CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This research study is titled “**Hydrogeochemical Study and Iron Removal of Groundwater in North Kelantan.** The utilization of groundwater in Kota Bharu started way back since 1935 (SMHB, 2000). Groundwater contributes about 90% of the total demand for drinking water in Kelantan (Suratman, 1997). The demand for groundwater increased 2.5% per year and for the year 2010 the production demand for the whole state was estimated at 165 MLD, (Suratman, 2010). In general, groundwater in North Kelantan area is abstracted from the shallow, first aquifer layer, with the exception of Tanjung Mas area and some areas in Pintu Geng water works.

The presence of iron has been noticed in Kelantan groundwater since initial investigation of groundwater resources by the Geological Survey Department (GSD) currently known as Mineral and Geosciences Department (MGD) in collaboration with the German Hydrogeological Mission (GHM) 1971 – 1975. Investigations showed that the iron concentration was above the potable limit of 0.30 mg/L. Continuous groundwater monitoring by MGD from 1989 until 1995 also recorded high iron concentration (Ang & Loh, 1996). Therefore, iron is a major problem in Kelantan groundwater. The said iron is suspected to be originating from the deposited sediment in the Kelantan delta. However a detailed study has not been carried out to confirm the statement.

High concentration of dissolved iron, Fe(II) is by far the most common problem in associated with groundwater potability (Chapelle, 2001). The World Health Organization (WHO) has set guideline values for iron in drinking water at 0.30 mg/L. Higher concentration would cause aesthetic considerations such as metallic taste, odor, turbidity, staining of laundry and plumbing fixtures (Dutta *et al.*, 2007). In human body, the normal iron content is three to four grams. Chronic iron overload, a genetic disorder (*haemochromatosis*) is possible if the amount of iron concentration exceeds the normal level (medicinenet.com). For agriculture, high iron content in soils will turn the agriculture land into a nonproductive area (Awadalla & Noor, 1990).

Air Kelantan Sdn. Bhd. is responsible in handling the full cycle of a drinking water supply system from sourcing, treatment and distribution of treated water to consumer right up to billing and collection. For the whole state of Kelantan there are 27 waterworks, which intake comes from surface water and groundwater (Table 1.1). In total, for North Kelantan areas, there are 6 waterworks intake from groundwater that contributes for the water supply (Figure 1.1). Presently, the groundwater is treated using conventional treatment method, (detailed in Chapter 4). The conventional process works fairly well for a total concentration of iron total below 5.00 mg/L and in the absence of dissolved organic matter (Ellis *et al.*, 2000). The problem with the conventional treatment is the precipitation of iron as ferric ion after the treatment process. Only 32% forms soluble iron. Thus, Air Kelantan only controls the level of total iron concentration to meet the standard guideline for drinking water. In order to find an alternative treatment method, room temperature ionic liquid (RTILs) was used as a medium in liquid – liquid extraction to remove iron in groundwater. RTILs have been studied over a decade as green solvent for the future due to their physicochemical characteristics.

Table 1.1: List of Waterworks in Kelantan

District	Waterworks	Capacity (MLD)	Intake	Longitude	Latitude
Tumpat	Wakaf Baru	19	Groundwater	102°12’ 17.93”E	6°07’ 15.57”N
Kota Bharu	Kg. Puteh	28	Groundwater	102°14’ 30.23”E	6°05’ 47.85”N
	Tanjung Mas	10	Groundwater	102°15’ 55.71”E	6°08’ 18.49”N
	Chicha	80	Groundwater	102°17’ 03.71”E	6°04’ 42.42”N
	Pintu Geng	9	Groundwater	102°14’ 06.55”E	6°05’ 51.11”N
Bachok	Kg. Chap	4.9	Groundwater	102°20’ 40”E	5°02’ 30”N
Pasir Mas	Kelar	64	Kelantan River	102°09’ 23.87”E	6°01’ 10.68”N
Tanah Merah	Batu Gajah	2.3	Jedok River	-	-
	Bendang Nyior	1.7	Jegor River	-	-
	Bukit Remah	28	Kelantan River	102°09’112.26”E	5°48’ 11.18”N
	Kemahang	3.38	Muring River	-	-
	Kuala Tiga	1.13	Kelantan River	-	-
Machang	Merbau Chondong	40	Kelantan River	102°14’ 41.80”E	5°52’ 40.45”N
Pasir Puteh	Wakaf Bunut	9	Rasan River	-	-
Jeli	Air Lanas	2.6	Lanas River	-	-
	Jeli	4	Pergau River	-	-
	Kuala Balah	2.3	Terang River	-	-
Kuala Krai	Kg. Tualang	8.69	Kelantan River	102°11’ 34.06”E	5°31’ 18.90”N
	Pahi	16	Lebir River	102°13’ 18.57”E	5°29’ 14.95”N
	Manik Urai	7	Lebir River	102°14’ 18.43”E	5°22’ 46.95”N
	Dabong/Stong	3.77	Stong River	-	-
Gua Musang	Bertam Baru	0.5	Galas River	-	-
	Limau Kasturi	1.2	Galas River	-	-
	Aring	1.8	Aring River	-	-
	Chiku	6	Chiku River	-	-
	Sg. Ketil	13	Ketil River	-	-
	Panggung Lalat	0.7	Betis River	-	-

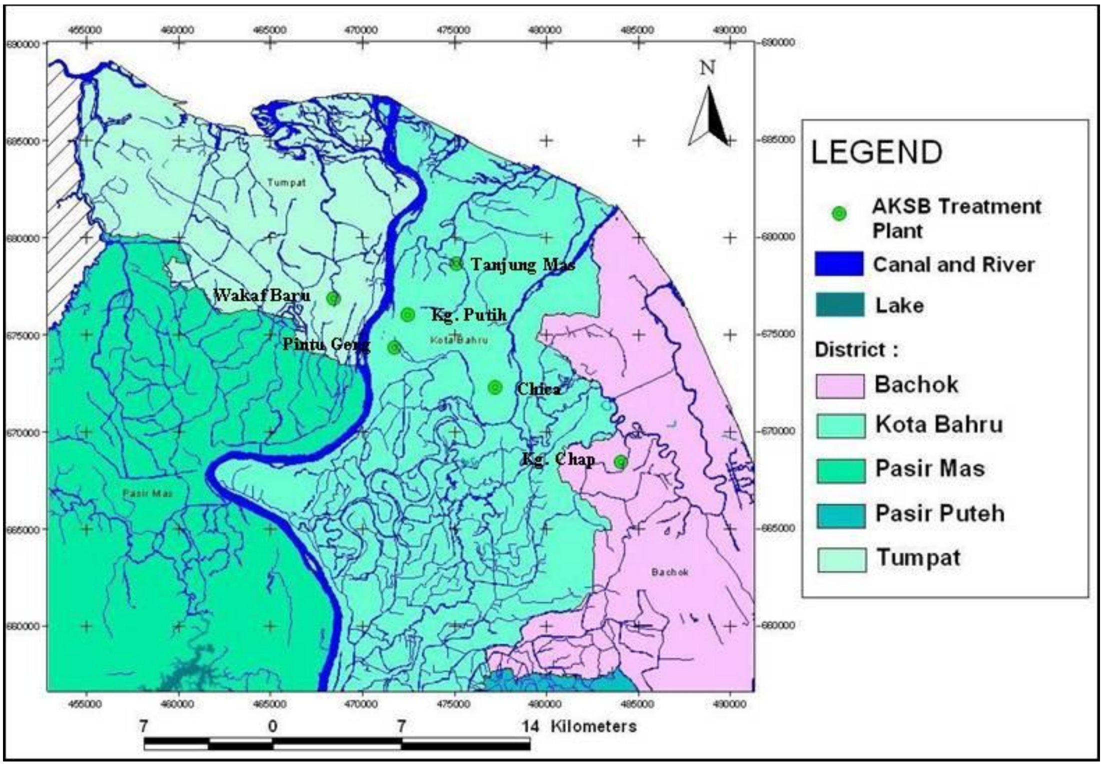

Figure 1.1: Waterworks Location in North Kelantan

1.2 OBJECTIVES

The aims of the study are:

i. To map the heavy metals concentration in each aquifer layers

ii. To study the hydrogeochemistry and evolution of the groundwater system

iii. To assess the suitability of ionic liquids based treatment method for Kelantan groundwater resources

1.3 STUDY AREA

The study area lies between longitude 102.05°E until 102.40°E and latitudes 6°N until 6.25°N (Figure 1.2). It is located at the northern part of the Kelantan state known as North Kelantan River Basin. The basin is bounded by the South China Sea in the north and east, while to the west is bounded by Thailand. Hulu Kelantan at the south marks the border of Kelantan State from Pahang State, Perak State at the south-west, while at the south-east it borders with Terengganu State.

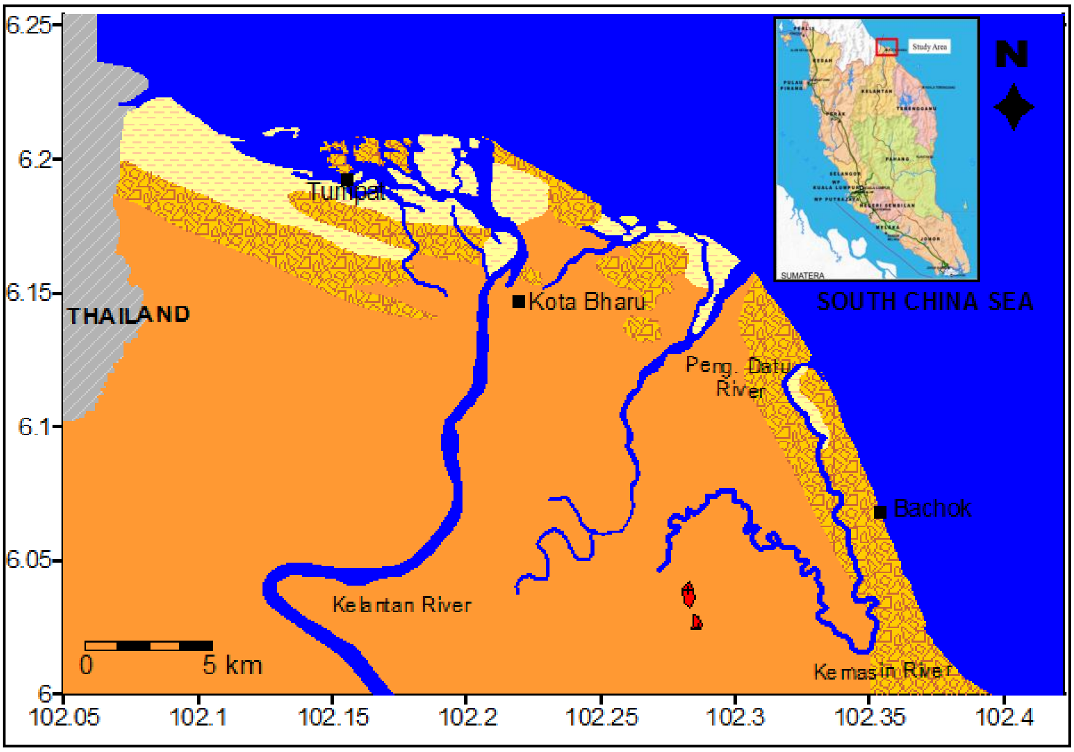

Figure 1.2: Location of the Study Area

1.4 GEOMORPHOLOGY

1.4.1 Topography

In general, the topographic features of Kelantan can be seen in Figure 1.3. This Digital Terrain Model (Ng, 2008) has been differentiated into 5 units based on mean elevation as noted in Table 1.2. Overall, the topographic features of North Kelantan is low lying unit with mean elevation less than 15 m as marked by pink rectangles in Figure 1.3. These low-lying areas represent depositional terrain and overlying unconsolidated alluvial, coastal and marine sediments of variable thickness. While the mountainous terrain mean elevation is more than 301 m. These mountains exist in the southeast part as granite intrusion (MacDonalad, 1967) known as Bukit Marak and Bukit Kechik with elevation of 373 m and 307 m.

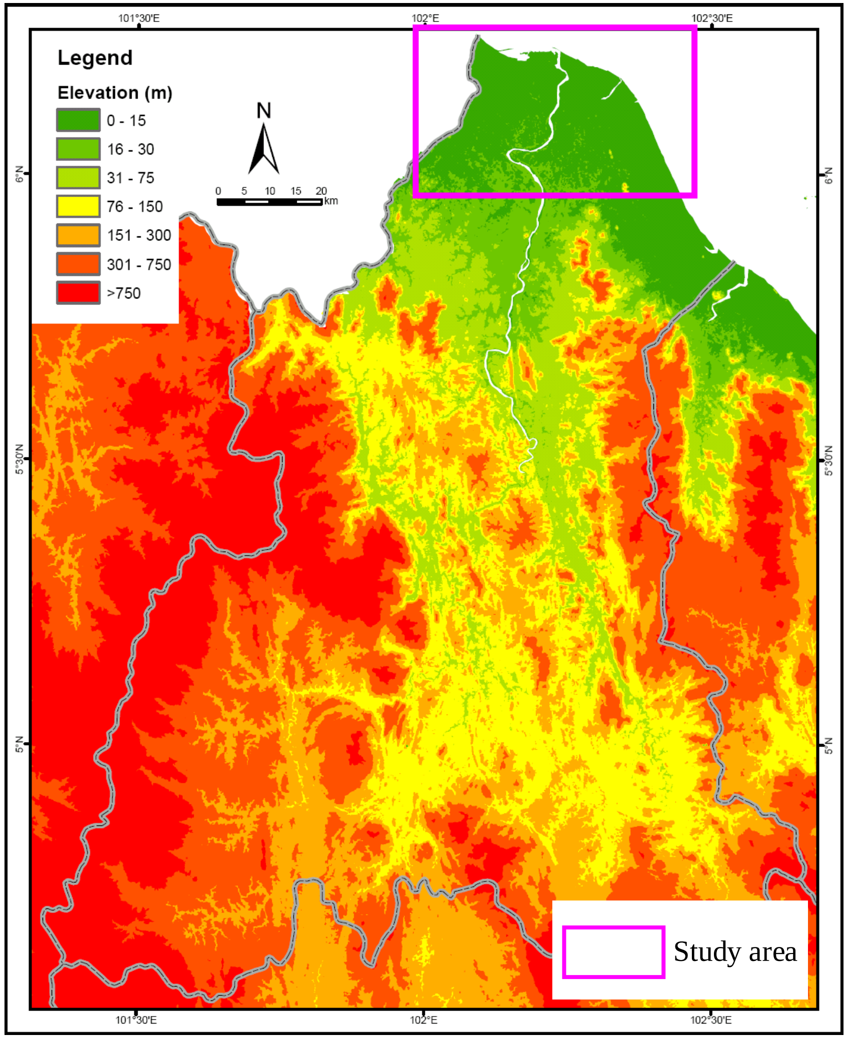

Figure 1.3: Digital Terrain Model of Kelantan Showing Mean

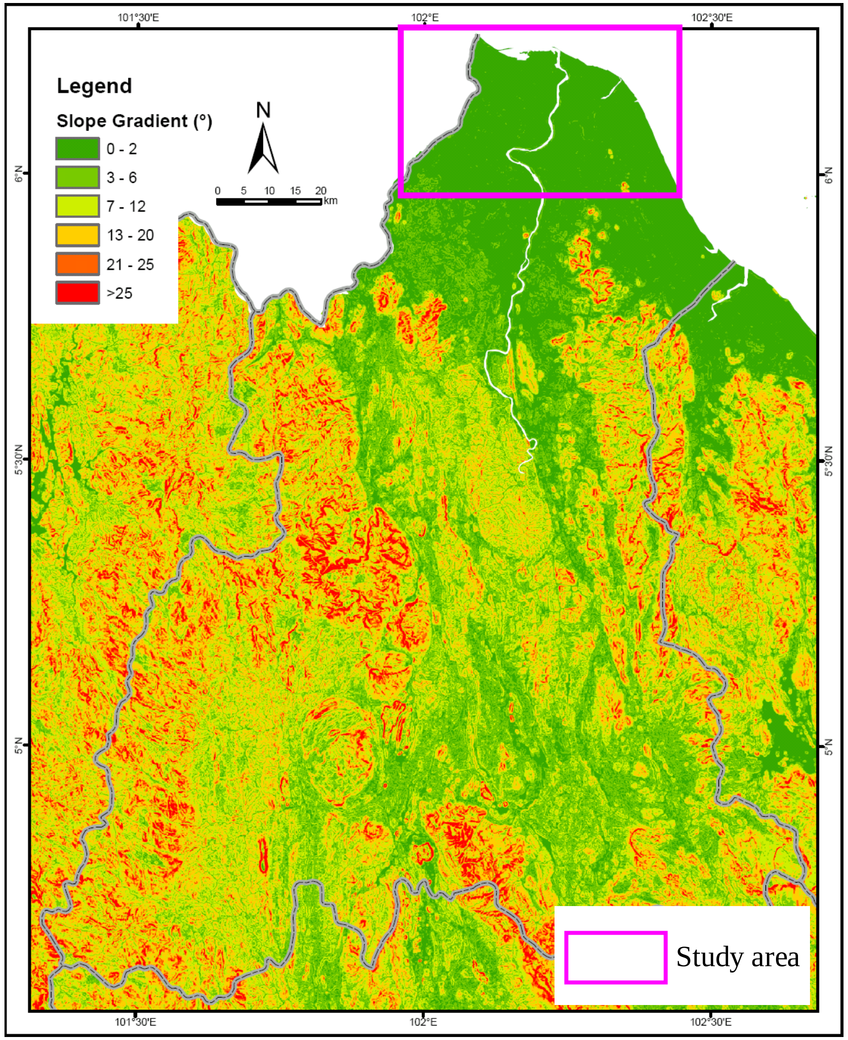

Figure 1.4: Digital Ground Slope Model of Kelantan

Table 1.2: Topographic Units according to Mean Elevations

	Topographic Unit	**Mean Elevation (m above sea level)**
1	Low lying	<15
2	Rolling	16-30
3	Undulating	31-75
4	Hilly	76-300
5	Mountainous	>301

Table 1.3: Slope and Terrain Classes (Leamy & Panton, 1960)

	Slope Angle	**Terrain Class**
1	0-2°	Level or nearly level
2	2-6°	Undulating
3	6-12°	Rolling
4	12-20°	Hilly
5	20-25°	Steep
6	>25°	Very Steep

A detailed view of the topographic features can be seen using Digital Ground Slope Model (Ng, 2008). The slope has been classed into six slope angles based on the Soil Survey Division of the Malaysia Ministry of Agriculture as noted in Table 1.3. The low lying area of North Kelantan is marked by pink rectangles (Figure 1.4) and is classed as level or nearly level terrain with very gentle ground slopes less than 2°.

1.4.2 Climate

The study area is situated in the East Coast of Peninsular Malaysia with a tropical rainforest climate. Two types of monsoon regime control the areas which influences the monthly and annual rainfall. The south west monsoon occurs from February till October with less rainfall thus hot and dry area. The north east monsoon occurs from November till March bringing heavy rainfall and contributing to high soil moisture. During this period, rainfalls are high in intensity and bring heavy storms over a large area of low lying coastal plain. Figure 1.5 shows the annual rainfall index of Kota Bharu measured at Sultan Ismail Petra Airport within year 1979 - 2008. The highest rain falls in 1999 with 3734.50 mm and the lowest rainfall in 1989 with 1540.50 mm. The mean annual rainfall is 2543.87 mm.

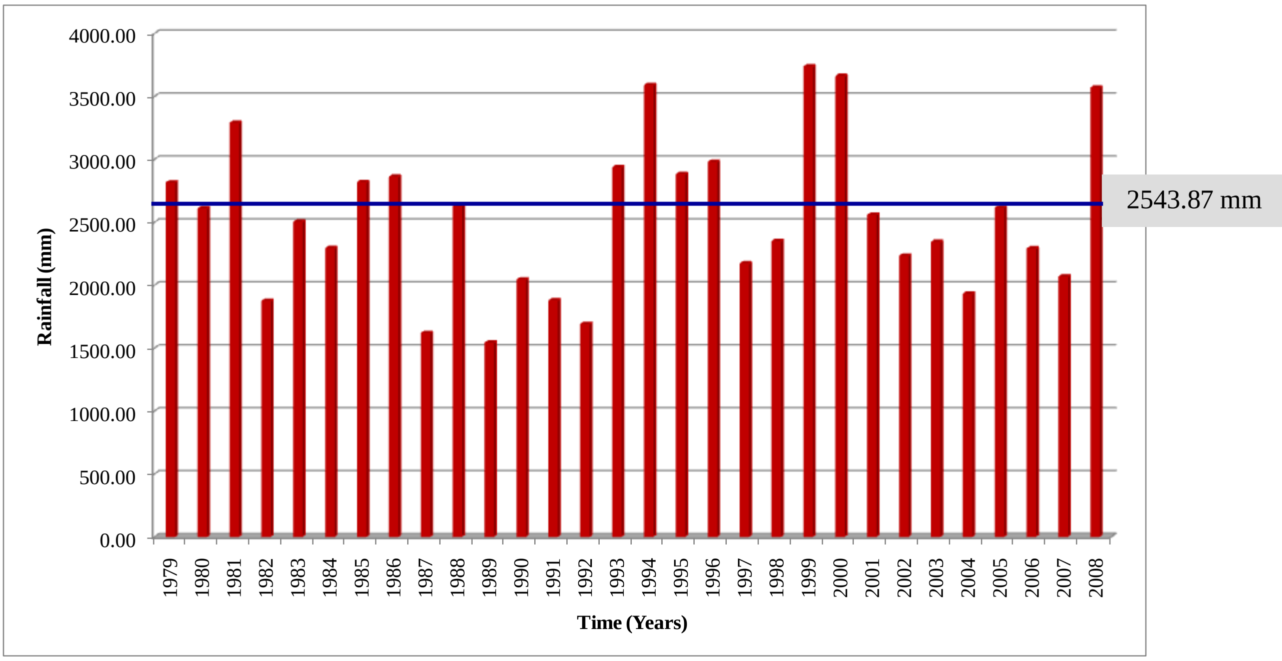

Figure 1.5: Annual Rainfall (1979 - 2008) of Kota Bharu.
Mean Annual Rainfall is 2543.87 mm

1.4.3 Drainage System

As shown in Figure 1.6, three rivers irrigate this study area. These rivers are Kelantan River, Pengkalan Datu River and Kemasin River. It demonstrates the dendritic pattern and flow from south to north-east. The Kelantan River is the main river for the state of Kelantan with 248 km length and covering an area of 11900 km^2 (Ibbitt *et al.*, 2002). This river flows northward into the South China Sea. To the east of Kelantan River are Pengkalan Datu and Kemasin river with 13.33 km and 52.60 km length, respectively. Kuala Besar, Kuala Sungai Besar and Kuala Kemasin are the main estuary. In the coastal area, there are a few beaches like Pantai Cahaya Bulan, Pantai Mek Mas and Pantai Sabak.

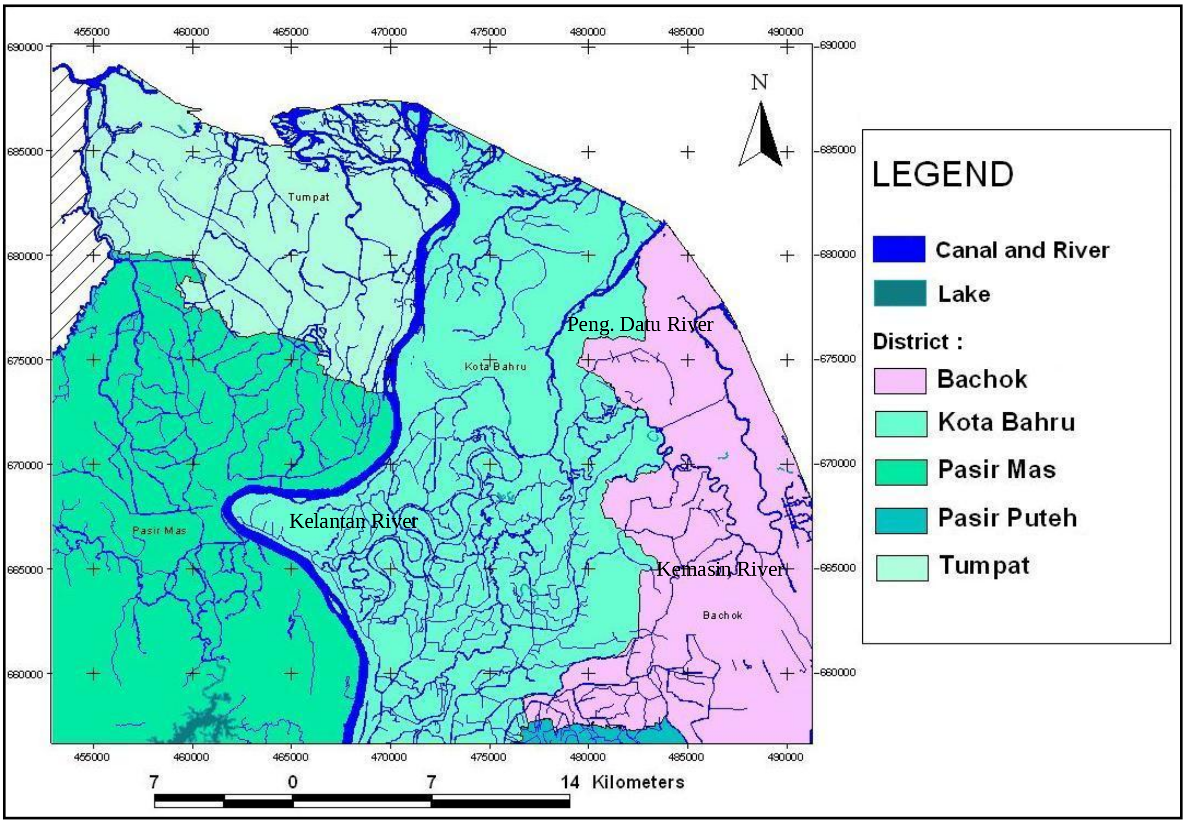

Figure 1.6: Map of Drainage System in North Kelantan

1.4.4 Land Use

Statistic shows that the total land use area is 86 343 hectare (Ha) (Department of Agriculture, 2006) which occupies the district of Kota Bharu, Tumpat and Bachok with 40 138 Ha, 18 519 Ha and 27 686 Ha, respectively. Figure 1.7 gives the percentage of main land use for Kota Bharu, Tumpat and Bachok districts. Short term crops make 34.04% of the total land use for the whole district. This is followed by plantation areas (23.77%), tree, palm and other permanent crops (15.63%), abundant grassland areas (7.02%), swamps (5.99%), settlement and associated non-agriculture areas (5.88%), water bodies (4.89%) forest (1.02%), others (1.40%) and livestock area (0.37%).

Agriculture land covers only 73.80% of the whole district with an area of 63,724 Ha. Meanwhile, the areas of land use are changed according to necessity due to continuous human activity such as municipal, housing, agricultural and others.

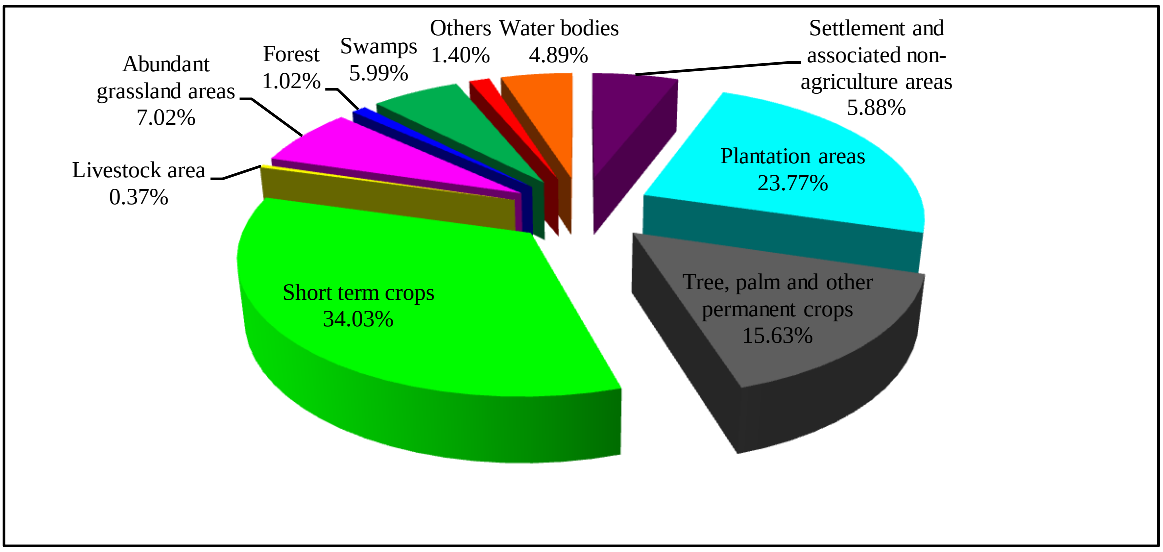

Figure 1.7: Main Land Use for Kota Bharu, Tumpat and Bachok Districts (2006)

1.5 LITERATURE REVIEW

In previous studies, numerous works had been done in this area including geology (e.g. MacDonald, 1967; Bosch, 1986 & 1988 and Noor, 1979), geomorphology (e.g. Soh, 1972; Teh, 1976; Bosch, 1988 and Raj *et al.*, 2007a & b) and hydrogeology (e.g. Ang & Kwan, 1979; Noor, 1979; Chong & Tan, 1986; Hamzah *et al.*, 1997). However, no studies have been reported on hydrogeochemistry and iron removal from groundwater.

1.5.1 Geology

The study area is a part of the coastal plain alluvium deposits during Quaternary as described by MacDonald (1967). The coastal plain was divided into marine deposits and fluviatile deposits. Complications occurred near the larger rivers in delineating these two types of deposits because large areas of marine alluvium could be swept away or covered by the river sediment. The depth, lithology and the extension of the coastal alluvium was obtained from the boring program. The alluvium extends at depth up to one hundred feet and more.

Further study by Bosch (1986 & 1988) suggested that the Quaternary deposits are divided into three formations, composed of Gula Formation, Beruas Formation and Simpang Formation.

The Gula Formation is Holocene marine deposits. This formation is made up of clay, silt, and sand with minor amounts of gravel, shell and coral deposited from the most recent major low sea level. Beruas Formation is Holocene terrestrial deposits. It consists of clay, silt, sand, gravel and peat that are deposited after the most recent major low sea-level between 15000 and 18000 years BP (before present). It is also named as the Pengkalan Member as peat is formed from *in situ* vegetation with minor intercalations of clay and silt deposited in paludal environment. This formation is also equivalent to the Young Alluvium in other parts of the Peninsular. It has been proposed to replace the Young Alluvium with the Beruas Formation. Simpang Formation is a terrestrial deposition of Pleistocene age. This formation consists of clay, silt, sand, gravel and peat that are deposited before the most recent major low sea level. It also proposed that the Old Alluvium to be replaced by the Simpang Formation. Beruas and Simpang Formation are deposited as a river channels during Holocene and Pleistocene.

Most part of the alluvial plain is underlain by Mesozoic granites but in some locality metamorphic rocks are encountered as bedrock (Noor, 1979).

1.5.2 Geomorphology

The geomorphology of North Kelantan is influenced by various physical and hydrological processes especially during north east monsoon. Kelantan delta can be divided into two geomorphic regions; to the west and east side of Kelantan River. The west region is characterized by the almost parallel three sand ridges and two distinct parallel depressions in the main land area. While the east region is made up of two vaguely areas of alluvial deposits separated by an elongated depression (Soh, 1972). In addition, Teh (1976) has classified sand ridges into Old Series and Young Series. The Old Series comprises discontinuities, parallel beach ridges about 2 km and more inland. The Young Series consists of a massive sand body with continuous parallel ridges and a few narrow swales within 2 km of the coastline. These sand ridges are the indicators of sea level changes during Holocene. The sand ridges consist of moderately sorted gravel coarse sand to poorly sorted, silty, and very fine sand. In the swales, greyish green marine sandy clay, silt and peat may be present locally. To the south of Kelantan delta stiff, white grey continental clay fills the swales (Bosch, 1988).

The coastal changes between Kuala Sungai Besar - Kuala Besar and Kuala Kemasin in consequence of breakwater construction during 1986 - 1987 and 1989 – 1991 has been studied (Raj *et al.*, 2007a & b). Littoral drift plays an important role of recession and accretion of the shorelines before and after construction. The construction of breakwater on the both sides of Kuala Sungai Besar affects the littoral drift with accretion of sediments up-drift of the southern breakwater while erosion and shoreline recession down-drift of the northern breakwater. In the present day, the littoral drift continues causing shoreline recession at Pantai Sabak and Pantai Cahaya Bulan. Northwestward transport of the eroded beach sediments result in the shoreline to advance at Pantai Mek Mas and the northwestward extension of sand spits and off-shore bar at and in the vicinity of Kuala Besar. The littoral drift has led several past coastal changes that mainly involve variation in the size of sand spits on both side of Kuala Kemasin estuary where accretion of shoreline occurs in the south side and shoreline recession occurs in the north.

1.5.3 Hydrogeology

First investigation on groundwater resources was carried out by Geological Survey Department (GSD) currently know as Mineral and Geosciences Department (MGD) working together with the German Hydrogeological Mission (GHM) on the Second Malaysian Plan (1971 - 1975). The plans cover the area of Kelantan, Terengganu, Pahang, Perlis and Sarawak. The works done during the plan involved detailed hydrogeological and geophysical studies including the construction of test and production wells.

A hydrogeological Map of Peninsular Malaysia on a scale of 1:500000 was published in 1975 by MGD as shown in Figure 1.8. This map classifies the Peninsular into various groundwater regions in accordance with their estimated yield. This classification put the coastal plains as one of the region with the highest groundwater yield (Noor, 1979). The investigation of groundwater continued to the Third Malaysian Plan (1976 - 1980) collaboration between MGD and GHM. The investigation was successfully completed for Kelantan, Terengganu, Pahang, Kedah and Perlis.

For North Kelantan River basin, early investigation in 1974 focused on the alluvial area at the east part where substantial reserves of groundwater have been proven in areas of Kota Bharu, Pengkalan Chepa, Bachok, and Pasir Puteh. During 1974-1977, detailed work in the coastal areas of Tumpat, Pengkalan Kubor and more inland of Wakaf Bharu was successfully completed. Continuous work was carried out for Pasir Mas district with construction of exploration boreholes and test well (Ang & Kwan, 1979).

Figure 1.8: Hydrogeological Map of Peninsular Malaysia

The depth aquifer layers are described by previous studies (e.g. Ang & Loh, 1975; Noor, 1979; Chong & Tan, 1986; Pfeiffer & Tiedemann, 1986; Mohammad, 1992; Mohammad & Ang, 1996 and Hamzah *et al.*, 1997). Layer 1 lies at the depth of approximately 20 m from the ground surface. Layer 2 lies at depth of 20 to approximately 50 m while Layer 3 lies at depth of more than 50 m. In some places Layer 4 has also been recognized. All aquifer layers are separated by impervious clay layer.

Previous hydrogeochemical studies (e.g. Ang & Loh, 1975; Noor, 1979; Awadalla & Noor, 1990; Mohamad, 1992; Bachik, 1994; Suratman, 1997; Mohd Aziz, 2007 and Mohd Rizalpahlavy, 2008) showed that iron concentration occurred naturally in groundwater. In general all aquifer layers showed iron concentrations exceed the WHO standard of 0.30 mg/L. The chloride concentration reported was also above the WHO standard of 250.00 mg/L especially in second layer aquifer. Nitrate concentrations in all aquifer layers were below the WHO standard of 45.00 mg/L. Certain areas in first aquifer layer had nitrate concentration above 10.00 mg/L. *E.coli* bacteria was found in the first aquifer layer. The bacteria colony was almost 40 to 230 bacteria in 100 mL groundwater samples. Hydrochemical facies indicated that groundwater changed from $NaHCO_3$ to NaCl from inland towards the coastal area.

1.5.4 General Iron Removal from Groundwater

In the past few decades, various methods have been used to remove iron from groundwater using either the conventional or advanced method. The conventional method is used for groundwater treatment in Kelantan state. This method consists of aeration, coagulation, sedimentation, filtration and disinfection. For iron removal, during aeration process, oxygen is brought into the water to convert the dissolved ferrous compound into insoluble ferric hydroxides. Then, the ferric hydroxide is removed by sedimentation and filtration processes.

Advanced method consists of (i) Ion-exchange method; (ii) Oxidation and filtration; (iii) Charcoal/ash-sand filtration; (iv) Bioremediation, as mentioned below.

In the ion exchange method, batch study using an inorganic ion exchanger of sodium titanate ion (CoTreat) was used to remove iron and other metal ions (Mn, Zn, Cu, Ni) from groundwater. The breakthrough values were below 45% and tends to decrease from 27% to 10% with the increase in the bed volume processed (Vaaramaa & Lehto, 2003).

In the oxidation combined with filtration method, oxygen or stronger oxidants such as chlorine and potassium permanganate ($KMnO_4$) are generally used for Fe^{2+} and Mn^{2+} oxidation. The solid products of oxidation ($FeOOH.H_2O$ and MnO_2) are then filtered through a granular bed, commonly green sand (Ellis *et al.*, 2000).

Charcoal/ash-sand filtration is a traditional method for iron removal. The ash-charcoal mixture is obtained from different types of firewood including bamboo. Water obtained from hand tube-well or ring-well is put in the filter system and filtered immediately, did not seem to retain iron. The use of ash or charcoal is expected to facilitate removal of iron by making the water alkaline, which precipitates iron as goethite or ferrihydrite (Dutta *et al.*, 2007)

Bioremediation for iron and manganese removal from groundwater pumped out of a hydrocarbon-contaminant obtained by oxidation and precipitation in a biological treatment plant. Iron was oxidized through aeration while manganese through the nitrification and autocatalysis process (Berbenni *et al.*, 2000).

1.5.5 Ionic Liquid as Medium for Removal of Metal Ions in Groundwater

As of date, no conclusive literature review is available on the removal of metal ions from groundwater using ionic liquids. Only batch experiments of ionic liquids with various metal ions stock solution have been reported so far.

1.6 GENERAL METHODOLOGY

To facilitate this study, techniques and methods were developed to ensure the study is scientifically sound. Figure 1.9 gives the flowchart of general methodology applied in this study.

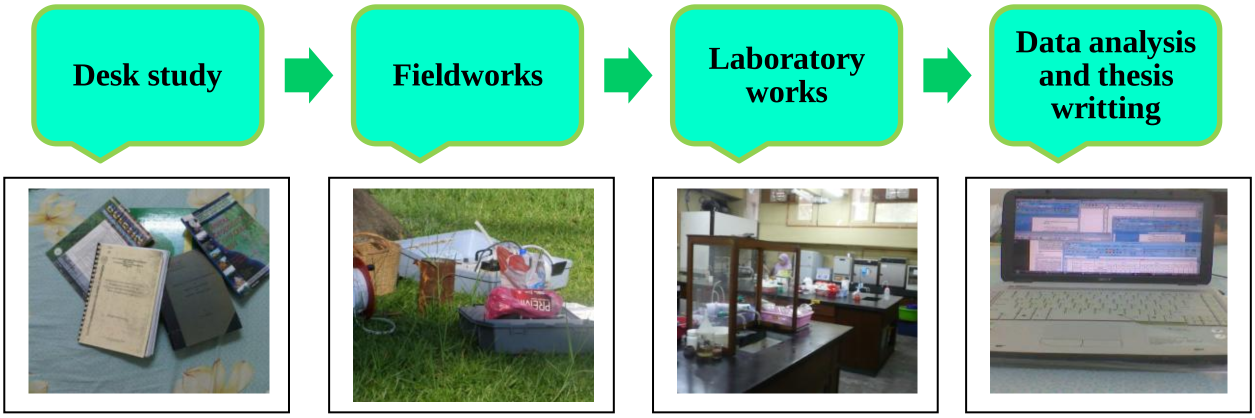

Figure 1.9: General Flow of Methodology in this Study

1.6.1 Desk Study

The first phase includes literature review, checklist and data collection for the study areas. Sources of data used in this phase were from both published and unpublished reports and journals, local or international. This phase provided a clear overview regarding the study area and gave a better understanding on the concepts and the situation of groundwater resources in Kelantan River Basin as noted in Table 1.4.

Table 1.4: Type of Data Used in this Study

Data	Scale	Department
Topography Map	1: 63360	Geology Department, University of Malaya
Geology Map	1: 50000	Minerals & Geoscience Department (MGD)
Hydogeology Map	1:500000	
Borehole Log	-	
Hydrology	-	Malaysian Meteorology Department (MMD) Department of Irrigation and Drainage (DID)
Land Use	-	Department of Agriculture (DOA)

1.6.2 Fieldwork

During fieldwork, data from literature review were validated and verified from the sampling locations. Only water level and field parameter was measured in the field. Groundwater samples were collected and preserved for laboratory analysis.

1.6.3 Laboratory

Laboratory analysis was done in Geology and Chemistry Department, University of Malaya. In Geology Department, the groundwater samples were tested for cation and anion. For cation analysis, Inductively Coupled Plasma Optical Emission Spectrometer (Perkin Elmer Optima 5300 ICP-OES) was used. Cation (13 geology elements) such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Cd^+, Mn^{2+}, Fe^{2+}, Pb^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+}, As^+ and Se^+ were determined using ICP. For anion analysis, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^- and F^-, Ion Chromatography (IC) supplied by Metrohm was used. The detailed analysis regarding metal ion removal from the standard solution was done using ionic liquid as the solvent medium for liquid-liquid extraction treatment method. Then, method analysis was applied to the groundwater samples.

1.6.4 Data Analysis and Thesis Writing

All data collected from fieldwork, laboratory experiment and government department were analyzed and interpreted. Software used were Didger 3, Surfer 7, Surfer 8, AquaChem V 5.1 integrated with PHREEQC, ArcGIS, AutoStitch and Adobe Photoshop CS3. This was followed by thesis writing.

1.7 THESIS OUTLINE

Thesis outline is guidance for thesis writing that consists of 5 chapters for this study. Chapter 1 (Introduction) discusses general overview of the study area including introduction, objective, study area, geomorphology, literature review, and a brief outline of the methodology. From here, chapter 2 – 4 has its own methodology. Chapter 2 (Geology and Hydrology), discusses about the geology, and hydrology of the study areas. Chapter 3 (Hydrogeochemistry), discusses the hydrochemical facies, groundwater quality and chemical evaluation for the three aquifer layers. Chapter 4 (Iron Removal) discusses about the treatment method with ionic liquid as a medium. Ionic liquid as a green solvent is used as a medium for this treatment with aqueous stock solution and groundwater samples. Chapter 5 (Conclusion and Recommendation), will conclude the whole of research and advocate for research improvements in the future.