CHAPTER 4

GROUNDWATER TREATMENT FOR IRON REMOVAL

4.1   INTRODUCTION

This chapter emphasizes on an alternative method of iron removal in cases where there is an abundance of iron in groundwater. At present conventional groundwater treatment is used for iron removal. Room temperature ionic liquid (RTILs) has long been used as solvents for numerous applications. Therefore, this chapter will briefly investigate the ability of ionic liquids to act as solvents for iron removal in groundwater using liquid-liquid extraction method.

4.1.1 Problems faced in Kelantan Groundwater

In Chapter 3 (Table 3.5), the presence of iron has been detected in Kelantan groundwater. The mean concentration of iron in aquifer layers ranges from 0.54 to 80.00 mg/L. The natural source of iron and other heavy metals are said to be originating from the deposited sediment in the Kelantan basin during Holocene time. More iron enters into the solution as the groundwater ages. This is because iron is released slowly from geologic materials through rock-water interaction process.

For example, in Minnesota groundwater; concentrations of iron exceed 1.00 mg/L in aquifers occurring in geologic materials that contain large amounts of iron, such as Cretaceous and some Precambrian deposits. High concentration of iron also can be found in aquifer with reducing condition such as the buried Quaternary aquifers. The reducing conditions of aquifer are characterized by low concentrations of oxygen, nitrate and Eh values less than 250 mV. Under these conditions, microbes utilize ferric

ion during food consumption. Conversion of ferric ion to ferrous ion results in dissolved iron concentrations that exceed the standard values. Aquifers occurring in low iron rocks, such as some of the Precambrian deposits, and aquifers containing oxygen, will have iron concentrations less than 0.10 mg/L (Minnesota Pollution Control Agency, 1999).

Iron is the major concern in the study area because even small amounts will seriously affect the usefulness of water for domestic and industrial purpose (Awadalla & Noor, 1990). Although iron is an essential mineral for human body, high iron also causes chronic iron overload-genetic disorder (*haemochromatosis*). According to Centers for Disease Control (CDC), a disorder can result in organ damage because of significant and excessive absorption and storage of iron from the daily diet. Over time, this excess builds up in organ tissues such as the heart, liver, pancreas, joint and pituitary. The advanced stages of *haemochromatosis* are:

   i. arthritis

  ii. liver disease, including an enlarged liver, cirrhosis, cancer, and liver failure

 iii. damage to the pancreas, possibly causing diabetes

 iv. heart abnormalities, such as irregular heart rhythms or congestive heart failure

  v. impotence

 vi. early menopause

 vii. abnormal pigmentation of the skin, making it look gray or bronze

Statistics from Hospital Universiti Sains Malaysia (HUSM) show that only 13 cases of *Haemochromatosis* have been reported from 1996 to 2009 as stated in Table 4.1. Only 2 cases involved on children while the rest cases involved on adult.

Table 4.1: Statistics of Haemochromatosis cases from 1996 – 2009

Haemochromatosis	Children (below 12 year old)		Adults (above 12 year old)	
	Male	**Female**	**Male**	**Female**
Cases	1	1	5	6
Total	2		11	

In term of irrigation, if the iron contents are accumulated in the irrigated soils over a long period of time, the soil properties as well as the nutrient uptake will be affected because iron bearing waters favors the growth of iron bacteria which can change certain forms of dissolved iron into insoluble ferric state. The insoluble iron is deposited in the voids of soil and can seriously clog the pores of water bearing formation and the opening in a well screen which ultimately restricts the movement of water. This will reduce the soil permeability (K). Once the agriculture soils are affected due to high iron content, further utilization will turn the agriculture lands into nonproductive areas. Thus, the World Health Organization, WHO (2008) has set the guideline value of 0.30 mg/L of iron in drinking water.

4.1.2 Groundwater Abstraction in Kelantan

In northern Kelantan, most of the groundwater has been exploited from shallow aquifer for public water supplies. In total there are 6 well-fields as noted in Chapter 1 which cover the districts of Kota Bharu, Bachok and Tumpat. Table 4.2 shows that the groundwater abstraction in North Kelantan from 1974 until 1995 (Mohammad & Ang, 1996). The value was estimated from 60 monitoring wells during the time period. It shows an increase in groundwater abstraction as a result of increase in the population in these districts for water supply. While Table 4.3, show the estimated demand of groundwater in Kelantan for 2010 (Suratman, 2010). As mentioned in Chapter 1, 165 MLD is the estimation values of groundwater demand in Kelantan 2010. According

Table 4.3, the total groundwater abstraction in North Kelantan is estimated about 148 MLD. Comparing from 1995 to 2010, the demand of groundwater has increased about 75 MLD. Over the years, it shows an increase in trend of groundwater demand for water supply in North Kelantan. These trends are expected to continuously increase in the future.

**Table 4.2:** Groundwater Abstraction in North Kelantan from 1974 – 1995

District	Well field	Groundwater abstraction (MLD)						
		1974	1980	1985	1988	1991	1994	1995
Kota Bharu	Tanjung Mas	-	3.18	3.18	2.59	9.00	9.00	9.00
	Pintu Geng	-	4.55	3.64	2.50	12.13	19.85	19.85
	Kampung Puteh	10.46	26.14	28.94	28.94	30.75	30.75	30.75
	Total	10.46	33.87	35.76	34.03	51.88	59.60	59.60
Bachok	Kampung Chap	0.09	0.14	1.68	1.68	4.55	4.55	4.55
	Total	0.09	0.14	1.68	1.68	4.55	4.55	4.55
Tumpat	Wakaf Bharu	0.18	0.09	5.45	3.77	8.73	8.73	8.73
	Total	0.18	0.09	5.45	3.77	8.73	8.73	8.73
	Grand Total	*10.73*	*34.10*	*42.89*	*39.48*	*65.16*	*72.88*	*72.88*

Table 4.3: Estimated Kelantan Groundwater Demand for 2010

District	Population 2010	Population %	Groundwater user (%)	Groundwater users	Groundwater Demand (m³/day)
Kota Bharu	509600	30.37	95	484120	96824
Bachok	142100	8.47	100	142100	28420
Tumpat	173200	10.32	65	112580	22516
Pasir Mas	212000	12.63	20	42400	8480
Pasir Puteh	134200	8	10	13420	2684
Machang	101300	6.04	10	10130	2026
Tanah Merah	133400	7.95	10	13340	2668
Jeli	48000	2.86	2	960	192
Kuala Krai	120800	7.2	2	2416	483
Gua Musang	103300	6.16	2	2066	413
KELANTAN	*1677900*	*100*	*-*	*823532*	*164706*

4.1.3 Groundwater Treatment in Kelantan

Groundwater in Kelantan is being treated using conventional treatment method. This conventional method consists of aeration, coagulation, sedimentation, filtration and disinfection. An aeration process precedes oxidation for oxygenation and removal of carbon dioxide (pH increase), sulfurs and other volatile substances. The coagulation will remove dirt and other particles suspended in water. Sedimentation takes place where heavy particles (floc) settle to the bottom and the clear water moves to the filtration. During filtration, the water passes through dual sand filtration made up with layers of fine and coarse sand that help remove small particles. Then, it is followed by the disinfection process where small amounts of chloride are added to kill any bacteria or microorganism present. Figure 4.1 shows the schematic flow of groundwater treatment done by Air Kelantan Sdn. Bhd.
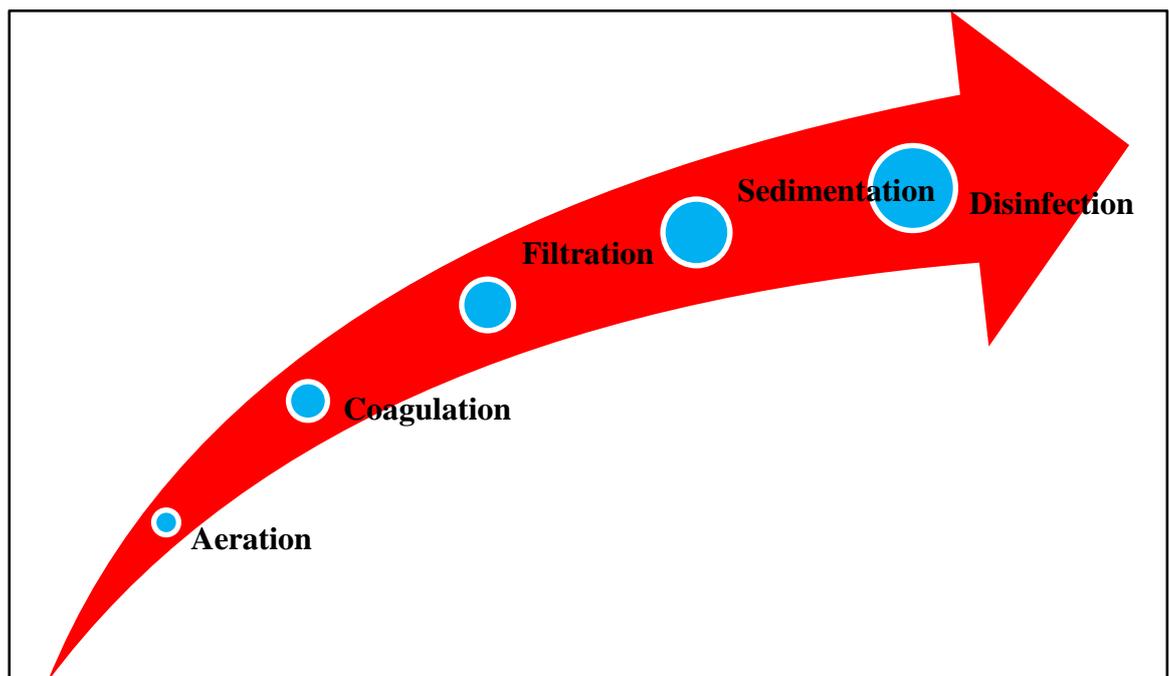
**Figure 4.1:** Schematic Flow of Conventional Groundwater Treatment

Recently, Air Kelantan Sdn. Bhd proposed another treatment method for groundwater. This new method is called ozonation groundwater treatment. The purpose of this method is to improve taste and color as well as to remove the organic and inorganic matters in groundwater (Kasprzyk-Hordern *et al.*, 2003). The disadvantages of ozonation are relatively its low solubility and stability in water. The application of ozonation might not be feasible from an economic point of view because of high cost and only partial oxidation of organic compound present in water. Ozone is known to be a powerful oxidant, but it reacts slowly with some organic compounds such as inactivated aromatics. In many cases, it does not provide complete oxidation of organic compounds (e.g. natural organic matter (NOM)), which results in the formation of biodegradable organic matter (carboxylic acids, carbonyl compounds).

4.1.4   General Description of Ionic Liquids

Room temperature ionic liquid (RTILs) do not contain any molecules, but they are made of ions. Ions are present in the liquid with an exactly equal number of positive and negative ions so that the whole liquid is electrically neutral (Carda-Broch *et al.*, 2003). The first RTIL, ethyl ammonium nitrate $[EtNH_3][NO_3]$ with a melting point of 12°C was discovered in 1914 during World War I (Ping Sun & Armstrong, 2010). A new class of RTILs has been reported in the 1980's consisting of dialkylimidazolium chloroaluminate. However, these chloroaluminate ionic liquids did not receive considerable interest due to their reactivity to moisture and many chemicals (Wilkes *et al.*, 1982). The true emergence of ILs as broadly useful solvents occurred with the first development of air and moisture-stable imidazolium salts in 1992. Most of the synthesized stable RTILs contain weak complexing anions, such as BF_4^- (Wilkes & Zaworotko, 1992). RTILs have increasingly attracted attention as green, high-tech

reaction media of the future. Ionic liquids (ILs) have aroused increasing interest for their promising role as alternative media for volatile solvents (Wei *et al.*, 2003).

The most common cations in ionic liquids are imidazolium, pyrrolidinium, pyridinium, tetraakylphosphonium and tetraakylammonium. While the most common anion includes halides (X^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), trifluoromethylsulfonate (TfO^-), nitrate (NO_3^-), acetate (OAc^-) and bis(trifluoromethanesulfonyl)imide (NTf_2^-). The combinations of such cation and anion can lead to a larger number of ionic liquids that can provide considerable flexibility in the selection of the most suitable pair for a specific chemical application. Figure 4.2 shows the common cations and anions in ionic liquids.
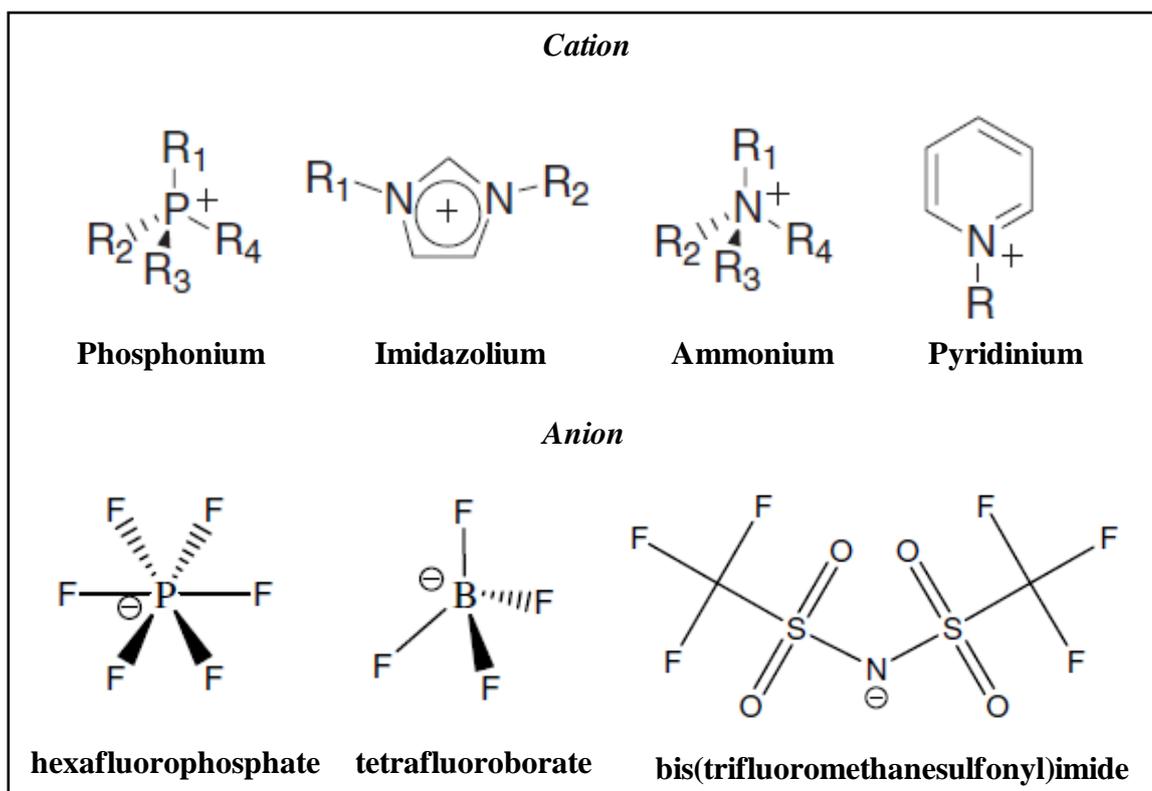
Figure 4.2: Common Cation and Anion Used in Ionic Liquids
(James & Davis, 2004; Sharma, 2008)

Ionic liquids account for their application in many fields such as catalysis, biocatalysis processing, extraction, electrochemistry or separation (Stepnowki & Zaleska, 2005). The applications of ionic liquid have expended over the past year due to their variable physicochemical properties. The main attractive physicochemical properties of RTILs are (Jonathan *et al.*, 2005 and Calda-Broch *et al.*, 2003): (i) nonvolatile at elevated temperatures; (ii) wide range electrochemical potential windows; (iii) high thermal and chemical stability; (iv) nonflammability under ambient condition; (v) media for various reaction; (vi) wide range viscosities and (vii) can be made miscible or immiscible with water and/or a number of organic solvents. Usually the term of 'Green Solvents' always refer to non-volatile, non-flammable and thermally stable ionic liquids that make such as promising replacement for the volatile organic solvents (Huddleston *et al.*, 2001).

For separation technique, the selection of RTILs is based on one of the physicochemical properties; immiscibility in water, nonvolatility and nonflammability. Water immiscibility is an important criterion because RTILs that are incorporating with hydrophobic cations and anions appear to be available for the liquid – liquid extraction (LLE) process. The nonvolatile and nonflammable RTILs is an important advantage over the conventional organic solvents (Goto *et al.*, 2003 and Goto & Shimojo, 2004).

### 4.1.5   Ionic Liquid as a Medium in Liquid-Liquid Extraction

Over the last ten years, numerous studies on the application of imidazolium ionic liquids as solvents for separation processes has been carried out. [C_4mim][PF_6] was first applied as a solvent for the extraction of organic benzene (Roger *et al.*, 1998). Several studies show the application of ionic liquids as a medium for extraction of metal ions using LLE technique (e.g. Roger *et al.*, 2001; Visser *et al.*, 2002; Wei *et al.*, 2003;

Sheng *et al.*, 2004; Li *et al.*, 2007 and Zou *et al.*, 2008). Using the functionalized ionic liquids as an extractant and hydrophobic phase (Roger *et al.*, 2001), cadmium ($Cd^{2+)}$ and mercury (Hg^{2+}) were successfully extracted from an aqueous medium via the formation of an IL-metal complex (Visser *et al.*, 2002). The [C_4mim][PF_6] as an alternative solvent and dithizone as a metal chelator formed metal-dithizone complex with heavy metal ions. The extraction, separation and pre-concentration were achieved by controlling the pH (Wei *et al.*, 2003). BOBCalixC6 in ILs provides efficient extraction of cesium ions from aqueous solutions without the introduction of an organophilic anion in aqueous phase (Sheng *et al.*, 2004).

Successful extraction and back-extraction of inorganic mercury with [C_4tmsim][PF_6] ionic liquid using CDAA as chelating agent are also reported. This method is used to determine trace inorganic mercury in natural water with satisfactory results (Li *et al.*, 2007). The extraction of Ce(IV) along with Th(IV) and Ln(III) (Ln = Ce, Gd, Yb) nitrate by pure ionic liquid [C_8mim][PF_6] has also been tested. [C_8mim][PF_6] only showed good extraction ability for Ce(IV), poor for Th(IV) and negligible for Ln(III). Thus, the most probable extraction mechanism proposed for the study is by was anion exchange mechanism (Zuo *et al.*, 2008).

In this study, ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [C_4mim][NTf_2] was used as a solvent medium in LLE together with the 1, 10-phenanthroline as an extractant (Figure 4.3). An extractant has a crucial effect on the separation and extraction efficiency (Goto & Shimijo, 2004). Therefore, the extractant that is added into an ionic liquid has to attain high distribution coefficients for cations in the LLE process (Praunitz *et al.*, 2008). In the analytical

application, an extractant plays an important role because it can determine metal ions in an acid medium. It also forms complexes with metal ions in the system.
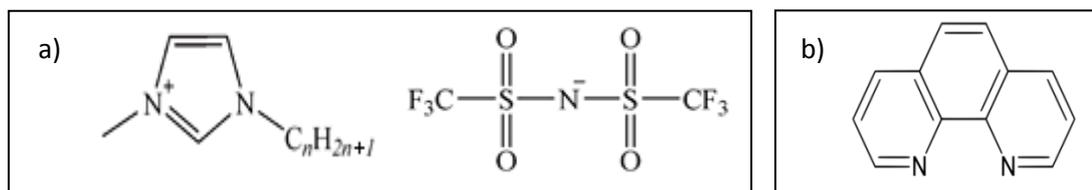
Figure 4.3: a) Structure of [C$_4$mim][NTf$_2$] and b) 1, 10-phenanthroline

4.2 METHODOLOGY

4.2.1 Sampling Points

Seven groundwater samples were collected from Department of Mineral and Geoscience (MGD) wells and private supply wells. Selection of well were based on high iron concentration for each layer of aquifer. Figure 4.4 shows the sampling locations of the selected wells. The groundwaters were sampled using peristaltic pump. Before any samples can be taken, the well should be pumped for 10 minutes or until the TDS reading give constant value to assure only a representative samples were collected. Then, the groundwater samples were filtered through Eijkelkamp filters paper (0.45 µm) into 1L polyethylene bottle. The samples were preserved in two ways; acidified or raw. The acidified samples were preserved with nitric acid at pH <2 and the raw samples were kept in a cold box with a temperature below 4°C. This samples preservation will kept the samples almost at the same condition as its actual state. The sampling and preservation method followed the APHA (1995).

Table 4.4 shows the general characteristic of the selected sampling points. The depth of wells varies from 15.0 m to 131.4 m. All layers are comprised a mixture of sand from fine to coarse and gravel in sizes.

Figure 4.4: Groundwater Sampling Point Locations

Table 4.4: General Characteristic of the Selected Sampling Points

Well	Location	Total depth (m)	Aquifer layer	Formation
KB 39	Kg. Binjai	17.0	1	Quaternary (Sand; fine to medium, greyish)
KB 54	Kg. Bawah Lembah	15.0	1	Quaternary (Sand; coarse, brownish)
KB 05	Pengkalan Chepa	30.0	2	Quaternary (Sand; fine to medium)
KB 13	Tanjung Mas	31.5	2	Quaternary (Sand; medium to coarse, grey)
KB29	Pintu Geng	62.2	2	Quaternary (Sand; coarse to very coarse with some gravel)
KB 01	Pengkalan Chepa	114.0	3	Quaternary (Sand; coarse to very coarse)
KB31	Beris Kubor Health Centre	131.4	3	Quaternary (Sand; coarse to very coarse with some gravel)

4.2.2 Chemicals and solutions

All chemicals and solvents were reagent grade and were used without purification. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide $[C_4mim][NTf_2]$, 1,10-phenanthroline, and iron standard solution (1000 ppm) were supplied by Merck (Darmstadt, Germany). Lithium bistrifluoromethanesulfonylimide was supplied by Acros Organic (New Jersey, USA). Chlorobenzene (99% purity) and chloroform (99.8% purity) were obtained from Lab-Scan (Dublin, Ireland), sodium carbonate and natrium hydrogen carbonate from BDH Limited, England. Acetonitrile was supplied by Fisher Scientific (United Kingdom). Hydrochloric, sulphuric and nitric acids were obtained from Fisher Scientific (United States). Aqueous solutions were prepared using ultra-pure water with specific resistance of 18.2 MΩ-cm (PURELAB Classic by ELGA Labwater).

4.2.3 Instrumentations

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) by Perkin-Elmer (USA) was used for the determination of iron and other cations. The detection limit for ICP-OES ranges from <0.1 pbb to >10pbb depending on the elements in the periodic table. Calibration for samples analysis was done using 1ppm, 2 ppm, 3 ppm, 10 ppm and 20 ppm that contain 13 geology elements (as noted in Chapter 1). The calibration curve for standard solution should be linear through zero with correlation coefficient, r > 0.995. Each sample was replicate three times. The anion and ionic liquid phase were measured by 850 Professional Ion Chromatography Metrohm (Switzerland). The pH value of the extraction systems were measured with Eutech Instruments Cyberscan pH meter (Singapore) that was calibrated with pH 4.00 and 7.00 buffer standards. The conductivity, salinity and total dissolved solids (TDS) were measured

using Hach sensION5 Portable Conductivity Meters (Colorado) that was calibrated with 1000 µS/cm standard solution.

4.2.4 Extraction Procedures

Figure 4.5 shows the simplified laboratory experiments. To perform the extraction mechanism, an aqueous standard solution of Fe(II) and Fe(III) ion was prepared with concentration of 20 ppm. 1 mL of [C_4mim][NTf_2] and 0.05 M of 1, 10 phenanthroline were mixed with ultrasonic agitation. Two phases will be observed when the aqueous solution is added into the ionic liquid. The biphasic system was shaken for 5 hours. The upper aqueous phase was filtered out for analysis. The initial and final solutions were analyzed using ICP-OES to determine the concentration of iron that was left in the aqueous phase. The percentage extraction of iron was calculated using Equation 4.1.

$$\text{Extraction (\%)} = 100D \,/\, [D+(V_{aq}/V_{org})], \quad D = (I-F)/F \tag{4.1}$$

where; D = distribution ratio

V_{aq} = volume aqueous (mL)

V_{org} = volume organic (mL)

I = initial concentration of aqueous (mg/L)

F = final concentration of aqueous (mg/L)

4.2.5 Stripping Procedures

For the stripping procedure of the Fe(III) ions, H_2SO_4, HNO_3 and HCl were used as stripping reagents as shown in Figure 4.5. In the extraction procedure, only 10 mL of aqueous phase containing 5 ppm of Fe(III) ion was used. The aqueous phase was shaken with 1 mL of an ionic liquid containing 0.05 M of 1,10 phenanthroline. After shaking

vigorously for 5 hours, the aqueous phase was removed by filtration to separate the two phases. A 0.5 mL portion of the ionic liquid phase which contained iron-phen complex was stripped back with 2 mL of aqueous acid solution. This was followed by further vigorous shaking until equilibrium was reached. The acid solution was removed and 1 mL acid solution was diluted into 10 mL volumetric flask. The amount of iron was measured using ICP-OES to determine the recovery of the iron. The recovery factor was estimated from the ratio of metals ion in acid solution to aqueous with the correction of dilution factor (Wei *et al.*, 2003). The percentage recovery of iron was calculated using Equation 4.2.

$$\text{Recovery (\%)} = \frac{\text{Concentration of iron in acid after stripping process}}{\text{Extracted iron in IL phase}} \qquad (4.2)$$
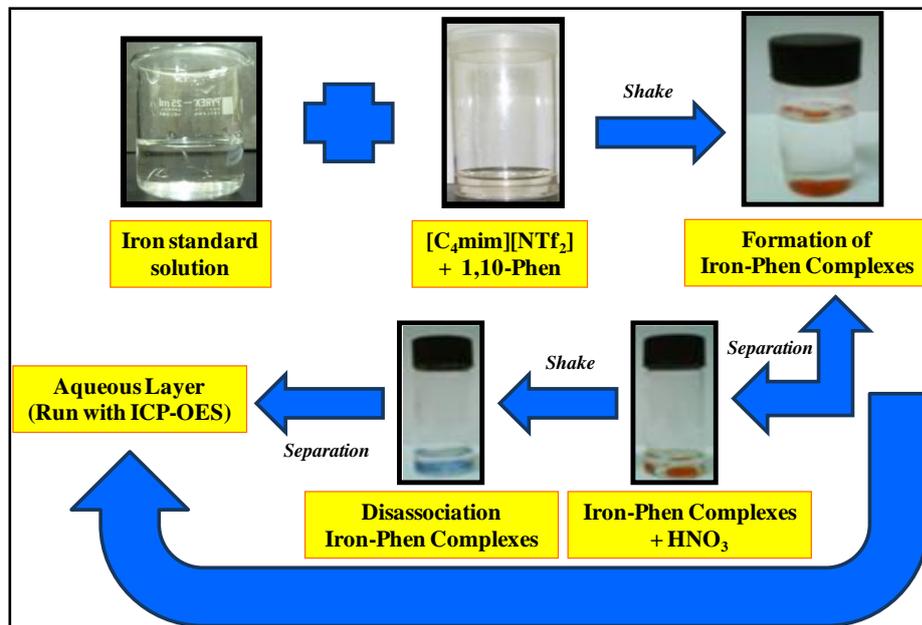
Figure 4.5: Schematic Flow of Iron Extraction and Stripping Process

4.2.6 Reuse/Recycle Procedures

Regeneration of ionic liquid take places after the extraction and stripping process were repeated for a few cycles. The recovery from each cycle shows the applicability of the ionic liquid itself for reuse.

4.3   RESULTS AND DISCUSSION

Two stages of study are involved, the first stage is using the iron standard solution and the groundwater samples is used in the second stage. In order to investigate the potential of $[C_4mim][NTf_2]$ ionic liquid as a medium in liquid – liquid extraction several parameters were studied as listed below:

i.	effect of pH	iv.	effect of phase ratio
ii.	effect of solvent	v.	effect of stripping agent
iii.	effect of time shaking		

4.3.1 Effect of pH

In order to determine the optimal pH required for the extraction, it is important to study the effect of pH on the extraction efficiency of iron-phen complex with $[C_4mim][NTf_2]$ in a wide range of pH as shown in Figure 4.6. It seems that the extraction is strongly dependent on the pH value of the extraction system (Wei *et al.*, 2003). The quantitative extraction (100%) is obtained approximately at pH around 2.5
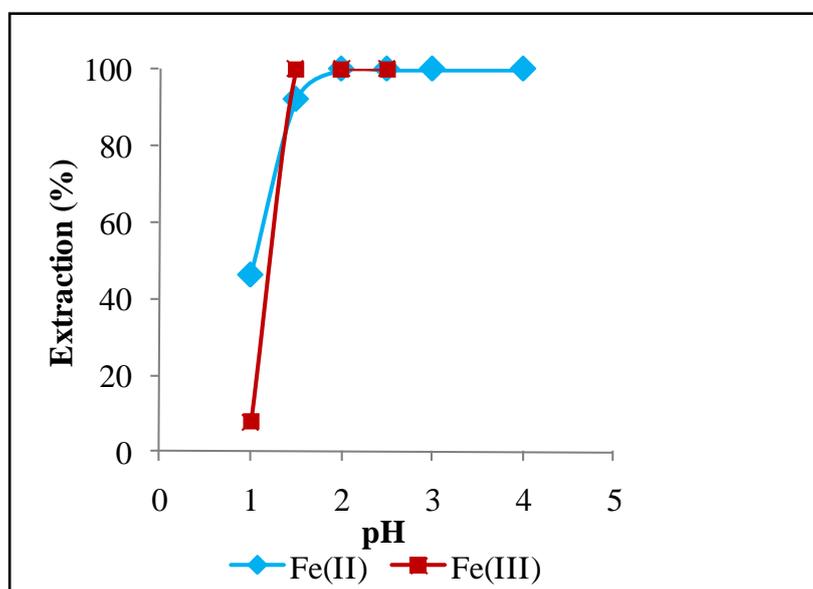
Figure 4.6: Effect of pH on the Extraction Percentage (%) of Fe(II) and Fe(III) Ion (Condition: [Fe(II)] and [Fe(III)] = 20 ppm; [phen] = 0.05 M; $V_{aq}:V_{IL}$ = 10:0.5)
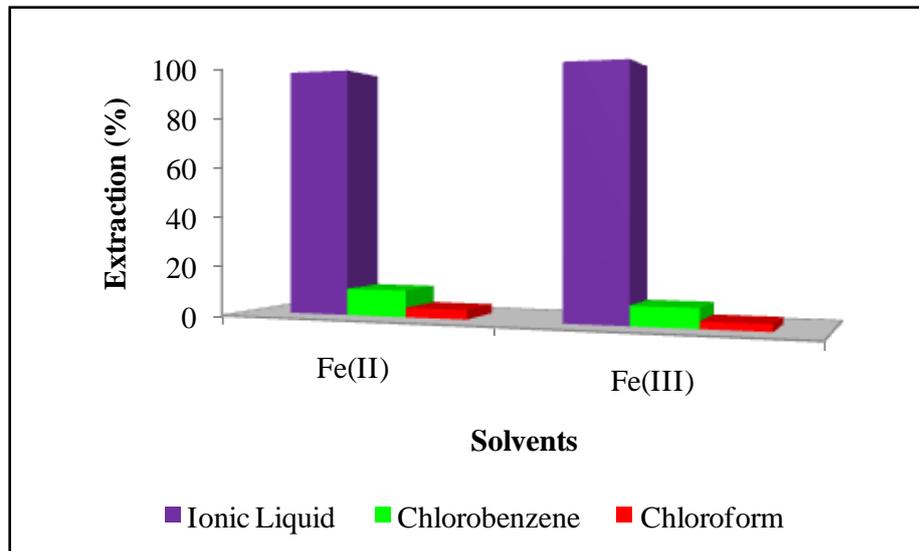
4.3.2 Effect of Solvents

The selection of solvents as the medium for extraction in this study is an important factor and it has to meet the following characteristics:

  i.   it should be heavier than water,

 ii.   it should form a binary homogenous system with water (Farajzadeh *et al.*, 2009)

iii.   it should dissolve the chelating agent.

In this study, other conventional organic solvents such as chloroform ($CHCl_3$) and chlorobenzene (C_6H_5Cl) were used to carry out the extraction efficiency of Fe(II) and Fe(III) in the binary system. Figure 4.7 shows the binary phase of solvents. Ionic liquid ([C_4mim][NTf_2]) gives a clear phase of binary system compared to chlorobenzene and chloroform which are volatile organic compounds (VOCs). The changes in color of ionic liquid from clear to red indicate the formation of iron-phen complex. In chlorobenzene and chloroform the iron-phen complexes are still in the aqueous phase after the extraction but in ionic liquid, the iron-phen complex associates with ionic liquid. Figure 4.8 shows that the ionic liquid has higher extraction efficiency compared to chloroform and chlorobenzene at low pH. It shows that iron-phen complex has higher distribution in ionic liquid phase compared to traditional solvents.
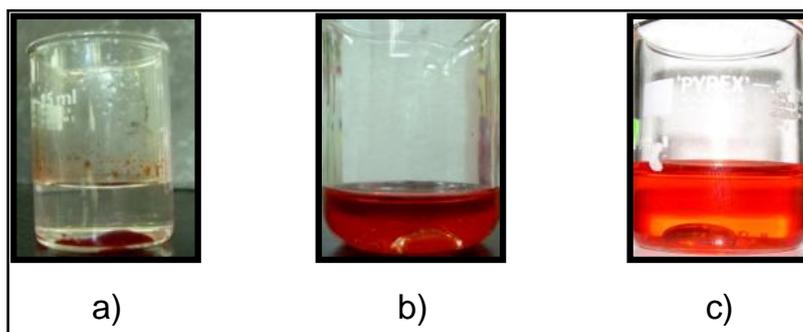

Figure 4.7: Phase Separation a) [C4mim][NTf2]; b) Chlorobenzene; c) Chloroform

Figure 4.8: Effect on Types of Solvent on the Extraction of Fe(II) and Fe(III) Ions (Condition: [Fe(II)], and [Fe(III)] = 20 ppm; [phen] = 0.05 M; $V_{aq}:V_{IL}$ = 10:0.5; $V_{aq}:V_{CHCl3}$ = 10:0.5; $V_{aq}:V_{C6H5Cl}$ = 10:0.5)

4.3.3 Effect of Time Shaking

The extraction time were performed at 5, 10, 15, 20, 60, 120, 180, 240, 300, 480, 960 and 1440 min. Figure 4.9 shows that the extraction efficiencies of Fe(II) and Fe(III) ion with [C_4mim][NTf_2] increases with time. The extraction reaches equilibrium around 300 min but the extraction time was set at 1440 min for all the experiments to ensure that all irons are fully extracted into the ionic liquid.
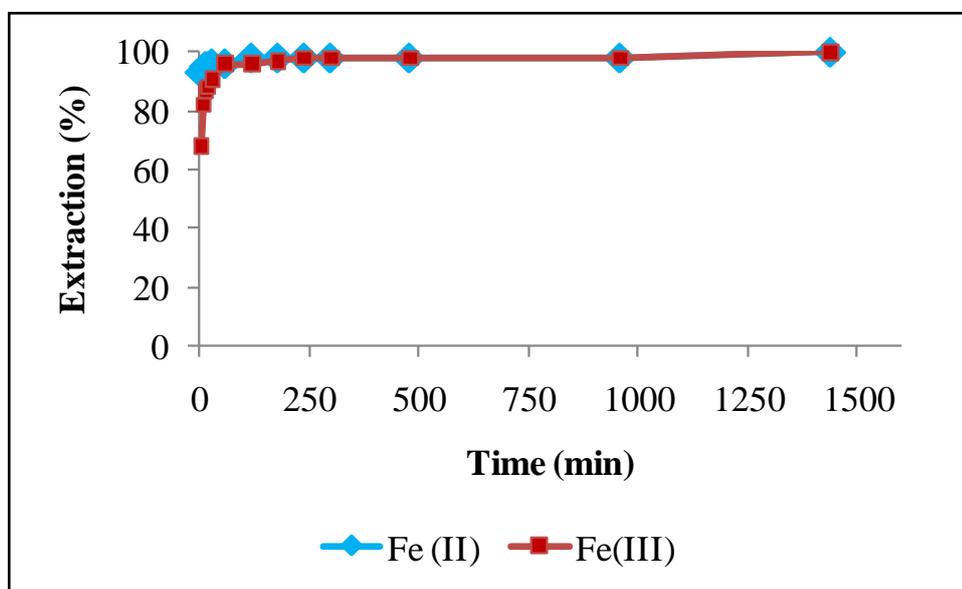
Figure 4.9: Effect of Time Shaking on the Extraction of Fe(II) and Fe(III) Ion (Condition: [Fe(II)] and [Fe(III)] = 20 ppm; [phen] = 0.05 M; $V_{aq}:V_{IL}$ = 10:0.5)

4.3.4 Effect of Phase Ratio

The volume of ionic liquid was fixed at 0.5 mL. The extraction efficiency was obtained by changing the volumes of the aqueous phase at 10, 25, 50, 75 and 100 mL. Figure 4.10 shows the curve of extraction efficiency with different phase ratio. It shows that by increasing the ratio values, the extraction efficiency decreases. Ratio volume of aqueous to volume of ionic liquid (V_{aq}/V_{IL}) at 20 was the optimum condition for extraction. It seem that the ionic liquid shows an economic value in terms of consumption because 0.5 mL ionic liquid can extract Fe(II) and Fe(III) ion in 10 mL of aqueous phase. The percentage extraction of Fe(II) and Fe(III) ion starts to decrease at ratio V_{aq}/V_{IL} of 85. The decrease of the extraction is the result of loss in ionic liquids as volume of the aqueous phase increases.
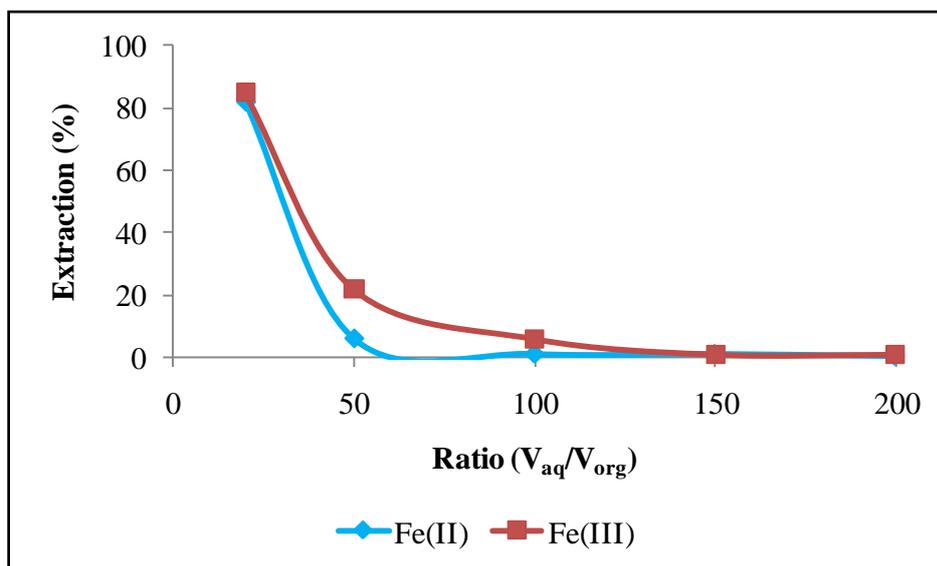

Figure 4.10: Effect of Ratio Aqueous/Organic on the Extraction of Fe(II) and Fe(III) Ion (Condition: [Fe(II)] and [Fe(III)] = 20 ppm; [phen] = 0.05 M; V_{aq}:V_{IL} = 10:0.5, 25:0.5, 50:0.5, 75:0.5 and 100:0.5)

4.3.5 Effect of Stripping Agent

The purpose of stripping process is to ensure that the ionic liquid used for extraction is applicable for reuse. For this study, three types of acid were been selected, HNO_3, H_2SO_4 and HCI. During the extraction process, iron-phen complex were formed at pH value of 2.5. At pH 1.0, due to the disassociation of the iron-phen complex, low extraction value is obtained as proven by Figure 4.6. Therefore, a decrease in pH values, causes iron-phen complexes to disassociate and Fe ion removed from ionic liquid.

Figure 4.11 shows the recovery of Fe(III) with different stripping agents. It was observed that the order of stripping ability was found to be: $HNO_3 > H_2SO_4 > HCI$. HNO_3 was the most effective stripping agent for quantitative recovery. HNO_3 also acted as an oxidizing agent therefore stripping increases with the increase on the concentration of oxidizing agent in this LLE (Alam, 1997). 8 M HNO_3 was found to be suitable for stripping the extracted Fe(III) ion with 100% recovery. However, this stripping process leaves a problem of impurities of ionic liquid. There was no results for Fe(II) ion as regards to the inconsistent reading during the analysis.
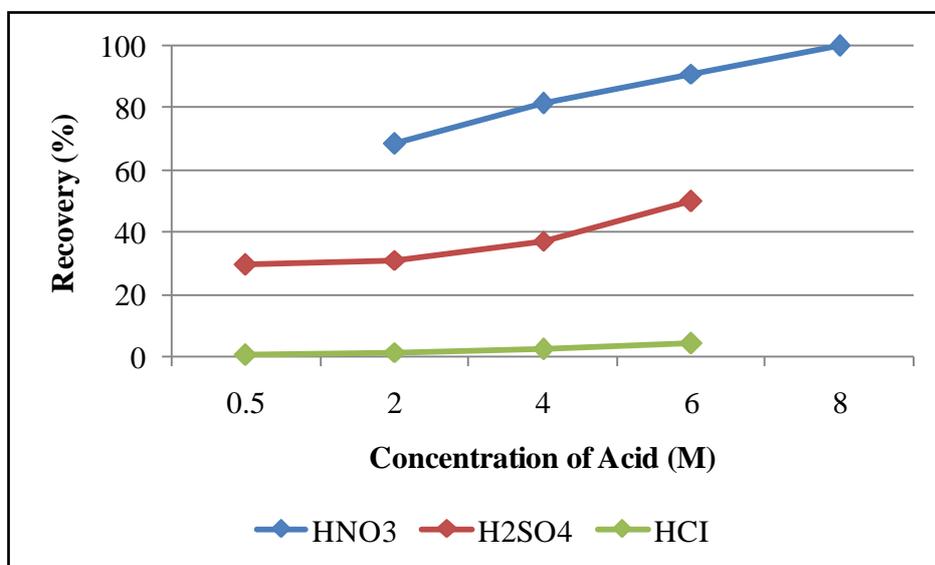
Figure 4.11: Effect of Stripping Agent on the Extraction of Fe(III) Ion
(Condition: [Fe(III)] = 5 ppm; [phen] = 0.05 M; [HNO_3] = 0.5 M, 2.0 M, 6 M & 8 M; [H_2SO_4] = 0.5 M, 2.0 M & 6 M; [HCI] = 0.5 M, 2.0 M & 6 M; V_{aq}:V_{IL} = 10:1; V_{acid}:V_{IL} = 2:0.5)

4.3.6 Regeneration of Ionic Liquid

As mentioned before, the purpose of regeneration is to study the applicability of the ionic liquid itself for reuse. This will reduce the cost of using ionic liquids in LLE process. Figure 4.12 shows the recovery efficiency for each regeneration cycle. The feasibility of recycling $[C_4mim][NTf_2]$ in LLE was determined. In the recycle process only HNO_3 solution was used. After the extraction process, the Fe(III) ion was stripped back from the ionic liquid. Then, the ionic liquid was recycled for reuse to extract Fe(III) ion in the aqueous phase. The extraction and stripping process was repeated for three cycles. The percentage of recovery decreased from cycle 1 to cycle 3 with 100%, 30% and 4% recovery. After the 2nd cycle, the ionic liquid was not suitable for the extraction of Fe(III) ion. The decrease in the recovery was observed as might be due to the loss of ionic liquid during the filtration and impurities in ionic liquid after the stripping process. Further investigation was carried out by analyzing the anion in aqueous and ionic liquid phase (Section 4.3.7).
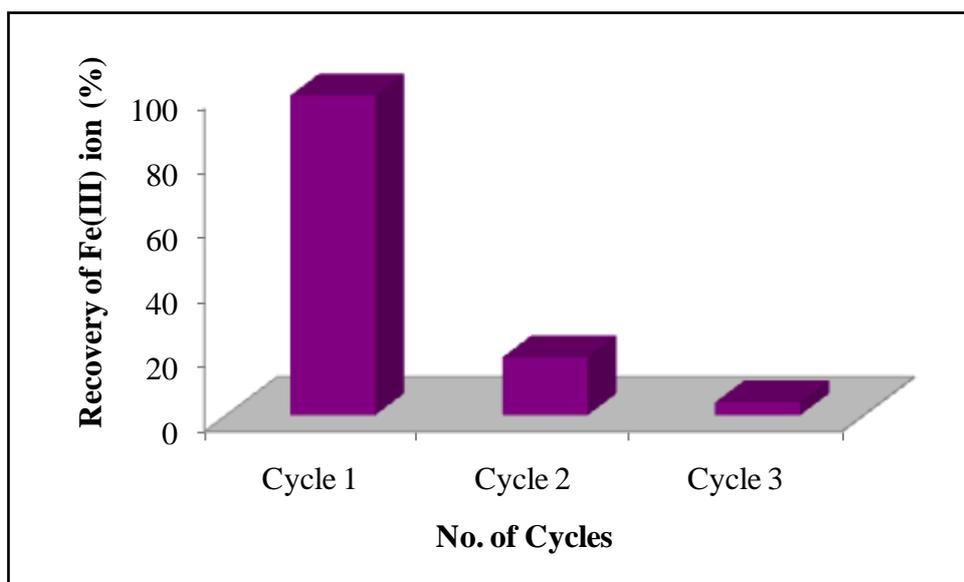
Figure 4.12: Recovery (%) of Fe(III) Ion
(Condition: [Fe(III)] = 5 ppm; [phen] = 0.05 M; $[HNO_3]$ = 8 M;
$V_{aq}:V_{IL}$ = 10:1, 10:0.5 & 10:0.2; $V_{acid}:V_{IL}$ = 2:0.7 & 2:0.4)

4.3.7 Application of Ionic Liquid using Groundwater Samples

Physical and Chemical Parameters

Table 4.5 shows the mean values of physical and chemical parameters of groundwater samples. In general the pH ranges from 5.42 to 6.26 that show slightly acidic groundwater condition. Most of the groundwater samples were classified as fresh water. Only KB05 was classified as brackish water as according to Freeze & Cherry, (1979) the total dissolved solid (TDS) value was more than 1000 mg/L. For sodium (Na), only KB05 showed concentration above the standard limit of 200.00 mg/L for drinking water. Most of the layers show iron (Fe) and manganese (Mn) concentration above the standard limit of 0.30 mg/L and 0.10 mg/L respectively. For anion, only chloride (Cl) showed concentration above the standard limit of 250.00 mg/L for selected groundwater samples. The standard limits are based on World Health Organization (WHO, 1984).

Removal of Metal Ions

To prove the applicability of the results obtained using the iron standard solution, study was carried out using the groundwater samples. All of the experimental conditions were chosen based on the results discussed previously.

Figure 4.13 shows that the percentage of removal of iron and other heavy metals in groundwater samples. It shows that more than 95% of iron can be removed from the groundwater samples according to the initial concentration of iron in each layer as noted in Table 4.5. Besides iron, other metal ions; Zn, Mn, and Cd too can be removed from the groundwater samples by using $[C_4mim][NTf_2]$ ionic liquid as a solvent medium in liquid-liquid extraction treatment method.

Table 4.5: Mean Values of Physical and Chemical Parameters of Groundwater Samples

| Samples		KB54	KB39	KB13	KB5	KB29	KB1	KB31
Aquifer		Layer 1	Layer 1	Layer 2	Layer 2	Layer 3	Layer 3	Layer 3
Physical parameters	Water level (m)	-	1.69	4.89	4.75	-	5.39	2.54
	pH	5.79	5.42	6.03	6.26	5.93	5.94	6.15
	Temp (^{o}C)	29.00	28.00	29.60	29.60	27.80	29.90	28.50
	Conductivity (uS/cm)	182.75	104.50	1226.00	4950.00	151.10	615.00	1352.00
	Total Dissolved Solids (TDS) (mg/L)	88.25	49.75	603.50	1413.50	71.70	299.50	669.00
	Dissolved Oxygen (DO) (mg/L)	3.55	3.65	3.80	3.15	5.50	3.35	3.10
	Salinity ($^{0}/_{00}$)	0.10	0.00	0.60	2.65	0.10	0.30	0.70
Chemical Parameters — Cation (mg/L)	Na^{+}	22.09	18.30	122.80	885.20	10.81	49.76	145.30
	K^{+}	7.89	1.86	14.49	47.23	3.29	12.21	42.01
	Mg^{2+}	4.28	1.24	30.39	32.90	2.79	15.94	22.92
	Ca^{2+}	20.86	1.12	46.78	26.21	20.40	18.85	32.67
	Fe_{total}	0.03	0.53	24.49	22.74	3.21	23.40	58.69
	Mn^{2+}	0.06	0.25	0.65	0.17	0.14	0.41	0.70
	Zn^{2+}	0.06	0.04	0.04	0.06	0.10	0.07	0.05
	Cd^{2+}	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	Pb^{2+}	0.02	0.01	0.01	0.02	0.01	0.01	0.02
	Se^{2+}	0.02	0.02	0.00	0.01	0.01	0.01	bdl
	Cu^{2+}	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	As^{2+}	bdl	bdl	bdl	0.05	0.01	bdl	bdl
	Al^{3+}	bdl	0.25	0.03	bdl	bdl	bdl	bdl
Chemical Parameters — Anion (mg/L)	F^{-}	0.07	bdl	0.13	0.08	0.40	0.14	0.05
	Cl^{-}	28.25	20.25	320.40	11.16	1561.19	187.30	376.90
	SO_4^{2-}	19.17	8.61	bdl	18.39	1.07	bdl	bdl
	HCO_3^{-}	120.10	26.60	62.40	85.70	201.60	72.80	52.60
	CO_3^{2-}	bdl	bdl	bdl	bdl	bdl	bdl	bdl
	NO_3^{-}	1.81	bdl	bdl	0.96	bdl	bdl	bdl
	Br^{-}	0.80	0.44	0.63	0.61	0.36	0.23	0.81

bdl: below detection limit
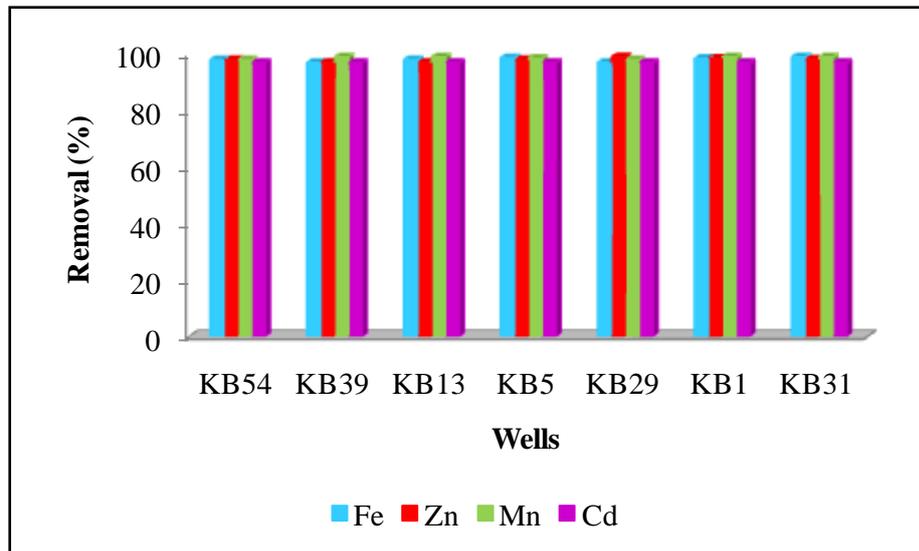
Figure 4.13: Removal of Iron and Other Heavy Metals in Groundwater Samples
(Condition: [phen] = 0.05 M and $V_{aq}:V_{IL}$ = 10:0.5)

Stripping of Ionic Liquid

In this study, 8 M of HNO_3 was used as a strippant. Figure 4.14 shows the recovery of iron from the groundwater samples. In general, the recovery ranges from 25% to 60%. The recovery values were lower compared to the laboratory experiment with iron standard solution of 100% recovery. It can be concluded that it is not very promising to reuse ionic liquid in groundwater samples because of low recovery at early stage.
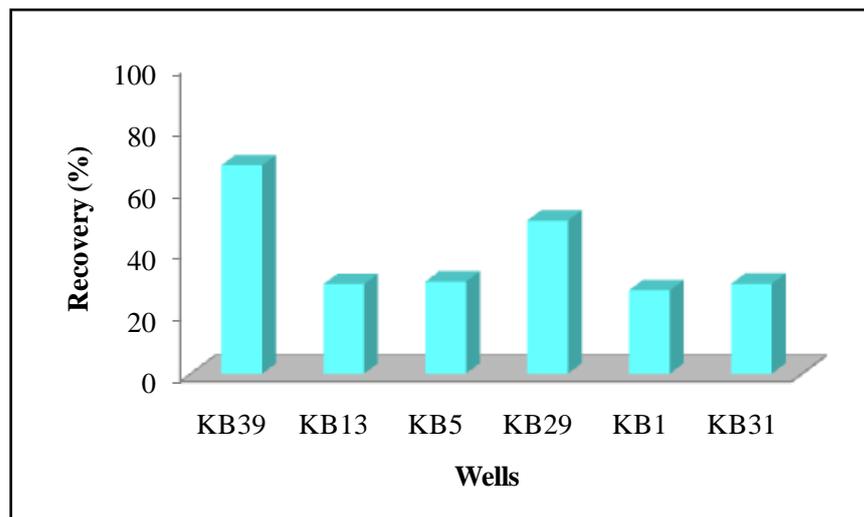

Figure 4.14: Recovery (%) of $Iron_{total}$
(Condition: $V_{aq}:V_{IL}$ = 10:1; $V_{acid;}V_{IL}$ = 2:0.5)

Analysis of Anion

Anion analysis was done using 850 Professional Ion Chromatography (IC) from Metrohm (Switzerland). Figure 4.15 and 4.16 shows the peak of NTf_2 anion appearing at retention time of 24.00 min (50% window) for samples KB31. It shows that NTf_2 anion from ionic liquid entered into the aqueous phase after the extraction and stripping processes. The concentration of NTf_2 in aqueous phase after the extraction was 6.43×10^{-3} M while after the stripping was 6.90×10^{-2} M. The concentration of NTf_2 in ionic liquid after the extraction was 7.84 M while after the stripping was 6.49 M. The lost of NTf_2 anion from ionic liquid suggests that the forces of attraction between the $[C_4min]$ cation and $[NTf_2]$ anion are not sufficiently strong enough to hold them together. Therefore NTf_2 anion of ionic liquid easily exchanges with the counter-ion in groundwater samples. Anion exchange occurs in this system as groundwater samples contain various anions as stated in Table 4.5.

Furthermore, the high concentration of strippant (8 M of HNO_3) is the main factor of impurities in IL after the stripping process. Figure 4.16 clearly shows that the presence of NO_3^- ion (retention time 4.93 min) and the loss of NTf_2 in ionic liquid phase after the stripping process. The presence of high concentration of anion in groundwater samples and strippant are the main limitations in the reuse of IL in groundwater samples. Further studies are needed to eliminate this limitation.
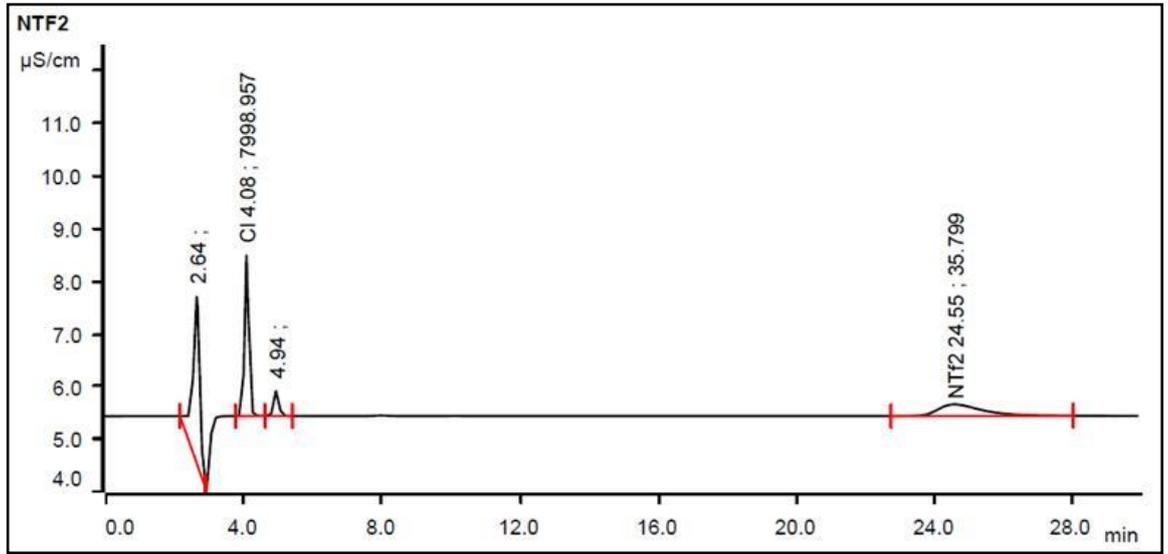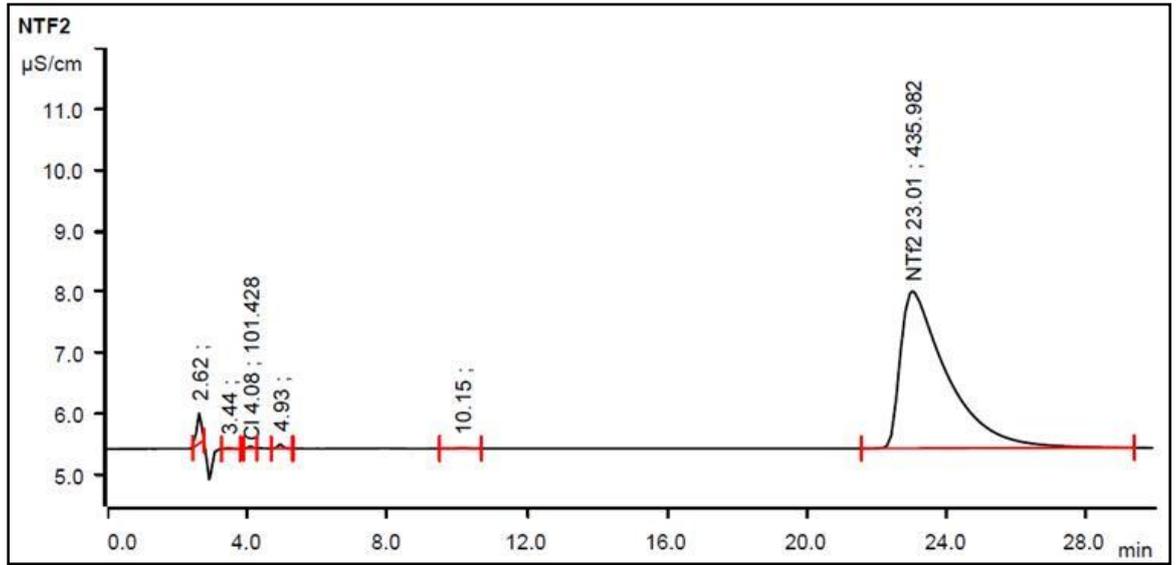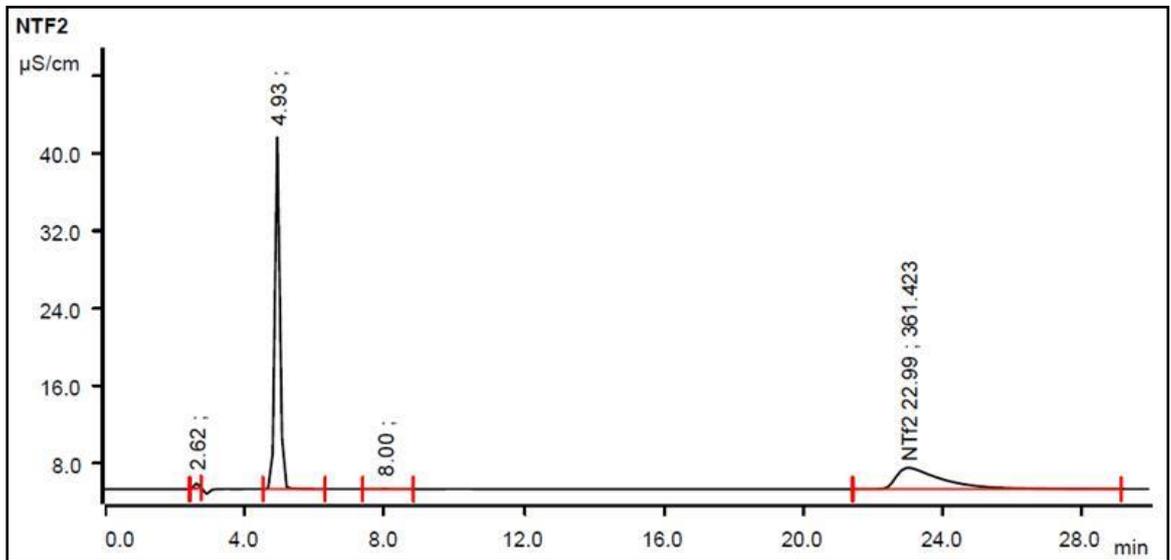
a) Aqueous phase after extraction
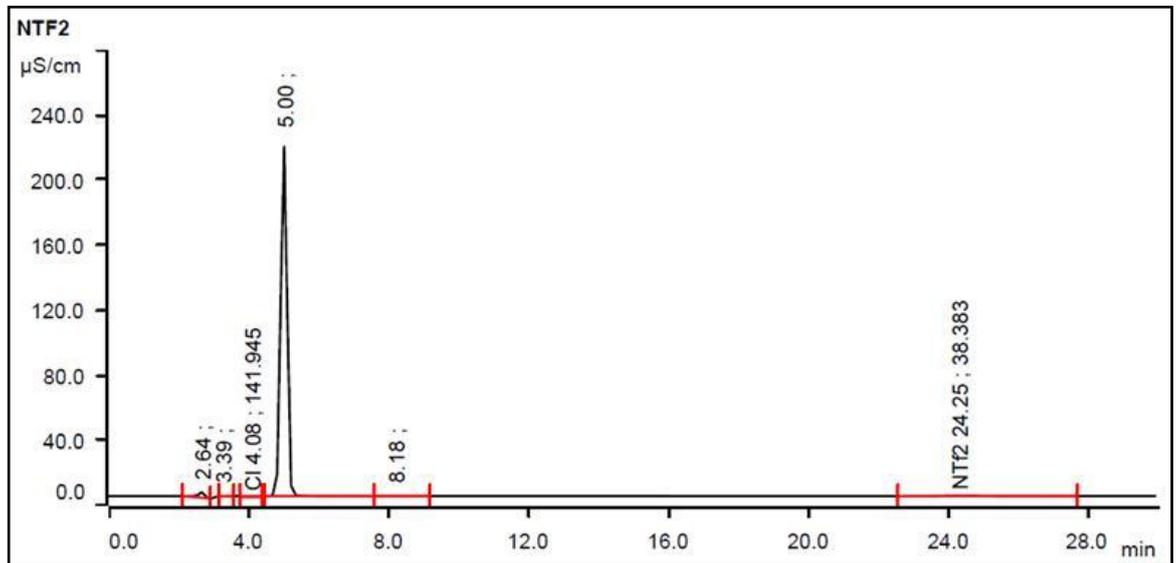
b) Aqueous phase after stripping with HNO$_3$ acid

Figure 4.15: Aqueous Phase Sample KB31

a) Ionic liquid phase after extraction

b) Ionic liquid phase after stripping with HNO_3 acid

Figure 4.16: Ionic Liquid Phase Sample KB31

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This chapter deals with the major conclusions drawn on the basis of hydrogeochemical study and iron removal of groundwater in the study area. Recommendations will be made based on the findings.

Conclusion

The following conclusions are drawn from the study:

1. The whole area of North Kelantan River basin is underlain by Quaternary deposits with sub formation of Gula and Simpang Formations. The thickness of the Quaternary deposits is 25 m inland and up to 200 m to the coast. This deposit is underlain by granite and metamorphic bedrock in certain locality. Bukit Marak and Bulit Kechik at the south east part appear as patches resulted from the intrusion of Boundary Range Granite in the basin.

2. This basin is drainage by Kelantan River with a length of 248 km and area of approximately 11900 km^2. The base-flow index (BFI) value of 0.54 is due to diverse geological, morphological and climatological aspects in the basin. For the whole basin, 70% of the river flows on the hard rock in the upper part of the basin and 30% of the river flows on the alluvium in the lower part of the basin. The main interaction of surface water – groundwater only occurs at the lower part of basin that is covered by alluvium deposits. While in the upper part of the basin the surface runoff dominates the process. The basin receives precipitation of 30.95×10^9 m^3/year. Potential evapotranspiration shows that about 40% (12.34×10^9 m^3/year) of water loss from the basin with runoff coefficient of 50%. Recharge to the aquifer basin is

estimated about 11% (3.27 x 10^9 m^3/year) of the total precipitation based on the water balance study.

3. The alluvium deposits form an aquifer system in North Kelantan. Three aquifer layers have been identified; Layers 1, 2 and 3 with depth of approximately 20 m, 20 m to approximately 50 m and more than 50 m, respectively. These aquifer layers are separated by semi permeable clay layer and hydraulic connection exists between the layers but the uniform of the continuity is still undetermined. The permeability, transmissivity of the aquifer ranges from 28 m/day to 337 m/day, 336 m^2/day to 9431 m^2/day with specific yield is 0.06. At present, Layer 1 plays an important role as the main source of water supply for North Kelantan area.

4. Water chemistry shows that all layers have high iron concentration up to 80 mg/L and most of wells in Layers show iron concentration exceeding the WHO guideline standard of 0.30 mg/L. TDS value, classify Layers 1 and 3 as fresh water while Layer 2 as a mixture between fresh and brackish water (TDS > 1000 mg/L). As depth increases selected ions show a variation in water chemistry. Depth intervasl below 20 m shows high concentration of nitrate and ammonium. High concentration of sodium, chloride and iron are found at depth interval of 20 – 50 m. Iron remained high at depth interval of more than 50 m. Water quality shows that groundwater in Layers 1 and 3 are more suitable for drinking water purposes compared to Layer 2. Action must be taken in order to maintain the water quality as parameters above the standard limit that will result in side effects for human. While for irrigation purposes, groundwater in Layer 1 is more suitable compared to Layers 2 and 3. Layer 1 is classified as low sodium hazard (S1) with low to medium salinity hazard (C1-C2), while Layer 2 and 3 are classified as low sodium (S1) with low to high salinity hazard (C1-C3). Treatment is needed in order to control the groundwater quality of irrigation.

5. Hydrochemical facies reveal two main facies; Na-HCO$_3$ facies in the inland area while Na-Cl facies towards the coastal area. The intermediate facies of CaHCO$_3$, AlHCO$_3$, MgCl and CaCl has been observed in between the main facies. Based on AQUACHEM and PHREEQC analysis, the origin and evolution of groundwater in North Kelantan is influenced by weathering, dissolution, ion exchange and precipitation. An excess of sodium in groundwater are governed by silicate weathering of albite followed by dissolution. Ion exchange process especially with the clay minerals which act as impermeable layer in aquifers also increased the sodium concentration. An excess of chloride ion is attributed as a minor product due to weathering. In Layers 1 and 2, an excess of sodium and chloride ions are due to tidal effect from the river and entrapped seawater in the marine sediment during Holocene. Groundwater saturation index shows that iron minerals of hematite and goethite tend to precipitate in aquifer medium while pyrite is highly soluble in groundwater that gives high iron concentration in aquifer layers. The ferromagnesian minerals originates from the bedrock that has undergone physical and chemical weathering process.

6. The conceptual model of the aquifer system for North Kelantan River Basin is proposed and simplified in Figure 5.1. The simplification is based on the geological set up, hydrology, hydrogeology and hydrogeochemical information obtained from this study.
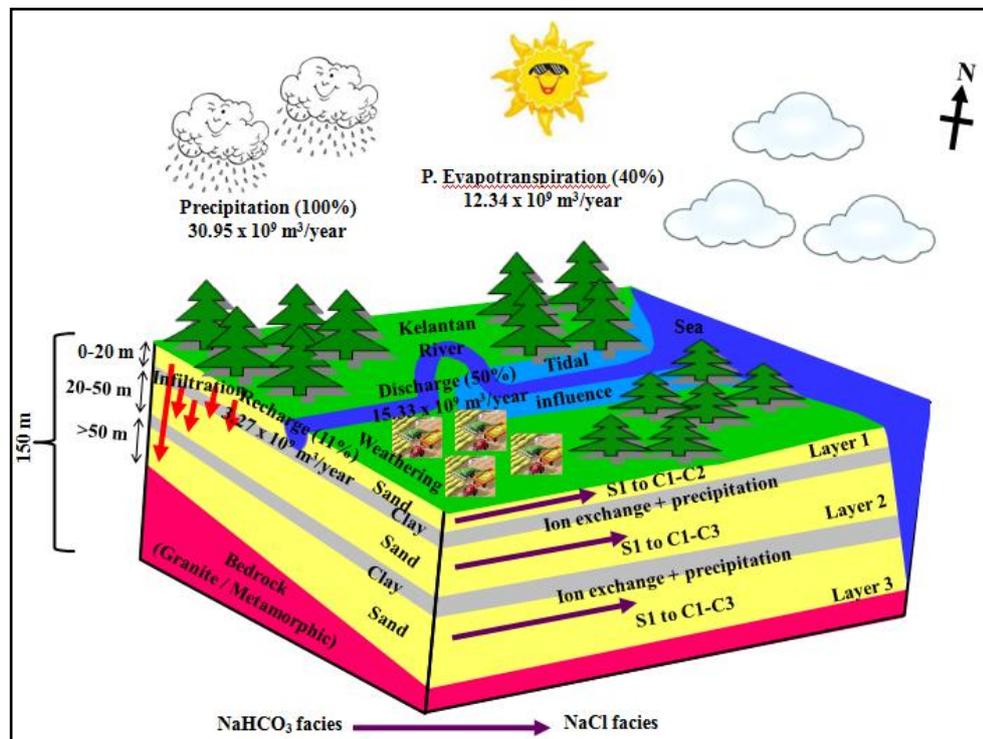
Figure 5.1: Conceptual Model of North Kelantan

7. The ionic liquid ($[C_4mim][NTf_2]$) as a medium in liquid – liquid extraction and 1, 10-phenanthroline as a chelating agent has been studied as an alternative method of conventional groundwater treatment. Iron was successfully removed with more than 95% removal according to the initial concentration of iron in groundwater. This method was also applied to remove manganese, cadmium and zinc from groundwater. However, $[C_4mim][NTf_2]$ ionic liquid is not suitable to be reused for iron removal as low recovery obtained ranging from 25% to 60% in stripping process for groundwater samples. This is in regard to the appearance of $[NTf_2]$ anion in groundwater samples as ion exchange process occurs between $[C_4mim][NTf_2]$ ionic liquid and counter ions in the groundwater samples.

Recommendation

The following are recommendations to improve the feasibility of ionic liquid as a treatment method for groundwater with high iron concentration:

1. Further research must be done using different types of ionic liquid with different alkyl chain in order to improve the feasibility of ionic liquids as a medium in liquid – liquid extraction based on parameters studied.

2. Mass production of ionic liquids needs to be explored in the future in order to investigate field scale size of treatment.