment techniques may be necessary to change, remove or reduce the excess mineral constituents before the water can be used for its intended purposes.

1.3 Iron in drinking water

Removal of Iron from groundwater is a major concern for most water supply companies. Various regulatory agencies have put forward standards or guidelines to control iron concentrations in water supplies. An American Water Works Association task group suggested the limits of 0.05 mg/L for iron as an “ideal quality water” for public use [18]. Based on the taste and nuisance considerations, the Ministry of Health in Malaysia [19] recommends a maximum level of 0.3 mg/L iron concentration in drinking water. This standard is similar to the standard proposed by the World Health Organization (WHO) [20]. In Netherland, the permissible limit for iron in drinking water is less than 0.05 mg/L, and several water supply companies are aiming at a level below 0.03 mg/L in order to minimize the maintenance cost of the distribution system [21].

1.4 Existing Treatment System

Several methods have been developed for the treatment of iron. The first method of iron removal is an aeration process with sand filtration. Other applied methods that has been successfully used to remove iron are ion-exchange [22], stabilization or sequestering process (with polyphosphates and silicates) [23], lime softening [24], manganese greensand process [25], in situ oxidation [26], membrane processes [27] and reverse osmosis [28]. Aeration and chemical oxidation with sand filtration is the most common method for the treatment of iron.

1.5 Problem Statement

Groundwater usually contains minerals, including iron. At low concentration, iron does not pose any threat to the consumer. However, at high iron concentration, groundwater becomes unsuitable for many purposes such as drinking, agriculture irrigation and textile industry. At concentrations above the permissible limit, water characteristics such as color, taste (bitter), stain are affected especially in water-supply [29]. Excessive iron concentration can also have adverse health consequences. The Ministry of Health, Malaysia, (MOH) [19] has set the permissible limit of iron in potable water at 0.3 mg/L as recommended by WHO [20]. Many methods for treatment of iron have been developed starting from aeration process with sand filtration, ion-exchange [22], stabilization or sequestering process (with polyphosphates and silicates) [23], lime softening [24], manganese greensand process [25], in situ oxidation [26], membrane process [27] and reverse osmosis [28].

Among all these methods, aeration and chemical oxidation with sand filtration is the most common method for the removal of iron. The method is cost effective and uses oxygen for oxidation. This conventional method is usually suitable for big treatment plants. However, conventional rural water treatment plants in developing countries often fail to provide safe drinking water [30]. In water treatment plants, a smooth operation and maintenance of the installations are often hindered by many reasons such as lack of trained operators, an unreliable supply of chemicals and spare parts, and financial problems [30]. Major urban water supplies are also not always capable of maintaining a regular supply of qualitative water, the distributed water and it is often considered unsafe for direct consumption. A study conducted from November 2007 to July 2009 has shown that 8 villages from 5 different states in West Coast Malaysia lack clean water [31]. Malaysia is a country in category 3 with the need to increase the water development to meet future demands specifically in rural areas that lack clean water [32]. Thus, it is necessary to find a more cost effective way of removing high concentration iron from groundwater for small and rural areas

Sulfide precipitation and electrochemical (EC) precipitation are other methods of removing iron. The removal of iron from groundwater by sulfide precipitation is not yet developed, whereas it is more effective in removing chromium. [33]. One of the advantages of this method is the absence of secondary waste [34]. Electrochemical-coagulation process (EC) is an effective wastewater treatment technique. EC treatment is

already being used in South America and Europe for treating industrial wastewater containing metals. EC is believed to be economically more feasible than conventional chemical oxidation [35]. Furthermore, EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit is possibly sufficient to carry out the process [25]. This study investigated the efficiency of iron removal from groundwater using sulfide precipitation and electrochemical precipitation method.

1.6 Objectives

The main objective of this study is to produce another approach for iron removal by sulfide precipitation and electrochemical precipitation with simple and minimal involvement of chemicals. The specific objectives are as follows:

- i. To examine the potential of iron removal by sulfide precipitation and electrochemical-coagulation (EC) methods.
- ii. To determine the optimum parameters and operating processes for sulfide and electrochemical precipitation method.
- iii. To compare the efficiency of both sulfide and electrochemical precipitation methods.

1.7 Significance of study

- ✓ This study will provide an alternative technique for treatment of groundwater for small scale water supply.
- ✓ To proffer a solution to the problems associated with iron in groundwater which renders groundwater unusable.
- ✓ The finding of this study is applicable for water supply in remote communities.

1.8 Scope of the study

This research focuses on iron removal by using sulfide precipitation and electrochemical-coagulation methods. The selections of these methods were based on their comparative advantage over the existing treatment processes. These include cost, availability of

materials, ease of operation and maintenance. Thus, comparative study for both methods has been done.

The experiment started by collecting data regarding the iron concentration in groundwater at different depth of the wells. The groundwater sample was collected from selected groundwater wells. The iron concentration in the water samples was analyzed. Simultaneously, other quality parameters of the water samples were also analyzed.

This study covers removal of iron by sulfide precipitation and electrochemical precipitation. The preliminary study was conducted using synthetic wastewater to ascertain the optimum process variables for both methods. In Sulphide precipitation method, native sulfur and water was used to produce hydrogen sulfide gas. The nitrogen gas was primarily purged into the sample in order to release the oxygen. It is continued by purging hydrogen sulfide gas to precipitate the iron in the samples. In the final phase, removal of iron by sulfide precipitation was conducted using real groundwater samples containing iron.

In electrochemical method, iron removal process was done through electrochemical precipitation. Aluminium plates were used as anode and cathode respectively to remove the iron in the sample. The operating parameters for iron removal by electrochemical precipitation include inter-electrode distance, voltage, surface area, initial concentration and sample volume. An initial preliminary study was conducted with synthetic wastewater and the obtained optimum parameters were applied to the real groundwater.

The precipitates from sulfide precipitation and electrochemical precipitation methods were analyzed to obtain the size and shape of the iron, including chemical composition. In this analysis, Field Emission Scanning Electron Microscopy (FESEM) was used to find the surface and precipitated elements, called Energy Dispersive Analysis of X-Ray (EDAX).

The results of the experiment using actual groundwater were used to analyze the kinetics order of the reactions.

1.9 Thesis Outlines

This thesis consists of five chapters and details of the each chapter are described as follows:

CHAPTER 1: In this chapter, the introduction of the study is provided including the background, problem statement, objectives and scope of the study.

CHAPTER 2: This chapter presents the review of iron in groundwater and its treatment. The review covers sources of iron, types of iron, iron removal in conventional and non-conventional methods.

CHAPTER 3: Chapter 3 describes the methodology and experimental procedures that were used in this study. The methods of iron removal by sulfide and electrochemical precipitation and coagulation are described in this chapter.

CHAPTER 4: This chapter presents and discusses the results from the experiment of the effect of iron removal from groundwater. The structure, surface morphological of iron formation and the types of kinetics of iron removal are discussed in this chapter.

CHAPTER 5: This chapter summarizes and concludes the findings of the study. Some recommendations for future study are suggested in this chapter.

CHAPTER 2

LITERATURE REVIEW

This literature review covers groundwater quality, iron and its sources in groundwater and removal methods.

2.1 Quality of groundwater

Groundwater quality is influenced by its existence with aquifer materials which affects the concentrations of water particles such as iron, sulfide, fluoride, hardness, total dissolved solids and pH. Groundwater usually contains dissolved mineral ions. Certain particles can be existed in excess amount or higher than the limit set by the World Health Organization (WHO). Some of the dissolved minerals are essential for good health but others if abundant can cause problem such as odor and stain [13]. For this reason, it is important to know the characteristics of the groundwater before it is used either for domestic, industrial, agricultural or livestock consumption. To achieve these ends, WHO has set different standards of water quality for different usages.

Physical and chemical characteristics of groundwater are described based on some parameters such as pH, total dissolved solids, hardness, color, turbidity, conductivity, calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, iron and fluoride. Table 2.1 shows the standard for drinking water quality set by the Malaysia Ministry of Health (MOH) [19] and World Health Organization, WHO [20].

Table 2.1: WHO and Malaysia Drinking Water Quality Standards

Parameters	Unit	WHO	Malaysia Standard
pH		6.5 – 8.5	6.5 – 8.5
Turbidity	NTU	1	5
Total Dissolved Solid	mg/L	600	1000
Color	Pt.Co	15	15
Hardness	mg/L as CaCO ₃	100 - 300	500
Iron (Fe ²⁺)	mg/L	0.3	0.3
Sodium (Na ⁺)	mg/L	200	200
Calcium (Ca ²⁺)	mg/L	200	-
Magnesium (Mg ²⁺)	mg/L	150	-
Aluminium (Al ³⁺)	mg/L	0.2	0.2
Sulphate (SO ₄ ²⁻)	mg/L	250	250
Chloride (Cl ⁻)	mg/L	250	250
Sulfide (S ²⁻)	µg/L	50	-
Nitrate (NO ₃ ⁻)	mg/L	50	10

2.2 Iron

Iron is one of the four most abundant element and second most abundant metal in the earth's crust [36]. It 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 sulfide [37, 38]. When iron exists in groundwater at high concentration as divalent ions (Fe²⁺), it is considered as contaminant mainly because of its organoleptic property [27]. Its contamination can cause many problems such as produce insoluble rusty, taste becomes bitter, staining problem to wet processing industries (textile, dyeing, white paper), results in more growth of micro-organism in distribution pipes which can cause clog and increase operational cost and has side effects on human's health [39].

Iron usually exists in two oxidation states, reduced soluble divalent ferrous (Fe²⁺) and oxidized trivalent ferric (Fe³⁺). Iron may be present in groundwater in various forms including dissolved as iron (II), inorganic complexes, organic complexes, colloids and suspension. Water containing ferrous iron used to be clear and colorless because the iron is completely dissolved [40].

2.3 Sources of iron

The most common sources of iron in groundwater are natural iron bearing minerals and rocks such as amphiboles, ferromagnesian micas, iron sulfides, magnetite, oxides, carbonates, and iron clay minerals [41]. Iron often presents in deeper wells where the groundwater is under anaerobic condition and in areas where groundwater flows through soils which are rich in organic matter.

In Malaysia, most dissolved iron can be found in granite and metasedimentary aquifers. Report of iron content in 23 wells of granite aquifers from two states (Penang and Johor) in Peninsular, Malaysia indicates that concentration of total iron in the water varies from undetectable levels to as high as 5.25 mg/L [42]. However, 60% of the wells contain iron concentration below the drinking water standard of 0.3 mg/L (Figure 2.1).

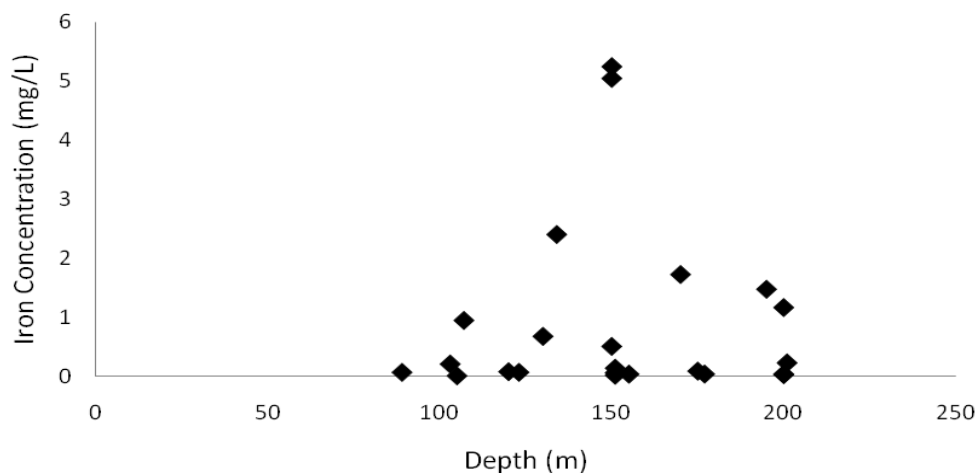
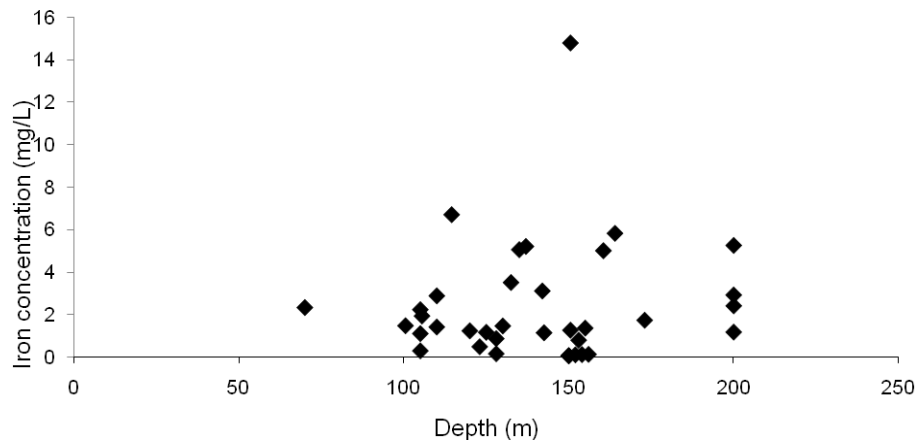


Figure 2.1: Iron concentrations from various depth of fractured granite aquifers[42]

This shows that water from fractured granite often can be used without treatment. Higher concentration of iron up to 47 mg/L was reported for groundwater granite aquifers in the City of Harere, Zimbabwe [43]. In Southern Africa, iron concentration in groundwater of 11 mg/L was detected [44]. The different concentration of iron may be due to the source rock and climatic condition of the area.

In Malaysia, data from 36 wells of metasedimentary aquifers in the state of Melaka, Negeri Sembilan, Selangor and Kedah indicate that iron concentration varied from 0.04 mg/L to 6.70 mg/L [45]. Only 19% of the wells contain iron less than the drinking

standard. This shows that most of the wells in fractured metasedimentary rocks produce water that require iron removal before it can be used for drinking water supply (Figure 2.2).



concentration in groundwater from 26 wells of sand aquifer at Akwa Ibom in Nigeria ranged from undetected level to 0.28 mg/L [52]. It is possible that sand in both places can acts as efficient filter and reduces the iron concentration in groundwater without treatment.

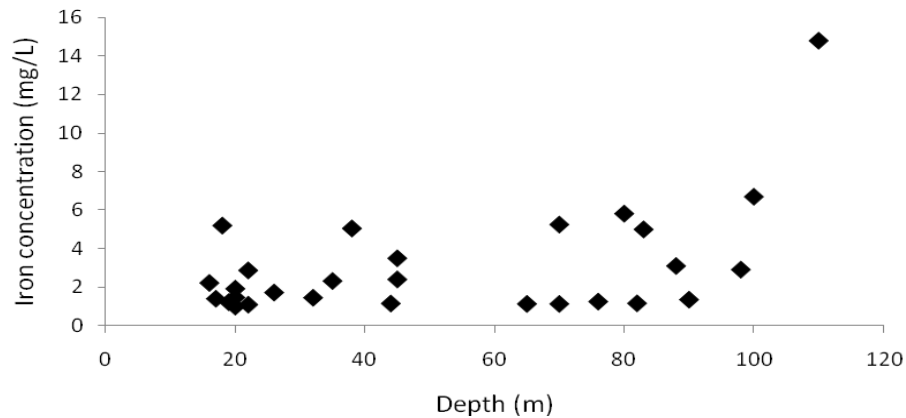


Figure 2.3: Iron levels from sand aquifers

Iron in groundwater may also come from man-made sources such as industrial effluent, acid-mine drainage, sewage and landfill [53]. Other man-made sources that may contribute iron include well casing, piping, pump parts, storage tanks, cast iron or steel that may be in contact with water. Table 2.2 shows iron concentration in groundwater from various places in the world. The groundwater was taken for analysis or laboratory experiment using various methods according to year. It indicated that iron concentration in groundwater varied from 1 mg/L to 20 mg/L. These concentrations are above the drinking water standard of 0.3 mg/L and need to be treated before it can be used.

Table 2.2: Various iron concentration from different places

Researcher	Source of Groundwater	Iron concentration (mg/L)
Stumm and Lee, 1961 [54]	Coal mining, Pysylavania, USA	1.0
Michalakos et al., 1997 [55]	Well in University of Patras, Greece	5
Gouzinis et al., 1998	Well in Patras, Greece	1.5

[56]		
Roden and Urrutia, 1999 [57]	North Carolina, USA	2
Berbenni et al., 2000 [58]	Lombardia, Italy	20
Hug et al., 2001 [59]	Well in Dubendorf, Switzerland	19
Katsoyiannis and Zouboulis, 2004 [60]	Well in FEA, Berlin, German	8
Choo et al., 2005 [61]	Gosan Treatment Plant, South Korea	7.2
Pacini et al., 2005 [62]	Avellaneda and Las Garzas, Argentina	2.15
Stembal et al., 2005 [63]	Northern Croatia	2.75
Tekerlekopoulou et al., 2006 [64]	Agrinio City Treatment Plant, Greece	10
Das et al., 2007 [65]	Assam, India	2.2
Chaudhuri and Sapari, 2008 [66]	Well in UTP, Malaysia	2.66
James T. Fish [67]	Fairbanks, Alaska	6.5

2.4 Types of iron

Three forms of iron can be found in groundwater, i.e. soluble, insoluble and organic forms.

2.4.1 Soluble Iron

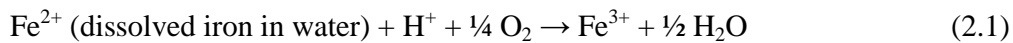
Soluble Iron in groundwater is commonly found in the form of Ferrous (Fe^{2+}). This iron structure has an octahedral hydration shell of six water molecules [68]. The monohydroxide complex $\text{Fe}(\text{OH})^+$ can be predominant at pH 9.5 and above [69]. At pH 11, $\text{Fe}(\text{OH})_3^-$ or HFeO_2^- can exist in water in various concentrations. However, at high pH, it cannot exist in natural systems [70]. The other soluble iron is in the form of complexes. Ferrous complexes can form in many organic molecules where some of the complexes may be considerably more resistant to oxidation compare to free ferrous ion [71].

Soluble iron or ferrous can be identified by the formation of reddish brown particles that eventually settle at the bottom. This type of iron is also often called "clear water iron" since it is not visible during pumping of groundwater. It is found in water under anoxic condition, such as water from deep wells or groundwater. Carbon dioxide reacts with iron

in the ground to form ferrous bicarbonate, which subsequently produces ferrous ions (Fe^{2+}) [72].

2.4.2 Insoluble Iron

Ferric is the insoluble form of iron. Near neutral pH, ferrous in groundwater converts to ferric as shown in the following equation:



When iron in groundwater comes in contact with air or oxygen, the water turns reddish in color and iron becomes iron oxide or ferric oxide $\text{FeO}(\text{OH})$:



Ferric or insoluble iron poses serious problems when it appears rusty or has red or yellow color. Although not very common, insoluble iron can create serious taste and appearance problems for water users [25].

2.4.3 Organic Iron

Organic iron or Heme iron may exist during combination of iron with different naturally occurring acids [73]. The combination of acid and iron or organic iron can be found in shallow wells and surface water [74]. Organic iron also formed during decomposition of vegetation. This kind of iron can be colorless. However, it can also appear in yellow or brown color. Organic iron cannot be removed by a cation exchange (water softener) method [25].

2.5 Issues of iron in groundwater

Iron in groundwater can cause severe color problem. When water is exposed to the atmosphere, dissolved iron turns indissoluble and leaves the water with brown-red color. This sediment is in the ferric form where iron is not dissolved in the water [75]. Presence of Iron in water supplies is undesirable because it causes various aesthetic, industrial and health problems as listed below:

- Iron produce ugly and insoluble rusty oxide; red, yellow or brown stains and streaks on laundry and plumbing fixtures [76].
- Iron imparts typical bitter taste to the water. The taste threshold of iron in water is 0.04 mg/L [77, 78].
- Turbidity and color may develop in piped systems at iron levels above 0.05-0.1 mg/L [71].
- The presence of iron is disastrous in some industrial wet processing operations. Water used in textile dyeing, beverage and white paper industries should contain less than 0.05 mg/L of iron [79].
- Iron-rich water applied to cultivated fields can lead to low-pH ferric hydroxide-rich soils that may severely damage agricultural productivity [79].
- Iron in the distribution system may promote growth of micro-organisms, accumulation of hydrous iron oxide and bacteria, increases the friction loss and power consumption, requires higher chlorine dosage, depletes dissolved oxygen, reduces the carrying capacity and may eventually clog the distribution pipes [80]
- Sloughing or re-suspension of iron deposits in distribution pipes by high flow causes high turbidities [81].
- Iron can have an effect on human health when it is overdosed in the body. Iron in the body of adults gradually increase for men while for women, iron stores start to increase after menopause. Total iron averages about 3.8 g in the body of men and 2.3 g in women [82].
- High concentration of iron in the body can cause anaemia due to reduction of red blood cell production, thus the amount of oxygen carried in the blood is decreased [83].
- Excessive iron concentration can lead to oxidative stress, tiredness, headaches and pale [84].

2.6 Overview of conventional iron treatment methods

Conventional treatments are widely used methods for iron removal. Conventional methods provide treatment processes in bigger scale, focusing on the communities and population growth. To date, there are several treatment methods for iron removal. The type of treatment method mostly depends on the quality of the raw water, availability of capital and the philosophy of the water company [85]. The summary of the development

of typical conventional methods for iron removal from groundwater is shown in Table 2.3. The methods are aeration, sequestering, ozone, membrane filter, ion exchange, lime softening, biological treatment and reverse osmosis. These methods are applicable in various types of industries including agriculture, tourism, education and water supply.

One of the earliest recorded groundwater treatment method for iron removal was constructed in 1874 in Germany, using aeration and filtration [37]. Until today, aeration or chemical oxidation and rapid sand filtration are the most widely used methods for groundwater treatment. Aeration or oxidation is a process that removes undesirable gases dissolved in water and at the same time converts undesirable substances to a manageable form, such as soluble ferrous (Fe^{2+}) into insoluble ferric (Fe^{3+}) which can be filtered afterwards [86]. Many treatment plant systems employ this process to remove iron. Aeration is generally recommended for ferrous iron with concentration more than 5 mg/L in order to avoid high treatment costs using chemical [87]. Recently, other processes has been used to remove iron by aeration such as chemical oxidation (precipitation and filtration), adsorption (oxidation with oxygen and filtration) and adsorption with chemical oxidation followed by precipitation and filtration [81]. An experiment of the aeration process for iron removal was conducted by Stum and Lee in 1961 [54]. The iron solution was prepared in acidic solution and the pH was adjusted using NaCO_3 . In this experiment, water containing iron was bubbled by introducing oxygen at a pressure of 76 mmHg and 155 mmHg. Iron oxidized and its concentration reduced in 10 minutes with 80% removal efficiency. Stum indicated that the reduction of iron with oxygen leads directly to ferric oxides or hydroxides based on the chemical equation below:

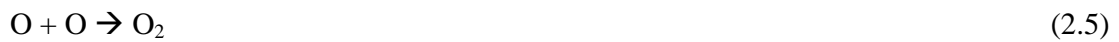


They also mentioned that the process is influenced by the pH. At pH greater than 6, iron reduction was rapid and more rapid at pH 7.24.

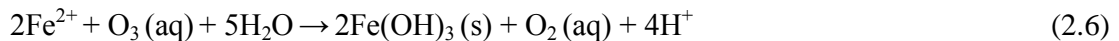
Sequestration is a process where chemicals are added to groundwater in order to control problems caused by iron. These chemicals such as polyphosphates or sodium silicates are added to groundwater at well head or pump intake before the water comes in contact with air or chlorine to ensure that iron stays in a soluble form [88, 89]. However, it is prohibited in some regions in the United States and Canada because it can accelerate eutrophication of surface waters [85]. Iron removal study using sequestering process was conducted by Klueh and Robinson [88]. In this process, polyphosphate (PO_4) solution was

introduced as the sequester agent to remove iron under anoxic condition. It was observed that Polyphosphate can effectively reduce iron from initial concentration of 2 mg/L to 0.1 mg/L in 5 days with 95% filterability. The applied dosage of PO₄ in this process was 1 mg/L with turbidity less than 0.5 NTU at pH 7.

Removal of iron by chemical oxidation using ozone has been investigated by few researchers [90-94]. The ozone process is also known as advance oxidation [95]. Ozone has an odor, most often described as the smell of air after a spring electrical thunderstorm [96]. Ozone is an unbalanced molecule and has potential to divest its third or release oxygen atom through the following reaction [97]:



Iron removal using ozone is similar with aeration where iron is oxidized from the soluble form to insoluble and can be filtered out of the water according to the following reaction:



The use of Ozone in iron treatment was conducted by Niemiski and Evans [92]. A generator was used to produce ozone (O₃) from oxygen (O₂). In this experiment, a sample with iron concentration of 0.4 mg/L was reduced below detection limits in one minute when ozone of 2 mg/L dose was purged into it. Another experiment was conducted by El-Araby using ozone process. Iron concentration of 2.6 mg/L was reduced to 0.1 mg/L resulting to 96% removal efficiency at 3 mg/L ozone dose [94]. The pH of the sample was increased from pH 5 to pH 12. However, El-Araby reported that ozone should not be overdosed to prevent it from dissolving [94] and increase manganese which can create another problem. The oxygen atoms generated by these reactions are effective medications that can remove iron from the oxidation process. Compare to other chemical purifying processes, ozone leaves no environmentally harmful residues [94].

Microfiltration and membrane filtration have been applied for iron removal. Membrane filters are uniformly thin membranes (typically 150 µm) with high porosity (about 80%) and provides high gas and liquid flow per unit area. Semi-permeable membranes have pores in the range of 0.5 nm to 5 µm [98]. Most filter membranes are produced by physical or chemical methods where the pores are formed by chemical

processes. In this process, water containing iron is allowed to pass through special filter media which physically retain the iron present in the water [99]. An experiment was performed to prove the effectiveness of membrane filter by Ellis et al. [27]. Iron concentration of 10 mg/L was reduced using membrane filter with 0.2 μm membrane size. However, in the initial stage, the sample was air bubbled and the pH was increased to 8.1 in order to accelerate the oxidation of iron. The process took 240 minutes to reduce iron below 0.1 mg/L resulting into 99% removal efficiency and final pH of 8.7.

Later development of the treatment method involves the use of zeolite. Zeolite is used as a medium for ion-exchange particularly in small water systems and individual homes. Normal zeolite or natural zeolite consists of three dimensional structure which are silicon, aluminium and oxygen ions [100]. Ion-exchange process involves the exchange of one ion to another in the water. For instance, zeolite exchanges sodium for calcium and magnesium [101]. Van Halem et al. [102], recommended that ion exchange process should be considered only for the removal of iron when the concentration is less than 5 mg/L. In particular, the removal efficiency of iron is between 22-90% using zeolite – clinoptilolite [103]. The use of zeolites in iron removal is capital intensive and requires skilled personnel [81]. Mohammed and Zaid studied the use of natural zeolite as ion exchange for iron removal [104]. Batch study was used to perform Jordan Natural Zeolite (JNZ) as an ion exchange agent. In this process, the zeolite with particle size of 45 μm can reduce iron concentration from 400 mg/L to 112 mg/L with removal efficiency of 72%. The contact time of this process was 150 minutes. The removal process was efficient in acidic solution and the final pH in this experiment was 2. It indicates that zeolite can be used to remove iron in acidic solution with high stability [100]. The problem of this process is that the precipitates can coat and foul the media [25].

Lime softening is often used to reduce the hardness of water and sometimes to enhance clarification prior to filtration. Iron precipitates rapidly, when lime dissolves. When pH is increased to alkaline, it reduces the iron concentration below 0.1 mg/L [105]. Ferrihydrite $\text{Fe}(\text{OH})_3$, goethite (FeOOH) and hematite (Fe_2O_3) was formed under this condition [105]. Iron concentration in groundwater can be reduced by lime softening process using crushed limestone. At high concentration of 1500 mg/L, iron decreased to 0.1 mg/L in 10 weeks using limestone. The size and volume of limestone was 1mm and 785 cm^3 , respectively [105]. In an experiment conducted by Wang et al. [106] using dynamic flow column, the sample was pumped into the column using peristaltic pump at a flowrate of 5 mL/min. The size and volume of the column was 8 mm and $1.4 \times 10^{-3} \text{ m}^3$

respectively. A synthetic groundwater with iron concentration of 50 mg/L was used. At 2 hours retention time, iron decreased below 0.3 mg/L and the final pH was 6.27. However, the use of limestone as permeable reactive barrier for iron remediation can be disadvantageous or show limitations such as slow reaction time and loss in efficiency of the system due to coating of limestone particles with iron precipitates [107].

Biological method for iron removal has been investigated since the early 90s. [60]. This method is based on the presence of particular species of indigenous bacteria in groundwater which are capable of oxidizing and removing iron [108]. Bacteria living in environments where there is no light require an alternative energy source to achieve growth. Iron bacteria that occur naturally in groundwater specifically make use of the small amounts of energy released when oxygen reacts with soluble un-oxidised iron (Fe^{2+}). The bacteria use the energy to assimilate carbon dioxide, achieve biological growth while iron accumulate around bacterial cells [109]. The oxidation reaction of ferrous iron to ferric iron by biological means is similar to that of the physico-chemical reaction [110, 111]. Polystyrene is one of the materials that was used as medium of biological process for iron removal. An experiment was conducted by Katsoyiannis on arsenic and iron removal using polystyrene beds as filter media [112]. The size of polystyrene was 3 mm and the condition of dissolved oxygen (DO) was set up to 2 mg/L. The concentration of iron decreased from 2.8 mg/L to 0.1 mg/L. The use of biological process to remove iron from groundwater is quite effective. However, it is ineffective when groundwater contains hydrogen sulfide, nitrate, cadmium and lead because the microorganisms cannot absorb them [25, 81, 107].

Reverse osmosis (RO) is a treatment process where membranes are used to separate dissolved solutes from water [95]. A membrane is a semi-permeable material that is permeable to some components in the feed stream and impermeable to other components [113]. The feed water to an RO system is pressurized and some water called permeate passes through the membrane [114]. Pawlak et al. [115] investigated the removal of hazardous metal including iron at a concentration of 0.17 mg/L. The treated water indicated that iron was removed below 0.02 mg/L and final pH dropped from 7.33 to 5.99. However, there are two concerns about this method; membrane fouling and membrane concentrate. Membrane fouling comes from foulant accumulations on the membrane surface and this is the major cause of RO system failure [28]. Membrane fouling has several effects, including a decrease in water production because of a gradual decline in flux, an increase in applied pressure required for a constant rate of water

production, a gradual membrane degradation which results in a shorter membrane life, and a decrease in the permeate quality [116].

Table 2.3: Development process of typical conventional method of iron removal from groundwater

Author	Method	Int. Conc.	Final Conc.	Effc. (%)	Final pH	Ret. Time	Remarks
Stumm and Lee, [54]	Aeration	1 mg/L	0.2 mg/L	80 %	7.4	10 min.	PO ₂ 76 and 155 mmHg
Klueh and Robinson, [117]	Sequester process	2 mg/L	0.1 mg/L	95%	7	5 days	PO ₄ (2 mg/L)
Nieminski and Evans, [92]	Ozone	0.4 mg/L	< 0.3 mg/L	> 90%	7-8	1 min.	Ozone (2 mg/L)
El-Araby et al., [94]	Ozone	2.6 mg/L	0.1 mg/L	> 96%	5-12	5 min.	Ozone (3 mg/L)
Ellis et al., [27]	Membrane filter	10 mg/L	0.1 mg/L	99%	8.7	240 min.	Membrane size 0.2µm
Mohammed and Zaid, [104]	Ion exchange	400 mg/L	112 mg/L	72%	2	150 min.	Zeolite size 45µm
Komnitsas et al., [105]	Lime softening	1500 mg/L	0.1 mg/L	99%	8.5	10 week	Limestone (Size, 1 mm, 785 cm ³)
Wang et al., [106]	Lime softening	50 mg/L	> 0.3 mg/L	> 90%	6.27	10 week	Limestone (Size, 8 mm, 1.4 × 10 ⁻³ m ³)
Katsoyiannis and Zouboulis, [60]	Biological process	2.8 mg/L	0.1 mg/L	96%	7.2	90 hours	Polystyrene (3 mm size, DO, 2 mg/L)
Pawlak et al., [115]	Reverse osmosis	0.17 mg/L	< 0.02 mg/L	> 90%	5.99	1 hour	Pressure (350 psi)

2.7 Non-conventional method for iron treatment

Non-conventional methods of iron removal are developed particularly for personal benefits and research. The acceptance of this method has a limit and its application is not in big scale. The process is cost effective, simple, easy and can be done using natural materials from natural environment or surrounding areas such as banana leaf, rice husk and bamboo [65]. Rocks like carbonaceous shale also can be a medium for iron removal [66]. In this section, two types of non-conventional methods are reviewed as follows:

- a) Sulfide precipitation
- b) Electrochemical coagulation

2.7.1 Sulfide precipitation

Iron can be removed by precipitation with H_2S and filtration by forming iron sulfide in aqueous solution [118]. When sulfide was introduced as hydrogen sulfide (H_2S) at pH 8.5, the metal ion combined with aqueous bi-sulfide ion to form precipitates as solid sulfide. [119]. Sufficient sulfide ion can precipitate heavy metals to a safe level of concentration [120]. In acid solution, precipitation is not possible, because sulfide ion concentration (S^{2-}) is insufficient to exceed solubility products of iron sulfide. Sulfide ion concentration can be made available by the addition of sodium acetate solution to allow precipitation of black iron sulfide to occur [121]. In inert atmosphere or absence of oxygen, sulfide reacts with metals in solution to form precipitate that is highly insoluble which can then be disposed [122].

The chemical composition of iron-sulfide is equivalent to pyrrhotite (FeS). However, as compared to other iron sulfide, pyrrhotite was formed at high temperature from 155°C to over 210°C . The crystal formation of pyrrhotite is easily visible from microscope with a size of 1 to 2 mm in diameter [123]. When iron reacts with sulfide, a black FeS is formed and precipitated [124]. The chemical reactions of the process are described as follow:



The reactions produce hydrogen ions which lead to the drop in pH. Thus buffering is necessary. Sodium acetate is one of the buffers that is applied for FeS precipitation based on an equation below [121] :



Hydrogen sulfide are formed by the combination of hydrogen and sulfur. Hydrogen sulfide can also be produced by boiling sulfur at 200°C [125]. This reaction is called self-oxidation and reduction reaction (shortly self-redox reaction). In self-redox reaction, reactant is reduced and oxidized by itself simultaneously. In case of sulfur–water interaction, elemental sulfur is reduced to hydrogen sulfide (H₂S), which dissociates to HS⁻ and S²⁻ in alkaline solution, and the elemental sulfur is also oxidized to sulfuric acid [126]. These chemical reactions are described as follow:



The formation of iron sulfide can occur within redox potential of – 10 to – 50 mV at pH 5.7. This study was conducted by introducing 0.1M sulfide gas into the iron solution [127]. Another study on the formation of iron sulfide was examined by Wilkin and Barnes [128]. At concentration of 5–20 mM of sulfide gas, the gas was introduced into the iron solution. Precipitation of iron sulfide was observed at pH 6–8 at 70°C. According to Peterson et al. [129], removal of iron in sulfide formation can take place at redox potential of around 0 mV to -100 mV under anoxic condition. Butler and Rickard [130] found similar results from the study conducted by Wei and Osseo-Asare [127]. The formation of iron sulfide by H₂S in aqueous solutions occurred at pH 6 but oxidation reduction potential (redox potential) or Eh value should be in the range of –250 mV and above 60°C in the absence of detectable oxygen (O₂). There is a potential for iron to be oxidized at Eh value of -250 mV during the formation of iron sulfide. However, since the condition is highly reducing, sulfide gas will take place due to strong reductant and it can be done in inert atmosphere [131]. The growth of the iron sulfide requires Eh level from –200 to –350 mV at pH 7 [132] as shown in Figure 2.4. Redox potentials as low as –400 mV, can be effective for metal removal process [133].

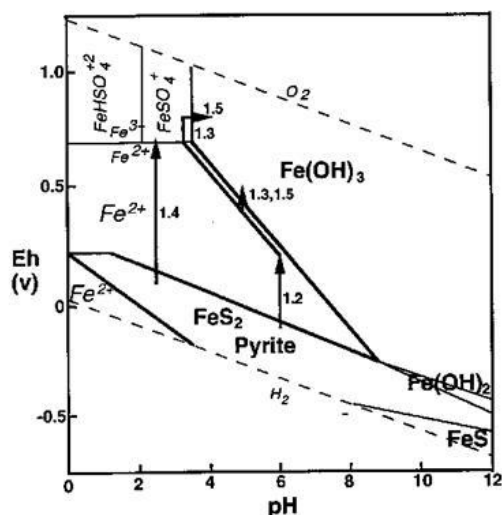


Figure 2.4: Effect of Eh-pH on stability of iron mineral [133]

2.7.1.1 Previous studies on metal treatment process by sulfide precipitation

Studies for metal removal by sulfide precipitation have been conducted by many researchers. Sulfide precipitation can be formed by using either solid (FeS , CaS), aqueous (Na_2S , NaHS , NH_4S) or gaseous sulfide sources (H_2S) [119]. The operating parameters for sulfide precipitation were also evaluated such as pH, temperature, sulfide and metal concentration.

The removal or precipitation of selenium in sulfide form was examined by Geoffroy and Demopoulos [134]. 300 mg/L concentration of selenium (IV) solution was prepared in weakly acidic sulfate solutions at 23°C and pH 1.3. The sulfide concentration was prepared by dissolving sulfur in a volume of deionized water. Then the sulfide solution was added at once in the Se (IV) solution and the mixture was agitated with a magnetic stirrer. The results showed that below pH 7.0, precipitation reaction was complete with less than 0.005 mg/L of soluble residual selenium in the solution after 10 minutes of the process. According to the authors, when pH was increased, the oxidation reduction potential or ORP (Eh) dropped to the value of -110mV. At high pH above 7 and up to 9.5, precipitation of selenium was incomplete.

Pettine et al. [135] also studied the reduction of selenium (IV) by hydrogen sulfide in aqueous solutions. Hydrogen sulfide in the range of 0.08–0.11 M was produced by dissolving sodium sulfide anhydrous ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) crystals in degassed Millipore Q water.

The sulfide gas was added in 1.26 mM selenium solution. The selenium reduction shows the process depends on pH. At pH 4 and 8, a H₂S concentration of 20µm reduced selenium to 1µM.

The precipitation of zinc in sulfide form was examined by Veeken [136]. The precipitation of Zn²⁺ with S²⁻ was studied at room temperature in a continuously stirred tank reactor (CSTR) of 0.5L by size. The solutions of ZnSO₄ containing 800–5800 mg/L of zinc (Zn²⁺) was used and sulfide was supplied by using sodium sulfide (Na₂S) solution. The pH was controlled at 6.5 and S²⁻ concentration in the reactor was controlled at values ranging from 3.2×10⁻¹⁹ to 3.2×10⁻⁴ mg/L. The experiment was conducted in 30 minutes of hydraulic retention time (HRT) before the precipitation of zinc sulfide was analyzed. The result showed that zinc concentration reduced from 5800 mg/L to below 0.03 mg/L in 29 minutes of the HRT and the sulfide concentration dropped from 3.2×10⁻⁴ to 3.2×10⁻¹⁸ mg/L. The ZnS particles was formed and measured while the value of a mean geometric diameter was about 10 µm. The result also indicated that below 3.2×10⁻¹¹ mg/L, sulfide (S²⁻) concentration was insufficient to make complete zinc precipitation while the effluent zinc concentration increased due to the formation of soluble zinc sulfide.

Esposito et al. [137] investigated zinc removal by sulfide precipitation in the form of zinc sulfide (ZnS). A 600 mL continuously stirred tank reactor was used to assess the performance of a zinc sulfide precipitation process using sodium sulfide (Na₂S) solution as sulfide source. At sulfide (S²⁻) concentration of 10⁻¹⁵ M, zinc concentration of 3 g/L was reduced to 0.07 mg/L which was optimal reduction. The mean particle size of the ZnS precipitates at pH 6.3 was 10.2µm.

Similar study was conducted for precipitation of zinc and copper in sulfide formation by Mokone et al. [138]. The experimental work was carried out in laboratory scale by using continuously stirred tank reactor (CSTR) as shown in Figure 2.5. A 500 mg/L concentration of zinc sulfate and copper sulfate solution was used in this experiment for both zinc (Zn²⁺) and copper (Cu²⁺).

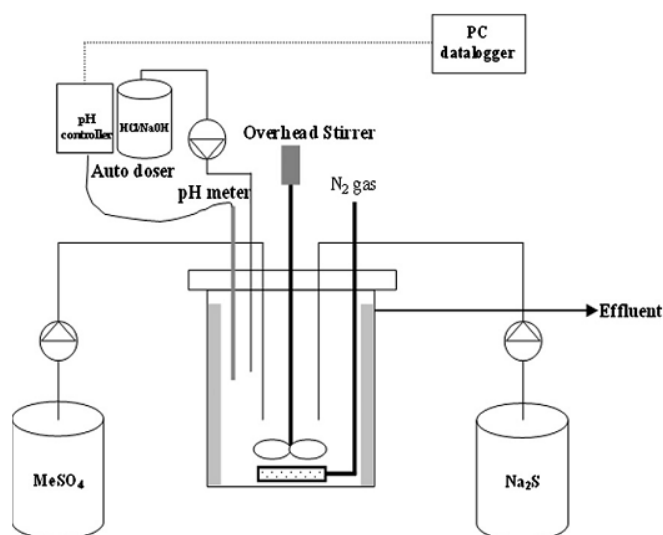


Figure 2.5: Schematic diagram of experimental setup [138]

In the initial stage, the reactor was first filled with 900 mL of Millipore water and the water was stripped of oxygen by bubbling with nitrogen gas (2L/minutes) for 20 minutes. After 20 minutes, the nitrogen gas flow-rate was adjusted to a lower level (0.1L/min) to minimize bubble formation and possible particle flotation. Then the solutions were pumped into the reactor. A 25-mL sample was collected from the effluent stream every 10 minutes over a period of 90 minutes. The results show that at pH 6, removal efficiency of copper and zinc increased to 97% and 93% respectively from initial concentration of 500 mg/L. The authors concluded that effective precipitation depends on pH.

Kim et al. [139] investigated chromium reduction by hydrogen sulfide in aqueous phase. Cr (VI) stock solution was prepared with $K_2Cr_2O_7$ in an amber bottle with degassed water. While sulfide stock solution was prepared by dissolving $Na_2S \cdot 9H_2O$ crystal in degassed water. The result showed that chromium concentration was reduced from 200 μM to 128 μM using 106 μM of sulfide concentration. The total amount of Cr (VI) reduced in the experiment is approximately 72 μM while the ratio of consumed H_2S to reduced Cr (VI) is about 1.5. Similar justification was made that reduction process depends on pH while the process occurred at pH range of 6.5 –10 as shown in Figure 2.6.

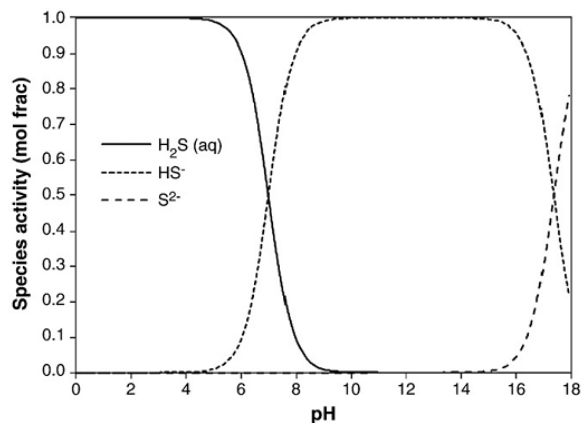


Figure 2.6: pH dependence of sulfide speciation [119]

Tokuda et al. [140] investigated the precipitation of Cu, Zn, Ni and Sn with H₂S. The synthetic solution used in this study was prepared by dissolving CuSO₄·5H₂O, ZnSO₄·7H₂O, NiSO₄·6H₂O and SnCl₂·2H₂O in distilled water and the concentration adjusted to yield 100 mg/L. A 1300 mL volume of wastewater was used in the experiment (Figure 2.7) and the solution pH was maintained at a predetermined value (Cu, Sn: pH 1.5, Zn: pH 4.5, Ni: pH 6.5–7.0) using 0.1 M NaOH. The concentration of H₂S gas varied in the range of 2500–5000 mg/L. During the process both nitrogen (N₂) and hydrogen sulfide (H₂S) gas was purged into the wastewater to maintain the condition of inert atmosphere. The results obtained by purging H₂S/N₂ gas at flow rate of 350 mL/min and 5000 mg/L concentration of hydrogen sulfide indicated reduction of metal during sulfidation process. The removal efficiency was 96.6% for Cu at pH 1.5, 96.0% for Zn at pH 4.5 and 99.4% for Ni at pH 6.5 from 100 mg/L of initial concentration after about 50–100 minutes of the process.

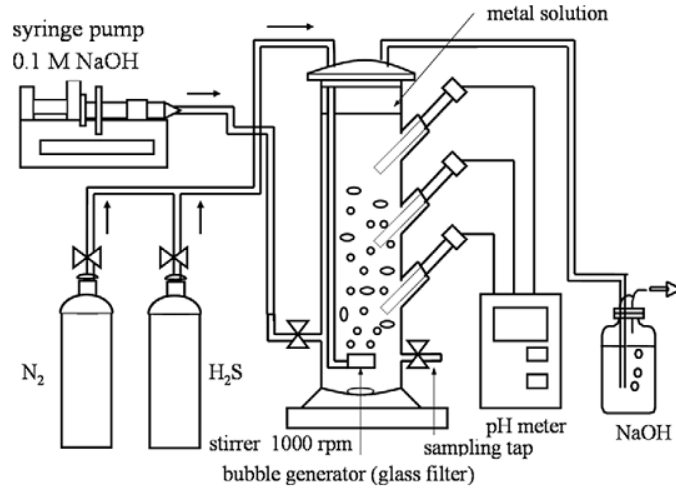


Figure 2.7: Experimental apparatus used in sulfidation treatment [140]

Lewis and Van Hille [141] investigated sulfide precipitation method and its effect on metal sulfide removal. The investigated metals were nickel and cobalt. Their solutions were produced by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. The experiment was conducted in semi-batch column reactor as shown in Figure 2.8.

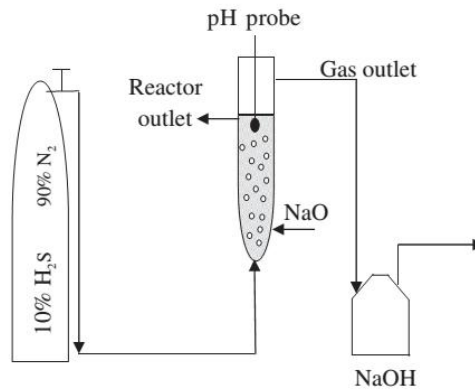


Figure 2.8: Schematic diagram of semi-batch column reactor [141]

The sulfide gas source was 10% of H_2S and 90% N_2 . The N_2 – H_2S mixture was passed through the precipitation reactor with gas distribution to the bottom of the column. The solution contains cobalt (Co^{2+}) and nickel (Ni^{2+}) concentrations of 100 and 200 mg/L respectively. The pH was adjusted to 7.1. During this process, the removal efficiency of both cobalt and nickel was 99.8% and 99.9% at 60 minutes of retention time. The authors reported that during the process at pH 7.1, hydrogen sulfide gas dissolved into the liquid and undergo a deprotonation reaction into equal concentrations of dissolved H_2S and aqueous bisulphide ion HS^- based on this equation:



2.7.2 Electrochemical-coagulation treatment (EC)

Electrochemical-coagulation (EC) is another alternative method for iron removal from ground water. This is a process of destabilizing suspended, emulsified or dissolved contaminants in aqueous medium by the introduction of electric current [142]. In results, it flocculates the contaminants and can subsequently be removed by sedimentation or flotation. EC treatment has been found to be a promising process for solid liquid separation with simple equipment [143]. It also requires comparatively less treatment time, effective removal efficiency, low cost and the possibility of complete automation with simplified operation [25, 144]. There are many benefits of applying electrochemical-coagulation techniques which include environmental compatibility, versatility, energy efficiency, safety, selectivity, amenable to automation, and cost effectiveness [145]. The advantages of EC technology include [146] :

- The treated water by EC is palatable, clear, colorless and odorless water.
- Sludge formed by EC tends to be settled and easy to de-water, because it is composed of mainly metallic oxides or hydroxides.
- Formations of flocs by EC are similar to chemical floc and therefore can be separated faster by filtration.
- Produces less total dissolved solids (TDS) compared with chemical treatments. If the water is reused, the low TDS level contributes to a lower water recovery cost.
- EC process can remove the smallest colloidal particles, because the applied electric field sets them in fast motion, thereby facilitating the coagulation.
- The EC process avoids the use of chemicals.
- The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
- The electrolytic processes in the EC cell are controlled electrically without moving parts. Thus it requires less maintenance.
- The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

EC process does not require the addition of chemicals or produce secondary pollutants [147]. It only requires a sacrificial metal anode (mostly iron and aluminium) transformed into metal ions by direct electric current and simultaneously evolves hydrogen at the cathode in order to precipitate iron and other metal [148]. In an EC

process, the coagulating ions are produced ‘in situ’ and involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the ‘sacrificial electrode’, (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs [149]. Coagulant species aggregate the suspended particles and precipitate or adsorb dissolved contaminants [150]. The pollutants are floated to the top of the solution during reaction by hydrogen bubbles released from the cathode. [148]. The mechanisms of operation in EC may involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption, precipitation and flotation [151]. In this process, variables or parameters can influence the efficiency of the EC treatment. These variables are pH, current density or electrical potential, contact time, concentration, electrode gap, surface area and electrode type. In order to conduct electrochemical-coagulation process in the laboratory, there are few basic components needed. The components required for the experiments include; 1) electrical power supply, 2) variable resistance, 3) Cathode electrode, 4) Anode electrode, 5) reactor or beaker, 6) magnetic stir bar, 7) magnetic stir controller, 8) ammeter as shown in Figure 2.9.

EC treatment has been used in treating fluoride [152], arsenic [151], copper, manganese, zinc [153], boron [154], cadmium [144], chromium [147], mercury [155], nickel, silver [156], strontium [157], lead [158], diazinon [159], nitrates [160] and natural organic matter (NOM) [161]. This treatment process has increasingly been used in South America and Europe for treating industrial wastewater containing metals [146]. However, the process is still not fully utilized for removal of metals in groundwater. EC is expected to be economically more feasible than conventional chemical oxidation [35].

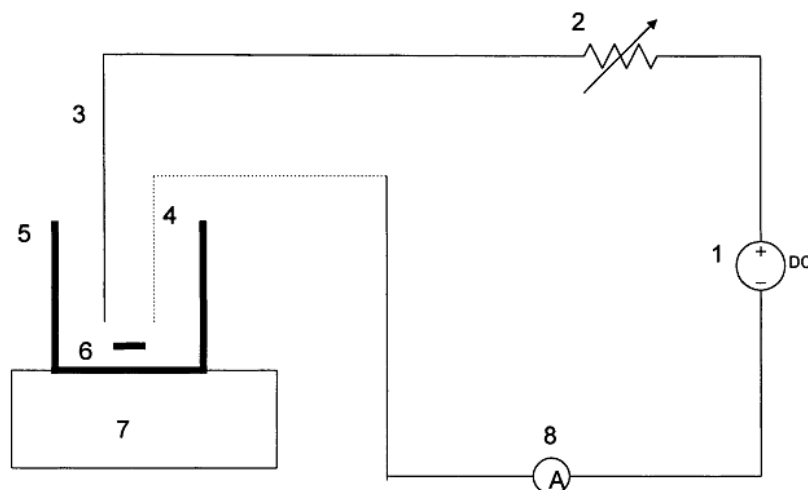


Figure 2.9: Schematic diagram of the electrochemical experiment [35]

2.7.2.1 Mechanism of EC process

Electrochemical-coagulation accompanied by electro-floatation is an emerging electrochemical water treatment technology. In these treatment mechanisms, the process involves electrochemical-coagulation/flotation. There are electrode oxidation, gas bubble generation, flotation and sedimentation of flocs formed [142]. In EC process, an applied potential generates the coagulant species in situ as the sacrificial metal anode (aluminium or iron) dissolves, simultaneously hydrogen ions evolves at the cathode [162]. Coagulant process is responsible for particle aggregation as well as precipitates suspended particles and simultaneously adsorbs the dissolved contaminants. Hydrogen and oxygen bubble formation during water electrolysis collides with air bubbles and float the pollutant particles as shown in Figure 2.10 [163]. Selection of electrode material depends on various criteria such as cost, low oxidation potential and inertness towards the system under consideration.

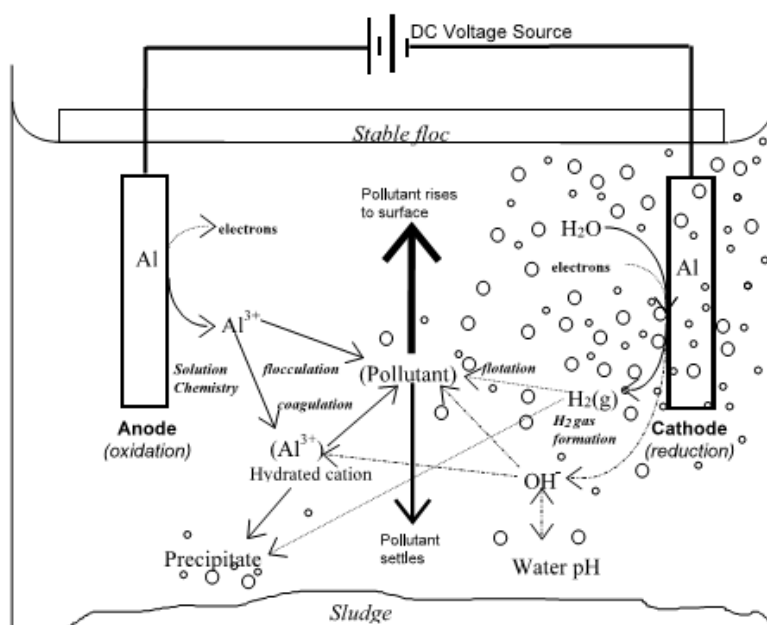


Figure 2.10: Interactions occurring within an EC reactor [163]

2.7.2.2 Electrode

Electrode is a pole of metal which undergoes redox reaction during electrolysis. The electrode materials can be of different types such as aluminium [152, 153, 157], iron [143], magnesium, zinc, alloy [164], titanium [165], carbon felt [166], graphite felt [167]

and platinum [168]. Most of the electrodes used in electrochemical process were either in the shape of a plate or bar.

Studies have shown that, aluminium plates used as electrolyte cell can generate high oxidation potential compared to other metals [146]. The use of aluminium as an electrode is due to high coagulation efficiency (Al^{3+}) ions [169]. It has been reported to be very effective and a successful process for metal removal [25]. The electrochemical reactions which occur at the electrode surface during electrolysis are summarized as follows [147]:



In general, the Al^{3+} and OH^- ions generated from both anode and cathode will form various monomeric species such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_4^-$ and polymeric species such as $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$, which transform finally into $\text{Al}(\text{OH})_{3(\text{s})}$, according to the complex precipitation kinetics “aluminium hydroxide” $\text{Al}(\text{OH})_3$ [170]. This is because during electrolysis, the applied current force the OH^- ions move towards the cathode and combine with hydroxide ions according to the chemical reaction below [171]:



Formation of amorphous $\text{Al}(\text{OH})_{3(\text{s})}$ occurs as “sweep flocs” which have large surface areas [148]. These flocs are active in adsorption of soluble organic compounds and trapped colloidal particles are easily separated from aqueous medium by sedimentation or H_2 flotation [162]. These flocs polymerizes as $n\text{Al}(\text{OH})_3 \rightarrow \text{Al}_n(\text{OH})_{3n}$ [25].

In addition, the electrolysis of water also occurs at both anode and cathode. The chemical reaction is represented as follows:



The performance of EC process is also influenced by the arrangement of the electrode. These arrangements can be done in a few ways such as bipolar, monopolar and dipolar (Figure 2.11, 2.12 and 2.13) respectively. In a related study, it was observed that

bipolar electrode pattern requires more contact time than monopolar electrode pattern [172]. However, the remediation process in bipolar mode has a limitation due to high cost and large consumption of electrode [149].

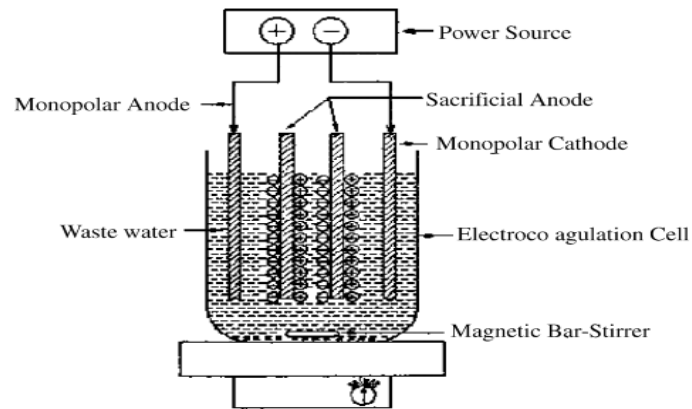


Figure 2.11: Bench-scale EC reactor with bipolar electrodes [173]

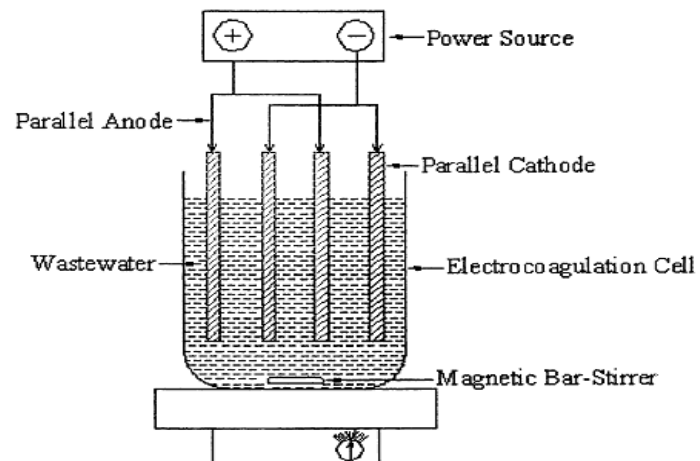


Figure 2.12: Bench-scale EC reactor with monopolar electrodes [173]

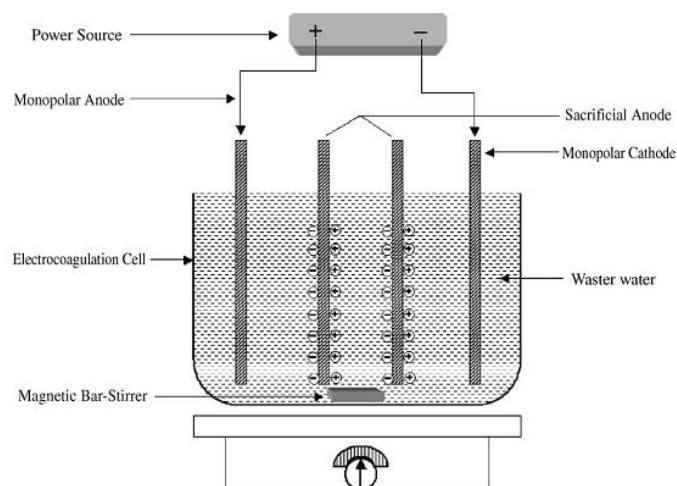


Figure 2.13: Bench-scale EC reactor with dipolar electrodes [174]

As shown in Figure 2.12, the monopolar mode is an arrangement where each pair of ‘sacrificial electrodes’ is internally connected with each other and no interconnections with the outer electrodes. The ‘sacrificial electrodes’ are conductive metal plates used in EC process [149]. The ‘sacrificial anode’ functions to lower the dissolution potential of the anode and minimizes the reductive deposition of elemental metals on the cathode [146]. The sacrificial anode and the cathode may be made up from the same or different materials. The arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections [174]. The parallel arrangement basically consists of pairs of conductive metal plates placed in between two parallel electrodes and a DC power supply [175]. The experimental set-up requires a resistance box to regulate the flow of current and a multimeter to read the current values [142].

2.7.2.3 Electrical potential (Applied voltage and current density)

Among the various operating variables, the applied voltage and current density from power supply are important factor which strongly influences the performance of electrochemical-coagulation [162]. It also affect the systems response time and strongly influence the dominant pollutant separation mode [176]. These parameters are used to control the anode dissolution speed and to form the hydrogen ions [177]. The power supply generates voltage and current to the electrode, thus the electrolysis process of metal is initiated. The supply of electrical potential of the EC system determines the amount of ions (Al^{3+} or Fe^{2+}) released from the electrodes [155]. For instance,

electrochemical equivalent mass for aluminium is 335.6 mg/(Ah) while for iron, the value is 1041 mg/(Ah) [175]. At high electrical potential, it is expected to generate large amounts of ions (aluminium or iron), where it will trap more pollutant and enhance removal efficiency [178]. It also increases the production rate of coagulant and the amount of metal hydroxide available in solution to form complexes and precipitate ions. A large electrical potential means a small electrochemical-coagulation unit [175]. However, when larger electrical potential is used, there is a high chance of wasting electrical energy in heating up the water [179]. The important part is, when large current density is used, current efficiency decreases [180].

2.7.2.4 Previous electrochemical-coagulation studies using aluminium electrodes

Various studies have been conducted with electrochemical-coagulation process using aluminium electrode. The studies show that the process was done with different normal operating parameters such as pH, surface area, and electrical potential. However, the continuing studies provided more information on operating parameters in order to improve the process. The remediation of various metals or pollutant using EC process also provided different removal efficiency and can be compared.

Gomes et al. [181] investigated arsenic removal using aluminium electrodes in EC treatment. The experiment was conducted using 200 mL arsenic solution and 0.8 g sodium chloride was added to prevent any drop in conductivity. The electrodes were 30 mm spaced from each other with 3–30 mA/cm² applied current density. The pH was varied from 4–10. It was found that arsenic was removed at pH 6 and applied current density of 30 mA/cm² after 30 minutes treatment time. The removal efficiency was 97.5% from initial concentration of 13.4 mg/L.

Ghosh et al. [182] studied iron removal from tap water by EC technique using aluminium electrode. Operating parameters were varied consisting of current density and inter-electrode spacing while pH, conductivity and salt concentration were kept constant. The study observed that increase in current resulted in an increase in removal efficiency at the lowest inter-electrode distance. Iron was removed after 35 minutes treatment time with a removal efficiency of 99.2% from an initial iron concentration of 25 mg/L.

Boron removal from synthetic wastewater by electrocoagulation (EC) using aluminium electrodes was studied by Sayiner et al. [143]. Aluminium electrodes were set

at electrode distance of 3 mm in laboratory scale reactor. Boron concentration was varied in 1000, 500, 250 and 100 mg/L. The current density values were taken as 10, 20 and 30 mA/cm². 10 mL of 1% sodium chloride (NaCl) solution was added to the solution to improve the conductivity. The authors reported that chloride ions will activate the metal dissolution. The results show that EC process for boron removal strongly depends on current density, initial concentrations, and time. When current density was increase to 30 mA/cm² at 60 minutes of the process, about 90% removal efficiency was observed.

Remediation of mercury (II) by electro-coagulation using aluminium electrodes was initially conducted using synthetic solutions of concentration 2×10^{-5} M. This study was conducted by Nanseu-Njiki et al. [155]. The effects of distance between electrodes, current density, charge loading and initial pH on the removal efficiency were investigated. The removal efficiency of mercury (II) was above 99.9% at the distance of 3 cm between the electrodes. The current density ranged from 2.5 to 3.125 A dm⁻². By varying the pH of the mercury (II) solutions from 3 to 7, it showed that removal efficiency remained higher than 99%. The study was further applied in river water and the results obtained showed that the presence of organic matter did not influence the efficiency of the treatment while the efficiency of mercury (II) removal was 99.85% after 25 minutes of the process using aluminium electrodes.

The removal of chromium Cr(IV) by electrochemical-coagulation process with aluminium electrodes was investigated by Mouedhen et al. [147]. The parameters investigated in this study include initial pH, current density and supporting electrolyte. The 3 mm thickness electrodes were cut yielding a total surface area of 54 cm². The electrodes were then connected with DC power supply. The range of current and voltage was 0–3A and 0–60 V. The electrodes were kept constant at electrode gap of 4 cm. Chromium was completely removed in acidic condition at pH 2 after 45 minutes of the process. The effect of current density showed that chromium reduced to undetected levels from initial concentration of 180 mg/L in 40 minutes when current density was increased to 2 A/dm². When 0.5 g/L sodium chloride (NaCl) was added to the solution containing 45 mg/L of Cr (IV), chromium was removed within 15 minutes.

Murthy and Parmar [157] evaluated the removal of strontium from synthetic wastewater by EC treatment. The operating parameters investigated include retention time, current density, electrolyte added, pH, distance between electrode, temperature and initial concentration of strontium. Results showed that the optimum operating variables

are 50 minutes of process time, 8 mA/cm² current density, solution pH 5 and 1 mL sodium chloride (NaCl) to increase the conductivity. However, the removal efficiency was found to be 77% using aluminium electrodes at 10 mg/L of initial concentration. The authors reported that removal process can be achieved up to 99% efficiency using stainless steel electrodes.

A study on cobalt (Co²⁺) removal by EC process with aluminium electrode was conducted [169]. Cobalt solution was used to study the removal efficiency by EC process using aluminium electrodes. The effect of several parameters such as pH, current density, time, conductivity and initial concentration on the performance of EC process was investigated. The results indicated that Co²⁺ removal efficiency exceeded 99% from 100 mg/L initial concentration at pH 8.0 after 15 minutes of the process. The effect of current density shows that at 6.25 mA/cm², the removal efficiency can reach 86% and cobalt was completely removed after 30 minutes of the process. The authors reported that the solution conductivity has no significant effect on removal efficiency of cobalt. The conductivity of cobalt solution was increased from 2.5 to 6.5 µS/cm by adding sodium chloride.

The performance of an EC system with aluminium electrodes for removing heavy metal ions like Zinc (Zn²⁺), Copper (Cu²⁺), Nickel (Ni²⁺) and Silver (Ag⁺) on laboratory scale was studied systematically by Heidmann and Calmano [156]. The study was conducted in batch experiment using 2000 mL beaker and four electrodes were installed vertically at fixed spaced of 5 mm in order to minimize the IR-drop. Parameters such as initial metal concentration, numbers of metals present, charge loading and current density and their influence on the EC process was investigated. At initial concentrations of 250 mg/L, zinc and copper was completely removed after 20 minutes of the process. While nickel took only 15 minutes to decrease completely. Silver took higher time rate. At 50 mg/L of initial concentration, only 30 mg/L was reduced and the corresponding residual concentration was 20 mg/L after 50 minutes of the process. The current density at 3.3 and 33A/m² indicates that zinc, nickel and copper were highly removed at higher rate compared to silver. The authors concluded that removal rates for Zn, Cu, Ni and Ag were independent of their initial concentration.

Tezcan et al. [183] studied fluoride removal using EC treatment with a unique design. A rotating impeller aluminium was employed which is connected for fluoride removal as shown in Figure 2.14. Various operating parameters such as the current density (in the

range of $0.5\text{--}2\text{ mA/cm}^2$), the duration of electrolysis, the supporting electrolyte dosage (in the range of $0.01\text{--}0.03\text{ M Na}_2\text{SO}_4$) and the initial pH (in the range of $4\text{--}8$) was examined to achieve optimal performance of the process. From fluoride initial concentration of 5 mg/L , the removal efficiency of fluoride was found to be 94.2% in 30 minutes corresponding to residual concentration of 0.29 mg/L .

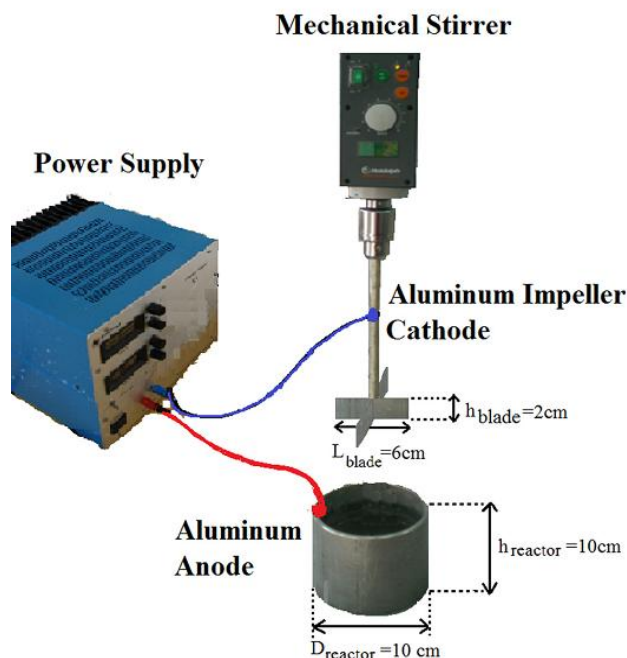


Figure 2.14: Experimental set-up for fluoride removal adopted [183]

The fluoride concentration was reduced from the initial value of 5.0 to 0.12 mg/L , with a removal efficiency of 97.6% after 30 min treatment at current density of 2 mA/cm^2 , pH 6 and $0.01\text{ M Na}_2\text{SO}_4$ as electrolyte support. The result also showed that the required EC time to reach the WHO recommended fluoride limit of 1.2 mg/L at 0.5 mA/cm^2 was 5 minutes .

CHAPTER 3

MATERIALS AND METHODS

3.1 Water Quality Study

In the initial stage of this research, the locations with tube wells that contain water with high iron concentration were selected. The locations were identified based on previous researches that have been conducted [66] and the theory of groundwater which usually contains iron [184]. The wells are located at Universiti Teknologi PETRONAS (UTP) monitoring well in Perak and groundwater treatment plants in Kelantan. In UTP, the monitoring wells are located behind the Academic Complex of Civil Engineering Department as shown in Figure 3.1. The well's size was 7 inches in diameter and 10 meters deep.

Figure 3.2 shows the location of groundwater treatment plants of Kampung Chicha, Tanjung Mas and Kampung Puteh, Kelantan. The Groundwater treatment plant of Kg. Chicha is located in Kubang Kerian district Kelantan at longitude 100°57'54.36"E and latitude 4°22'52.80"N. The plant has been in operation since 2002, with raw water supply from 34 wells. The depth of the wells varies from 16 meters to 110 meters. The wells are divided into Zone 1, 2, 3, and 4 of groundwater production area with yield of 1285 m³/hr, 568 m³/hr, 335 m³/hr and 327.5 m³/hr, respectively. The total production capacity of Kg. Chicha treatment plant is 80 million liter per day (MLD).

The Groundwater Treatment Plant in Kg. Puteh is located in Kota Bharu district, Kelantan at longitude 102°14'30.23"E and latitude 6°06'47.85"N. Its operation started in 2006 and contains 28 wells. Twenty wells were drilled inside the plant area while 8 wells were drilled outside the plant area. The size of wells for shallow aquifer is 6 inches in diameter with production of 28 m³/hr – 148 m³/hr per well. The size and

depth of well is 8 inches in diameter with yield of 230 m³/hr per well. The plant can produce up to 45 million liter per day (MLD).

Tanjung Mas groundwater treatment plant is located in Pengkalan Chepa at longitude 102°15'55.71''E and latitude 6°08'18.49''N and it is the oldest groundwater treatment plant in Kelantan. It started its operation in 1985 and have 8 wells with depths ranging from 32 to 127 m and a total production rate of about 9-10 million liter per day (MLD).

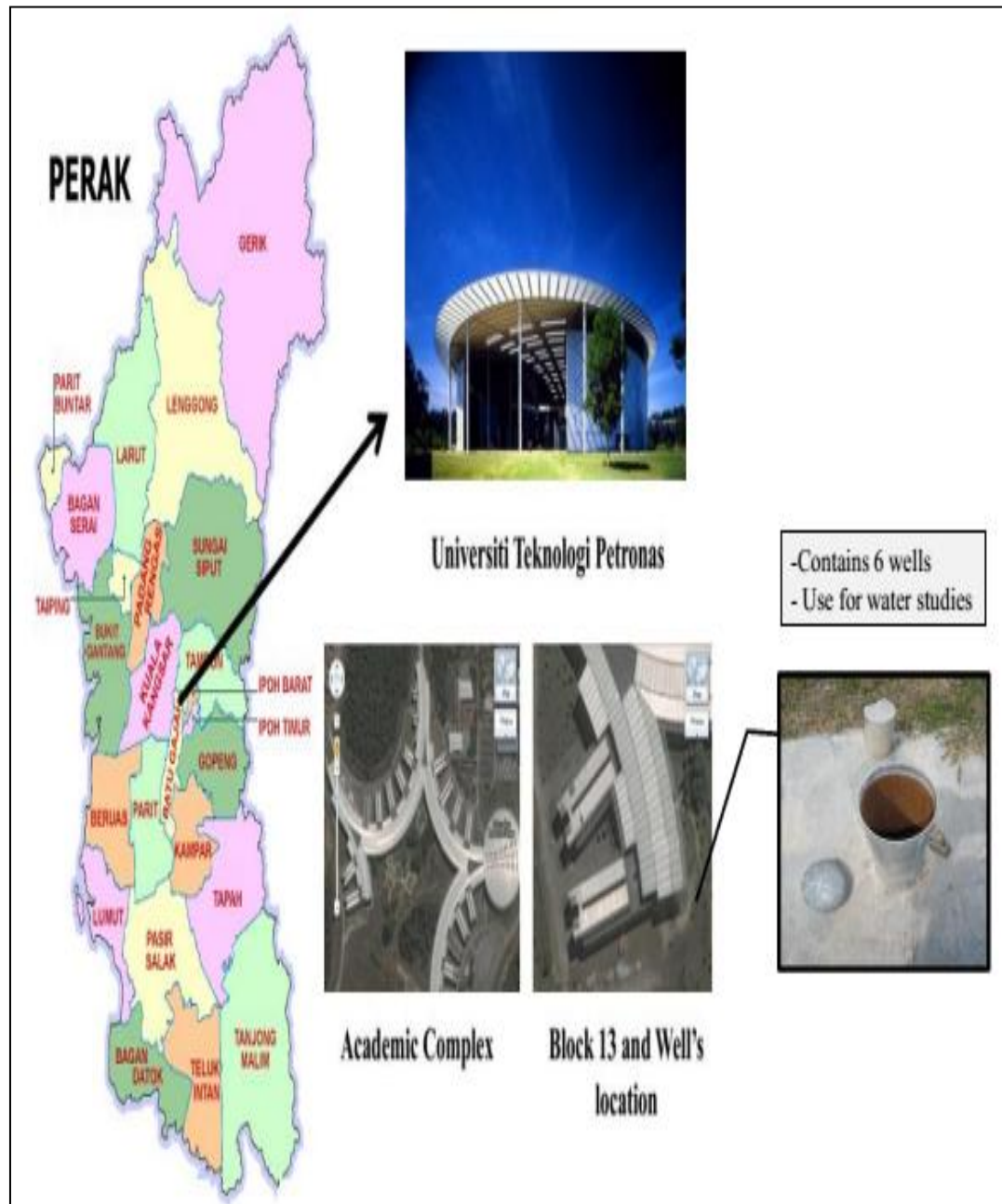


Figure 3.1: Location of Universiti Teknologi PETRONAS in Perak

3.1.1 Groundwater Sampling and Data collection

Syarikat Air Kelantan Sdn. Bhd (SAKSB) has provided the data of iron concentration in groundwater from the wells. The management of SAKSB approved the collection of groundwater sample from the wells at the treatment plant in Kelantan. The samples were collected from Groundwater Treatment Plant located at Kg. Puteh, Kg. Chicha and Tanjung Mas in Kelantan at once.

At the Kg. Chicha plant, two samples were collected from their laboratory. The raw water samples were collected directly from the water tap connected to the wells while at Kg. Puteh and Tanjung Mas treatment plants, two samples of different wells from each plant were collected respectively from a monitoring well connected to a tap. The water was discharged for few minutes before sampling (Figure 3.3). This was to ensure that the collected water samples were from the ground of the wells. All samples were stored in 5 liter plastic container and preserved with nitric acid at pH 2 according to preservation method [185]. A few parameters (pH, Eh, conductivity, turbidity, total dissolved solids (TDS) and total iron) were measured in-situ at a laboratory plant.



Figure 3.3: Groundwater from two wells discharged before sampling

For UTP monitoring well samples, (Figure 3.4a), the groundwater was collected five times using water sampler (Figure 3.4b). The water sampler is a cylinder container with a cap at its top and bottom. The water sampler was submerged into the well beneath the water surface for few minutes. Once the cylinder is full, a hammer is released through the string to knock the top of the lid and close the cap at the bottom. The samples were placed in a container and sealed tightly to avoid precipitation of iron. The samples were brought

to the laboratory and filtered using 45 mm diameter filter paper to remove the insoluble particles. The iron content was analyzed immediately and simultaneously preserved with nitric acid.



Figure 3.4a: UTP monitoring well



Figure 3.4b: Water sampler

3.1.2 Analytical Method

The groundwater samples were characterized using different analytical instruments. Initially, the samples were filtered using 25 mm paradisc syringe filtration unit with 0.45 μm filter paper before characterization. The filtered samples were placed in a beaker to measure physical water quality such as pH, oxidation redox potential (ORP/Eh), dissolved oxygen (DO), turbidity, conductivity, total dissolved solid (TDS) and color.

The pH was measured using a pH meter (Hatch sension4) and another meter was used to measure Eh (Hanna H98121). One Combo meter purchased from Irma Canguie Sdn. Bhd. (Hanna HI-98130) was used to analyse both conductivity and total dissolved solid (TDS). These meters were immersed into the beaker containing the groundwater samples and the corresponding data recorded.

Dissolved oxygen (DO) meter (YSI 5000-230V) was used to measure the amount of free oxygen in the sample. The DO meter was first calibrated by dipping the DO probe into 300 mL DO glass bottle filled with distilled water. The DO probe was subsequently dipped into the groundwater samples to measure the oxygen content.

The turbidity of the groundwater samples were measured using (Hatch 2100P) turbid meter.

The chemical properties of the groundwater samples was characterized using Spectrophotometric method (atomic absorption spectrophotometer (AA-6800) purchased by Shimadzu. Color, total iron (Fe^{2+}), calcium (Ca^{2+}) and magnesium (Mg^{2+}) was measured using a spectrophotometer. 10 mL of the filtered samples were placed into the cuvet. To measure the color of the water, two cuvetts (cubic cell) were needed (one for blank and the other for real sample). This test was conducted using Platinum-Cobalt method [186].

The spectrophotometric method was used to measure total iron in the sample. Specifically, this method is called ferrover or phenanthroline method adapted from standard method [187]. In this experiment, two cuvetts (cubic cell) were needed (for blank and real sample). These cuvetts were filled up with 10 mL sample. The Blank was used to zero the instrument followed by the second cuvet. Ferrover reagent was added to the real sample in the second cuvet and swirled. After three minutes, the total iron concentration in the sample was analyzed.

For calcium (Ca^{2+}) and magnesium (Mg^{2+}), the concentration was characterized with a spectrophotometer (DR 2800) using standard method (Calmagite Colorimetric method). From this experiment, the concentration of calcium and magnesium was used to determine the hardness of the sample. Four reagents were used to run this experiment which include alkali solution of calcium and magnesium test, calcium and magnesium indicator solution, Ethylenediaminetetraacetic acid (EDTA) solution and ethylene glycol tetra acetic acid (EGTA) solution. The hardness level of the sample can be calculated based on concentration of calcium and magnesium (see Appendix A) according to the equation [188]:

$$\text{Hardness, as CaCO}_3\left(\frac{\text{mg}}{\text{L}}\right)=2.497\left[\text{Ca},\frac{\text{mg}}{\text{L}}\right]+4.118\left[\text{Mg},\frac{\text{mg}}{\text{L}}\right] \quad (3.1)$$

The aluminium concentration was characterized with a spectrophotometer using the Standard Methods for the Examination of Water and Wastewater [189]. For this analysis, three reagents were used which are Aluminium Reagent Powder Pillow (AluVer 3), Ascorbic Acid Powder Pillow and Bleaching 3 Reagent Powder Pillow. These reagents are manufactured by Hach (22420-00) and purchased by Arachem Sdn. Bhd.

Another method to characterize the action or metal content of the sample was using Atomic Absorption Spectrophotometer AAS (AA-6800) as shown in Figure 3.5. Sodium (Na^+) and potassium (K^+) concentration was characterized using this method. To run this

experiment, solution of sodium and potassium (Merck 1000 ppm) was prepared and diluted at a range of 0.05, 0.1 and 0.15 mg/L while distilled water was used as blank. The samples were diluted at a ratio of 1:10 to get an accurate result within range.



Figure 3.5: Atomic Absorption Spectrophotometer (AAS, AA-6800)

For anion content, bicarbonate (HCO_3^-) was characterized using titration method. 250 mL sample was titrated with 0.02 normality (N) of sulfuric acid (H_2SO_4) until the pH reduced below 4.5. The readings were then plotted in a graph as pH vs mL of titrant. The intercept line at pH 4.5 and mL titrant is calculated as follow:

$$\text{Bicarbonate } \left(\frac{\text{Mg}}{\text{L}} \right) = \frac{\text{ml titrant} \times \text{normality of acid} \times 50000}{\text{ml sample}} \quad (3.2)$$

The total alkalinity was also characterized using titration method. In this measurement, 100 mL sample was placed into 250 mL conical flask. 0.1 normality (N) of hydrochloric acid (HCl) was placed into a burette. Two drops of phenolphthalein solution was introduced into the flask containing the sample followed by 2 drops of methyl orange solution and color change was observed. HCl was added into the flask and simultaneously swirled until the sample turns red. The amount of titrant from burette was recorded. The reading was calculated based on the equation below [190]:

$$\text{Total alkalinity, as CaCO}_3 \left(\frac{\text{mg}}{\text{L}} \right) = \frac{\text{ml titrant} \times \text{normality of acid} \times 50000}{\text{ml sample}} \quad (3.3)$$

Chloride (Cl^-), sulphate (SO_4^{2+}) and nitrate (NO_3^-) was characterized using ion chromatography (Metrohm-318) as shown in Figure 3.6. In this process, the ions and polar molecules allows the separation based on their charge [191]. Similar with AAS, the standard solutions for the analyzed anions was prepared. Deionized water was used as blank. The readings of the sample were recorded.



Figure 3.6: Ion Chromatography

Total sulfide (S^{2-}) was characterized using a spectrophotometer. Total sulfide include dissolved hydrogen sulfide (H_2S) and hydro sulfide (HS^-) [192]. In this experiment, the total sulfide was characterized by applying Methylene Blue Method [185]. Two reagents were used to operate this method. The sample was placed into the cuvet and 0.5 mL sulfide reagent 1 was added and swirled, followed by 0.5 mL of reagent 2. The sample was expected to turn blue if sulphide was present. The summary of analytical method of the groundwater are shown in Table 3.1 [185].

Table 3.1: Groundwater quality analysis methods

Parameters	Methods
pH	Electrometric
Turbidity	Electrometric
Conductivity	Electrometric
Color	Spectrophotometric
Dissolved Oxygen	Electrometric
TDS	Electrometric
Alkalinity	Titrimetric
Hardness	Spectrophotometric
Calcium (Ca^{2+})	Spectrophotometric, Calmagite Colorimetric Method
Iron (Fe^{2+})	Spectrophotometric, Ferrover Method
Magnesium (Mg^{2+})	Spectrophotometric, Calmagite Colorimetric Method

Sodium (Na ⁺)	Atomic absorption spectrophotometer
Aluminium (Al ³⁺)	Spectrophotometric, Aluminon Method
Sulphate (SO ₄ ²⁻)	Ion chromatography
Chloride (Cl ⁻)	Ion chromatography
Sulfide (S ²⁻)	Spectrophotometric, Methylene Blue Method
Nitrate (NO ₃ ⁻)	Ion chromatography

The calculated cation and anion in the samples are presented in a bar diagram. The bar diagram is displayed in rectangular form divided by two rows with upper row as cation and lower row as anion. The concentrations for both cation and anion are in cumulative. Bar diagram shows the relative concentrations of the major cations and anions. The upper bar shows cations (Ca²⁺, Mg²⁺, and Na⁺) while the lower bar shows anions (HCO₃⁻, Cl⁻ and SO₄²⁻). This is called ion balance. The effect of ion balance can be shown by calculating the percentage of error which should not be less than 10% between total cation and anion (Appendix A) [86]. The total concentrations of calcium, magnesium, potassium, sulphate, bicarbonate and chloride was converted from milligram per liter (mg/L) to milliequivalent per liter (meq/L) and plotted to bar diagram. A bar diagram shows a comparison of cation and anion concentrations. The plotted results in a bar diagram for the analysis of ion contents in samples can show their water type.

3.2 Procedures for proposed methods

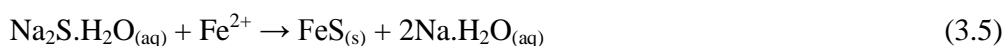
Laboratory experiments were carried out by applying two methods of treatment namely sulfide precipitation and electrochemical method. The purposes of these experiments were to determine the optimum dosage, optimum contact time and optimum pH for iron removal by these methods. Initially the experiment was conducted using synthetic iron solution (Merck 1000 ppm). The 1000 mg/L iron solution was diluted to reach required concentration such as 1 mg/L by using the following equation [193]:

$$M_1V_1 = M_2V_2 \quad (3.4)$$

The calculation of dilution is attached in Appendix A. Subsequently, real groundwater was used to validate the process.

3.3 Treatment by Sulfide Precipitation

A preliminary study was conducted using a synthetic iron solution and H₂S gas. These experiments were conducted in order to determine the optimum pH and contact time of iron removal by sulfide precipitation. An iron solution of 1 mg/L was prepared according to Eaton [194]. Two flasks (A and B) was placed and capped with rubber stopper. Flask A contains native sulfur with water while Flask B contains an iron solution. Sulfur was used because it is readily available especially in hardware shop. Additionally, the use of sodium sulfide creates another problem. The sodium content increases which can retard the precipitation rate of iron sulfide. This problem is explained by the chemical formula below:



In Flask A, 30 gram native sulfur was used and placed in a conical flask containing 350 mL of water while 250 mL iron solution containing 1 mg/L iron concentration was place in conical Flask B. The concentration of producing sulfide gas was calculated (Appendix A). The Flasks were mounted with rubber stopper attached with steel rods connected with a plastic tube. At Flask A, the steel rod was connected with tube and valve and connected again to the regulator of nitrogen cylinder gas. Both flasks were purged with nitrogen to remove oxygen for 30 minutes as shown in Figure 3.7. At the end of the purging process, the valve at Flask A was closed. The Flask B then was purged with hydrogen sulfide. Concurrently, the solution was agitated at 60 rpm. Hydrogen sulfide (H₂S) was prepared by boiling the native sulfur in water at 200°C according to Tsuchiya [126].

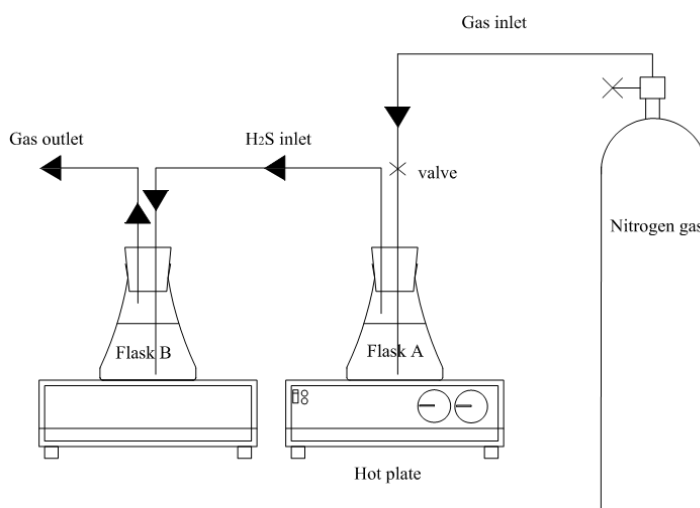


Figure 3.7: Arrangement of experiment on anaerobic treatment of iron
(Flask A for boiling sulfur and Flask B for sample)

3.3.1 pH Optimization

Sulfide precipitation method was conducted by varying the pH from 2 to 9. The pH was adjusted using sodium hydroxide (NaOH) to a specified pH level. Initially, the experiment was conducted using a jar test to obtain the optimum pH. The pH of the synthetic iron solution was regulated while H_2S was added to the flask as earlier mentioned in the sulfide precipitation method during the experiment. The experiments were repeated with different pH. The concentration of total iron was analyzed at one hour interval for six hours to determine the residual iron concentration using phenanthroline method. The results were plotted and the optimum pH was determined.

3.3.2 Contact time Optimization

A similar procedure as pH optimization was used for contact time optimization. In this experiment, 250 mL of synthetic iron solution containing 1 mg/L iron concentration was placed in the conical flask and the pH was adjusted to the optimum. The solution was purged with nitrogen to remove oxygen for 30 minutes followed by H_2S as shown in Figure 3.5. The concentration of total iron in the sample (Flask B) was analyzed at every 30 minutes interval to determine the effect of contact time using phenanthroline method. The experiment was conducted until the residual iron concentration was below drinking water standard of 0.3 mg/L [20].

3.3.3 Iron removal from groundwater by sulfide precipitation

Experiment on iron removal from groundwater using sulfide precipitation method was conducted at room temperature. Three groundwater samples were collected from monitoring wells in Universiti Teknologi PETRONAS campus. DR 2800 Spectrophotometer was used to determine the total iron concentration using phenanthroline method (APHA 1980).

The experiment was conducted using a stainless steel reactor. The reactor is shown in Figure 3.6 with a volume of 3 L. The reactor was equipped with pH (Hach Sension2) and Eh (Hanna H98121) probes to monitor hydrogen ion activity and redox potential as shown in Figure 3.8. 3 L of groundwater sample was placed in the reactor. 30 g of sodium acetate was added to the samples and stirred using a magnetic stirrer. Sodium acetate was used as a buffer solution to control the pH. The sample was purged with Nitrogen gas for 30 minutes at 60 rpm to remove the oxygen from the reactor. Subsequently the sample was purged with H_2S for 6 hours. Supernatants were collected at every 30 minutes interval from the valve at the bottom side of the reactor to analyze residual iron concentration over the 6 hours period. Simultaneously, the sulfide content and Eh of the water in the reactor were determined.

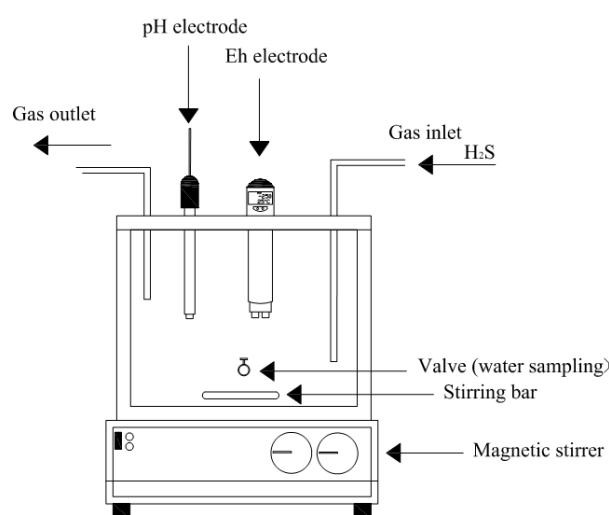


Figure 3.8: Experiment on sulfide precipitation using real groundwater

3.4 Electrochemical Treatment

The electrochemical experimental setup consists of 500 mL PYREX reactor, aluminium electrodes, DC power supply device, multimeter and magnetic stirrer. Aluminium plates of size 10 mm x 100 mm x 2 mm was used as electrodes (cathode and anode) for electrochemical precipitation. The plates were immersed into the beaker and held firm with crocodile clips connected through a wire to the DC power supply as shown in Figure 3.9. The magnetic stirrer was used to get a homogenous mixture of the sample during the process. The current was supplied by the DC power supply (Danzheng PS-305D) with adjustable current and voltage. During the experiments, the synthetic iron solution was

introduced into the reactor while the DC power supply was used to supply current at specific voltage to the electrodes. The experiments were performed at constant temperature of 25°C and stirring speed of 60 rpm. Supernatants was collected at different time intervals and filtered using 25 mm puradisc syringe filtration unit using 0.45 μm pore size filter paper before analyzing residual iron concentration through phenanthroline colorimetric method or ferrover method. A preliminary study was conducted using the synthetic iron solution with varying concentration of 1 mg/L to 5 mg/L. Hence, pH, distance of electrode, applied voltages, surface areas; initial concentration and volume of the sample were optimized.

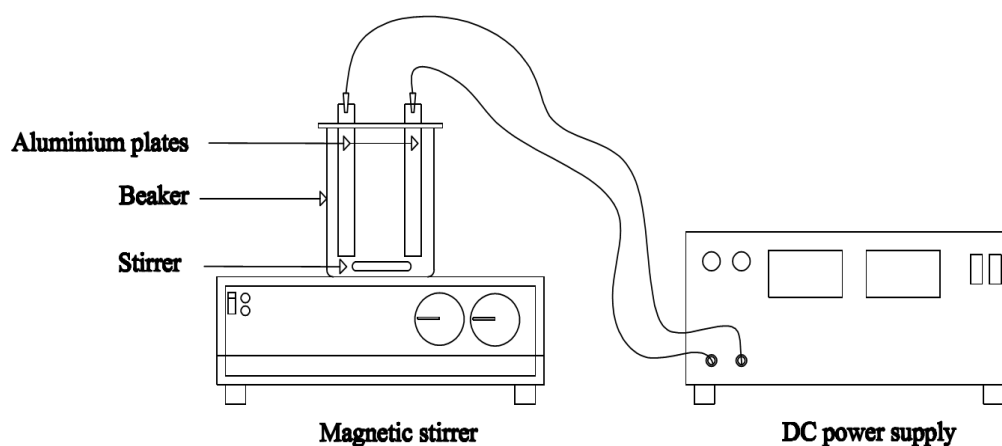


Figure 3.9: Schematic diagram of the experiment setup

3.4.1 Effect of pH

A 500 mL synthetic iron solution with varying concentrations of 1, 3 and 5 mg/L was used to find the optimum pH. The pH was varied from 2, 3, 4, 5, 6, 7, 8 and 9. The pH was adjusted using sodium hydroxide (NaOH) and measured using pH meter (Hach Sension4). The sample was continuously stirred at 60 rpm. Current density of 150 mA and electrode potential of 2 V was supplied to the electrodes at 35 mm inter-electrode distance with a total surface area of 11.2 cm². During the experiment, 15 mL of supernatant was sampled using a pipette at every 60 minutes interval to measure residual iron concentration. The process was repeated with different pH and different initial iron concentration.

3.4.2 Effect of distance between electrodes

The optimization of distance between the electrodes was carried out with 5 mg/L of the synthetic iron solution. The reactor was filled with 500 mL of the synthetic iron solution at pH 7. A pair of aluminum electrodes with surface area of 11.2 cm² was dipped into the solution and the distance between them was set at 5 cm apart at electrode potential of 4 V and current density of 0.5 mA. The residual iron concentration was measured at every 30 minutes interval until the concentration decreased below 0.3 mg/L. The collected samples were filtered before it was analyzed. The experiment was then repeated with an electrode distance of 4 cm, 3 cm, 2 cm, and 1 cm.

3.4.3 Effect of applied voltage

The experiment was further conducted to obtain the optimum voltage for the electrochemical precipitation process. 500 mL synthetic iron solution containing 5 mg/L iron concentration was placed into the reactor at pH 7. The experiments were conducted with inter-electrode distance of 1 cm and electrode surface area of 11.2 cm². 1 cm electrode distance was chosen due its removal efficiency from previous preliminary experiment. The current was allowed to flow through the electrodes. Supernatant was collected at every 30 minutes interval and filtered for residual iron concentration analysis. The experiment was repeated 5 times using different electrode potentials of 6, 8, 10, 15 and 20 V.

3.4.4 Effect on electrode surface area

The preliminary experiment on electrochemical analysis was conducted using different electrode surface area. 500 mL synthetic iron solution containing 5 mg/L iron concentration was placed into the reactor at pH 7. The electrode gap was 1 cm with electrode potential of 20 volts. 20 volts was selected based on results from previous experiment. The surface areas of the electrodes used in this experiment were 11.2, 22.4, 33.6, 45, 60, 75 and 90 cm². The residual iron concentration was measured at every 30 minutes interval.

3.4.5 Effect of initial iron concentration

500 mL of synthetic iron solution containing 5 mg/L iron concentration at pH 7 was placed in the reactor. The voltage was kept constant at 20 volts with inter-electrode distance of 1 cm and electrode surface area of 90 cm². These parameters were selected based on results obtained from previous experiment. The residual iron concentration was measured at every 30 minutes interval after filtering the supernatant. Subsequently, experiments were repeated with different initial iron concentration of 10 mg/L, 15 mg/L and 20 mg/L.

3.4.6 Effect of volume on iron removal

The final preliminary study was conducted to determine the effect of volume on iron removal. Sample volume of 300, 500, 800 and 1000 mL was used in this experiment. Each sample contains 20 mg/L of iron solution and pH was adjusted to 7. Aluminum electrodes consisting of 90 cm² surface area were dipped into the solution. Electrode potential of 20 V was supplied to the electrodes. Residual Iron concentration was determined at every 30 minutes interval after filtering the supernatant.

3.4.7 Iron removal from groundwater by electrochemical treatment

Groundwater samples from UTP monitoring well (GW-T) and groundwater treatment plant from Kg. Chicha (GW-C) were filtered through 25 mm puradisc syringe filtration unit using 0.45 µm pore size filter paper prior to the experiment. The iron concentrations were determined by phenanthroline colorimetric or ferrover method using a spectrophotometer (DR 2800). The iron concentrations from GW-T was found to be about 3.5 and 5.5 mg/L while the iron concentrations from GW-C was about 8.8 and 10 mg/L. A batch experiment was conducted using a sample of 1000 mL. A pair of aluminium electrodes with a total surface area of 90 cm² was dipped into the reactor containing the sample as shown in Figure 3.10. The electrodes were connected to a DC power supply at electrode potential of 20 Volts, regulated with a multimeter. This procedure was repeated for different iron concentrations of various groundwater samples. The total iron concentration in the sample was determined at every 30 minutes interval. Simultaneously, the other parameters were measured which include pH, Eh, current density, and aluminium concentration.

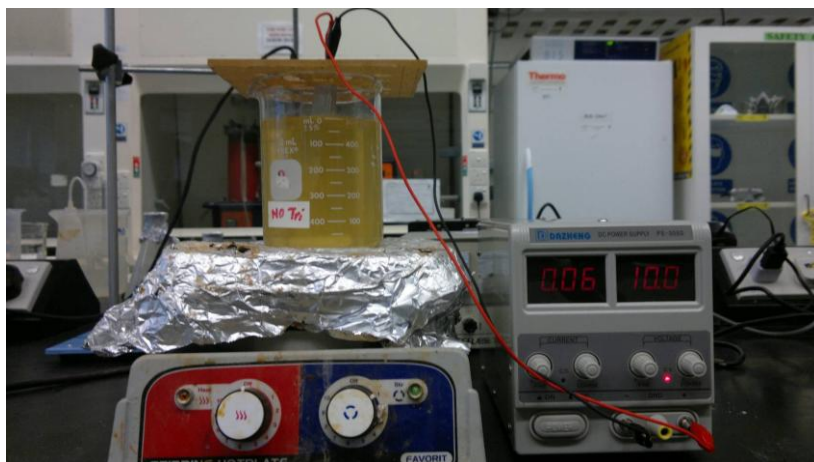


Figure 3.10: Experimental setup for electrochemical precipitation using aluminium electrode

3.5 Surface and chemical composition analysis

Filtered samples from both the anaerobic and electrochemical treatment were examined using EDAX (Energy Dispersive Analysis of X-Ray) and FESEM (Field Emission Scanning Electron Microscopy) as shown in Figure 3.9. The FESEM was used to visualize the very small topographic details on the surface of the precipitates. In this examination, the structure and surface morphology of the precipitated elements were examined.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Water quality of the groundwater samples

The characteristics of the groundwater samples collected from UTP (GW-T) well, Kg. Chicha (GW-K), Kg. Puteh (GW-P) and Tanjung Mas (GW-M) are shown in Table 4.1. The concentration of each parameter is compared with World Health Organization (WHO) and Malaysia Standard. The pH range of the samples varied around 6.9 to 7.8 and is in agreement with WHO and Malaysia Standard. The concentration of dissolved oxygen (DO) is 0.45 mg/L and the average conductivity of the samples is 153 μ S/cm. Water conductivity is usually related to total dissolved solids (TDS) or sodium chloride (NaCl) concentration of the sample [195]. The presence of salt (NaCl) or TDS in water forms a solution from the dissociation process of ions [196]. These ions are the charge carriers and allow the flow of current. Thus, as the number of charge carriers increases, the conductivity proportionally increases. The turbidity value of groundwater from Kg. Chicha indicates an allowable drinking water standard of 1 NTU while for GWT, GW-P and GW-M, their turbidity was found to be 6.57, 3 and 4 NTU respectively. The colors of two groundwater samples are below the allowable standard of 15 Pt.Co. The value of the color of the groundwater sample from Kg. Chicha and Kg. Puteh was 5 and 4 Pt.Co. The rest of the groundwater samples from UTP monitoring well and Tanjung Mas was 20 Pt.Co respectively. The main interest in the samples is total iron. The iron concentrations were high compared to the allowable standard of 0.3 mg/L. The iron values were found to be 4.5, 8.8, 6.75 and 8.8 mg/L for groundwater of GW-T, GW-C, GW-P and GW-M respectively. The high iron concentration in groundwater was reduced by the proposed treatment techniques.

Table 4.1: Characteristics of groundwater from UTP (GW-T), Kg. Chicha (GW-C), Kg. Puteh (GW-P) and Tanjung Mas (GW-M)

Parameters	Units	GW-T	GW-C	GW-P	GW-M	WHO Standard	Malaysia Standard
pH		6.79	6.55	7.50	6.80	6.5– 8.5	6.5 – 8.5
DO	mg/L	0.42	0.35	0.45	0.59	-	-
Conductivity	μS/cm	250	110	150	101	-	-
Turbidity	NTU	6.57	1	3	54	1	5
Color	Pt.Co	20	5	4	20	15	15
Total iron (Fe)	mg/L	4.50	8.80	6.75	5.5	0.3	0.3
Calcium (Ca ²⁺)	mg/L	18.11	6.00	5.50	2.70	200	
Magnesium (Mg ²⁺)	mg/L	4.15	2.10	2.44	2.10	150	-
Sodium (Na ⁺)	mg/L	23	10	13	13.10	200	200
Potassium (K ⁺)	mg/L	0.46	1.20	1.20	1.50	-	
Sulphate (SO ₄ ²⁻)	mg/L	5.00	5.00	8.60	8.88	250	250
Bicarbonate (HCO ₃ ⁻)	mg/L	122	36.6	48.8	24.4	-	-
Chloride (Cl ⁻)	mg/L	2.55	8.00	1.20	10.15	250	250
Sulfide (S ²⁻)	μg/L	4	1	3	2	50	-
Nitrate (NO ₃ ⁻)	mg/L	1.67	5.00	2.11	3.00	50	-
Hardness	mg/L as CaCO ₃	62.29	24.00	23.75	8.76	100-300	500
TDS	mg/L	120	50	62	111	600	1000
Total Alkalinity	mg/L as CaCO ₃	100	30	40	20	-	-

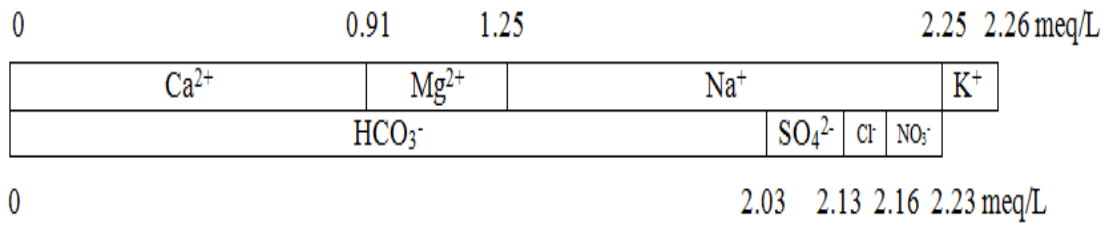
All the groundwater samples have low total dissolved solid (TDS). The standard TDS of WHO and Malaysia are 600 mg/L and 1000 mg/L respectively. The TDS for groundwater samples of GW-T, GW-C, GW-P and GW-M are 120, 50, 62 and 111 mg/L respectively. The total alkalinity for groundwater samples of GW-T, GW-C, GW-P and GW-M are 100, 30, 40 and 20 mg/L respectively. The sulfide and nitrate concentration of the samples indicate the values were below 50 mg/L of allowable standard. The concentrations of sulfide and nitrate of GW-T sample was 4 μg/L and 1.67 mg/L respectively. The concentration of ion sulfide and nitrate in GW-C, GW-P and GW-M samples was 1, 3, 2 μg/L and 5, 2.11, 3 mg/L respectively.

The total concentrations of calcium, magnesium, potassium, sulphate, bicarbonate and chloride were converted from milligram per liter (mg/L) to milliequivalent per liter (meq/L). The upper bar shows cations (Ca^{2+} , Mg^{2+} , and Na^{+}) while the lower bar shows anions (HCO_3^{-} , Cl^{-} and SO_4^{2-}). The plotted results in a bar diagram for the analysis of ion contents in GW-T, GW-C, GW-P and GW-M showed their water type. The ratio of cation and anion for corresponding samples were 0.6, 4, 0.5 and 0.5 % which is less than 10% of standard calculation. Thus, it implies that the samples were accurately characterized [86]. All four samples indicate that the groundwater is sodium bicarbonate type as shown in a bar diagram (Figure 4.1a, 4.1b, 4.1c and 4.1d). This is due to the high level of sodium and bicarbonate concentration in the samples compared to others ions. The sodium concentration of GW-T, GW-C, GW-P and GW-M was 23, 10, 13 and 13.10 mg/L, respectively while the bicarbonate concentration was 122, 36.6, 48.8 and 24.4 mg/L for respectively for corresponding samples.

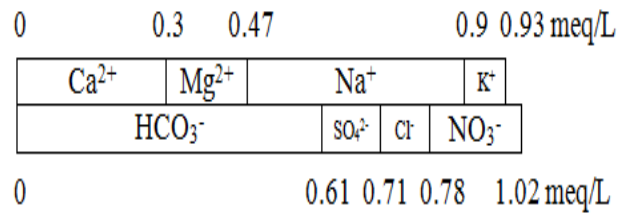
The calcium and magnesium concentration was characterized and concurrently calculated in order to find the hardness of the sample. The GW-T groundwater can be classified as moderately hard while the water from GW-C, GW-P and GW-M were soft. The total hardness was 61.9, 23.5, 23.6 and 15.3 mg/L respectively. These levels fall within the category of very soft and moderately hard water which is in the range of 60 mg/L to 120 mg/L. These hardness levels in the samples are in the allowable limit of 500 mg/L recommended by WHO. The sulphate and chloride levels are below the standard of WHO and Malaysia for both parameters at a permissible limit of 250 mg/L.

4.2 Results for iron removal from laboratory experimental work

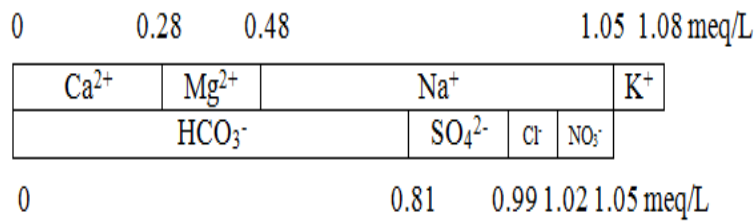
Results for iron removal during laboratory work were determined. These results covered the efficiency of iron removal by sulfide precipitation and electrochemical precipitation process. Both treatment methods were first operated in a preliminary study using synthetic wastewater before applying them to real groundwater.



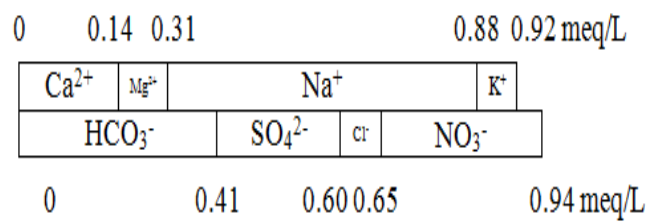
(a)



(b)



(c)



(d)

Figure 4.1: Bar diagram of the water: (a) GW-T; (b) GW-C; (c) GW-P; (d) GW-M

4.3 Results on iron removal by sulfide precipitation

4.3.1 Results on pH optimization

The effect of pH on iron removal is depicted in Figure 4.2. The pH was varied from 2 to 9. Supernatant was collected at every one hour interval during the process and residual iron concentration analyzed. Hydrogen sulfide was purged into the solution at a 0.18 M concentration during the experiment.

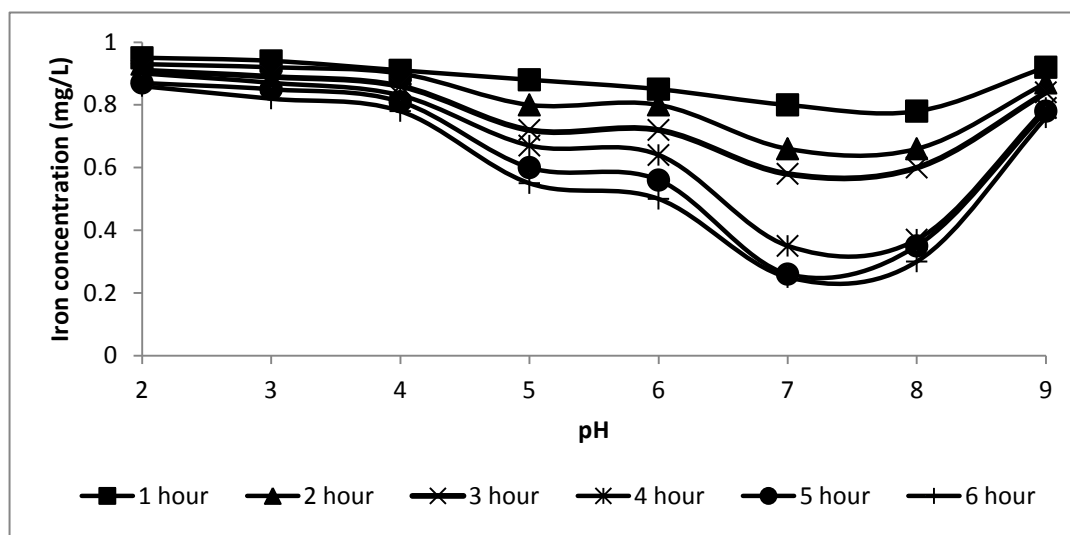


Figure 4.2: Effect of pH on iron removal. Conditions: initial concentration 1 mg/L, temperature 25°C, 0.18 M H₂S, and agitation speed 60 rpm.

During the experiment at pH 2 and 3, iron concentration decreased to 0.86 and 0.82 mg/L resulting to a removal efficiency of 14% and 18% respectively. The removal efficiency at these pH levels was very poor and did not even remove half of the initial concentrations. At low pH, the removal rate was slow due to low solubility of hydrogen sulfide to react with iron to enhance precipitation [197]. When the pH was increased to 4, 5 and 6, the iron concentration decreased to 0.78, 0.55 and 0.5 mg/L which resulted in the removal efficiencies of 22%, 45% and 50% respectively. At pH 7, iron concentration further decreased to 0.25 mg/L corresponding to 75% removal efficiency after 6 hours treatment time. At pH 8, slight increase in removal rate was observed as residual iron concentration approximately reached the allowable standard of 0.3 mg/L limit. pH 7 is therefore considered the optimum pH because it has the highest precipitating effect. These results are in agreement with Berner and Rickard and Luther [198, 199] where iron

precipitation was observed between pH 7 and pH 8 in sulfide forms. At pH 9, removal efficiency decreased further with a residual iron concentration of 0.76 mg/L corresponding to a removal efficiency of 24%. This is due to an adsorption surface negatively charged hydroxy ions that makes the removal process slow in inert atmosphere [200]. The results indicate that removal of iron through sulfide precipitation depends on pH. Removal efficiency increases as pH is increased until optimum pH is attained [201]. Thus, the pH level has a significant effect on iron removal since the rate of H_2S dissolution is faster at higher pH levels [119].

4.3.2 Reduction on iron from 1 mg/L at pH 7

The iron removal by sulfide precipitation was conducted with single experiment using synthetic iron solution at pH 7. The solution contained 1 mg/L of iron and purged with hydrogen sulfide at 0.18 M. The residual iron concentration monitored at every 30 minutes interval was plotted and depicted in Figure 4.3.

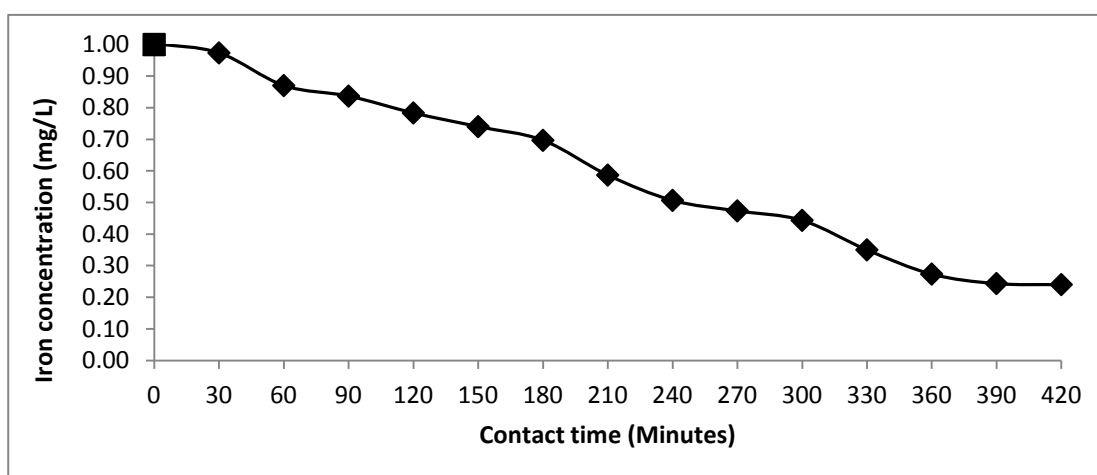


Figure 4.3: Iron removal Vs time. Conditions: initial concentration 1 mg/L, pH 7, 0.18 M H_2S and agitation speed 60 rpm.

The results indicate that iron concentration decreased from 1 mg/L to 0.24 mg/L below the allowable standard of 0.3 mg/L in 420 minutes. The removal efficiency was found to be 76 %. However, at 360 minutes, residual iron concentration (0.27 mg/L) was below 0.3 mg/L corresponding to a removal efficiency of 73%. Thus, the process attained equilibrium within 360 minutes. Final pH of the sample after treatment at pH 7 and 8 was observed to be around pH 7.8. Simon [202] also reported that iron decrease in sulfide form at pH 7.5. However, increase in initial concentration may affect the removal

efficiency. The removal process took longer time to reach the standard due to the slow bonding of sulfide gas with iron. In inert atmosphere, longer time (12-24 hours) is required for iron to precipitate in sulfide form [203].

4.3.3 Results of experiment using real groundwater

The experiment on iron removal by sulfide precipitation was further conducted by using real groundwater. The groundwater from UTP monitoring wells (GW-T) was used with three different concentrations. The removal of iron at a concentration of 1.5, 3.55 and 5.01 mg/L versus time was plotted as shown in Figure 4.4. The figure indicates the reduction patterns of iron from corresponding iron concentrations over 360 minutes of contact time. The results shows that increase in contact time resulted in the increase in removal efficiency.

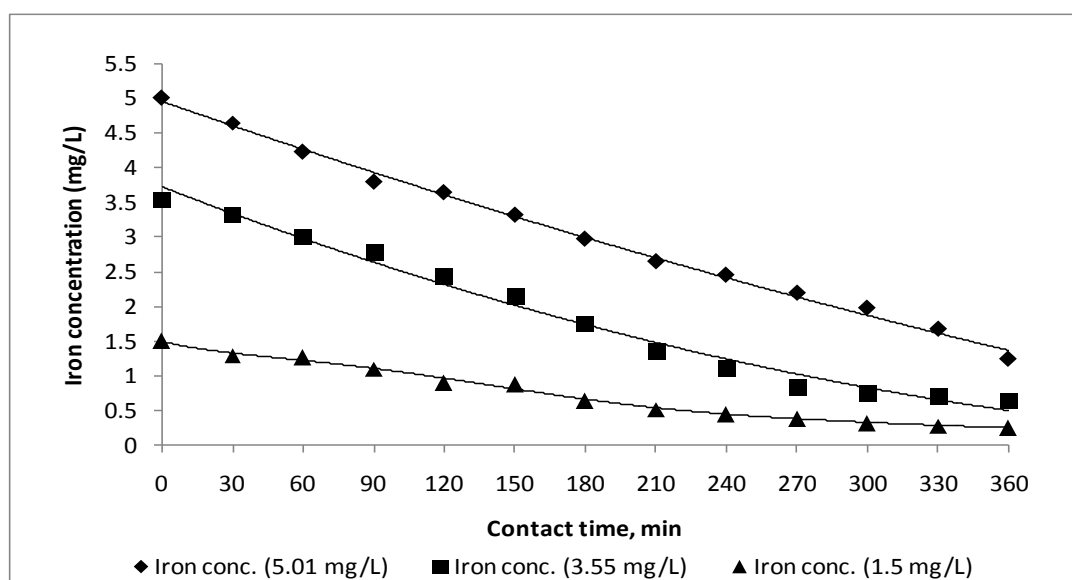


Figure 4.4: Effect on initial concentration of iron. Conditions: 0.18 M H_2S and agitation speed 60 rpm.

At 5.01 mg/L of iron concentration, the removal efficiency was observed to be 75%. However, final residual concentration after treatment was 1.24 mg/L which is above the 0.3 mg/L allowable standard. The removal efficiency increased as the concentration of iron in the groundwater reduced. The groundwater containing 3.55 mg/L iron concentration had a removal efficiency of about 82%. The residual concentration at the end of the process was 0.65 mg/L at pH 7.55. The groundwater containing 1.5 mg/L iron concentration had a residual concentration of 0.25 mg/L after treatment corresponding to

about 83% removal efficiency and below the allowable standard of drinking water (0.3 mg/L). The final pH at the end of the process was 7.68. From these results, it can be concluded that increase in concentration decreases the removal efficiency. However, there is a possibility of iron removal at high concentration but the contact time could be increased. It is therefore suggested that iron removal by sulfide precipitation method should be applied only at groundwater containing low iron concentration.

4.3.3.1 Sulfide concentration during iron removal in anaerobic process

The residual sulfide concentration in the groundwater was measured and plotted as shown in Figure 4.5. The sulfide levels in the treated water was determined and compared to the drinking water standard. Initially, the average groundwater concentration of sulfide for three samples was 4.3 µg/L. This sulfide content was present due to underground decomposition of organic matter such as decaying plant material or by chemical reduction of sulfate [204].

For the groundwater containing iron concentration of 5.01 mg/L, the sulfide concentration increased from 7 µg/L to 31 µg/L after 360 minutes of contact time. For the groundwater containing 3.55 mg/L of iron concentration, the sulfide concentration increased from 4 µg/L to 23 µg/L.

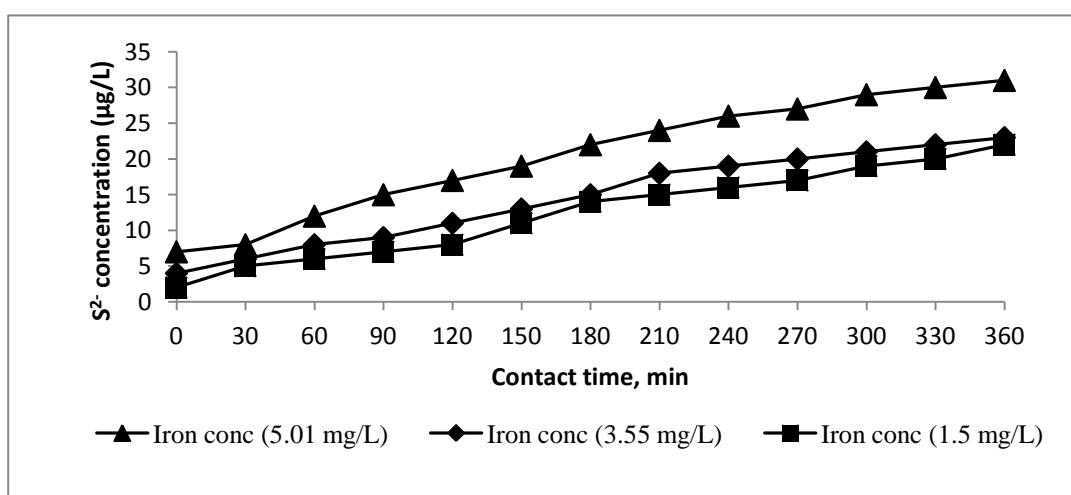


Figure 4.5: Effect of initial concentration of sulfide at pH 7

For the groundwater containing 1.5 mg/L of iron concentration, the sulfide concentration increased from 2µg/L to 22µg/L. Overall, these concentrations are still below the WHO standard (50µg/L) for drinking water [71]. Thus, this process does not harm or give secondary problem to the treated water. The sulfide level has increased during the process when the samples were purged with hydrogen sulfide gas. The increased sulfide concentration was due to an increased volumetric sulfate reducing activity resulting in more sulfide being produced [205]. This hypothesis is based on the following chemical equation:



Sulfide concentration increased due to an excess of hydrogen sulfide gas in the water. When iron was saturated with sulfide to form iron sulfide, there is the possibility for sulfide gas redissolve and form a polysulfide species in the aqueous solution [119]. Hence, increases the sulfide concentration in the groundwater.

4.3.3.2 Redox potential during sulfide precipitation process

The iron removal by sulfide precipitation was conducted in an inert atmosphere or absence of oxygen. Thus, oxidation reduction (redox or Eh) potential for different initial iron concentration was measured during the process and the results are illustrated in Figure 4.6.

Figure 6 shows Eh had an initial average of 50 mV from three groundwater samples containing iron at a concentration of 5.01, 3.55 and 1.50 mg/L respectively. In the first 30 minutes of purging with nitrogen gas, the Eh value decreased to an average of -80 mV. It gradually decreased to -300 mV after 360 minutes of the process. It shows that the groundwater samples were already in anoxic or inert atmospheric condition [129]. The Eh values during the experiment using groundwater with iron concentrations of 1.5, 3.55 and 5.01 mg/L were -290, -280 and -272 mV respectively.

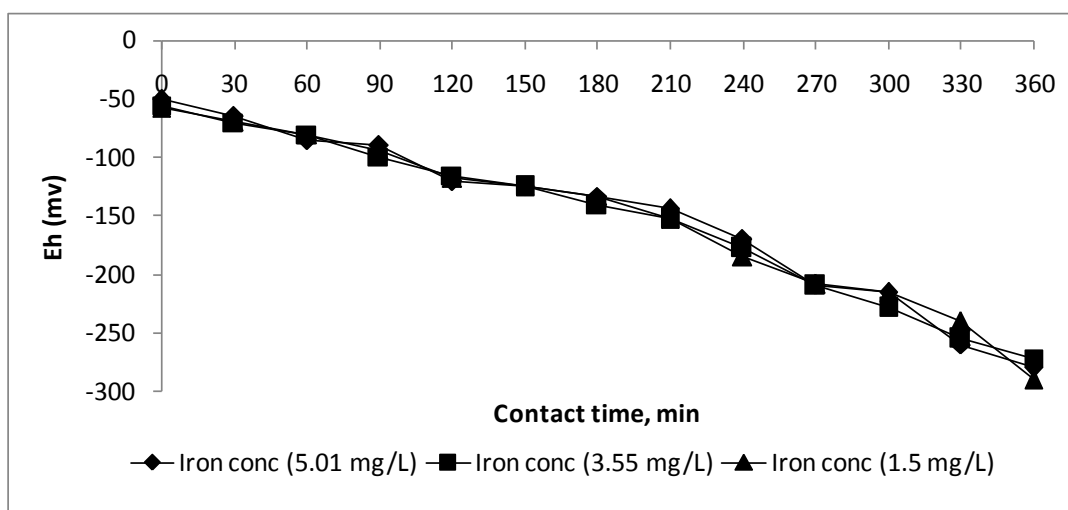


Figure 4.6: Redox condition during treatment at pH 7

These results were in agreement with the requirements in sulfide precipitation process. These conditions should be constantly maintained at Eh value from -200 to -400 mV for iron to be effectively removed [206]. The decrease of Eh value is due to the starting sulfate reduction in the groundwater which results to the dissolution of iron to form iron sulfides [207].

4.4 Results on iron treatment using electrochemical precipitation

In this section, the results of iron removal using electrochemical precipitation are presented based on two experimental approaches, namely:

- i) Results of preliminary study using synthetic iron solution, and
- ii) The results of the experiment using real groundwater.

4.4.1 Effect of pH on iron removal using EC treatment

The effect of pH on iron removal was analyzed using three different synthetic iron solutions with initial concentrations of 1, 3 and 5 mg/L. The pH is an essential parameter to consider when EC treatment is proceeding in aqueous solution [208]. When pH varies, iron can exist in the following oxidation states; Fe^{2+} , $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. Figure 4.7 shows the result of residual iron concentration after 2 hours of contact time at different pH. At the beginning of the process, pH was adjusted from pH 2 to 3, 4, 5, 6, 7, 8, 9 and

10 similar to sulfide precipitation experiment. The results after 2 hours of reaction time indicate iron residuals at different pH.

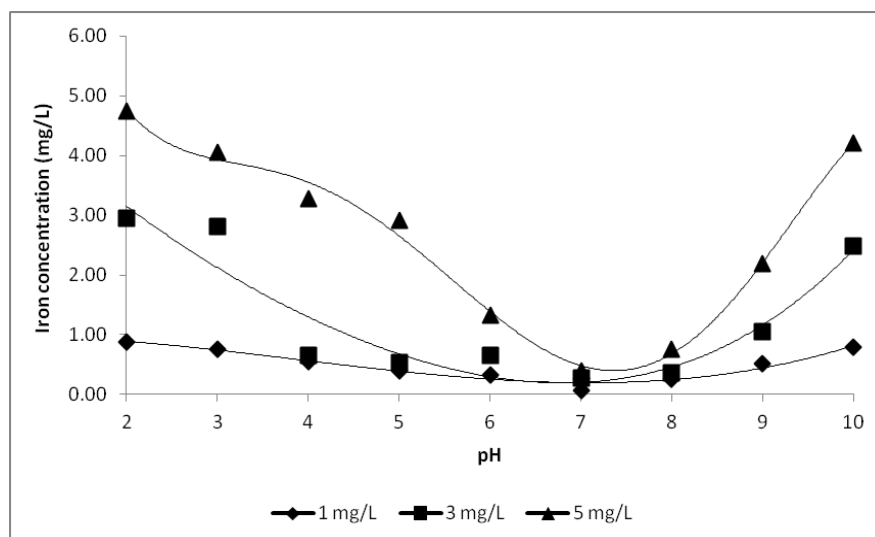


Figure 4.7: Effect of pH on iron removal. Condition: Temperature 25°C, stirring speed 60 rpm; volume 500 mL; electrode surface area 11.2 cm² of; applied potential 2 volts

Iron removal efficiency increases with the increase in initial pH. Experiments below pH 3 should be avoided because the hydroxyl ions formed will not be stable enough to react with aluminium cations [155]. The removal efficiency of iron at pH below 3 was less than 10%. This situation is similar to sulfide precipitation where iron removal was less than 20% from the total concentration. Iron removal efficiency has increased when pH was increased from 4 to 8. This was likely due to the release of more hydroxyl ion in acidic condition that can precipitate iron as iron hydroxide. Between pH 6 to 8, iron concentrations decreased below 0.3 mg/L. In sulfide precipitation, the removal efficiency increased up to 50% between pH 4 to 6. In this process, sulfide gas was dissolved in the solution and bond with iron to precipitate. However, iron was effectively removed between pH 7 and 8 forming ferric in the alkaline range. The removal efficiency was up to 95% for each different concentration. In this range, the aluminium electrodes produced aluminium hydroxide $\text{Al}(\text{OH})_3$ with higher weight and density that can settle iron faster and acts as better enmeshment in a precipitate [209]. It was reported that the removal of iron from tap water by EC treatment effectively occurred at pH 7.70, 7.77, 7.82 and 7.88 respectively [148]. In comparison with sulfide precipitation, iron was reduced at the same pH with EC treatment. The removal efficiency of iron at pH 7 and 8 was 75% and 70% respectively for sulfide precipitation. However, the contact time required for sulfide

precipitation (6 hours) to attain WHO allowable standard of 0.3 mg/L was higher compared with the contact time required using electrochemical precipitation (2 hours). It was acknowledged that formation of iron sulfide is considered to be a slow process under an inert atmosphere or without oxygen conditions and may not occur at the timescale of the experiments [210].

Above pH 8, the removal efficiency started to decrease. This is because of the amphoteric behavior of metal hydroxides caused by the generation of soluble monomeric cations and anions released at lower and higher pH [157]. When the initial pH was kept in neutral, all the aluminium produced at the anode formed polymeric species ($\text{Al}_{13}\text{O}_4(\text{OH})^{7+}_{24}$) and precipitated as $\text{Al}(\text{OH})_3$ which resulted in greater removal efficiency [211]. The decreasing removal efficiency at pH 9 and 10 also happened in sulfide precipitation process with only about 24% removal efficiency observed. This was due to an adsorption surface negatively charged hydroxyl ions that made the removal process slow in inert atmosphere as has been explained in sulfide precipitation section.

4.4.2 Effect of electrode-distance on iron removal

The effect of electrode distance was investigated to determine the best electrode distance for iron removal. The results of iron removal from initial concentration of 5 mg/L in 500 mL solution at pH 7 are shown in Figure 4.8. The results show residual iron concentration in water sample treated by electrochemical precipitation using aluminium electrode at different electrode distance of 1, 2, 3, 4 and 5 cm.

In general, the results obtained from the different electrode distance investigated showed removal efficiency near to each other. However, the removal efficiencies can be compared to obtain the best electrode distance for effective iron removal below 0.3 mg/L. At 5 cm electrode distance, process reaction was slow. A residual iron concentration of 0.27 mg/L was observed after 210 minutes from an initial concentration of 5 mg/L. When the electrode distance was reduced to 4 and 3 cm, contact time for iron removal below 0.3 mg/L remained the same (210 minutes). The residual iron concentration was observed to be about 0.25 mg/L at these conditions. When the electrode distance was reduced to 2 cm, a residual iron concentration of 0.28 mg/L was observed at 180 minutes. This is below the WHO permissible limit. Further reduction of the electrode distance to 1 cm resulted in residual iron concentration of 0.28 mg/L and a decrease of treatment time to 150 minutes.

The electrode distance of 1 cm indicated that iron can be removed at a lower treatment time compared to other electrode distances. The slow removal process at high electrode distance can be due to lower anodic oxidation. Thus, the number of cations also decrease since the cations are responsible for the coagulation process [150]. At a minimum electrode distance, resistance to current flow in the solution is low and facilitates the electrolytic process to enhance iron removal [148]. The removal process becomes more efficient due to strong electric field resulting in slower displacement of the ions formed during electrolysis. This helps to bind iron in the solution to aluminium hydroxide $\text{Al}(\text{OH})_3$ [155]. The electrode distance of 1 cm will be used for another experiment.

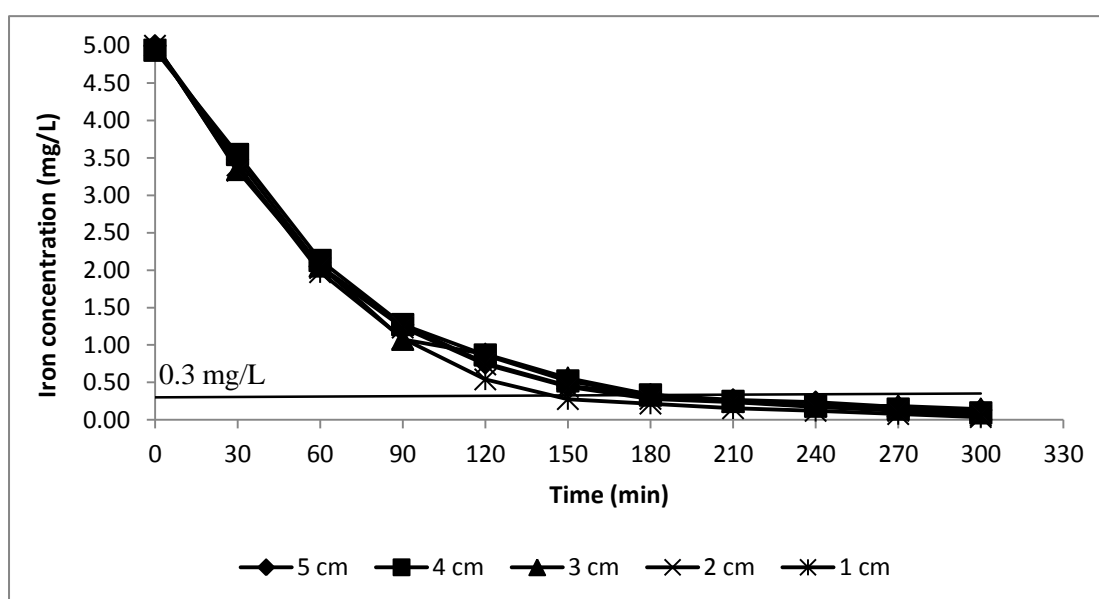


Figure 4.8: Rate of iron reduction at different electrode spacing. Conditions: Temperature 25°C, stirring speed 60 rpm; Volume 500 mL, electrode surface area 11.2 cm², applied potential 4 volts, pH 7.

4.4.3 Effect of voltage on EC treatment

An applied voltage is an important operating parameter than can influence the performance and increase removal efficiency of EC treatment [162]. The results on the effect of applied voltages on iron removal are shown in Figure 4.9. It indicates that removal of iron from initial concentration of 5 mg/L to below 0.3 mg/L occurred over a total period of 300 minutes. Five different voltages (6, 8, 10, 15 and 20 volts) were used in this experiment using a pair of electrode with surface area 11.2 cm². The pattern was

almost similar with the electrode distance result as the graph lines were on the same plane except at 6 volts electrode potential.

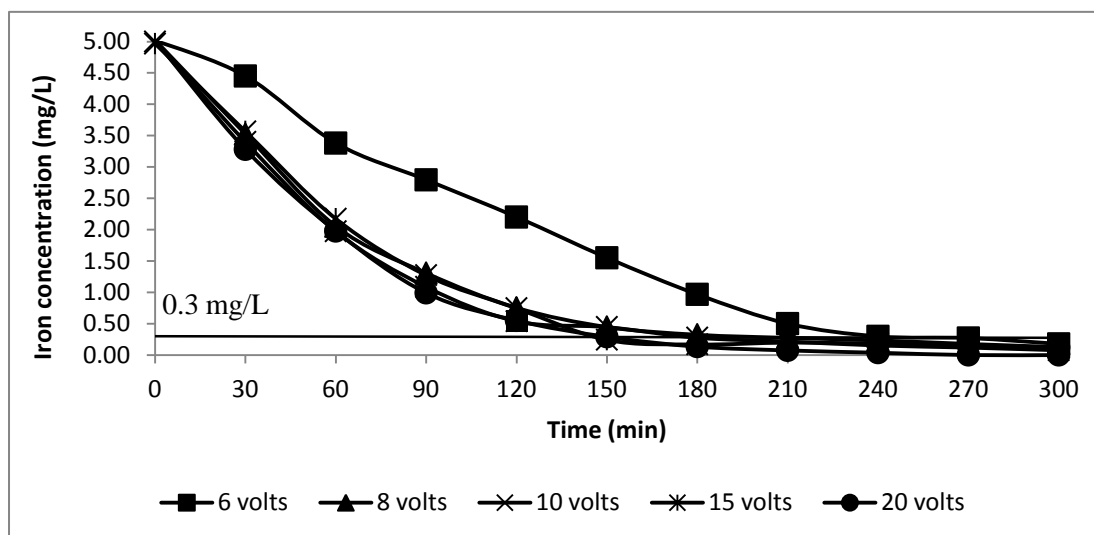


Figure 4.9: Effect voltage at 5 mg/L iron concentration. Condition: Temperature 25°C, stirring speed 60 rpm, volume 500 mL, electrode surface area 11.2 cm², pH 7, electrode distance 1 cm

The applied voltages produced more bubbles and bigger size of flocs [159]. The oxidized aluminium increased rapidly and generated more hydroxyl ion that leads to precipitation of iron [160]. At 6 and 8 volts, iron was observed to be 0.3 mg/L and 0.27 mg/L after 240 minutes of the process. While at 10 volts, residual iron concentration was 0.28 mg/L after 180 minutes. This concentration is below the allowable limit of 0.3 mg/L. Similar results were observed at an applied potential of 15 and 20 volts with both applied voltages showing residual iron concentration below minimum limits of drinking water after 150 minutes of the process. Their concentrations were 0.24 and 0.29 mg/L respectively. However, at 20 volts, the result shows that iron was almost eliminated compared to applied potential of 15 volts after 210 minutes of the treatment. Considering the performance of the removal efficiency and specific energy consumption simultaneously, the applied voltage of 20 V with estimated energy consumption of 0.159 to 0.192 kWh/kg seems to be offering the best overall performance for this treatment with reasonable removal efficiency and relatively low specific energy consumption [162]. Thus, it is suggested to use 20V for continuous experiment.

4.4.4 Effect on electrode surface area

Results on the effect of electrode surface area for iron removal using 5 mg/L concentration in the solution are shown in Figure 4.10. The results showed the residual iron concentration after using aluminium electrodes with a total surface area of 11.2, 22.4, 33.6, 45, 60, 75 and 90 cm² at 1 cm electrode spacing in 500 mL solution. The electrodes were arranged in monopolar pattern. The total time for the process was 300 minutes. However, the time taken to reach below 0.3 mg/L of iron concentration was also considered.

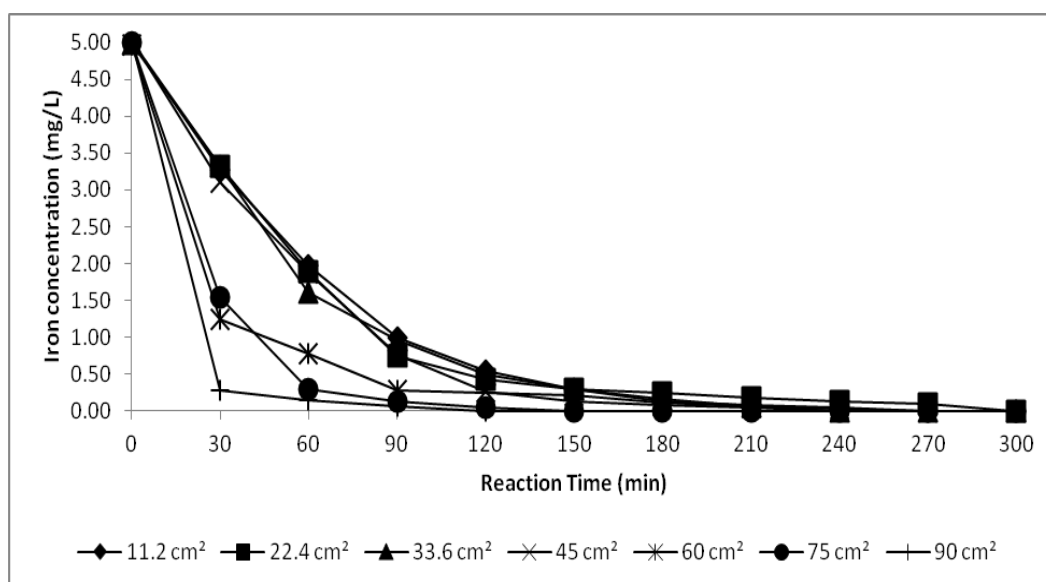


Figure 4.10: Effect of surface area on treatment of iron. Conditions: Temperature 25°C room, stirring speed 60 rpm, volume 500 mL, electrode distance 1 cm, pH 7, applied potential 20 V.

Iron concentration was reduced to or below 0.3 mg/L after 150 minutes of the EC treatment with an applied electrode surface area of 11.2, 22.4 and 33.6 cm². The iron concentrations were observed to be 0.29, 0.30 and 0.39 mg/L, respectively. While at 45 and 60 cm² surface area of the electrode, the iron concentration was observed to be 0.27 and 0.28 mg/L after 120 and 90 minutes respectively. As the surface area was increased, the treatment time for iron removal decreased. The applied surface area of aluminium electrode at 75 and 90 cm² shows that iron can be reduced to 0.29 and 0.28 mg/L after 60 and 30 minutes of process. During this process, when the surface area is increased, more electrons are transferred from production of massive hydroxyl ions which can oxidize iron faster through reduction or precipitation [212]. From the results, it can be concluded

that an effective surface area can reduce treatment time and increase removal efficiency [211]. Thus, surface area of 90 cm² was selected for further experiments.

4.4.5 Effect of different initial concentration

The effect of initial iron concentration on the EC treatment was investigated in the range of 5, 10, 15 and 20 mg/L in 500 mL synthetic iron solution at pH 7 using electrode spacing of 1 cm, electrical potential of 20 volts and 90 cm² surface area of aluminium electrode. As illustrated in Figure 4.11, iron removal rate decreases as iron concentration increased. It is clear that removal efficiency of iron decreased when the iron concentration was increased.

After 30 minutes of the EC process with initial concentration of 5, 10, 15 and 20 mg/L, residual iron decreased to 0.28, 3.45, 2.22 and 6.34 mg/L respectively from the solution. The removal efficiency was found to be 94, 66, 85 and 68% respectively. Residual iron concentration decreased below the admissible level of 0.3 mg/L after 30, 90, 90 and 120 minutes of corresponding concentrations. Again, the time required to reach the allowable standard increased. In EC process, iron can be removed by two steps. Iron (II) is converted into iron (III) or ferric and it is adsorbed in aluminum hydroxides [213]. At lower concentrations (5 and 10 mg/L), iron can be reduced in shorter treatment time (30 to 90 minutes) due to the availability and sufficiency of aluminum hydroxides with suitable oxidizing condition [148]. While at high concentration, the amount of hydroxyl ions generated was insufficient. Thus, the ability of aluminium hydroxides to adsorb iron was not enough to make the iron precipitate [148, 214].

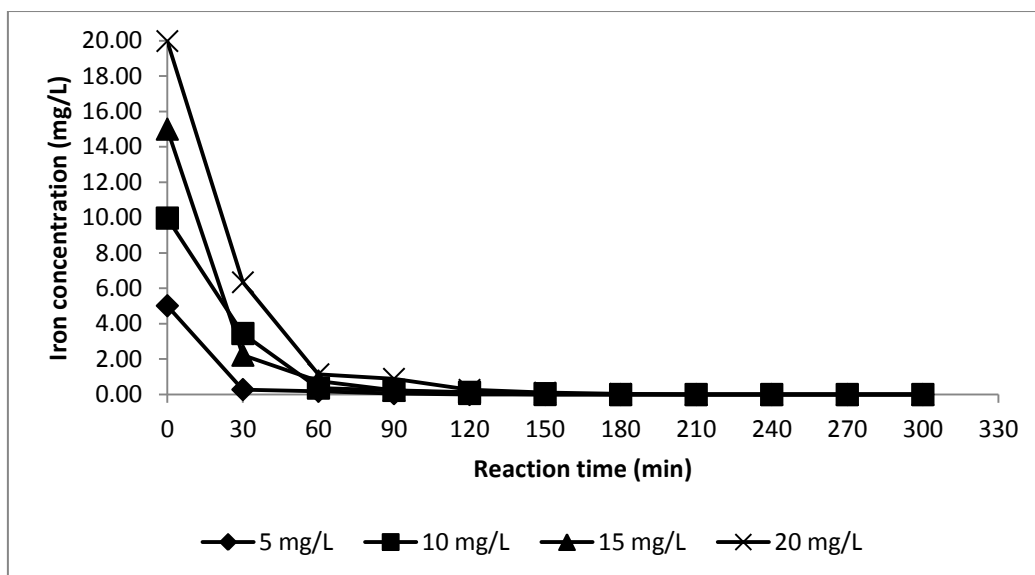


Figure 4.11: Effect of initial iron concentration. Conditions: Temperature 25°C, stirring speed 60 rpm, volume 500 mL, electrode distance 1 cm, pH 7, applied potential 20 V, electrode surface area 90 cm².

4.4.6 Effect of different volume

The effect of iron removal on different volumes of solution was investigated. The volume of iron solution was varied in 300, 500, 800 and 1000 mL with the same concentration of 20 mg/L at pH 7, 1 cm electrode distance, 20 volts applied voltage and 90 cm² surface area of aluminium electrode. The results are illustrated in Figure 4.12. The result indicates that treatment time is increased as the volume increases.

From the results, it was observed that iron removal at high concentration is influenced by the volume. Increase in volume resulted in the increase in contact time. At volume of 1000 mL, iron decreased to below 0.3 mg/L after 120 minutes with residual concentration of 0.28 mg/L. At volume of 800 mL, contact time of about 120 minutes was used to reduce iron concentration below allowable standard. The residual concentration of iron was 0.21 mg/L. At lower volume of iron solution (300 and 500 mL), contact time decreased as the volume of the solution was decreased. Treatment time was within 60 to 90 minutes for the process to reach below 0.3 mg/L. Iron concentration was found to be 0.22 and 0.24 mg/L respectively. It can be explained that treatment time of EC process is influenced by the volume of aqueous solution and also surface area. Ghosh et al. [182] showed 1000 ml tap water contained 25 mg/L iron concentration was reduced in 35 minutes by using aluminium electrodes with 150 cm² surface area.

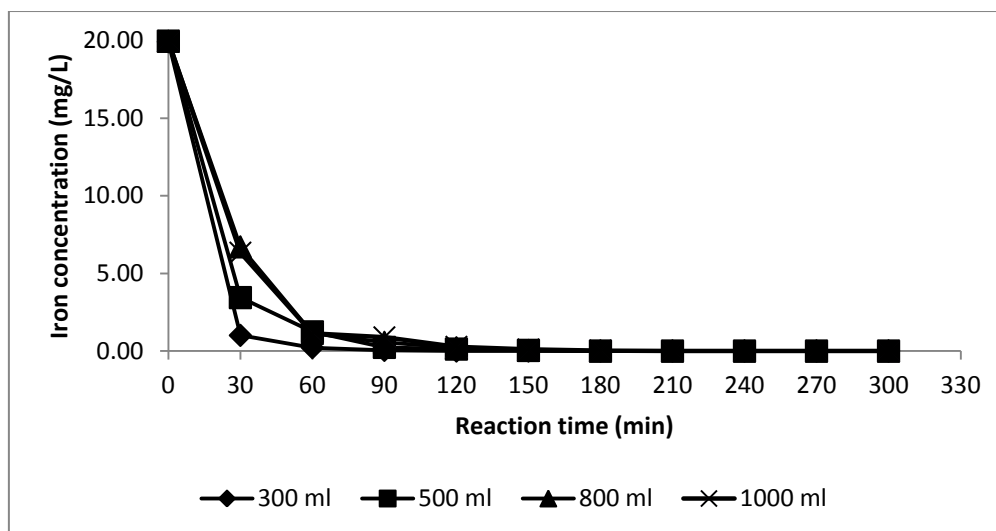


Figure 4.12: Effect of volume of iron solution. Condition: concentration 20 mg/L, temperature 25°C, stirring speed 60 rpm, volume 500 mL, electrode distance 1 cm, pH 7, applied potential 20 V, electrode surface area 90 cm²

4.4.7 Result of treatment using real groundwater

The validation of electrochemical precipitation treatment was conducted using real groundwater from different places containing iron. The groundwater samples from UTP monitoring wells (GW-T) contain 3.5 and 5.5 mg/L of iron while groundwater from Kg. Chicha (GW-C) contains 8.8 and 10 mg/L iron. The 1000 mL samples were placed in a reactor by immersing 90 cm² total surface area of aluminium electrodes at applied potential of 20 volts. The samples were agitated at a stirring speed of 60 rpm. The results of iron residual at various treatment time is shown in Figure 4.13.

The results indicate that iron was completely removed by EC process after 150 to 180 minutes of the process. The iron concentration of 10 and 8.8 mg/L in the groundwater (GW-C) was reduced to 0.24 and 0.27 mg/L respectively. The time taken to reach below 0.3 mg/L was 90 and 60 minutes respectively. While for groundwater of GW-T, at 5.5 and 3.5 mg/L of initial concentration, the iron decreased to 0.28 mg/L. The process took 60 minutes for both initial iron concentrations to reach below allowable drinking water standard of 0.3 mg/L. The iron removal in EC treatment was a little bit faster than sulfide precipitation. The highest iron concentration of 10 mg/L was completely removed in 180 minutes. However, in sulfide precipitation, at 5.01 mg/L, the iron concentration was reduced to 1.24 mg/L after 360 minutes of the process and it only reach below 0.3 mg/L

at the same period when the groundwater containing 1.5 mg/L was used. The removal efficiency versus time in sulfide precipitation shows that the process is slower than iron removal by EC treatment.

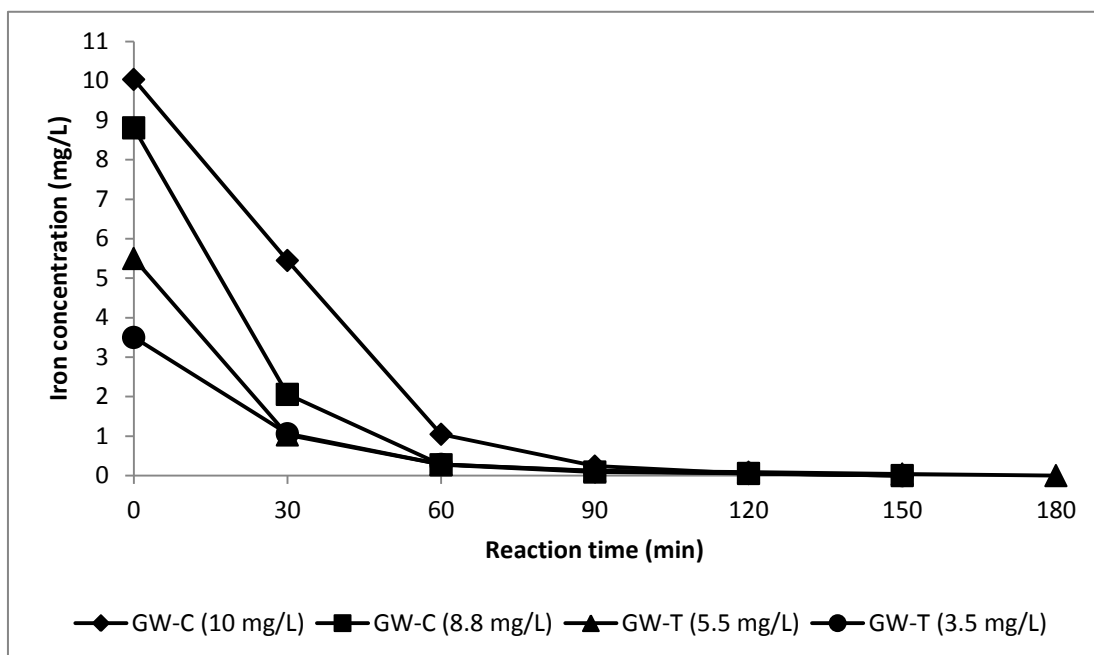


Figure 4.13: Treatment of iron using real groundwater. Conditions: Temperature 25°C, stirring speed 60 rpm, volume 1000 mL, electrode distance 1 cm, pH 7, applied potential 20 V, electrode surface area 90 cm².

As mentioned earlier in preliminary results of EC treatment, the treatment time for iron removal increased when the concentration was increased. However, in whole analysis, it can be concluded that the rate of iron removal using groundwater seems to be slower than the solution. In preliminary experiments, there were no other ions that can interfere in the removal process with the oxidizing and adsorption process of aluminium hydroxides focusing only on iron molecules. However, using real groundwater, there may be interference of ions due to the presence of other ionic elements which can react with the hydroxyl ions and result in a substantial reduction of metal removal [215]. Thus, the efficiency of iron removal in groundwater process is slower than the solution.

4.4.7.1 Profile pH during EC treatment using real groundwater

The pH of groundwater was monitored during the iron removal process using EC treatment. The pH changed from the beginning of the process until the end for both

groundwater from Kg. Chicha (GW-C) and UTP (GW-T) as illustrated in Figure 4.14. In the initial stages, the pH was observed to be 6.72 and 6.8 in groundwater (GW-C) containing iron concentration of 10 and 8.8 mg/L. While for groundwater of GW-T containing iron concentration of 5.5 and 3.5 mg/L, the initial pH was 6.8 and 6.89, respectively. The pH value increases with the increase in time and current density. This is due to the formation of higher concentration of OH^- generated by the electrolysis process in the EC reactor [150]. The increase in final pH is attributed to the generation of OH^- ions disassociated from water at the cathode according to the equation below:

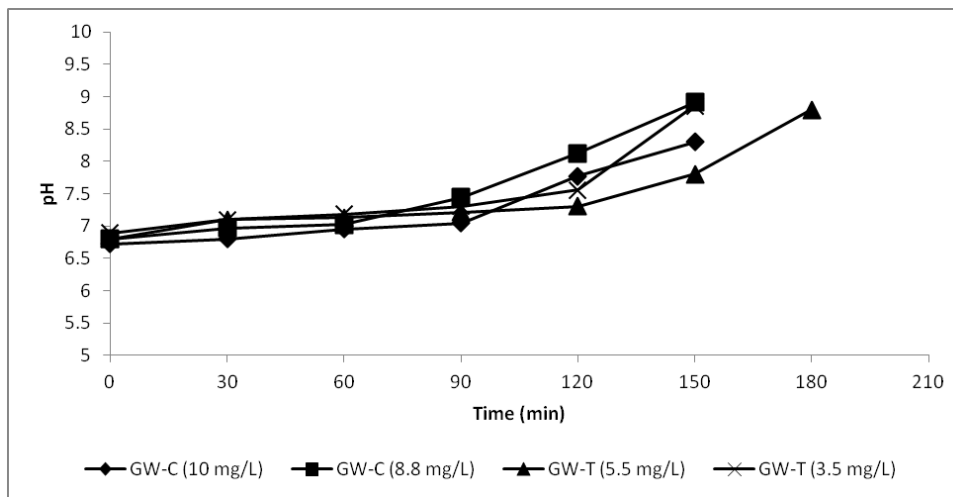
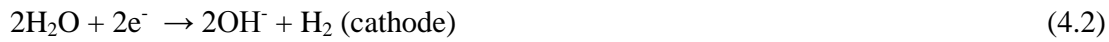


Figure 4.14: pH during EC treatment

At the end of the process, the pH of groundwater GW-C (containing iron concentration 10 and 8.8 mg/L) and GW-T (5.5 and 3.5 of iron concentrations) have increased. The pH was measured to be 8.3, 8.91, 8.8 and 8.86 for corresponding groundwater samples. All the pH readings of the samples were in the allowable range for drinking water standard [71]. It is confirmed that, when the pH is increased, the rate of removal also increased to a certain limit [209]. Thus, at this pH, formation of iron hydroxides happens in the alkaline region. It is also clearly shown that electrochemical treatment is highly affected by pH. A similar observation was also made by Murthy and Parmar [157] and Ratna Kumar et al. [165]. They discussed that pH is an important operating factor influencing the performance of electrochemical process. The pH of the groundwater during iron removal by sulfide precipitation process was found in the range of 7 to 8. It is different with EC treatment where the pH was between 8 and 9 even though the pH is still within WHO standard. The pH of the groundwater during sulfide

precipitation was constant at pH 7 because sodium acetate was used as a buffer to maintain the pH.

4.4.7.2 Profile Eh during EC treatment using real groundwater

The redox potential or Eh was measured during the removal of iron from groundwater using EC process. The results of the change in Eh value during EC treatment was plotted and shown in Figure 4.15. The initial Eh value of GW-T groundwater was about -20 mV. While the Eh value for GW-C groundwater was about 20 mV. Eh in ground water was generally low due to the absence of oxygen [216]. However, the Eh value of GW-C groundwater increased due to transportation of samples to the laboratory compared to the samples of GW-T. The GW-T samples were directly measured and used for the EC treatment since the well was located near the laboratory.

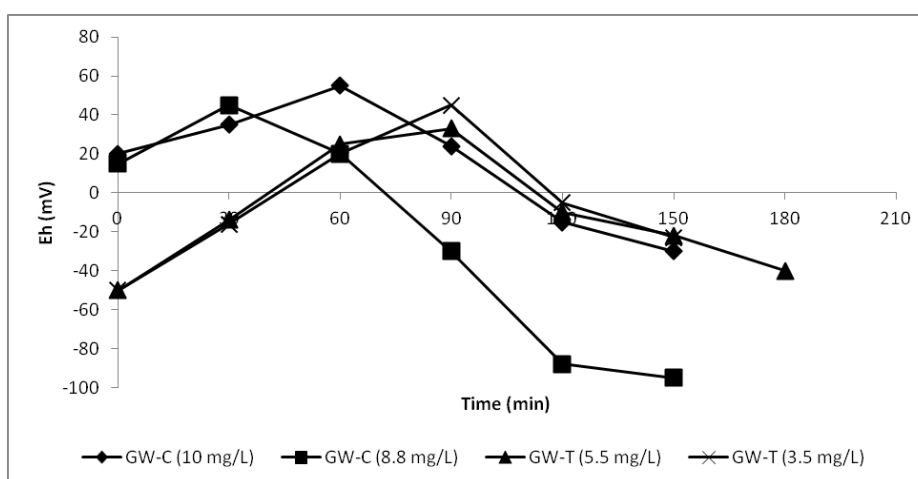


Figure 4.15: Eh during iron treatment using EC method

During the initial EC process, Eh increased rapidly to a maximum range between 40 mV and 50 mV after 90 minutes. The Eh value for GW-C with 10 and 8.8 mg/L of iron concentration increased to 55 and 45 mV respectively. While the Eh for GW-T with 5.5 and 3.5 mg/L of iron concentration increased to 33 and 45 mV for corresponding iron concentrations. However, towards the end of the process, the Eh dropped to below zero. The Eh dropped when the reaction reaches the limit as the applied voltage increases the temperature and lower the oxidation process [217]. At the end of the process, the Eh value for GW-C decreased to - 40 and – 95 mV for the two samples while the Eh value for GW-T decreased to – 23 and – 40 mV respectively. It is confirmed that iron can be formed into ferric or $\text{Fe}(\text{OH})_3$ either in high or low Eh value [218]. This formation is in

solid form [219]. In sulfide precipitation, the Eh continues to drop during iron removal process until it reached -300 mV which is almost 10 times higher compared with the Eh value in EC treatment. During sulfide precipitation process, the Eh dropped due to sulfate reduction activity that increased the sulfide gas as was mentioned earlier in section 4.3.3.2.

4.4.7.3 Profile current density during EC treatment using real groundwater

Current density was monitored during the EC treatment and the results are shown in Figure 4.16. Due to constant applied voltage, the current density is varied. In the beginning of the process, at applied voltages and surface area of 20 volts and 90 cm² respectively, the average current density for the treated groundwater of GW-C and GW-T was 0.03 and 0.029 A/cm². At this stage, high current density produced high amount of hydroxyl ion by forming a bubble around the electrode. The density of the bubble increases and the size is decreased to accelerate the removal process [156].

Increase in time resulted in decrease in current density and subsequently decrease in residual iron concentration. This is due to a slower reaction rate caused by concentration gradient. On the other hand, the bubble production rate and the size also decreased. Consequently, the flocs growth becomes slow resulting in a slower removal of iron at low concentration. The GW-C with iron concentration of 10 and 8.8 mg/L, the current density dropped to 0.022 and 0.025 A/cm² after iron was removed. The average current density at the end of the process for GW-T (5.5 and 3.5 mg/L of iron concentration) was found to be 0.021 A/cm². The reduction of current density followed by reduction of iron concentration occurs probably due to the formation of iron hydroxide and aluminium hydroxide during the process and the conductivity of the water getting low. The conductivity reduces because of the unavailability of metal coagulant which is aluminium that form aluminium hydroxide [220].

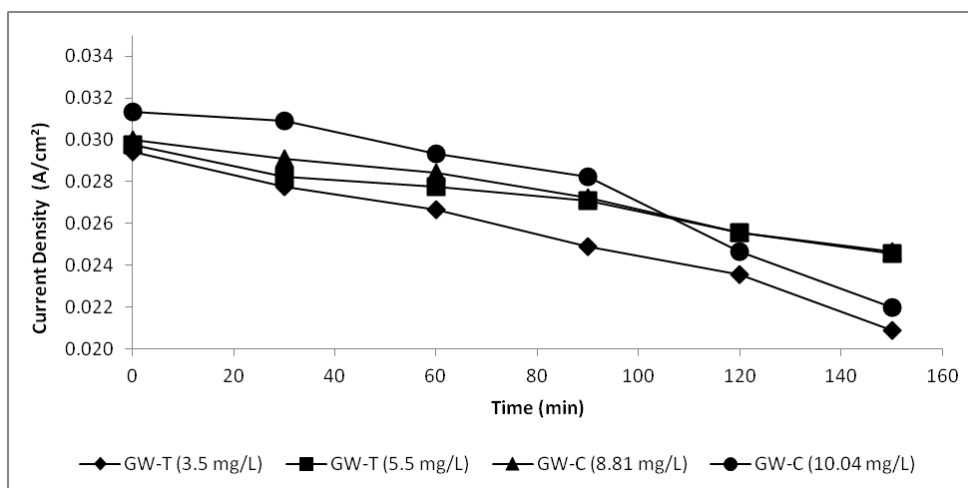


Figure 4.16: Result on current density during EC treatment

4.4.7.4 Profile of aluminium concentration during EC treatment using real groundwater

Iron removal by EC treatment using aluminium electrode is associated with aluminium concentration in treated water. The used aluminum electrodes can give an effect to the treated water. Due to oxidation of sacrificial anode, there is the tendency that dissolved aluminum can increase the concentration of aluminum in the effluent. Thus, this gives another problem for iron removal process. Aluminum dissolves due to the applied current. The aluminum concentration is monitored during this process and illustrated in Figure 4.17.

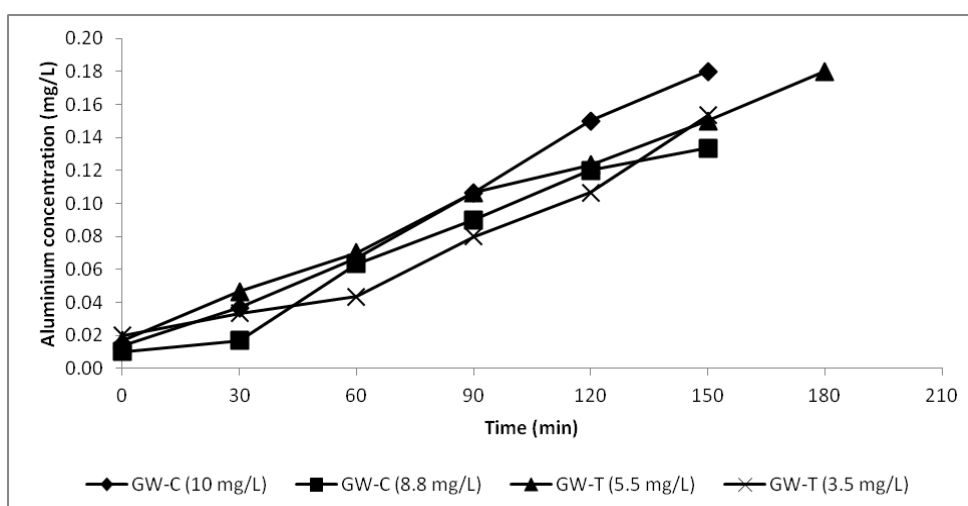


Figure 4.17: Aluminium concentration during treatment of iron

Initially, the average concentration of aluminium in groundwater samples of GW-C and GW-T was 0.01 and 0.02 mg/L. As the reaction proceeds, aluminium concentration also increased. During the process, aluminium released from the electrodes precipitated with iron. Due to solubility of aluminum, some of the aluminium ions released from the electrode did not precipitate thereby increasing residual concentration of aluminium in the groundwater samples. The average residual aluminium concentration for groundwater of GW-C was 0.16 mg/L and 0.17 mg/L for the groundwater of GW-T. This aluminum concentration implies that EC treatment can be operated without producing a secondary pollutant as being mentioned before [146]. The concentration is still within the WHO allowable standard limit of 0.2 mg/L [71]. The iron removal process by sulfide precipitation also indicated that residual sulfide concentration was below the allowable standard limit of 50 µg/L. Thus, both processes did not bring any secondary pollutant. However the use of EC treatment by aluminum electrode can be done in high iron concentration compared with sulfide precipitation process.

4.5 Result of surface and composition analysis

4.5.1 Results of FESEM analysis on sludge after sulfide precipitation

The sludge production is another important parameter in characterizing the sulfide precipitation and electrocoagulation (EC) process. The structure and surface morphology of the sludge for both processes was characterized by FESEM. The sludge image of sulfide precipitation process at 200 nm scale bar shows that sulfide minerals of iron was formed with grain sizes ranging from 2.8 µm to 4.8 µm as shown in Figure 4.18. This was aligned as mentioned before, since the size of pyrite is in the range of 2 µm to 5 µm [131]. The minerals show surface configuration of a cubic system. This proves that pyrite (FeS₂) was formed during sulfide precipitation in cubic shape similar to the mineral described by Rickard and Luther [199].

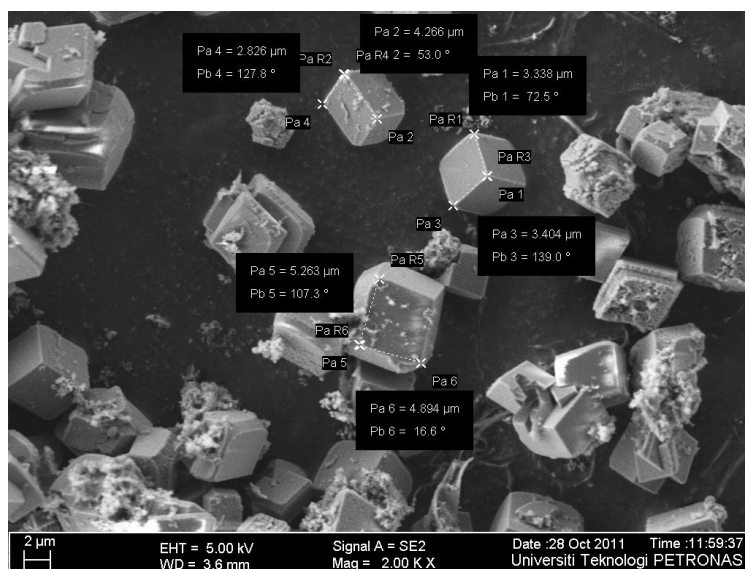


Figure 4.18: FESEM image of the sludge produced in the sulfide precipitation process

Figure 4.19 shows the results of EDAX analysis of the sludge that was formed by sulfide precipitation. The figure shows the metal elements that were precipitated during the experiment which include O, S, Si, Ca, C and Fe. In the EDAX image, the compositions yield was almost at the same peak.

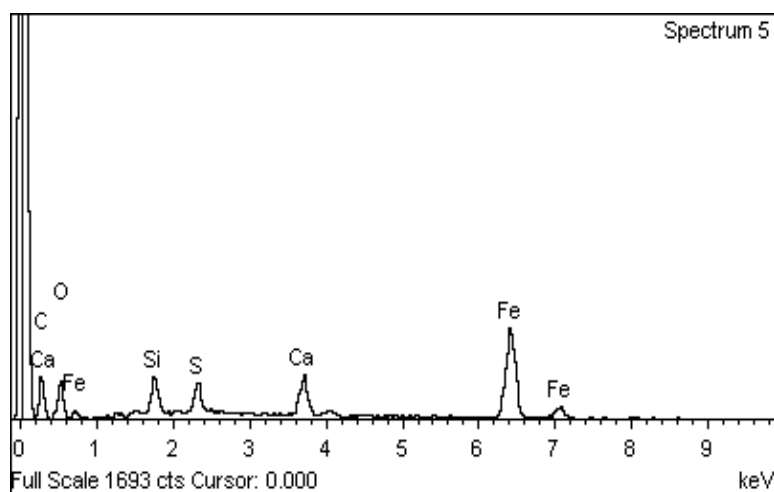


Figure 4.19: EDAX spectrum of the sludge produced during sulfide precipitation process

The weight and atomic percentage of compositions in the sludge produced during sulfide precipitation are listed in Table 4.2. The EDAX spectrum proves that pyrite or iron sulfide (FeS_2) was formed during the iron removal process. The weight and atomic percentage was analyzed to be 7.99 and 5.65%. The characteristics also indicated that the elements in the sludge contain iron having a weight and atomic percentage of 13.76% and

4.89%. During the sulfide precipitation process, other metals also were traced such as calcium. Calcium was found in a form of calcium carbonate and wollastonite. Wollastonite is one of the minerals that have composition of calcium silica oxides (CaSiO_3).

Table 4.2: Characteristics of the sludge produced during sulfide precipitation process in weight and atomic (%)

Element	Weight %	Atomic %
C - CaCO_3	11.44	18.91
O - SiO_2	43.58	54.09
Si - SiO_2	20.61	15.16
S - FeS_2	7.99	5.65
Ca - Wollastonite	2.62	1.30
Fe - Iron	13.76	4.89

4.5.2 FESEM and EDAX analysis of sludge after EC treatment

Compared to the sludge from sulfide precipitation, the FESEM analysis of the sludge from EC process at 200 scale bar shows grain sizes in the range of 23 nm to 37 nm (Figure 4.20). The sizes were randomly measured from 5 spots and they were bigger than the sludge of sulfide precipitation. The roundness of the crystals is sub-angular compared to sulfide precipitation crystal.

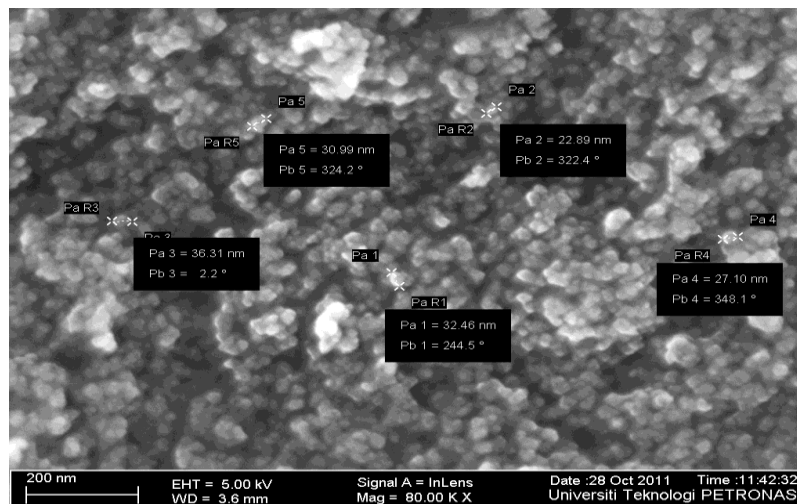


Figure 4.20: FESEM image of the sludge produced in the EC process

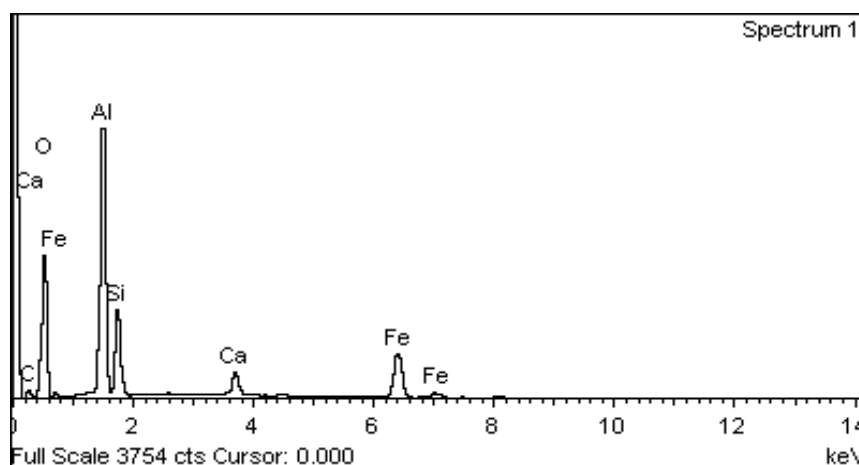


Figure 4.21: EDAX spectrum of the sludge produced during the EC process

Figure 4.21 shows the results of EDAX analysis of the sludge produced during the EC process. The composition analysis of the sample indicates that O, Al, Si, Ca, C and Fe are present in the sludge which is a confirmation of the formation of colloidal matter in the sludge. These compositions were almost similar with the sludge from sulfide precipitation except for aluminum (Al) and pyrite (FeS_2) composition.

The percentage of weight and atomic sludge characteristics are presented in Table 4.3. Based on the EDAX spectrum and the table, aluminium was one of the elements whose yields are prominent to the highest peak. It shows that aluminium is one of the major constituents that triggered the reduction of iron in groundwater by EC process.

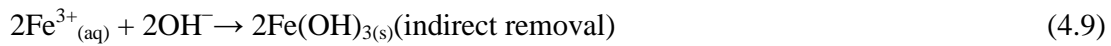
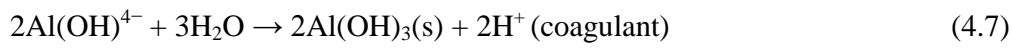
Table 4.3: Characteristics of the sludge produced during EC process in weight and atomic percentage (%)

Element	Weight %	Atomic %
C - CaCO_3	38.47	60.33
O - SiO_2	19.64	23.12
Si - SiO_2	3.26	2.19
Al - Al_2O_3	2.71	1.59
Ca - Wollastonite	4.86	2.28
Fe - Iron	31.07	10.48

Figure 4.21 and Table 4.3 also shows that calcium is precipitated. This suggests that this treatment can also effectively reduce water hardness. When pH increases, more hydroxyl ion (OH^-) will react with the bicarbonate ion (HCO_3^-) in groundwater to form calcium carbonate (CaCO_3) which precipitate according to the chemical formula below:



Iron precipitation took place either through direct removal or indirect removal. The direct removal could happen because at the cathode, Fe^{3+} accepts three electrons from Al and deposited. Meanwhile, Al^{3+} released into the water reacts with OH^- (formed during electrolysis of water) to form $\text{Al}(\text{OH})_3$ and coagulate with iron. Similarly, Fe^{3+} ions also react with OH^- and form $2\text{Fe}(\text{OH})_3$. The reactions of electrochemical removal of iron can be summarized as follows:



CHAPTER 5

CONCLUSION AND RECOMMENDATION

Minerals in groundwater can render the water unsuitable for various purposes. Iron can give an effect on such as stain, odor, taste and health. Various methods have been applied to treat the iron. Treatment of iron by sulfide precipitation and electrochemical-coagulation (EC) were conducted to treat the iron by using solution and groundwater. A preliminary study was conducted with iron solution for both methods and obtained the optimum conditions applied to real groundwater. The parameters investigated in sulfide precipitation method including pH and contact time while the parameters investigated in electrochemical-coagulation include pH, voltage, contact time, inter-electrode distance, electrode surface area and sample volume.

The pH was of significant importance for both methods. Increase in pH resulted in increase in removal efficiency for both methods. The pH 7 was optimum for both sulfide precipitation and EC process with a removal efficiency of 75% and 95% after 6 hours and 2 hours treatment time respectively. Increase in contact time increased removal efficiency for both methods. However, low contact time (2 hours) was required for electrochemical-coagulation than sulfide precipitation (6 hours). Increase in electrode distance decreased the removal efficiency and increased the treatment time in EC process. The optimum electrode distance was observed at 1 cm with a residual iron concentration of 0.28 mg/L after 150 minutes. Increase in applied voltage resulted to increase in removal efficiency in EC method. An optimum voltage of 20V was used in this study with a residual iron concentration of 0.24 mg/L after 150 minutes of treatment time. Increase in electrode surface area resulted to increase in removal efficiency. The optimum surface area was 90 cm² with a residual iron concentration of 0.28 mg/L below the permissible limit of 0.3 mg/L. Increase in iron concentration resulted in a decrease in removal efficiency. Increase in sample volume also resulted in a decrease in removal efficiency.

Groundwater from Universiti Teknologi PETRONAS (UTP) monitoring well Perak, groundwater treatment plants of Kampung Chicha, Tanjung Mas and Kampung Puteh, Kelantan was used and the efficiency of both methods was evaluated in batch study. Application of obtained optimum conditions to the real groundwater samples showed that sulfide precipitation and electrochemical-coagulation are both effective in removing iron from groundwater. Iron in groundwater can be removed up to 83% of the initial concentration of 1.5 mg/L by sulfide precipitation method. At higher initial concentrations of 3.55 mg/L and 5.01 mg/L the efficiency drop to 82% and 75%, respectively. In EC method, the iron concentration up to 10 mg/L (above 95% removal efficiency) requires 90 minutes contact time to drop below 0.3 mg/. While concentration between 3.5 and 5.5 mg/L corresponds to 91% and 94% requires 60 minutes to reach below the drinking water standard. However, EC treatment had a comparative advantage over sulfide precipitation with regards to treatment time and removal efficiency. While it is recommended that sulfide precipitation be applied to samples with low iron concentration due to slow reaction of sulfide and iron at inert atmosphere, electrochemical precipitation can be effectively used for samples with high concentration.

5.1 Recommendations for experiment on iron removal from groundwater by sulfide precipitation

In sulfide precipitation method, there are few recommendations could be applied in the future study to remove iron in groundwater as listed below:

- ☐ Determine the suitable temperature and pressure that can produce sulfide gas without reaching the toxicity level.
- ☐ Determine the produced sulfide concentration that can reduce mg/L of iron.
- ☐ Study other possible source which can produce sulfide gas or other materials in sulfide precipitation process.

5.2 Recommendations on iron removal from groundwater by electrochemical-coagulation (EC) method

For the further study of iron removal in groundwater by EC method, the following recommendations are proposed as listed below:

- Consumption of aluminum plates should be calculated to determine the durability and quantity of the plates to be used for the removal process.
- Identify cost of electricity and other related costs for water production.
- Conduct the treatment process in continuous flow and in-situ experiment or pilot scale of treatment plant.
- Study on iron removal by EC treatment by using other electrodes which can minimize the current applied parameters.

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LIST OF PUBLICATIONS AND ACHIEVEMENTS

In Refereed Journals:

1. Nasiman Sapari, Raja Zainariah Raja Azie and Hisyam Jusoh (2012). *Groundwater from Fractured Granite and Metasedimentary Rocks of the West Coast, Peninsular Malaysia*. *Pertanika Journal of Science and Technology*, 20 (2): 371 - 379
2. Hisyam Jusoh, Nasiman Sapari and Raja Zainariah Raja Azie (2011). *Removal of Iron from Groundwater by Sulfide Precipitation*. *International Journal of Chemical and Environmental Engineering*, Vol. 5 Issue 60, page 652 – 658, eISSN 2010-3778
3. Sapari, N., Raja Zainariah, R. A. and Hisyam Jusoh (2011). *Quantity and Quality of Groundwater in Fractured Metasedimentary Rocks of the West Coast of Peninsular Malaysia*. *Sains Malaysiana*, 40(6): 537-542
4. Sapari, N., Jusoh, H. and Raja Azie, R.Z. (2010). *Groundwater in fractured granite for water supply to remote areas in Malaysia*. *Water Practice and Technology Journal*, Vol. 5, Issue 2, doi: 10.2166/wpt2010.041.

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1. Sapari, N., Raja Azie, R.Z and Jusoh, H. (2010). *Groundwater from fractured granite and metasedimentary rocks in the west coast of Peninsular Malaysia*. *Proc. World Engineering Congress 2010*, 2nd-5th August, Kuching, Serawak.
2. Sapari, N., Azie, R. Z. and Jusoh, M. N. H. (2009). *Groundwater from granite aquifer for water supply to remote areas of Malaysia*. *Third Specialized Conference on Decentralized Water and Wastewater International Network of IWA*.

Presented Paper

1. Hisyam Jusoh, Nasiman Sapari, Asim Yaqub, Raja Zainariah Raja Azie (2012). *Electrochemical Removal of Iron (Fe) from Groundwater using Aluminium (Al) Electrode*. Proc. International Conference on Civil Offshore and Environmental Engineering (ICCOEE), World Engineering, Science & Technology Congress (ESTCON), Kuala Lumpur Conventional Centre, Malaysia.
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