FEASIBILITY OF USING IONIC LIQUIDS IN THE EXTRACTION OF ORGANIC/INORGANIC COMPOUNDS FROM REFINERY WASTEWATER

by

NORLIYANA BT KAMARUDIN

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for
BACHELOR OF ENGINEERING (Hons)
CHEMICAL ENGINEERING

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Moulay Rachid Babaa)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

CERTIFICATION OF ORIGINALITY

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

NORLIYANA BT KAMARUDIN
Final Year Final Sem,
Chemical Engineering Programme,
Universiti Teknologi PETRONAS.

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ABSTRACT

This work analyzed the feasibility of using ILs in the extraction of organic/inorganic compounds as well as heavy metals (Zn^{2+} and Pb^{2+}) from aqueous solutions of refinery wastewater. In this scope, imidazolium cation based ILs which are 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim$^+$][OTf$^-$], 1-Butyl-3-methyl-imidazolium trifluoroacetate [bmim$^+$][CF_3COO^-] and 1-Butyl-3-methyl-imidazolium chloride [bmim$^+$][Cl^-] were used. These ILs were founded that they allow the extraction and removal of organic/inorganic compounds including heavy metal ions contain in the aqueous solutions. The usage of ILs are emphasize in this project because it has an increasing interest in the industry since ILs are more environmental friendly and safer to be used as well as it has a lot of attractive and high potential of unique properties to offer. The ability of ILs as the chemical tenability had made them as a novel solvents with similar physical properties but having different chemical behavior. They have been demonstrated in previous studies conducted that ILs has more advantages in the extraction technology compared to the conventional solvents used currently as extraction medium in Liquid Liquid Extraction process in which achieving high efficiencies and selectivities upon the extraction. Based on the results achieved via this work, the extraction percentage of Zn^{2+} and Pb^{2+} were analyzed. It was observed that the IL of 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim$^+$] [OTf$^-$] allowed the highest removal of heavy metals with the extraction percentage of Zn^{2+} and Pb^{2+}, it is noted that high extraction percentage was achieved for Zn^{2+} (87.50 %) and Pb^{2+} (86.67%) compared to [bmim$^+$][CF_3COO^-] and [bmim$^+$][OTf $^-$]. For the removal of organic compounds analyzed by GCMS, it is shown that different ILs have capability to extract different of the selected hydrocarbons. This work is significantly important as the use of ILs is widely considered as high potential as alternative solvents in the industries.

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ABBREVIATIONS AND NOMENCLATURES

ILs - Ionic Liquids
ppm - parts per million
mL - milliliters
Zn^{2+} - Zinc
Pb^{2+} - Plumbum/Lead
Cu^{2+} - Copper
AAS - Atomic Absorption Spectroscopic
GCMS - Gas Chromatography Mass Spectroscopy
mg/l - milligram per litre
$g\ km^3$ - gram kilometer cube
Cr - Chromium
Mg - Magnesium
Ni - Nickel
rpm - rotation per minute

CHAPTER 1

INTRODUCTION

1.1 Project Background

Green solvent is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances *(Anastas & Warner, 2000)*. Green chemistry, also known as sustainable chemistry, describes the search for reducing or even eliminating the use of substances in the production of chemical products and reactions which are hazardous to human health and environment *(S. Keskin et al,May 2007)*. Nowadays, the search for green chemistry and technology is very crucial as the goal of it is to create cleaner and sustainable medium which is receiving more and more attention in recent years. The ideal situation that searches the alternative solvents, environmental friendly of ILs compared to traditional organic solvents which are at the same time increased the reaction rates, lower reaction temperature as well as higher selectivity.

The main objective of this work is to investigate the ability of using ILs to remove dissolves organic and inorganic compounds including heavy metals from refinery wastewater. There is a study made with regards to the removal of metal ions from aqueous solutions by extraction with ionic liquids done previously *(L.J. Lozano et al, 2010)*.Several technologies can be used to remove toxic metals from liquid effluents including precipitation, solvent extraction, ion exchange, etc. *(L.J. Lozano et al, 2010)*.

The studies of *(J.G. Huddleston et al.,1998; M.D. McKinley et al.,2000 & T.M. Letcher et al.,2003)* and so on show that for example, the cation 1-*n*-ethyl-3-methylimidazolium has been the most widely studied until 2001, and nowadays, 1-3-dialkyl imidazolium salts are the most popularly used and investigated class of ILs. From those works revealed that ILs have strong ability to interact with organic molecules and heavy metal ions via various mechanisms such as π-π interaction, dispersion, ionic exchange and hydrogen bonding.

On the other way, the change of ILs cation or anion can make these interactions finely adjusted to bring on elevated separation efficiency compared to traditional solvents. The development of ILs usage as solvents in extraction and separation industries is because it has several conditions that are promising to the industries.

Nevertheless, among of these technologies implemented, it is found out that solvent extraction is the most widely used in the separation/extraction technologies of the removal of organic/inorganic compounds and heavy metals from aqueous solutions. To meet the requirement of the project design aspect, the bench scale of experiment to obtain data that could be used in this field are carried out. Throughout this work, three (3) different types of hydrophilic ILs with imidazolium cation based which are 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim$^+$][Otf$^-$], 1-Butyl-3-methyl-imidazolium trifluoroacetate [bmim$^+$][CF_3COO^-] and 1-Butyl-3-methyl-imidazolium chloride [bmim$^+$][Cl^-] are used as extraction solvents.

This work is conducted to investigate the ability of ILs in extracting the unwanted compounds from particular aqueous solutions that are currently becoming quite important issues among the environmentalist. The equipments and procedures used are all created based on the research made and take into consideration of the scope of studies as the limitations of this project.

To date, ILs have recently been revealed as interesting clean alternatives to classical organic solvents in a wide range of chemical and biochemical processes *(A. Ruiz et al,2007)*.

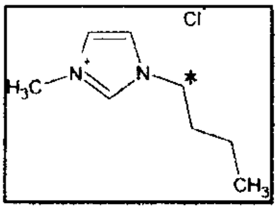


Figure 1.1: Structure of [bmim] [Cl]

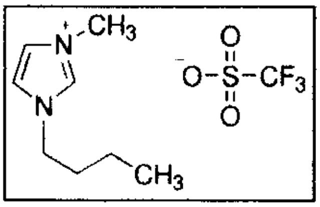


Figure 1.2: Structure of [bmim] [OTf]

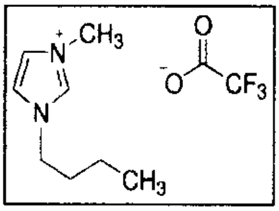


Figure 1.3: Structure of [bmim] [CF3COO]

1.2 Problem Statement

1.2.1 Problem Identification

The current extraction and separation technology in the industry is the usage of conventional organic solvents as extraction solvents. An organic solvent is a type of volatile organic compounds (VOC) which easily vaporizes at room temperature. One disadvantage discovered through solvent extraction is that the loss of organic diluents when they vaporized. This volatilization has a detrimental impact on the quality of environment and also human health. However, this disadvantage can be overcome by using ILs that recently offers safer and greener extraction solvents in extraction method.

These organic solvents normally comprises of Hydrogen bonding, Dipole-dipole and Van Der Waals interactions which most of them are weaker interactions. Thus, these conventional solvents are less capability in being immiscible with other polar substances.

Most of the conventional organic solvents may react with sunlight if expose in atmosphere producing air pollutant known as 'ground-level ozone'. High concentrations of this 'ground-level ozone' can seriously affect human, animal and plant health as well as harming the building materials, forests and crops. Many of the conventional organic solvents require large amount of high purity solvents, expensive, toxicity, carcinogenic and resulting in production of hazardous wastes. They can cause significant and water pollution as well as land contamination. An estimated 20 million tones of volatile organic compounds (VOCs) is discharged into the atmosphere each year as a result of industrial processing operations *(Allen and Shonnard, 2002)*.

Refinery wastewater is one example of aqueous solutions that contain a lot of organic and inorganic compounds as well as heavy metal ions. These compounds need to be removed because they are hazardous and vital to the environment and quality of peoples' life now and in future.

The key problem in most the developing countries is wastewater treatment in which contaminates the water bodies thereby increasing health risk and also due to increasing rate of depletion of water resources *(M. M. Aslam et al, 2010)*. In the industries currently, the removal of these metals has becoming a burning issue. For an instance, the wastewater used taken from Malacca Refinery contains for about seventy-seven (77) organic and inorganic compounds plus heavy metals that are hazardous and some are highly dangerous.

Heavy metals that contain in this contaminated wastewater are considered as the most important compounds in water pollution as it causes serious ill effects. These compounds need to be removed before releasing it to the environment.

The conventional solvent extraction is widely used previously despite of any other valuable developed in separation processes. *(A.Rajendran, D. Ragupathy, M. Priyadarshini, A. Magesh, P. Jaishankar, N.S. Madhavan, K. Sajitha And S. Balaji, 2010).* Unfortunately, the current technology used which is by using the conventional solvents is quite complicated to separate the aromatics and aliphatic hydrocarbon due to overlapping of boiling points and azeotropes formation in the aqueous solution. Hence, ILs has been used to replace these organic solvents since they can react well with low aromatic contents feed that is superior to conventional extraction solvents. The raw data of compounds contain in this wastewater is available in *Appendix 7.1* Throughout this experimental work, the determination of types of organic and inorganic compounds extracted will be determined. The maximum the number or compounds can be extracted, the better it is.

1.2.2 Project Significance

The development of this project will give contributions towards the extraction or separation technology industries. The contributions are as the following:-

1. Capability in identifying the potential of ILs as good extraction solvents in extraction technology.
2. Enhance the interest of study towards ILs applications in extraction technology.
3. ILs widely considered as alternatives solvents compared to conventional solvents.
4. The use ILs as an excellent choice for the development of a safer project and green technology.

1.3 Objectives

The main objectives of this project are:-

1. To investigate the ability of using ILS to remove dissolves organic and inorganic compounds including heavy metals from refinery wastewater.
2. To find out what type of organic/inorganic compounds and heavy metals can be extracted from three (3) different aqueous solutions used.
3. To determine and compare which types of ILs are most preferable in the removal of organic and inorganic compounds.

1.4 Scope of Studies

The usage of ILs in this extraction method is too wide and general based on industry. As to make it specifically, the scope of studies is narrowed down as following:-

1. Determine the water content absorbed by ILs initially from surrounding and determine its solubility in water.
2. Study the extraction percentage of organic and inorganic compounds extracted by liquid liquid extraction method with ionic liquids.
3. Study the capabilities of 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim$^+$][OTf$^-$], 1-Butyl-3-methyl-imidazolium trifluoroacetate [bmim$^+$][CF$_3$COO$^-$] and 1-Butyl-3-methyl-imidazolium chloride [bmim$^+$][Cl$^-$] towards the removal of organic/inorganic compounds and heavy metals contain in refinery wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

2.1.1 Introduction

Rapid industrialization had increased the serious aspects of water pollution throughout the world. Industrialization like refinery and petrochemical plants generate plenty of solid waste and sludge that composed a lot of organic and inorganic compounds including heavy metals.

The presence of pollutants in natural water alters the quality and often poses serious threats to aquatic life. Various studies have shown positive correlation between pollutions from petrochemical and refinery effluents and the health of aquatic organisms *(Warri, U. C et. al, 2011)*. Pretreatment of industrial wastewater to remove hydrocarbons is often required so that the hydrocarbons will not cause VOC emissions from Publicly Owned Treatment Plants (POTWs) to exceed regulatory limits *(K. S. Mohr, 1998)*. The type of wastewater used in this project is taken from a refinery in Malacca contains for about seventy-seven (77) both including organic and inorganic compounds altogether *(Refer appendix)*. Normally, a refinery relatively used a large volume of water especially in cooling systems including surface water runoff and sanitary wastewater.

Refineries generate polluted wastewater containing Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) levels approximately 150 – 250 mg/l and 300 – 600 mg/l respectively; phenols level of 20 – 200 mg/l, oil level of 300 – 600 mg/l in desanter water and up to 5000 mg/l in tank bottoms, benzene level of 0.1 – 100 mg/l, benzo(a)pyrene level of less than 1 to 100 mg/l, heavy metals levels of 0.1 – 100 mg/l for chrome and 0.2 – 10 mg/l for lead and other pollutants *(The World Bank Group, 1998).*

2.1.2 Organic/Inorganic compounds in refinery wastewater

Wastewater released from petrochemical and refineries industries are characterized by the presence of large quantity of polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface active substances, sulphides, naphthylenic acids and other chemicals *(Suleimanov, 1995).* Wastewater chemically composed of organic and inorganic compounds (including heavy metals) where it is considered as the hazardous materials among other types of water pollution. Organic contaminants include dissolved and undissolved volatile organic compounds consisting phenols, chlorobenzene, hydrols. In addition, it also contains dissolved and undissolved non-volatile organic

Organic compounds consist of carbohydrates, proteins, fats, greases, surfactants, oils, pesticides, phenols, etc. and may include another compounds of trace minerals, sulfides, chlorides, nitrogen and phosphorous. Since wastewater contains a higher position of dissolved solids than suspended about 85% to 90% of total inorganic component is dissolved and about 55% to 60% of total organic compounds is dissolved *(R.R. Bansode, 2002).*

According to POTW, these hydrocarbons in wastewater can cause troublesome to the environment because some of these hydrocarbons are volatile and contribute to VOC emissions to the surrounding. Moreover, too much hydrocarbons content in the incoming water would lower down the quality of life. Heavy metals in refinery wastewater are normally related to the group of metals with an atomic density of greater than 6 g km^3 such as Pb, Cr, Cu, Mg, Ni and Zn are widely recognized due to its association with pollution and toxicity problems. (*A.Rajendran, D. Ragupathy, M. Priyadarshini, A. Magesh, P. Jaishankar, N.S. Madhavan, K. Sajitha And S. Balaji, 2010*). Heavy metals include lead, silver, mercury, copper, nickel, chromium, zinc, cadmium and tin that must be removed to certain levels to meet discharge requirements *(Z. Yang, 2003).*

2.1.3 Environmental issues

Due to ineffectiveness of purification systems, wastewater may become dangerous leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem *(Bay et al., 2006).* Normally, the effluent coming from refineries contains oil when discharged into water body. It can cause depletion of dissolved oxygen due to transformation of organic component into organic compounds and loss of biodiversity of the aquatic life. This rapid increase of the presence of these compounds especially involving heavy metals is particularly hazardous since most of them are high in toxicity and persistent. The utilization of compounds from improper treatment or removal of these dangerous compounds into natural water resources is undesirable. It can upset the quality of the water and furthermore, the presence of these contaminants leads to a complex example of pollution because of its toxicity which affects aquatic life as well as human life. Industrial effluents often are released into the natural water resources comprises agricultural, industrial and domestic water.

The damage comes from the separation process that take place in large open air ponds which seep into groundwater and pollute fresh water resources like rivers. Mostly in the places where chemicals industries are placed, people nearby will easily get affected with chronic diseases by this contaminated water that mostly contain heavy metals and organic compounds discharged without proper treatment. With the presence of the excess concentration of these heavy metals can lead to the abnormal growth of living things and metabolic dysfunctional that can cause chronic illnesses.

According to *World health Organization (2000)*, amongst the toxic heavy metals, lead or Pb is one of the most serious environmental poisons throughout the worlds. Likewise in the removal of the heavy metals and organic compounds from industrial effluents especially waste water. For example, a part of contaminated water or waste water cause by petroleum industry has caused environmental damage.

2.2 Ionic Liquids

2.2.1 Physical and chemical properties of ILs

Ionic liquids (ILs), considered being a relatively recent magical chemical due their unique properties, having a large variety of applications in all areas of the chemical industries.

Ionic liquids (ILs) have been accepted as a new green chemical revolution which excited both the academia and the chemical industries *(S. Keskin et al,May 2007)*. The terms room temperature ionic liquid (RTIL), non-aqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase *(T. Welton, 1999)*.

Table 2.1 lists some data for several RTILs formed by the 1-butyl-3-methyl imidazolium cation associated with different anions. However the water solubility of RTILs is highly dependent on the anion such as chloride, bromide, trifluoroacetate ionic liquids are water-soluble *(Wassercheid P. et al., 2000; Dias A.P. et al., 1996; Hagiwara R. et al., 2000 & Muldoon M.J. et al., 2001).*

Table 2,1: Effect of the nature of the anion on physicochemical properties of 1-buthyl-2-methyl imidazolium salts.

1-butyl-3-methyl imidazolium salts					
gegenion	m.p. °C	d g/cm^3	N	Viscosity cP 20°C	Conductivity S/m
BF_4^-	-82 (g)	1.17	1.429	233	0.17
PF_6^-	-8	1.36	1.411	312	0.14
Cl^-	65	1.10*	solid	solid	solid
CF_3COO^-	-40 (g)	1.21	1.449	73	0.32
$CF_3SO_3^-$	16	1.29	1.438	90	0.37
$(CF_3SO_2)N^-$	-4	1.43	1.427	52	0.39
$C_3F_7COO^-$	-40 (g)	1.33	1.414	182	0.10
$C_4F_9SO_3^-$	20	1.47	1.405	373	0.045

Essentially, ILs is purely ionic, non-volatile molten salts with a low melting point less than 100°C or below room temperature where they composed in the majority of ions. This properties had gives ILs the potential to behave very differently when they are used as solvents which is capable for a clean technologies.

ILs are good solvents for a wide range of substances; organic, inorganic, organometallic compounds, bio-molecules and metal ions. They are usually composed of poorly coordinating ions which makes them highly polar but non-coordinating solvents. ILs are immiscible with most of the organic solvents, thus they provide a non-aqueous, polar alternative for two-phase systems *(D.C. Donata et al., June 2006).*

Although all other conventional solvents evaporate to the atmosphere, ILs do not evaporate and their nonvolatility gives an opportunity to utilize them in high vacuum systems. As solvents, ILs posses several advantages over conventional organic solvents, which make them environmentally compatible *(T. Welton, 1999; J.F. Brennecke et. al, 2001; Q. Yang et. al,2004; K.R. Seddon,1996; C. Lagrost et. al,2003 & H. Zhao et. al,2005).*

ILs have a few remarkable unique properties such as has a wide liquid range of 300°C compared with 100°C for water, good solvents for wide range of inorganic, organic and polymer materials, have negligible vapor pressure, high thermal stability up to 200°C, relatively inexpensive and easy to handle and prepare, capable of being a designer and tunable solvents, non-flammable and non-volatile. These most notably of ILs properties under normal operating conditions and therefore do not contribute to air pollution. It is also becoming an advantage in terms of solvents replacement for many industrial processes as it will not be lost due to evaporation as well as reducing the worker exposure. These reasons lead to well said 'green' in the sense that their negligible vapor pressure results in the reduction of waste chemicals and eases product extraction.

Not only the extraction efficiency is greater but also the other advantages like the following are entertained *(A. Rajendran, 2010)*:-

1. No requirement of volatile and flammable organic solvents.
2. More sustainability.
3. Eco and environmentally friendly procedure.
4. Fastness and reliability.
5. Recoverability and reusability of ionic liquid hence more economical.

The terms used as polar, nonpolar and apolar are generally related to the values of dielectric constants, dipole moments, polarizabilities. If a solvents has the ability to dissolve and stabilize dipolar or charged solutes, it is defined as a polar solvent. Under this simple definition, ILs are highly polar solvents, but it is not completely true to make such strict conclusions since there ILs can be designed in a vast range. As example, since polarity is the simplest indicator of solvent strength, researchers compared polarities of ILs and conventional solvents showed that 1-alkyl-3-methylimidazolium ILs with anions [PF6], [BF4], [(CF3SO2)2N], and [NO3] are in the same polarity region as 2-aminoethanol and lower than alcohols such as methanol, ethanol and butanol *(A.J. Carmichael et al, 2000).* Imidazolium ILs are solvents of main interest and have been comprehensively described. They are well defined and their synthesis is well established *(M. R. Rosocka, 2010).*

Different types of ILs give an opportunity to modify the physical and chemical properties of the IL. One of the most used cations is imidazolium. Charge distribution on the anions, H-bonding ability, polarity, dispersive interactions is the main factors that influence the physical properties of ILs *(F. Mutelet et al., 2005).* For example, imidazolium-based ILs are highly ordered hydrogen-bonded solvents and they have strong effects on chemical reactions and processes *(J. Dupont et al., 2005).* The overall properties of ILs result from the composite properties of the cations and anions and include those that are superacidic, basic, hydrophilic, water miscible/immiscible and hydrophobic. Usually, the anion controls the water miscibility, but the cation also has an influence on the hydrophobicity or hydrogen bonding ability *(J.G. Huddleston et al., 2001).* Since the anion chemistry has a large effect on the properties of IL, although the cations are the same, there are significant differences between ILs with different anions as what have been investigate in this work.

It has been demonstrated the task-specific ionic liquids (TSILs) have advantages compared to common solvents used as separation media in liquid-liquid extraction processes achieving high efficiencies and selective separation *(Mihkel Koel, 2007)*. They have ionic interactions (mutual electrostatic attraction/repulsion of charged particles) that make them very miscible with polar substances. At the same time, their solubility in less polar fluid is determined by the presence of alkyl chain on its cation. ILs constituents are constrained of columbic forces that lead to exhibition of no vapor pressure. For example, they are soluble with water and/or a number of organic solvents providing the flexibility for a number of reaction and separation schemes due to its high polarity.

A complete understanding of their physical properties, phase behavior and safety/environmental hazards is necessary when dealing and utilizing ILs in the process. Their physical and chemical can be tuned for a broader range of applications by varying its chemical constituents. For example like alklylimidazolium ILs that can vary over wide ranges due to its physical properties in which they are denser than water with density of 1.0 to 1.5 g/cm^3. Its viscosity is quite similar to oil with the values from 0.2 to 4.0 Poise at 25°C. refractive index of 1.3 to 1.5, electrical conductivity in the range of 60 to 250 S/cm. ILs not only can be applied in existing methods where improvement of sensitivity and selectivity of analysis is always needed, but their different behaviors and properties can offer original solutions in the chemical analysis and the search for new applications of ILs is growing in every area of chemistry *(Mihkel Koel, 2007)*.

According to Earle and Seddon published paper in IUPAC Journal Pure and Applied Chemistry, 2000, ILs can be recycled which can reduce the cost of a process. They are less wasteful than conventional solvents because they give higher yields and more selective for desired production.

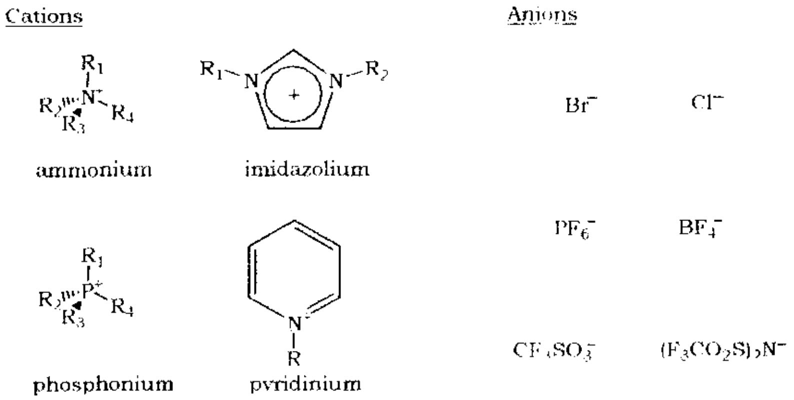


Figure 2.1: Typical Ionic Liquid Cations and Anions (Morton III S.A, 2008)

With respect to this separation technique, the most attractive characteristic of ILs is it can be designed to be immiscible in water by extending the alkyl chain length of its cations as well as its hydrophobic anions. The advantages of this extraction of organic compounds with ILs will require less process steps and less in energy consumption compared to conventional solvents since it is negligible of vapor pressure.

Hence, the use of ILs for the removal of heavy metals and organic compounds had growing its interest recently as a potential extracting agents and more successful compared to other conventional methods such as precipitation, reverse osmosis, adsorption and ion exchange as well as environmental friendly alternative to traditional solvents *(NSC, 2004)*.

2.2.2 Comparison of ILs with conventional solvents

Recently, the use of ILs is gaining more interesting recognition as a novel solvent in the extraction technology. ILs generally consists of a bulky and nonsymmetrical organic cations like imidazolium, pyrrolidinium, pyridinium, ammonium or phosporium and various other inorganic or organic anions such as tetrafluoroborate and bromide anions if compare to other conventional solvents. Considering high potential of ILs as solvents, they can easily replace other conventional organic solvents which are used in large quantities in chemicals processing industries to eliminate major environmental problems. Typical solvents used are polar components such as sulfolane *(J. Chen et al., 2000; L. Duanet al., 2000; Y.J. Choi et al., 2002 & Y. Yorulmaz et al., 1985)*, N-methyl pyrrolidone (NMP) *(R. Krishna et al., 1987)*, N-formyl morpholine (NFM), ethylene glycols *(W. Wang et al., 2003)* and propylene carbonate *(S.H. Ali et al., 2003)*. Compared to conventional solvents which are mostly comprises of weak interaction like Hydrogen Bonding, Dipole-Dipole And Van Der Waals interaction, ILs have strong interaction where it can electrostaticly attract or repulse charged particles which make them very miscible and polar substance.

ILs tend not to give off vapors in contrast to traditional organic solvents such as benzene, acetone, and toluene *(Kabo et al., 2004)*. In most of the studies, ILs are introduced as a great green solvents compared to conventional solvents which are mostly VOC type because of their great chemical and physical properties which they are not explosive due to its negligible vapor pressure and they may be feasible to recycle to be repeatedly reuse. Thus, it is convenient to work with ILs in the laboratory since the non-evaporating properties of ILs eliminate the hazardous exposure and air pollution problems. In addition, this volatility of existing extraction solvents not only contains hazardous contaminant to the environment instead it can lead to the difficulty on the recovery of extractant and subsequent purification of products when the solute volatile.

Hence, research for cleaner solvents is crucial to cope with these volatile liquids, the cost of replacing evaporation solvents and the bulk volume of solvents required in industries. Thus, it has been figured out that the use of ILs has potential as a clean and better replacement for common VOCs solvents in chemicals processes.

ILs is suggested to be used in solvents such as water that have a liquid range of 100°C which are impossible to be used with another traditional/conventional organic solvents. They are not only applied in existing methods in which improvement of sensitivity and selectivity is always needed, on the contrary of their different behaviors and properties can offer original solutions in chemical analysis and the search for the new applications of ILs that is increasing in chemical industries.

ILs are appear superior than another existing conventional entrainers and extraction solvents for it is can be customized in terms of its selectivity, capacity, viscosity and thermal stability. It is also found out to be able to break a variety of azeotropes systems. Comparing to conventional solvents, ILs are more viscous, dense and have less volume changes upon the change of operating conditions when mixing with another aqueous solutions.

2.2.3 Challenges of ILs

The viscosities of ILs are higher than most organic solvents and water, usually similar to viscosity of oils. This high viscosity may be responsible to produce a reduction in the rate of many organic reactions and even a reduction in the diffusion rates of species and also handling of ILs with high viscosities is difficult however; increasing temperature, changing anion–cation combinations may yield ILs with lower viscosities *(S. Keskin et al., 2007)*.

However, the advantageous (process) properties of ionic liquids notwithstanding, some of them have unfavorable chemical properties which disable their use on bigger scales than laboratory or pilot plant scale or limit their application window to only a few processes.

Those limitations are mainly due to instability as a result of corrosiveness and moisture instability as well as insolubility in water. Another point is the, often, high viscosity of ionic liquids; because elevated viscosity is unfavorable in many processes, too *(Antje Hansmeier, 2010)*. *(Arce et al., 2006)* concluded that IL presents the highest selectivity but close to the other organic solvents and they reported that the results for solute distribution ratio depend on the concentration range of extraction. The stability of ILs is crucial for optimum performance where many of them are both air and moisture stable, some are even hydrophobic.

On the other hand, most imidazolium and ammonium salts are hydrophilic and if they are used in open vessels, hydration will certainly occur *(S.N.V.K. Aki et al., 2001)*. These kinds of hydrophilic type of ILs are very sensitive and tend to absorb water from atmosphere.

2.2.4 ILs applications as an extraction solvent

In the literature, various studies were performed to extract metal ions using ILs *(A.E. Visser et al., 2000; S.V. Dzyuba et al., 2001; R.A. Bartsch et al., 2002; C.J. Chen et al., 2003 & H. Luo et al., 2004)*. In this work, extraction is used as medium for separation since it is an energy efficient technique in most of chemical applications. Most of organic solvents used in extractions are known with their flammable and toxically properties. In order to improve the safety and environmental friendliness of this conventional technique, ILs may be used as ideal substitutes due to their stability, nonvolatility and adjustable miscibility and polarity *(S. Xia et al., 2005)*.

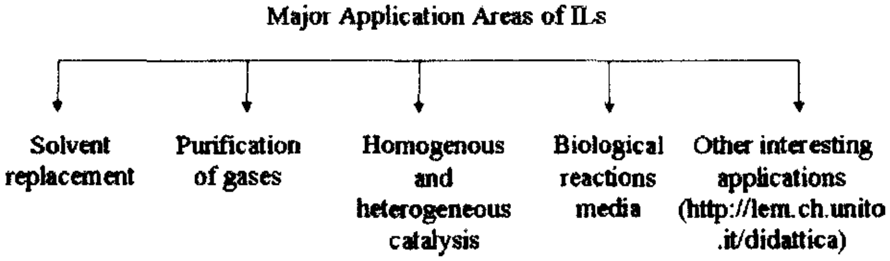


Figure 2.2: Major application areas of ILs (S.Keskin et al., 2007)

When a reaction is carried out in an ionic liquid, differences in the rates and selectivities of the process are often observed when compared to the corresponding reaction in molecular solvents. Being made up of ions, the principle interactions in such a solvent are electrostatic and the interactions between the component ions are typically much larger than between the ions and solute molecules *(J.B Harper et al., 2006).* Liquid-liquid (or solvent) extraction has been extensively employed in the recovery and separation of metal ions. Removal of organic, inorganic compounds and heavy metal ions from an aqueous phase by solvent extraction is normally achieved by contacting the aqueous phase with an organic phase.

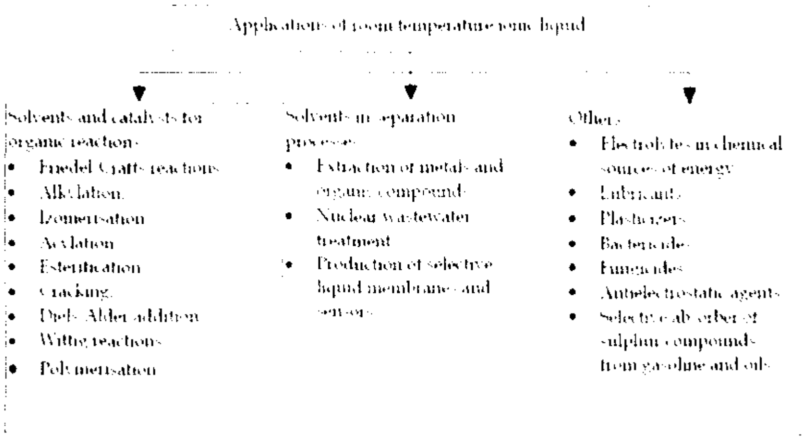


Figure 2.3: Scheme of ILs' applications (Adams, 2002; Holbrey & Seddon, 1999; Kosmulski et al., 2002; Pernak, 2003; Seddon et al., 2000)

Liquid-liquid extraction is an important kind of separation method in certain metal processing and the search for better solvents is continuing task that is based on the distribution of chemicals between two different liquid phases. It has been receiving more and more attention currently in the industries. Compares to other separation methods, LLE often has unique advantages for separation of chemicals that have high or similar boiling point with relatively large capacity and low consumption of material and energy *(Treybal, 1951)*. In this work, ILs such as $[bmim^+][OTf^-]$, $[bmim^+][Cl^-]$ and $[bmim^+][CF_3COO^-]$ were employed as solvents replacing current VOCs solvents in LLE of metal ions, organic compounds and inorganic compounds extraction. Some ILs are suitable to be done using conventional liquid-liquid extraction method due to their immiscibility with water in which allow the formation of biphasic systems and the high solubility of organic species in them. ILs also play a very important role in extraction technology as its design of safe and environmentally benign separation processes made it perform well in its ways.

ILs having a miscibility gap with water has been shown to be effective solvents for a range of organic compounds. The pH-dependent distribution of certain solutes (e.g. organic acids) can provide a route for reverse extraction *(Huddleston et al., 1998, Visser et al, 2000)*. ILs seems to be highly effective as replacements for conventional organic diluents in liquid-liquid extraction because they provide unique salvation environment for ionic species such as metal ion-neutral ligand complexes. Nevertheless in many cases, ILs can be superior to common solvents not only due to its nonvolatility features in fact to it other benefits like the designable physicochemical properties against specific tasks and unusual liquid-liquid extraction with conventional solvents.

The ILs come into contact with contaminated water and they snatch the metal ions out of water. Task-specific ionic liquids (TSIL) concept is introduced in order to synthesize ILs with desired properties to extract metal ions *(Visser et al., 2002)*.

CHAPTER 3

METHODOLOGY

The research method for this project will be on experimental methods which are carried out in the Chemical Engineering Laboratory and Ionic Liquid Research lab, Universiti Teknologi PETRONAS.

3.1 *Preparation of ionic liquids*

The ILs used in this experiment are 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate $[bmim^+][OTf^-]$ (purity>99%), 1-Butyl-3-methyl-imidazolium trifluoroacetate $[bmim^+][CF_3COO^-]$ (purity>99%) and 1-Butyl-3-methyl-imidazolium chloride $[bmim^+][Cl^-]$ (purity>99%) were obtained from Ionic Liquid Research Center (Universiti Teknologi PETRONAS). Initially before starting the experiment, the water content contained in ILs were measured by using Karl Fischer titrations. A fixed small volume of solution was then injected into the Karl Fischer coulometer and a reading of water content was obtained. This step is needed since the ILs used is hydrophilic type in which they tend to absorb the moisture from the surrounding. Then, the solubility of ILs in the water is determined by placing the ratio of ILs to water at 1:1 in the test tube. The mixture is mixed by using VORTEX Mixer (4000rpm) for about 5 minutes and then the mixture is centrifuged at 5000rpm for 10 minutes in order to allow the better phase separation to occur. The phases collected and the water content is measured again by using Karl Fischer titration. To ensure that the phase of ILs contain the minimum amount of moisture, they are kept in the vacuum oven until the next use during the extraction part.

3.2 *Liquid Liquid Extraction of Organic/Inorganic Compounds including Heavy Metals from Wastewater.*

Liquid-liquid extraction techniques used in this project/experiment is the most common technique to separate or isolate the desired organic and inorganic compounds including heavy metals from a mixture based on their relative solubility in two different immiscible liquids normally water and organic solvents.

The mixture of ILs and aqueous solutions are prepared. This technique initially carried out by preparing 5mL of ILs each with 2.5mL of wastewater each to be used. ILs and wastewater is then well mix together before proceeding to the extraction. The mixtures are then place in the separation funnel on a ring stand to perform liquid liquid extraction. The separation funnel is gently rock and followed by vigorously shake for about 30 seconds in order to allow the solutes to become equilibrium between the two solvents. Noted that along the process, slowly open the separation funnel stopcock by pointing up its stem. This is as to release the excess pressure buildup and avoid the hazardous chemicals from blowing out.

After the extraction procedure in this method is over, the ionic liquid present in the organic layer was separated using separating funnel under controlled pressure. The mixture is rested for 5-10 minutes until a clearly two separated layers are formed. Carefully open the stopcock and take the sample of the bottom layers which contains the aqueous solutions to be analyzed. This extraction steps will be repeated several times to have a better effect at the completion separation. Noted that ILs are used repeatedly in this work without regeneration.

3.3 *Analytical Method*

Samples at approximate 0.5mL will be taken from the phases and analyze by using AAS for determination of inorganic compounds including heavy metals (Pb^{2+}, Zn^{2+} and Cu^{2+}) and GCMS for organic compounds.

For AAS, all of the standard and stock solutions are prepared by using distilled water with the standard concentration (ppm) as required. Detail results for ternary phase behavior of the systems of interest at a temperature 295K are obtained for both wastewaters. All of the aqueous solutions were prepared using deionized water.

GCMS has been used in identifying the organic/hydrocarbons in wastewater samples. The GCMS setting are as following: Electron impact ionization, electron energy 70ev, scan range of 40 to 50 amu at 1scan/s, helium flow rate of 0.9 cm^3/min. The samples were then injected in the column in 30 m SGE BP1 capillary column, 0.25mm i.d, and the temperature held at 35°C for 1 minute the increased from 55 to 300 °C at 5 °C/min, thereafter held at 300 °C for 5 mins. All the data obtained both from AAS and GCMS were recorded and analyzed.

3.4 Tools

Instrumentations

1. Separation Funnel
2. Karl Fischer
3. Centrifuge
4. Atomic Absorption Spectroscopy (AAS)
5. Gas Chromatography Mass Spectrometry (GCMS)

Chemicals

1. Malacca Refinery Wastewater
2. Ionic liquids
   a) 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate,$[bmim^+][OTf^-]$
   b) 1-Butyl-3-methyl-imidazolium chloride,$[bmim^+][Cl^-]$
   c) 1-Butyl-3-methyl-imidazolium trifluoroacetate,$[bmim^+][CF_3COO^-]$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 *Determination of water content and solubility of ILs with Karl Fischer and Centrifuge.*

Hydrophilic type of ILs was selected as the extraction solvents to study the liquid liquid extraction of organic and inorganic compounds as well as heavy metals from wastewater. These type of ILs used are 'water-lover' solvents that enable the reaction in aqueous solutions with water basis. Most of ILs usually absorbs moisture from environment even it is kept in a low humidity place. Thus, the water content in ILs needs to be measured with Karl Fischer titration.

From the preliminary data obtained in *Table 4.1*, the water content in [bmim$^+$][Cl$^-$] is higher in percentage and ppm compared to [bmim$^+$][OTf $^-$] and [bmim$^+$][CF_3COO^-]. This water content might affect the efficiency of ILs in acting as extraction solvents. Thus, the water content need to be dried or removed initially in order to increase the efficiency and performance of ILs in extracting the unwanted compounds from aqueous solutions. Even though later these ILs will react with wastewater and they will absorb water content, but in this case, we want to ensure at the beginning of the experiment, the water content in ILs can be as minimize as it can. Hence it can perform better as solvents during the extraction process.

Table 4.1: Percentage of water content in ILs

Ionic Liquid	Weight (g)	Concentration (ppm)	Percentage of water content (%)
$[\mathrm{bmim}^+][\mathrm{OTf}^-]$	0.0075	76880.44	7.69
	0.0642	60634.58	6.06
$[\mathrm{bmim}^+][\mathrm{Cl}^-]$	0.0540	6458.77	0.65
	0.0722	9701.45	0.97
$[\mathrm{bmim}^+][\mathrm{Cf3COO}^-]$	0.0228	8243.42	0.82
	0.0270	8056.61	0.81

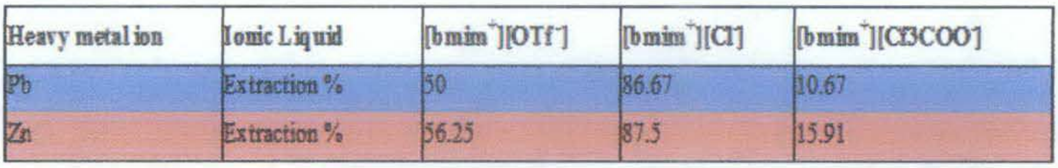
In regard to the solubility, the mixture of ILs and distilled water at ration of 1:1 was determined by using Centrifuge. The centrifugations were conducted repeatedly for three times and the results showed that the selected ILs were soluble in water. The mixture of ILs and distilled water then need to be dried in the vacuum oven for a few days in order to remove the amount of water before the ILs can be used again throughout this experiment.

4.2 *Liquid liquid extraction of organic and inorganic compounds including heavy metals from wastewater.*

4.2.1 Atomic Absorption Spectroscopy (AAS) result for inorganic compounds/heavy metal ions removal

In order to evaluate the capabilities and efficiencies of ILs as extraction solvents, the initial fraction for some of the heavy metals which are in this case, only the most two important heavy metals (Zn^{2+} and Pb^{2+}) were analyzed and obtained from AAS

Table 4.2: Effect of imidazolium cation based ILs on extraction percentage



Heavy metal ion	Ionic Liquid	[bmim$^+$][OTf$^-$]	[bmim$^+$][Cl$^-$]	[bmim$^+$][Cf3COO$^-$]
Pb	Extraction %	50	86.67	10.67
Zn	Extraction %	56.25	87.5	15.91

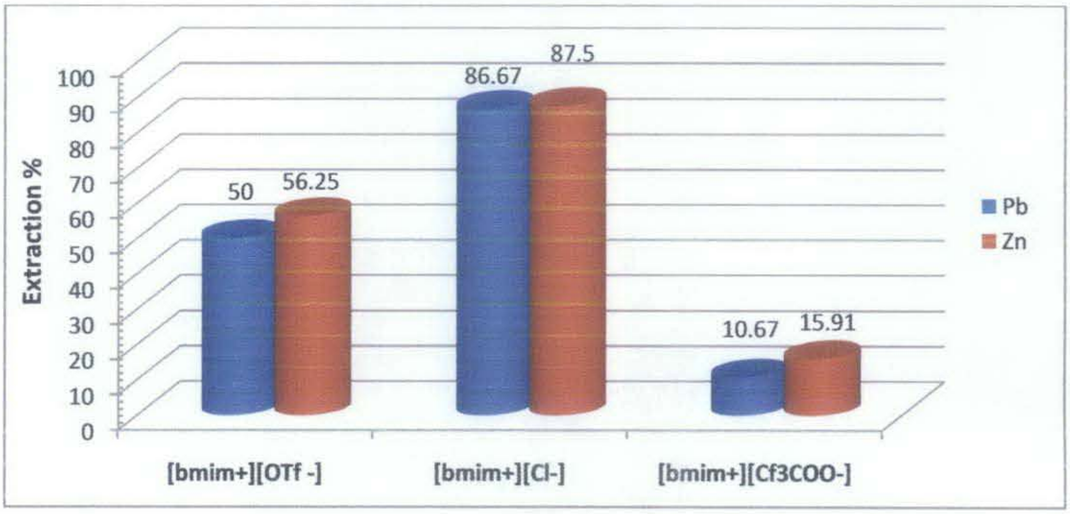


Figure 4.1: Extraction percentage of the Zn^{2+} and Pb^{2+} metals removal by using ILs

In the evaluation of the extraction percentage of Zn^{2+} and Pb^{2+}, it is noted that high extraction percentage was achieved for Zn^{2+} (87.50 %) and Pb^{2+} (86.67%) with [bmim$^+$][Cl $^-$]. However, less extraction percentage of Zn^{2+} (56.25%) and Pb^{2+}(50.00%) was achieved with [bmim$^+$][OTf $^-$] and the lowest extraction of extraction percentage of Zn^{2+} (15.91%) and Pb^{2+}(10.67%) with [bmim$^+$][CF_3COO^-]. This shown that the imidazolium cation based ILs with [Cl $^-$] anion is more efficient as extraction solvent compared to [CF_3COO^-] and [OTf $^-$] anions. As far as the percentage of heavy metal ions are concerned, it is inferred that almost all of these ILs were proved to be used as potential extracting agents from aqueous solutions. Hence, [bmim$^+$][Cl $^-$] were found to be the better extraction solvents compared to the [bmim$^+$][OTf $^-$] and [bmim$^+$] [CF_3COO^-] to remove Zn^{2+} and Pb^{2+} metals.

The following is the decreasing order of the efficiency of removal of heavy metal ions (Zn^{2+} and Pb^{2+}) using three type of hydrophilic imidazolium cation based ILs:-

$$[bmim^+][Cl^-] > [bmim^+][OTf^-] > [bmim^+][CF_3COO^-]$$

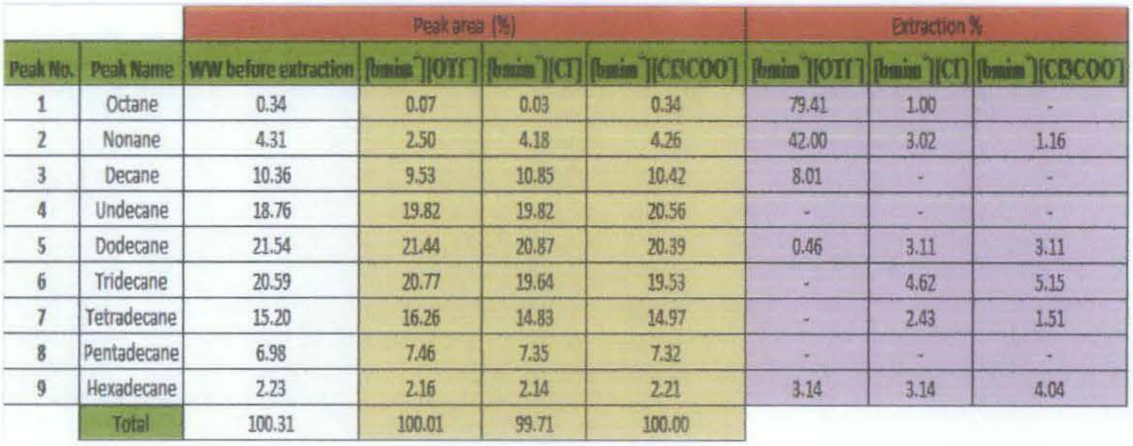
In *Table 4.2 and Figure 4.1*, by comparison made with regards to the different anions effects in ILs which based on imidazolium cations, the greatest effect on extraction percentage was observed when the nature of anion in ILs had changed. ILs seems possible to tailor for the use of as extraction solvents for specific metal ions separation. On the other hand, a high efficiency of Pb^{2+} and Zn^{2+} metals removal had reached with $[bmim^+][Cl^-]$ ILs. All of the above results were analyzed and determined in order to evaluate the influence of cation and anion compositions of ILs on the removal of heavy metals. These ILs used to remove Pb^{2+} and Zn^{2+} from the wastewater via liquid liquid extraction with efficient remarkably greater than other conventional methods such as chemical preparation, co-precipitation, coagulation, evaporator recovery process, reverse osmosis and etc. After liquid liquid extraction part is over, IL layer that presented in the organic layer was separated using separating funnel under a controlled pressure. The layers formed were based on the different density of ILs and wastewater. Currently, a great deal of interest in studying the interaction between metal ions and ILs is being shown *(L. J. Lozano, 2010)*.

4.2.2 GCMS result for organic/hydrocarbon compounds removal

The following *Figure 4.2 and 4.3* showed the result of GCMS analysis of the components presence in wastewater samples. Based on the analysis, the GCMS analyzed wastewater samples contain large number of hydrocarbon components (from peak 1 till 9) which are presented in *Table 4.3*.

In this work, only nine (9) of the highest and main peaks are taken into consideration for comparison since it will give more accurate results of organic/hydrocarbon compounds extraction percentage.

Table 4.3: Effect of imidazolium cation based of ILs with different anions towards organic/hydrocarbon extraction



		Peak area (%)				Extraction %		
Peak No.	Peak Name	WW before extraction	$[bmim^+][OTf^-]$	$[bmim^+][Cl^-]$	$[bmim^+][Cl_3COO^-]$	$[bmim^+][OTf^-]$	$[bmim^+][Cl^-]$	$[bmim^+][Cl_3COO^-]$
1	Octane	0.34	0.07	0.03	0.34	79.41	1.00	-
2	Nonane	4.31	2.50	4.18	4.26	42.00	3.02	1.16
3	Decane	10.36	9.53	10.85	10.42	8.01	-	-
4	Undecane	18.76	19.82	19.82	20.56	-	-	-
5	Dodecane	21.54	21.44	20.87	20.39	0.46	3.11	3.11
6	Tridecane	20.59	20.77	19.64	19.53	-	4.62	5.15
7	Tetradecane	15.20	16.26	14.83	14.97	-	2.43	1.51
8	Pentadecane	6.98	7.46	7.35	7.32	-	-	-
9	Hexadecane	2.23	2.16	2.14	2.21	3.14	3.14	4.04
	Total	100.31	100.01	99.71	100.00			

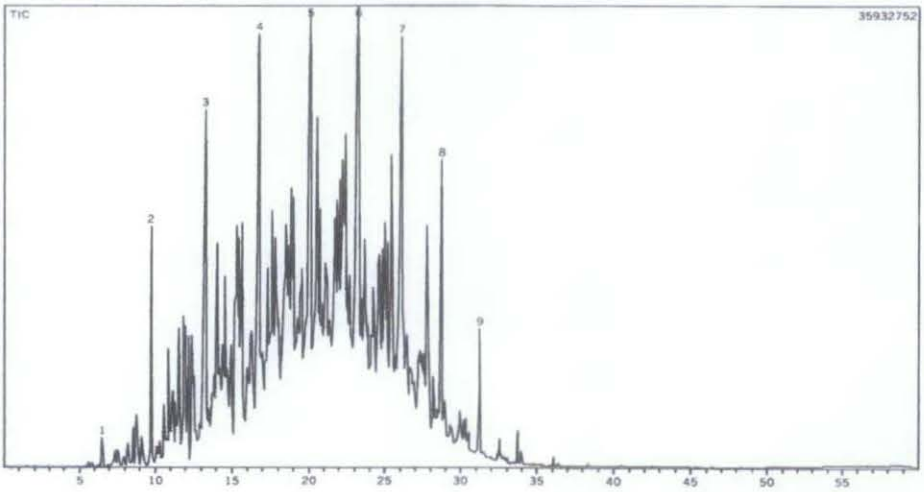


Figure 4.2: GCMS peak area fraction of organic/hydrocarbon compounds result for wastewater BEFORE extraction

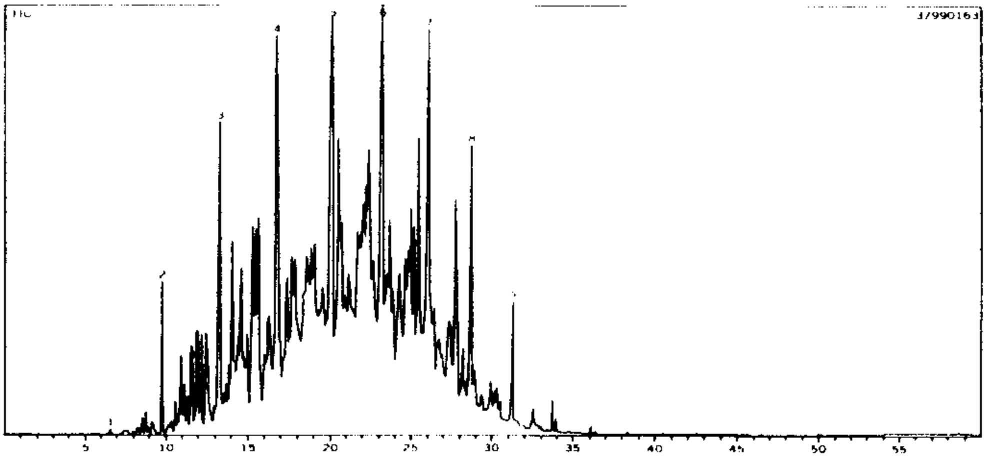


Figure 4.3: GCMS organic/hydrocarbon compounds result for wastewater AFTER extraction

In the evaluation of the extraction percentage of organic/hydrocarbon compounds analyzed by GCMS, it is shown that the selected ILs used via this work did removed the hydrocarbon compounds.

In order to evaluate better, the extraction percentage were determined by comparing the peak area percentage before and after extraction method took place as presented in *Table 4.3*. However, throughout this investigation, the results showed different ILs removed only different/some of the selected hydrocarbons. For example like [bmim$^+$][OTf$^-$], it is excellent in removing Octane and Nonane hydrocarbons as well as removing only a small amount of Decane, Dodecane and Hexadecane hydrocarbons. Despite of [bmim$^+$][OTf$^-$] IL, the other two ILs, [bmim$^+$][Cl$^-$] and [bmim$^+$][CF$_3$COO$^-$] also removed some of hydrocarbons in a low extraction percentage thus not really efficient. The following figure presented the effects of imidazolium cation based ILs on organic/hydrocarbon compounds extraction percentage.

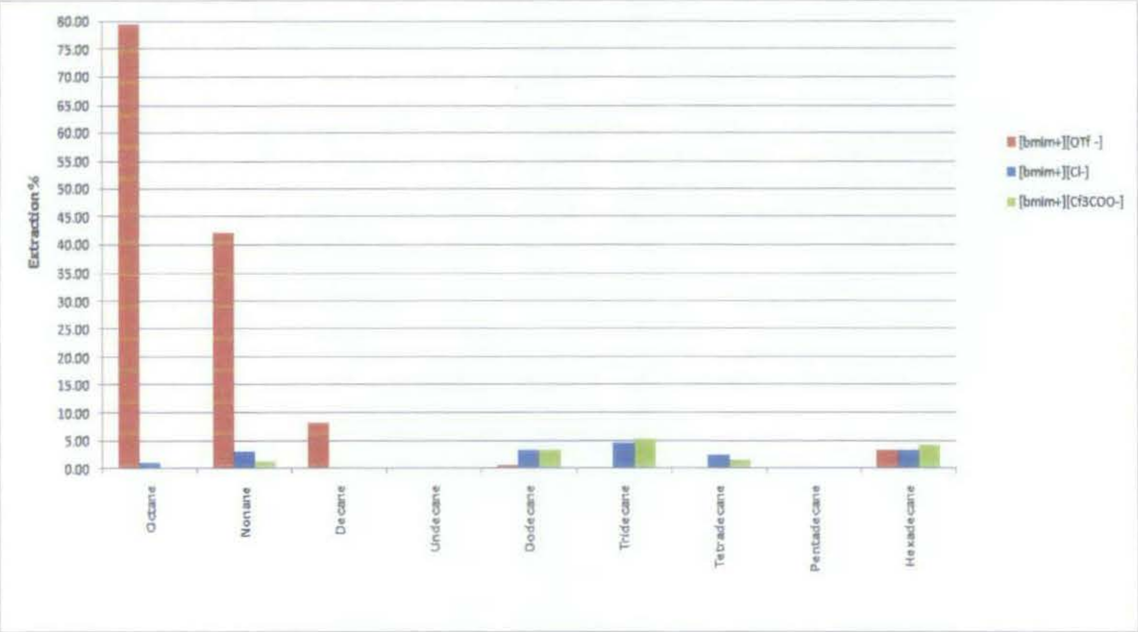


Figure 4.4: Effects of imidazolium cation based ILs on organic/hydrocarbon compounds extraction percentage

This removal process is regarded as more sustainable as no volatile and flammable solvents organic solvents needed as ILs had replaced them. During the extraction process, ILs had snatched away the unwanted compounds from refinery wastewater samples. Comparing ILs to the other conventional solvent/extracting agents, they are working well under neutral conditions. In the recently published studies shown that ILs which are proposed in this method display interesting advantages where their extracting efficiency lies greater than the other extracting solvents.

CONCLUSION

In this piece of work, in can be concluded that the most preferable imidazolium based cation IL to be used arranged in decreasing order is [bmim$^+$][Cl$^-$] > [bmim$^+$][OTf >[bmim$^+$][CF$_3$COO$^-$] for inorganic/heavy metal ions removal. However, for organic/hydrocarbon, all of these ILs react equally by removing certain of the hydrocarbon based on their selectivity and capability.

It is proven that ILs are capable in extracting solvents for organic/inorganic solvents as well as heavy metal ions from aqueous solutions. The attractive properties of ILs had given a flavor of what objectives can be achieved in this project. Due to its behavior, ILs can be designed by adjusting the combination of its anion and cation to suit with other solutions make them a better alternative solvent to be used in the industry. These ILs were proved to be used as alternative extracting agents for organic and inorganic compounds from their aqueous solutions. When the ILs are in contact with other aqueous solutions that highly contains organic and inorganic compounds, they will effectively attract the compounds from the solutions and sequester the in that ionic liquids.

The extraction and removal of organic and inorganic compounds by using ILs outnumbered the other conventional extraction processes such as adsorption, chemical precipitation, reverse osmosis, evaporator recovery process and electrolytic recovery in terms of its removal efficiency, fastness, ejection numbers of hazardous and inflammable chemicals and ability to recover and reuse. It was found out that the use of ILs as extraction solvents has becoming more exciting potential in developing greener extraction process.

This piece of work will enhance the enthusiasm among the environmentalists and chemists on the investigation of the feasibility of using ILs in the removal of organic and inorganic compounds from aqueous solutions as well as in the extraction technology.

FUTURE WORK AND RECOMMENDATION

Despite of ILs unique and promising properties that have highly potential in extracting industries, its nonvolatility , some amount of ILs may move or trap into the aqueous solutions whereas in this context wastewater inevitably during the extraction process. Hence, it might lead to the inaccuracy of the results during the work done.

Moreover, an extended research is needed on the leach and enrichment of ILs in environments as well as its toxicity and degradability or recovery of ILs. The recovered ILs can be reused successively to the same kind of extraction method. It was ascertained that the recovered ILs can sustain the extracting efficiency at the same at least four half-a-dozen times. On the contrary on the extraction, the other benefits like no requirement on volatility and flammability organic solvents, more sustainability, economical and environmental friendly procedure, fastness and reliability and capability of ILs to be recycle hence more economical are entertaining. Other than that, the diffusion of components, dispersion of biphasic systems, interfacial transport, process intensification and etc should also been studied thoroughly.

When it comes to the comparison of removal/extraction percentage of both organic and inorganic compounds, it is highly recommended for the future work to focus more on the effects of imidazolium cation based ILs in the removal of inorganic/heavy metal compounds from wastewater rather than focusing on the removal of organic/hydrocarbon compounds from this wastewater. The work of removal inorganic/heavy metal compounds can be extended and deeper research can be done on changing the parameters of the experiments such as varies the ratio of ILs and wastewater mixture or its reaction time.

As noted in most of the studies made, ILs have a few challenges that need to be taken into consideration when dealing with them in a certain process. Some of them especially hydrophilic ILs are very sensitive to moisture from the environment. They supposed to be dried and stored in a vacuum oven most of the time in order to ensure the water content is the lowest. Other constraint that must be noted are the cost of ILs, its control parameter (such as pH, Temperature, etc.) and its synthesis of task-specific ILs.

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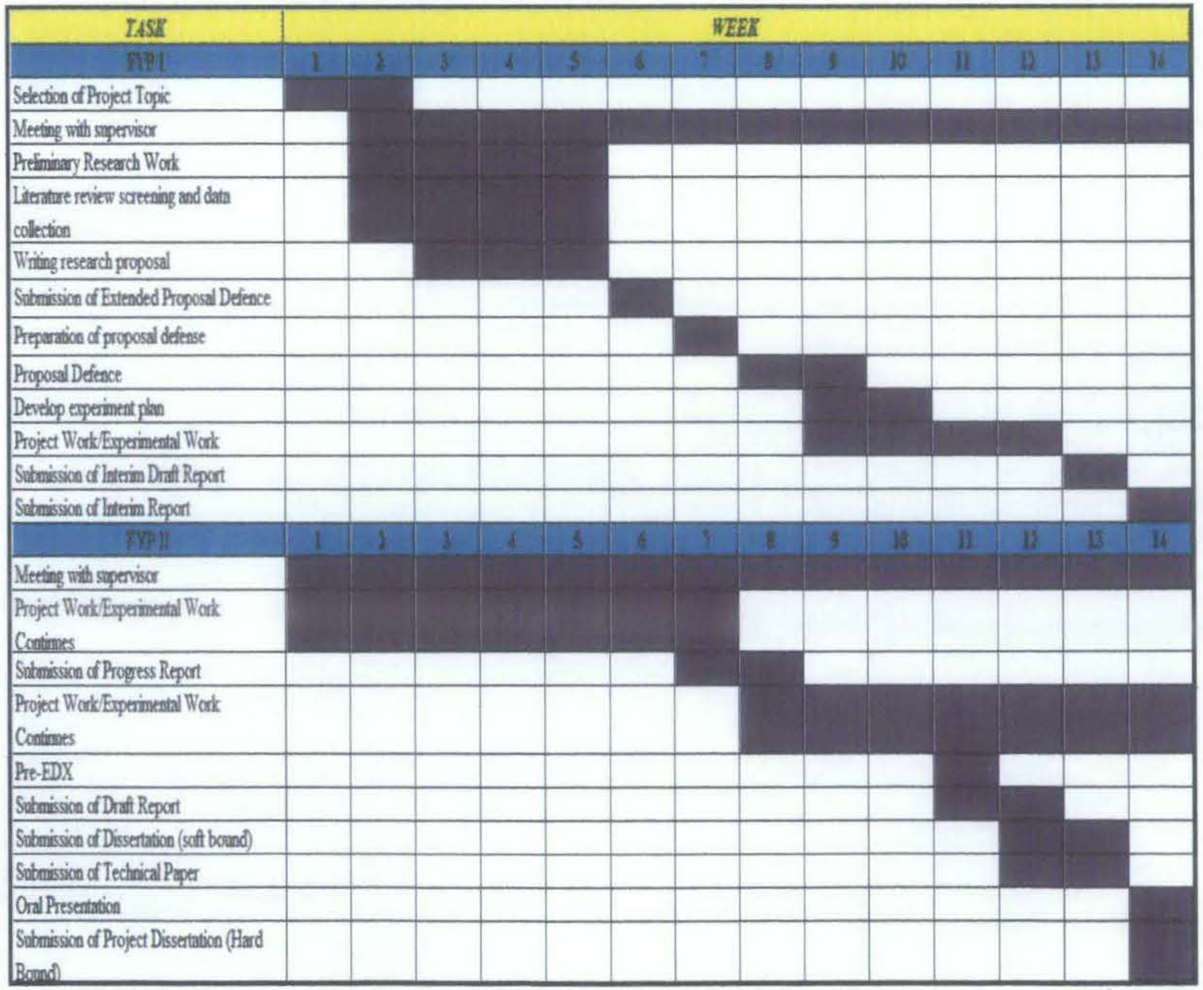
APPENDICES

Gantt chart and Milestone



TASK	WEEK													
FYP I	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Topic	■	■												
Meeting with supervisor		■	■	■	■	■	■	■	■	■	■	■	■	■
Preliminary Research Work		■	■	■	■									
Literature review screening and data collection		■	■	■	■									
Writing research proposal			■	■	■									
Submission of Extended Proposal Defence						■								
Preparation of proposal defense							■							
Proposal Defence								■	■					
Develop experiment plan									■	■				
Project Work/Experimental Work									■	■	■	■		
Submission of Interim Draft Report													■	
Submission of Interim Report														■
FYP II	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Meeting with supervisor	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Project Work/Experimental Work Continues	■	■	■	■	■	■	■							
Submission of Progress Report							■	■						
Project Work/Experimental Work Continues								■	■	■	■	■	■	■
Pre-EDX											■			
Submission of Draft Report											■	■		
Submission of Dissertation (soft bound)												■	■	
Submission of Technical Paper												■	■	
Oral Presentation														■
Submission of Project Dissertation (Hard Bound)														■

Raw Data of Organic/Inorganic Compunds in Malacca Refinery Wastewater

Note: *The red highlight represent the most hazardous compound contains in Refinery Wastewater*

Peak No.	Compound	Formula	Fraction, x_i (%)
1	Nonane	C_9H_{20}	0.6645
2	4-methyl-1-Decene	$C_{11}H_{22}$	0.7238
3	3,5-dimethyl-octane	$C_{10}H_{22}$	0.2891
4	2-methyl-Nonane	$C_{10}H_{22}$	0.2434
5	4-methyl-1-Decene	$C_{11}H_{22}$	0.3499
6	1,3,5-trimethyl-benzene	C_9H_{12}	0.2449
7	Nonane	C_9H_{20}	3.9881
8	Dodecane	$C_{12}H_{26}$	0.2548
9	4-methyl-decane	$C_{11}H_{24}$	0.9228
10	1-chloro-tetradecane	$C_{14}H_{29}Cl$	0.2231
11	1,3,5-trimethyl-benzene	C_9H_{12}	0.3004
12	3-methyl-tridecane	$C_{14}H_{30}$	0.2236
13	(E)-3-undecene	$C_{11}H_{22}$	0.2176
14	5-methyl-decane	$C_{11}H_{24}$	0.3959
15	4-methyl-decane	$C_{11}H_{24}$	0.7011
16	2-methyl-decane	$C_{11}H_{24}$	1.9011
17	3-methyl-decane	$C_{11}H_{24}$	0.9866
18	P-cymene	$C_{10}H_{14}$	0.3692
19	P-cymene	$C_{10}H_{14}$	0.6913
20	6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]heptane	C[illegible]H[illegible]	0.3974
21	Undecane	$C_{11}H_{24}$	7.8438
22	2-methyl-undecane	$C_{12}H_{26}$	0.9145
23	Tetradecane	$C_{14}H_{30}$	0.8780
24	P-cymene	$C_{10}H_{14}$	0.5659
25	N-tridecane	$C_{13}H_{28}$	0.2747
26	Cyclopentylcyclohexane	$C_{11}H_{20}$	0.5200
27	(E)-3-undecene	$C_{11}H_{22}$	0.4029
28	2-methyl-decane	$C_{11}H_{24}$	1.7060
29	4-methyl-undecane	$C_{12}H_{26}$	0.9446
30	2-methyl-undecane	$C_{12}H_{26}$	1.9277
31	3-methyl-tridecane	$C_{14}H_{30}$	2.0683
32	4,8-dimethyl-undecane	$C_{13}H_{28}$	0.5327
33	Cyclododecane	$C_{12}H_{24}$	0.5531
34	Undecane	$C_{11}H_{24}$	9.9396
35	2-ethenyl-1,3,5-trimethyl-benzene	$C_{11}H_{14}$	0.3243
36	2,6-dimethyl-undecane	$C_{13}H_{28}$	2.5607
37	N-decane	$C_{10}H_{22}$	0.5307
38	2-methyl-undecane	$C_{12}H_{26}$	0.4290

39	1-tetradecene	$C_{14}H_{28}$	1.3243
40	1-nonadecanol	$C_{19}H_{40}O$	0.4916
41	Cyclododecane	$C_{12}H_{24}$	1.6532
42	2,4-dimethyl-undecane	$C_{13}H_{28}$	2.1283
43	4-methyl-tridecane	$C_{14}H_{30}$	1.4355
44	2-methyl-heptadecane	$C_{18}H_{38}$	1.9511
45	tridecane	$C_{13}H_{28}$	3.3768
46	(E)-3-tetradecene	$C_{14}H_{28}$	0.5591
47	4-tert-butylstyrene	$C_{12}H_{16}$	10.4145
48	Octane, 2,3,7-trimethyl-	$C_{11}H_{24}$	0.2844
49	2,6-dimethyl-undecane	$C_{13}H_{28}$	0.6819
50	N-hexadecane	$C_{16}H_{34}$	0.3859
51	3-methyl-tridecane	$C_{14}H_{30}$	0.2843
52	1-Octanol, 2-butyl-	$C_{12}H_{26}O$	1.3928
53	2-methyl-octane	C_9H_{20}	0.4048
54	4-methyl-tridecane	$C_{14}H_{30}$	1.0628
55	2-methyl-tridecane	$C_{14}H_{30}$	1.6408
56	3-methyl-tridecane	$C_{14}H_{30}$	1.1027
57	2,6,10,14-tetramethyl-heptadecane	$C_{21}H_{44}$	1.9308
58	(E)-3-Tetradecene	$C_{14}H_{28}$	0.4756
59	N-tridecane	$C_{13}H_{28}$	7.6368
60	2,3,6,7-tetramethyl-octane	$C_{12}H_{26}$	0.6913
61	N-hexadecane	$C_{16}H_{34}$	0.2408
62	2,6-dimethyl-naphthalene	$C_{12}H_{12}$	0.5335
63	1,7-dimethyl-naphthalene	$C_{12}H_{12}$	0.2855
64	1,6-dimethyl-naphthalene	$C_{12}H_{12}$	1.0830
65	Decyl-cyclopentane	$C_{15}H_{30}$	0.2449
66	Heptadecane	$C_{17}H_{36}$	1.5143
67	2-methyl-heptadecane	$C_{18}H_{38}$	0.7990
68	3-methyl-tridecane	$C_{14}H_{30}$	0.4292
69	N-tridecane	$C_{13}H_{28}$	3.2871
70	1-Decanol, 2,2-dimethyl-	$C_{12}H_{26}O$	0.4649
71	4-Octanone	$C_8H_{16}O$	0.3095
72	4-methyl-undecane	$C_{12}H_{26}$	0.2306
73	2-methyl-pentadecane	$C_{16}H_{34}$	0.2950
74	3-methyl-hexadecane	$C_{17}H_{36}$	0.2549
75	N-tridecane	$C_{13}H_{28}$	1.1043
76	N-tetradecane	$C_{14}H_{30}$	0.2268
77	N-pentadecane	$C_{15}H_{32}$	0.3824