

CAB 4614: Final Year Project II

Treatment of Soil Contaminated with Ionic Liquids

by

Siti Nurain Roseli (9285)

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

JULY 2010

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CERTIFICATION OF APPROVAL

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TRONOH, PERAK

JULY 2010

CERTIFICATION OF ORIGINALITY

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

SITI NURAIN BINTI ROSELI

ABSTRACT

Ionic liquids (ILs) are molten salts consist of positive and negative ions. It is being utilized in many applications of industry especially as main solvents in green chemistry. This is mainly for reason that ILs have properties of non flammable chemical due to its low vapor pressure less toxic than conventional organic solvents. However, toxicity of these compounds is still under investigation by many scientists. In case these compounds released into environment especially soils and sea, it may cause bad impacts. Current investigations showed that ILs may become toxic toward other organisms. Thus, the aim of this work is to investigate the effectiveness of solvent washing method to treat ILs that contaminate in soils. In this study, soil is collected from dry area in Perak. The pH of soil is measured equal to 5.719. The acidity of soil may influence the leaching or movement of ionic liquid. This is because acidity of soil also indicates the total organic matter content in soil which influences the interaction between ionic liquids cations and organic matter of soil. The soil is then dried using oven and aliquot amount of ionic liquid is added into the soil. Then, the mixture is left for 72 hours for equal distribution of contaminant in the soil. Two ionic liquids are used in this experiments which are 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetraflouroborate. Methanol is used as the solvent to wash the soil. Few variables are being manipulated which are amount of methanol, concentration of contaminant and speed of shaking during treatment. After manual contamination procedure, soil is then washed with different amount of methanol and shaken for 2 hours at different shaking speed. Amount of methanol added are 60ml, 70ml, 80ml, 90ml, 100ml, 110ml, 120ml, and 130ml while shaking speeds are 150rpm, 160rpm, 170rpm, 180rpm, 190rpm, 200rpm, 210rpm and 220rpm. At the end of the experiments, washed soil is filtered and liquid sample is analyzed using HPLC analyzer to get final concentration of ionic liquid left in soil. Results obtained show that removal of ILs from soil are enhanced with the increase of methanol added during washing and increase of shaking speed of water bath shaker.

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CHAPTER 1

INTRODUCTION

1.1 Background

Ionic liquid is becoming popular chemical solvent and being utilized widely in industry. Its applications include in organic synthesis, catalysis, electrochemistry, analytical chemistry and separation science. This compound refers to molten salt with relatively low melting point (below 100°C) and consists of anion and cation and counterion, in either organic or inorganic form. Besides, it has low vapor pressure, excellent thermal stability, electrical conductivity and high polarity. Its stability benefits on its application, unfortunately, a negative aspect for its decomposition treatment after its usage. (Baranyai *et al.*, 2004; Goc-Maciejewska *et al.*, 2005). Toxicity study and detoxification study of ILs has been started since few years ago. This studies are still ongoing and under investigation by many scientists. However, current results shown that ionic liquid may toxic other organisms while the long time effects on human beings is still under studies (Latala *et al.*, 2005; Abramo *et al.*, 2006). It is also reported that this may harm ecology; water and soil systems.

ILs are often regarded as green solvent due to their negligible vapor pressure, and therefore a good alternative to reduce the emissions of toxic vapors from conventional molecular organic solvents. A low vapor pressure, however, is generally not enough to justify calling a process or even a whole technology “greener”. Certain amounts of ILs will soon be present in technological wastewaters where, because of their high stability, they could become persistent pollutants and break through classical treatment systems into natural waters. It harms soil when it spilled. Then, it contaminate the soil and at the same time acts as toxicant.

Great utilization of ILs in industries in condition which the study of this field is still young, may invite long term hazards to environment. A lot of toxicity studies had been conducted for several ILs over species of animals and plants (Stepnowski *et al.*, 2005; Bang-Jun *et al.*, 2009; Jian- Ji *et al.*, 2010). It was reported that ILs of 1-methyl-3-octylimidazolium bromide ((C₈mim)Br) may affects on the growth, reproductive ability and activity of earthworms *Eisenia foetida* (*E. foetida*). However, the concentration of the contaminant which is (C₈mim)Br was varied and the results from experiments shown only at higher concentration of C₈mim]Br may inhibits the growth and activities of *E. foetida* (Jian-Ji *et al.*, 2010). A similar phenomenon also tested on aquatic livings which is green algae of *Scenedesmus obliquus* (*S. obliquus*) and *Chlorella ellipsoidea* (*C. ellipsoidea*). The length of ILs of 1-alkyl-3-methylimidazolium bromide ((C_nmim)Br) was varied from C₄, C₆, C₈, C₁₀ and C₁₂ and same goes with its concentrations. Results showed increase of both alkyl chain and concentration may influence the primary production of the algae (Bang-Jun *et al.*, 2009).

1.2 Problem Statements

Several studies have been conducted to measure toxicity of ILs. However, not much of them are related on treatment of soil contaminated by ionic liquids. A research that investigated the transport process of imidazolium ionic liquids cations such as 1-butyl-3-methylimidazolium (BMIM) in soil by column leaching experiments shows that longer chain of imidazolium cations are bonded stronger to the soil than shorter chain of imidazolium cation such as 1-ethyl-3 methylimidazolium (EMIM). This is due to van der Waals interactions that play an important role in longer hydrocarbon chain. This also explains the effect of higher total carbon content (TOC) of soil that causes retardation in transport of ionic liquids cations. For these reasons, it will take longer to elute these ionic liquids from soil (Buszewski *et al.*, 2009).

In this study, it is proposed that removal of ILs from soil can be enhanced by using soil washing method and methanol is used as solvent. Parameters of amount of methanol added during washing and shaking speed of water bath shaker will be investigated to see their effects on ILs removal efficiency.

1.3 Objectives and Scope of Study

Main objectives of this study are:

1. To treat soil contaminated with ILs by using washing method.
2. To study several variables and their effects on ILs removal from the soil. The variables investigated include concentration of contaminant in soil, amount of solvent and speed of shaking during treatment.

1.4 Significant of Study

ILs are being engineered to fit in many applications in industry for examples as electrolytes, solvents in liquid–liquid extractions, acid scavengers, and many reactions including hydrogenations, oxidations, Diels-Alder cyclo additions, Friedel-Crafts acylations and alkylations and Heck reactions (Kathryn *et al.*, 2007). Wastes contain ionic liquids are not being properly managed. This is due to the reasons mentioned previously, that not much studies related to ILs hazard to the soil and the treatment of contaminated soil by ILs. Thus, this study is relevant as to figure out the efficiency of soil washing method in removing ILs.

1.5 Feasibility of Study

There will be four phases of work focus along this study:

- i. *Research for understanding and identify soil pollution, ILS behavior, soil treatment and its methodologies.*

These are done by reading literature, articles, surfing, books, journal and many other media as much as possible.

- ii. *Choosing several from available methodologies that suit to be applied for treatment of soil contaminated with ILS.*

Through good understanding and knowledge about the subjects of this project will make it easier for choosing treatments that suitable for ILS.

- iii. *Testing proposed experimental methods for treatment of soil contaminated with ILS.* These testing activities are done experimentally.

Derivatives that equate to the factor for degradation of ILS will be manipulated and results are observed for varying data and fitting conditions.

- iv. *Propose most suitable methodology for treatment of soil contaminated with ILS by solvent washing.*

This will be done after all experiments are conducted, repeated and ensured its validity and reliability. Then, results are compared to within each tested variables. Finally, best suitable treatment can be proposed.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Ionic Liquids

2.1.1 Properties and Characteristics

Ionic liquid is identified as excellent solvent for most chemicals as it is also a salt of which is poorly coordinated and results its low melting point under 100°C, or even at room temperature. The formation of its stable crystal lattice is prevented due to at least one ion delocalized charge and one component is organic. The properties and phase behavior vary for each type of ILs based on its pair of anion and cation. However, in general, ILs are electrically conductive and have low vapor pressure. Most of them have good thermal stability, low combustibility, miscibility with water, tunable viscosity and also high heat capacity. Those are the reasons ILs mostly used as catalyst for various chemical reactions (Koel *et al.*, 2006).

Some of these properties of ILs are advantageous to the experimental procedures. ILs as mentioned has low volatility thus is makes this chemical do not easily vaporized in room temperature. Thus, prevention for hazards can be increased because atmospheric solvent loss and flammability hazard is reduced. Its high thermal stability and large liquid range helps to ensure the ionic liquid exists as liquid during the dissolution process either at low temperature or high temperature. ILs are almost entirely recycled due to the low or near zero vapor pressure.

ILs in many cases have polar phases as the ability of the salt to act as hydrogen-bond donor and/or acceptor and the degree of localization of the charges on the anions. There are generally seventeen head groups (cations) of ILs including Guanidinium(Gu), Imidazolium(IM), Ammonium(N), Phosphonium(P), Pyridinium(Py) and Sulfonium(S) (Koel *et al.*, 2006). Imidazolium- based ILs are highly ordered hydrogen bonded solvents and have strong effects on chemical reactions and processes. The crystal structures of ILs are the result of strong interaction between nitrogens of imidazolium rings and special order of alkyl chains. The interaction is expected to be stronger in alcohol as alcohols are also good hydrogen bond donors and/or acceptors (Domanska *et al.*, 2004).

2.1.2 Potential Hazard of Ionic Liquids in Environment

New 'green' solvent usually regarded as 'innocent' chemicals. As many of the other chemicals; for example Methyl Tertiary Buthyl Ether (MTBE), is widely used as green additive in gasoline production to reduce engine knocking and auto emission and improve air quality. Later then, it was found to be hazardous having potential carcinogenic effects and increase groundwater pollution. As a result, MTBE used has been banned and a lot of expensive bioremediation studies conducted to find biodegradation method for MTBE (Hristova *et al.*, 2005).

Eventhough ionic liquids have not yet been released into environment in large scale, but extensive studies are being conducted including toxicity studies to figure out the impacts of ionic liquids in environment (Kathryn, 2006). Ionic liquids with halogens (anions) which have poor stability in water may become very corrosive and toxic because acid is formed. For example, anions such as Cl⁻ and F⁻, when mixed with water may form HCL and HF (Kenneth, 2003). Experiments of ionic liquids were conducted on marine bacterium Vibro Fischeri and inhibition of the bacteria increased as the longer chain of ionic liquids are tested (Ranke *et al.*, 2004).

Effects of ILs in an enzyme level was studied by several studies and summarized by Thuy Pham *et al.*(2010). The effect was learnt from animals including electric eel (*Electrophorus electricus*) and mouse. The enzyme studied was acetylcholinesterase and this enzyme plays important role in nerve response and function. It was reported that ILs can inhibit the enzyme from molecular up to organism levels of biological complexity. The enzyme inhibition assays suggested that longer alkyl chain of ILs cations can inhibit the enzyme much stronger. This is proven by experimental study which results that IL with pyridinium as cationic core structure inhibited the enzyme slightly stronger as compared to imidazolium.

2.2 Researched Treatments and Technologies

2.2.1 Oxidation by Fenton-like System

Degradation of toxicants can be done via oxidation process through Fenton-like System. Ionic liquids were also a subject of interest in advance of oxidation process, especially in Fenton-like System. This reaction for soil and groundwater remediation was proposed for degradation of ionic liquid residues in water, in particular, to determine the effect of hydrogen peroxide concentration on degradation rates of an exemplary ionic liquid oxidized in a Fenton-like system, and to determine the mechanism of its oxidation in a vigorous Fenton-like reaction successfully used for contaminated soil remediation (Siedlecka *et al.*, 2006).

Fenton's reaction is the catalytic decomposition of dilute hydrogen peroxide by iron (II) which results in the generation of hydroxyl radicals. Hydroxyl radicals are very reactive oxidizing agent especially with alkanes and aromatic compounds. However, they are unreactive toward perhalogenated alkane compounds with a high degree of nitro-substitution and other oxidized organic compounds (Rogers *et al.*, 2002). In a study

conducted by Kaczyński *et al.*, tells that in Fenton-like oxidation, ILs were oxidized in experiments that were conducted in a well stirred and thermostated batch reactor with volume of 0.30 dm³ at 25±1°C. All reactions were performed in dark to prevent photoreduction of Fe(III) (Kaczyński *et al.*, 2007).

2.2.2.1 Hydrothermal Mineralization and Photocatalytic Degradation Treatment

Photocatalytic degradation (PD) treatment was demonstrated to be effectively decomposing organic cations of ILs. This degradation treatment is carried out in a closed photocatalytic reaction system. On the other hand, hydrothermal mineralization (HM) is known to be efficient treatment in removing and recovering BF₄⁻ anion from aqueous solution (Itakura *et al.*, 2006). Both of these treatments are combined and experimented on ILs (organic cation part: butyl- methyl or ethyl-methyl imidazolium, and inorganic anion part: PF₆⁻, BF₄⁻ and Br⁻). Results obtained showed that examined ILs' anions were effectively decomposed and removed by HM treatment with Ca(OH)₂ mineralizer at 473K, while the cations were treated by PD treatment at room temperature. (Aori *et al.*, 2008).

2.2.3 Soil Washing by Using Appropriate Solvent

Soil washing treatment is a process used for remediating both organic and inorganic chemical constituents from contaminated soils, sludge and sediments. This process involves high energy contact between the contaminated soils and an aqueous based washing solution. Soil washing can be physical and/or chemical process which results in the separation, segregation and volume reduction of hazardous materials. It may also results in chemical transformation of contaminants to nonhazardous

substances. The effectiveness of soil washing is depending on type of soil and its contaminants (Reddy *et al.*, 1996).

Kuhlman *et al.* (1999) simplified the soil washing process in which high shear mixing, sprays, hydrosizing, flotation, and screening are integrated to counter currently clean sand, salt and clay. Chemical techniques are applied to remove the selected contaminant from soil and then treat the wash water for reuse. According to him, the soil washing process begins by breaking up the soil in attrition scrubber and fines and contaminants are separated from soil slurry by hydrosizing and flotation. The generic soil washing process is simplified as in the flowchart below:

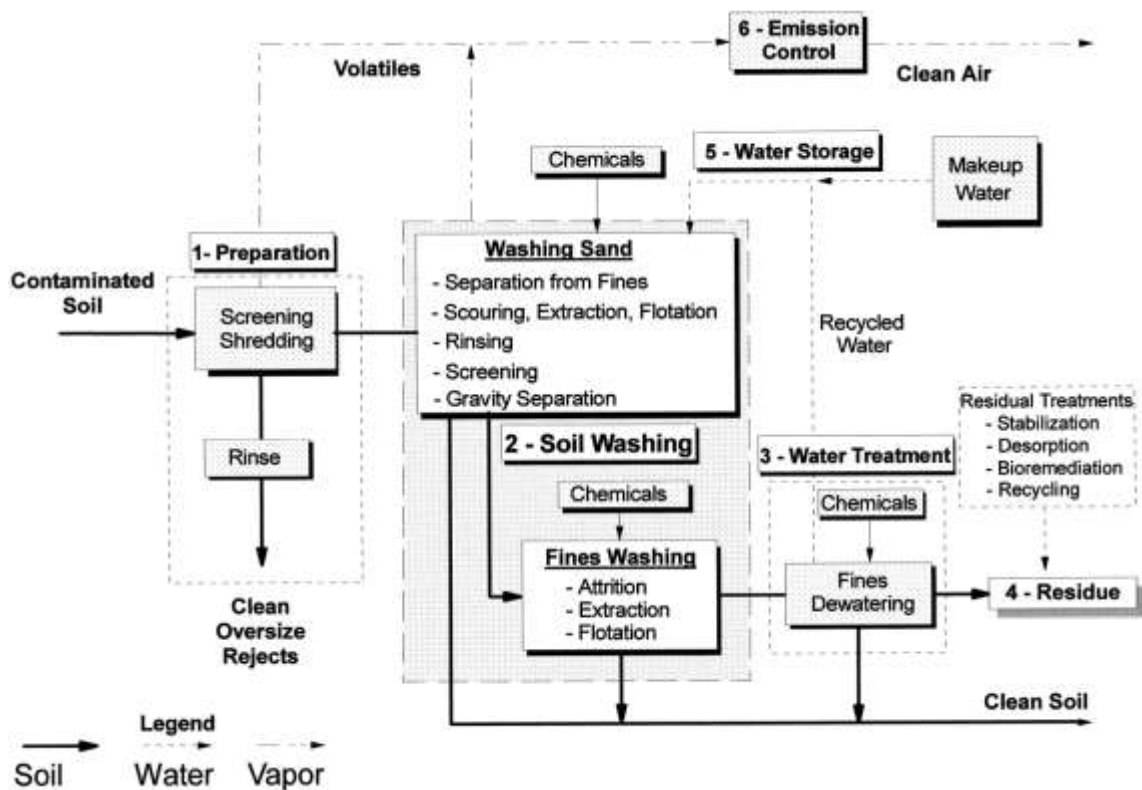


Figure 1.1: Flowchart of generic soil washing process (Kuhlman *et al.*, 1999).

Generally, soil washing is one technique of extraction. It is seemed to be relatively cheaper too. Recently, many other alternatives of solvents including surfactants and additives were engineered and utilized to be fitted in treating some contaminants. Ethanol was found as most suitable solvent for soil washing based on health effects and acceptable removal efficiencies (Hosomi *et al.*, 2001). Based on experiment conducted by *Haglund et al.*,(2010) portion of contaminated soil is taken and added with 60 ml of washing liquid in 250 ml glass bottle with Teflon-lined screw caps. It is then shaken to ensure well mixed solution. After appropriate period of shaking, the mixture is allowed to settle before the liquid phase was filtered. Contaminants is then were extracted using liquid-liquid extraction with three portion of 15ml n-hexane. Water is added to increase the difference in polarity which leads for ease of phase separation.

Soil washing treatment has been practiced onto crude oil contaminated soils. This treatment was conducted by using sodium dodecyl sulfate (SDS) to see the effects on the biodegradation. Kingsley *et al.* (2004) reported that the surfactant solution is used to transfer a matrix of crude oil contaminants to a liquid phase. The surfactant solutions were then used to enhance the biodegradation of the oil. In their research, effect of concentration of surfactant solution onto removal of contaminant efficiency was investigated. The results show that as the concentration of the surfactant solution increases, the overall performance of rhamnolipid and SDS in removing crude oil from the soil sample is also increase.

2.2.4 Biological Treatment Using Bacteria

Microbiological studies include wide and several of science and chemistry fields such as zoology, bacteriology, virology, protozoology, psychology and mathematics. A lot of researchers found that bacteria, fungi and some other microorganisms are very useful in protecting and preserving the environment. Their existence is significant and valuable. These groups of lives metabolize contaminants, toxicants into energy and all

those contaminants become their soul or main food to release energy. Industries nowadays implement this method widely because of its environmental friendliness and easy for waste handling. However, due to expensive costs for some bacteria for waste treatment, there are industries implementing chemical reaction treatment for faster effect and larger amount of waste to be handled (Ross, 2004).

Corynebacteria sp. was identified can degrade *N*-ethylpyridinium cation of ionic liquids. However no metabolize activities observed when examined on imidazolium groups (Dodge *et al.*, 2010).

2.2.5 Separation Using CO₂

Carbon dioxide can be used to separate ionic liquids from organic and inorganic compounds which are complement to supercritical extraction (Blanchard *et al.*, 2002). Liquid-liquid extraction is applied whereby layers of liquid phases exist consist of methanol and IL tested. However, it can be induced to form three phases in the presence of CO₂. The lower liquid phase is rich in IL. Methanol is then merged with vapor phase (carbon dioxide) with increase of pressure. This will form a phase that is completely free of ionic liquids as all ILs have been forced out of methanol into ILs rich phase at the bottom part. This interesting phase behavior has mechanistic and practical implications for both reaction and separation systems using ILs.

CHAPTER 3

METHODOLOGY

This study is to determine the best condition for treatment of soil contaminated with ILs. In this study, there will be two ILs of imidazolium group to be used which are 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-butyl-3-methylimidazolium tetrafluoroborate ([EEIM] BF₄).

3.1 Materials and Methods

3.1.1 Materials

3.1.1.1 Soil

Soil is taken from nearby area (Bandar Seri Iskandar, Malaysia). Since there is zero information about the sample soil taken, few characteristics of the soil needed to be investigated. The soil's pH determined by using pH meter. Soil is first sieved through 2 mm sieve mesh openings. Measurements on soils having larger particle size than 2 mm may give different value thus test method may be invalid. 10 g of soil is added with approximately 10 ml of distilled water. It is then mixed thoroughly and allowed to settle for an hour. Later, the sample is tested with pH meter (ASTM D4972-01).

Organic matter was measured with a total organic carbon (TOC) analyzer. TOC allow investigation of the influence of this parameter on the mobility of ILs cations in soil. Total carbon (TC) determined by catalytical combustion and oxidation of 200mg of soil sample at 900C, while inorganic carbon (IC) was analyzed in 100mg sample after

pre-acidification in the oven at 250C. TOC is calculated by difference of TC and IC (Buszewski *et al.*, 2009).

3.1.1.2 Chemicals

ILs that are being studied are 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] BF₄) obtained from Merck with both total mass of each ionic liquid is 25 g. They are used as it received without any pre-treatment except for [BMIM]Cl, since it presents in solid phase (powder) thus it needed to be heated until its melting point (65°C). Solvent used as mentioned earlier is methanol was obtained from Merck.

3.1.2 Methods

3.1.2.1 Tools and Equipments

Water bath shaker and high performance liquid chromatograph (HPLC) are all equipped by Universiti Teknologi PETRONAS Chemical Engineering Department's laboratory.

3.1.2.2 Preparation of Phosphate Buffer Solution

In order to prepare a phosphate buffer solution that is to be used in HPLC, Kaczyński *et al.* (2008) described the methods and calculation needed to be done in their research paper. Firstly, acid base and alkali base of disodium hydrogen phosphate are mixed. pH of desired solution being decided and pKa value of the acid/ conjugate base

will be used in order to calculate amount of both salt are to be mixed. The concentration of sodium di- hydrogen phosphate and disodium hydrogen phosphate were calculated by using Henderson-Hasselbach equation. One liter of buffer solution is prepared by mixing both acid/ conjugate base, and diluted in a little less than 1L of water. pH of the solution is then adjusted by using phosphoric acid to lower down the pH or sodium hydroxide to higher it up. Once the desired pH is reached, water is then added to bring up the total volume of phosphoric acid buffer to 1L.

3.1.2.3 Soil Washing Experiment

3.1.2.3.1 Preparation for Samples of Contaminated Soil

Samples of contaminated soil are prepared by adopting the procedures from experiment conducted by Daugulis *et al.* (2008). In the mentioned procedure, the total concentration of contaminant in the soil is expressed as weight percentage equal to 900 mg kg⁻¹. Since one of the ionic liquids; 1-butyl-3-methylimidazolium chloride (BMIMCl) is presence in solid form, it is melted by heating it in oven at temperature of 65°C. Due to the behavior of BMIMCl which has high tendency to absorb moisture from atmosphere, samples' containers must be sealed. Samples were kept for 72 hours for equal distribution of ILs in the soil and allow the imidazolium cations transport. In this study, three experimental conditions were investigated in this study including investigating the effect of total concentration of ILs in soil toward the amount of removed ILs after washing. In this condition only, different samples with different concentration are prepared.

3.1.2.3.3 Soil Washing Treatment

Enhanced soil washing treatment is conducted by applying complete procedure implemented experimentally by Haglund *et al.* (2010). In Haglund's studies, contaminant investigated was dioxin and the solvent used was ethanol. Portions (20 g) of contaminated soils were added with 60 ml of methanol to 250 ml glass bottles with Teflon-lined screw caps. The bottles were shaken laterally for 15 minutes by hand to ensure that the resulting slurries were properly mixed. Then, the bottles were placed in water bath shaker with appropriate temperature and speed of shaking. Water is used as to maintain the washing temperature at room temperature while shaking at the same time. Temperature parameter was not included in this study as methanol will be evaporated at higher temperature. The shaking process was conducted for 2 hours. Later, sample is allowed to settle for 24 hours at room temperature. Then, liquid phase was filtered by using filter paper Whatman (grade 44) before being analyzed by using HPLC analyzer.

In order to determine the content of ionic liquid at end of experiment, the sample is analyzed using High Performance Liquid Chromatograph (HPLC) analyzer. The procedure was conducted based on experimented procedure done by Kaczyński *et al.* (2007). It is reported that the analyzer (PerkinElmer Series 2000) consisting of a chromatographic Interface (Link 600), binary pump, UV/vis detector, vacuum degasser and Rheodyne injection valve. The ILs were separated on a Synergi Polar-Reverse Phase 150 mm x 4.6 mm column (4 μm ; pore size 8 nm; specific surface area $1.05 \text{ m}^2\text{g}^{-1}$; carbon load 11%; calculated bonded phase coverage $3.15 \mu\text{mol m}^{-2}$). The analyses were performed at ambient temperature at flow rate of $0.75 \text{ cm}^3 \text{ min}^{-1}$, and the elution profiles were monitored at $\lambda=218 \text{ nm}$. The separation column was equilibrated with the mobile phase until baseline stabilization, at which point the sample injection (0.01 cm^3) were made. The mobile phase was methanol mixed with 5 Mm phosphate buffer ($\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$) and adjusted pH 3.

The efficiency of the treatment in removing ILs in the soil is represented by using the following calculation:

$$\text{Efficiency of ionic liquids removal (\%)} = \left[\frac{(m_i - m_r)}{m_i} \right] \times 100\%$$

Where m_i is initial mass of ionic liquids in the soil and m_r is the mass of ionic liquids removed from the soil.

3.1.2.3.3. 1 Amount of Solvent (Methanol) Used

Initially, the volume of methanol added is fixed as 60ml. Then, for the second condition of the experiment which is to investigate the effect of amount of solvent added during washing toward ILs removal, this volume is varied for five different samples with five different volumes respectively; 70ml, 80ml, 90ml, 100ml, 110ml, 120ml and 130ml. Concentration of IL in soil is 900mg kg^{-1} while temperature and speed of shaking is at room temperature; 25°C and 150rpm.

Table 3.1: Different samples of different amount of methanol added during washing.

Sample	B1	B2	B3	B4	B5	B6	B7	B8
Total concentration (mg kg^{-1})	900±100							
Amount of methanol (ml)	60	70	80	90	100	110	120	130
Temperature of shaking ($^\circ\text{C}$)	25							
Speed of shaking (rpm)	150							

3.1.2.3.3.2 Speed of Shaking

Initially, the speed of shaking is set as 150rpm. Then, for the third condition of the experiment which is to investigate the effect of shaking's speeds toward ILS removal, this speed is varied for five different samples and each of them is shaken at speed of 160rpm, 170rpm, 180rpm, 190rpm and 200rpm respectively. Concentration of IL in soil is 900mg kg^{-1} while amount of methanol is 60ml and temperature of shaking is at room temperature; 25°C .

Table 3.2: Different samples of different speed of shaking set during washing.

Sample	C1	C2	C3	C4	C5	C6	C7	C8
Total concentration (mg kg^{-1})	900±100							
Amount of methanol (ml)	60							
Temperature of shaking ($^{\circ}\text{C}$)	25							
Speed of shaking (rpm)	150	160	170	180	190	200	210	220

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Soil Properties

pH of soil measured using pH meter is 5.719 ± 0.1 . This value indicates that the soil has weak acidic property. pH of soil is closely related to porosity and organic carbon content in the soil. More acidic soil (lower pH value) indicates higher organic carbon content (TOC). This effect is consequence of the dissociation of organic $-OH$ and $-COOH$ groups. High TOC also increase the sorption capacity for inorganic cations (Ca^+ , Mg^{2+} , Na^+ and K^+) and leads to their accumulation in soils rich in organic matter. In other words, it also means that the soil has moderate porosity and the interaction between imidazolium cations and the organic matter in the soils is not too strong to immobilize the imidazolium cations in soil.

4.2 Washing Experiments

The experiment is following the procedure adopted from Daugulius *et al.* (2008) and Haglund *et al.* (2010). This report is presenting the first part of the experiments since the author is needed to queue analyzing the sample using HPLC due to limited equipment. Thus, it is expected that complete result with HPLC analysis will be included in the final dissertation report.

There are two conditions that are being investigated which are effects amount of solvent added during washing and speed of shaking toward the efficiency of ILs removal from soil.

4.2.1 HPLC Data gathering

HPLC is used to analyze samples of liquid which are filtered after soil washing treatment. The filtered solution is then filled into a vial before it is being analyzed in HPLC. The working principle of HPLC is that when a mixture of various components enters a chromatography process, and the different components are flushed through the system at very high pressure at different rates. The migration occurs as the mixture moves over adsorptive materials and later it provides separation. High pressure allows better separation of the components. For reverse phase HPLC, the column used is made non-polar by attaching long hydrocarbon chains to its surface and polar solvent is used such as methanol. There will be strong attraction between polar solvent and polar molecules in the mixture passing through the column. Polar molecules in the mixture will spend the time moving in the solvent while the non polar molecules will tend to form attraction with hydrocarbon groups due to van der Waals interaction. Thus, these molecules will spend less time in the solvent and slow down its movement through the column.

Figures shown below are some of results given by HPLC after samples are being analyzed.

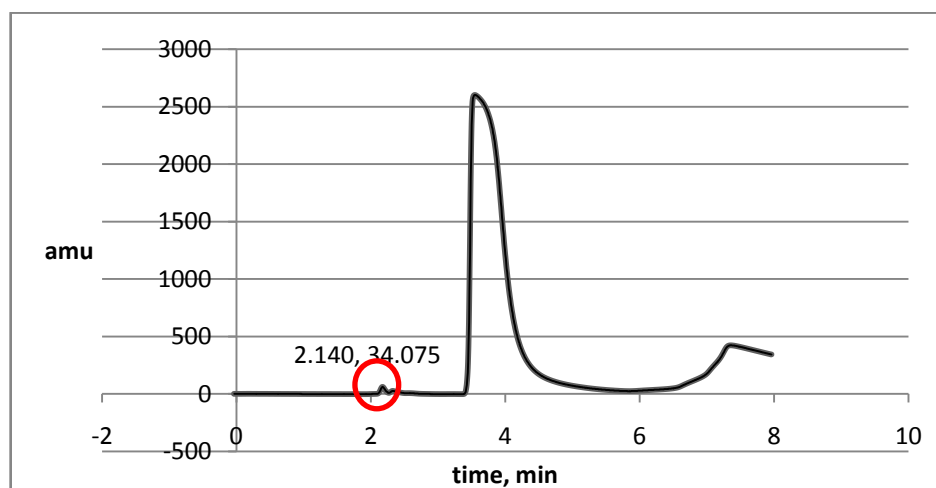


Figure 4.1: HPLC data for sample contains BMIMCl

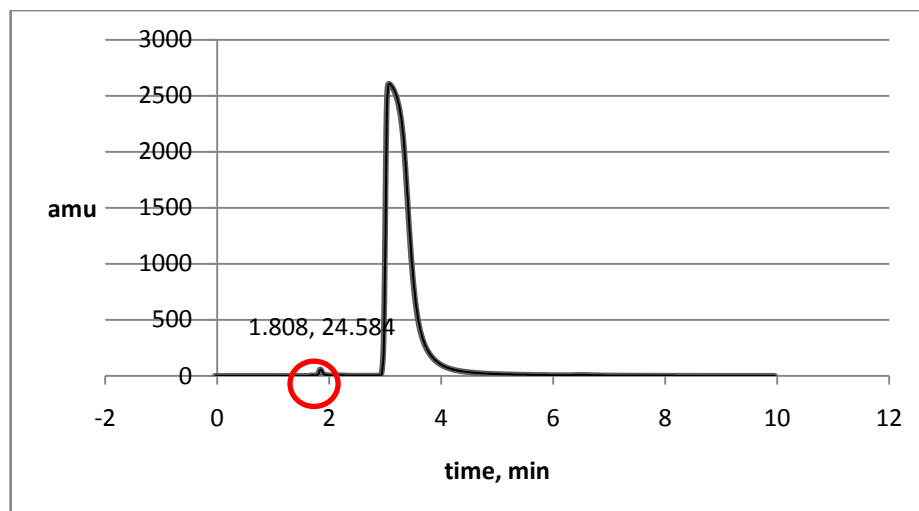


Figure 4.2: HPLC data for sample contains BMIMBF₄

HPLC is automated and highly sensitive too. The circled peaks indicate the peaks that each ionic liquid are detected. Area under the curves will be automatically calculated by this equipment and a calibration curve will be plotted based on standard solution analyzed. The calibration curves of each ionic liquid used in this project is shown below. This calibration curve is then used for each runs of sample analyzed as every area under curve calculated will gives the concentration of ionic liquid in the sample.

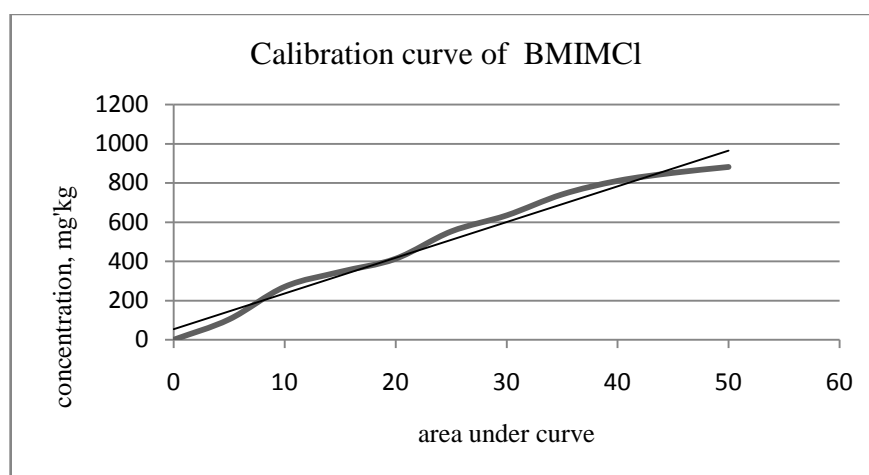


Figure 4.3: Calibration curve of BMIMCl

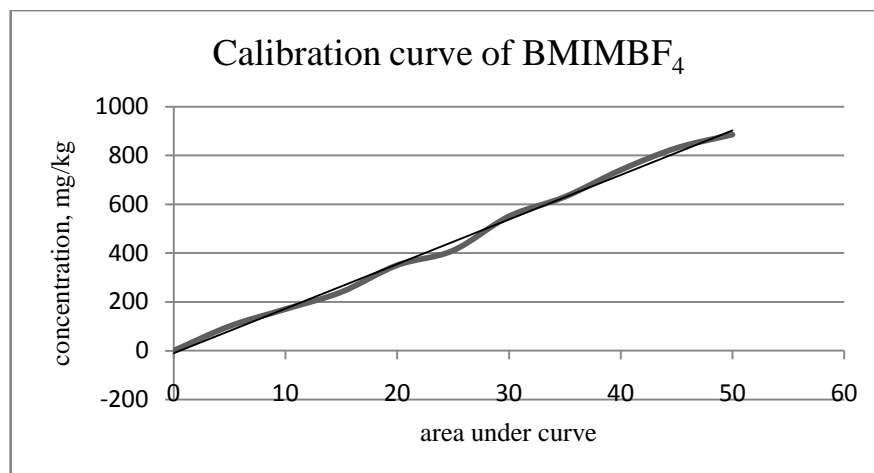


Figure 4.4: Calibration curve of BMIMBF₄

4.2.2 Effect of Amount of Solvent during Washing on Removal of Ionic Liquid

Experiment was conducted to investigate the effect of amount of solvent added during washing to the efficiency of BMIMCl and BMIMBF₄ removal from soil. Results show that the amount of BMIMCl removed from soil is increasing as more volume of methanol is added in the sample. However, the removal seems to be efficient for BMIMBF₄. It can be seen from tables and figures attached below. The efficiency is decreasing with the increment of amount of methanol added which indicates the more methanol is added, more ionic liquid is diluted and removed from the soil. In other words, ionic liquid that remains in the soil is getting less.

Table 4.1 Parameters that remain constant during experiment to investigate the effect of different amount of methanol added during washing onto amount of BMIMCl removed.

Total concentration (mg kg ⁻¹)	900±100
Temperature of shaking (°C)	25
Speed of shaking (rpm)	150

Table 4.2: Experimental data of washing method for BMIMCl by addition of different amounts of solvent.

Sample	A1	A2	A3	A4	A5	A6	A7	A8
Amount of methanol (ml)	60	70	80	90	100	110	120	130
Concentration of ionic liquid removed (mg/kg)	99.900	123.300	130.500	186.300	222.300	242.100	276.300	299.700
Concentration of ionic liquids remain in soil (mg/kg)	800.100	776.700	769.500	713.700	677.700	657.900	623.700	600.300
Efficiency	88.9	86.3	85.5	79.3	75.3	73.1	69.3	66.7

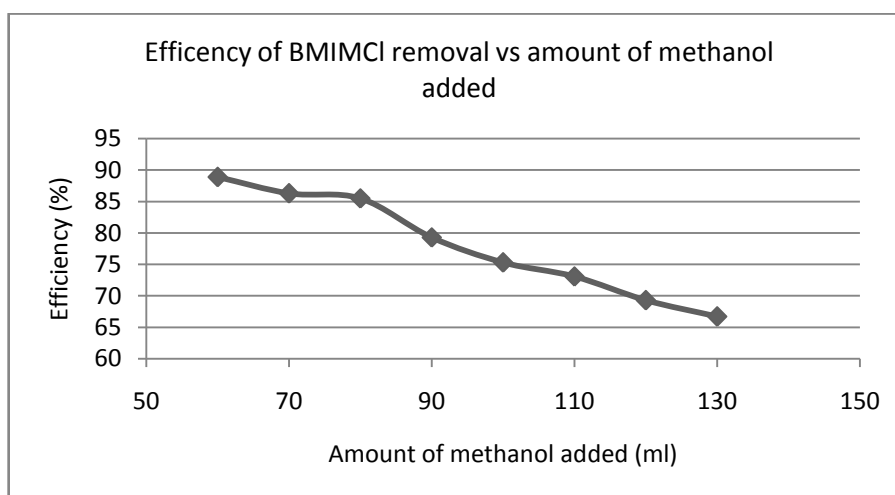


Figure 4.5: Relationship between amounts of methanol added during washing and the efficiency of BMIMCl removal.

Table 4.3: Parameters that remain constant during experiment to investigate the effect of different amount of methanol added during washing onto amount of BMIMBF₄ removed.

Initial concentration of BMIMBF ₄ (mg/kg)	900
Speed of shaking (rpm)	150
Temperature of shaking (°C)	25

Table 4.4: Experimental data of washing method for BMIMBF₄ by addition of different amounts of solvent.

Sample	B1	B2	B3	B4	B5	B6	B7	B8
Amount of methanol (ml)	60	70	80	90	100	110	120	130
Concentration of ionic liquid removed (mg/kg)	114.3	130.5	143.1	200.7	207.9	235.8	296.1	307.8
Concentration of ionic liquids remain in soil (mg/kg)	785.7	769.5	756.9	699.3	692.1	664.2	603.9	592.2
Efficiency (%)	87.3	85.5	84.1	77.7	76.9	73.8	67.1	65.8

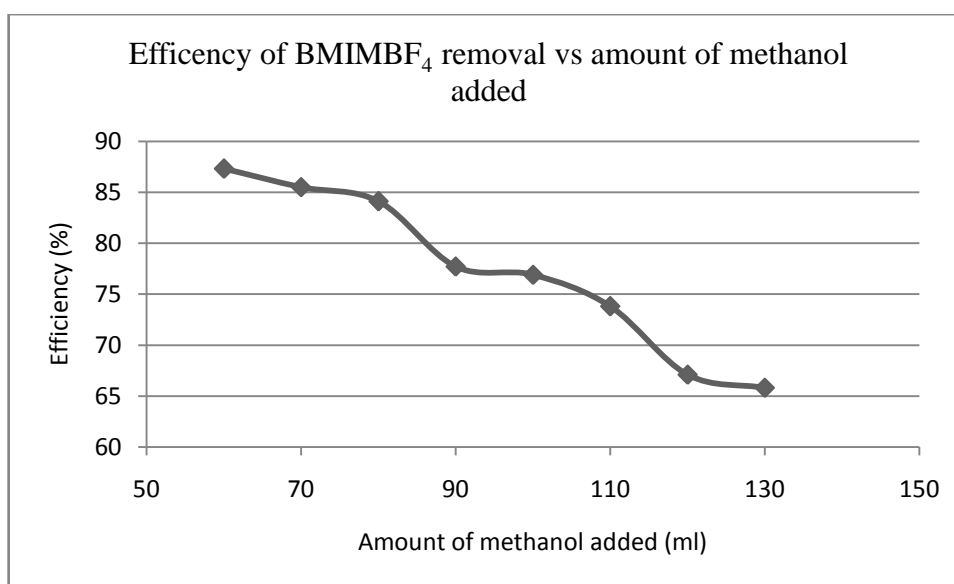


Figure 4.6: Relationship between amounts of methanol added during washing and the efficiency of BMIMBF₄ removal.

Dissolution phenomena of ionic liquids in methanol can be explained by using general rule that is “like dissolves like”. Eventhough this rule is not applying for all solvents, but it does for this case. The term “like” is referring to polarity of the solutions, for example water contains polar molecules that may dissolve other polar molecules. In other words, polar solutes dissolve in polar solvents and same thing as nonpolar solutes and solvents.

These can be explained by using analogy of table salt or sodium chloride (NaCl). In water (H₂O), NaCl breaks down into its ions, Na⁺ and Cl⁻. This phenomena is what termed as dissolving and it happens because the polar molecules of water are surrounding the individual ions in the solution until they are covered in water molecules.

Theoretically, there are three main events take place in dissolving a solute. Firstly, lattice of cations and anions collapse which then setting free the lattice ions into the solvent. Secondly, hydrogen bonds in the solvent are broken. Thirdly, solute ions are becoming hydrated by an interaction between the ions and the solvent dipoles. Thus solvent molecules will need to surround these ions loosely. For a salt to dissolve, the energy required to collapse the lattice and break hydrogen bonds in the solution must be compensated for by the energy set free during the hydration process. The overall process is finally balanced (Domanska *et al.*,2004).

4.2.3 Effect of Speed of Shaking on Removal of Ionic Liquid

Experiment was conducted by varying shaking speed of water bath shaker for different samples and each is shaken at different speed. This is simplified in Table 4.3 and Table 4.5 and results can be seen from Table 4.4 and Table 4.6. It is observed that as we increase the shaking speed of water bath shaker, the amount of ionic liquid removed from soil is also increase. The efficiency indicates the amount of remaining ionic liquid in the soil and it is decreasing with shaking speed. It is also can be seen that the efficiency of ionic liquid removal is better for BMIMBF₄ as compared to BMIMCl.

Table 4.5: Parameters that remain constant during experiment to investigate the effect of different shaking speed during washing onto amount of BMIMCl removed.

Initial concentration of BMIMCl (mg/kg)	900
Amount of methanol (ml)	60
Temperature of shaking (°C)	25

Table 4.6: Experimental data of washing method for BMIMCl by different speed of shaking.

Sample	C1	C2	C3	C4	C5	C6	C7	C8
Shaking speed (rpm)	150	160	170	180	190	200	210	220
Concentration of ionic liquid removed (mg/kg)	99.9	107.1	112.5	114.3	116.1	120.6	124.2	130.5
Concentration of ionic liquid remain in soil (mg/kg)	800.1	792.9	787.5	785.7	783.9	779.4	775.8	769.5
Efficiency (%)	88.9	88.1	87.5	87.3	87.1	86.6	86.2	85.5

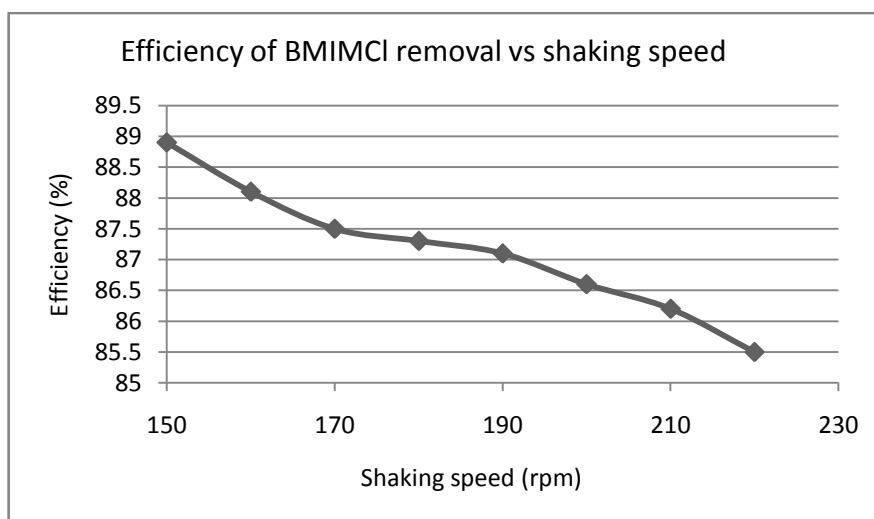


Figure 4.7: Relationship between speed of shaking during washing and the efficiency of BMIMCl removal.

Table 4.7: Parameters that remain constant during experiment to investigate the effect of different shaking speed during washing onto amount of BMIMBF₄ removed.

Initial concentration of BMIMBF ₄ (mg/kg)	900
Amount of methanol (ml)	60
Temperature of shaking (°C)	25

Table 4.8: Experimental data of washing method for BMIMBF₄ by different speed of shaking.

Sample	D1	D2	D3	D4	D5	D6	D7	D8
Shaking speed (rpm)	150	160	170	180	190	200	210	220
Concentration of ionic liquid removed(mg/kg)	108	133.2	138.6	146.7	156.6	162	166.5	184.5
Concentration of ionic liquid remain in soil (mg/kg)	792	766.8	761.4	753.3	743.4	738	733.5	715.5
Efficiency (%)	88	85.2	84.6	83.7	82.6	82	81.5	79.5

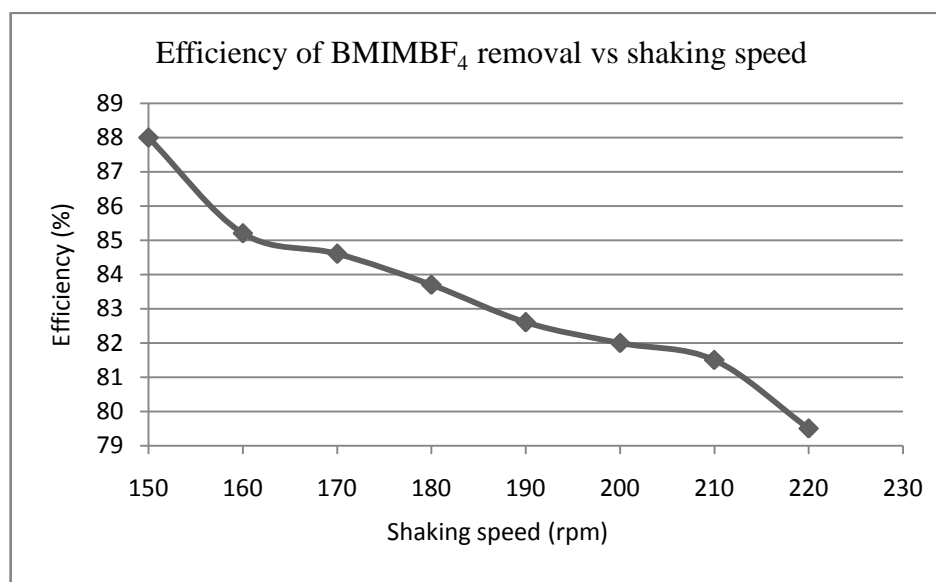


Figure 4.8: Relationship between speed of shaking during washing and the efficiency of BMIMBF₄ removal.

Many studies regarding effects of stirring onto rate of reaction has been conducted. Rost *et al.* (2002) and Hidekazu *et al.* (2009) are among researches who investigated the impact of stirring or shaking in their project. According to them, stirring or shaking could affect the rate of dissolution. This can be explained by using analogy of

dissolving sugar in water. With no stirring that layer of sugar is just going to sit on the bottom. However, at the interface between liquid and solid phase of the mixture, the sugar is actually dissolving. There will be fluid veins of different densities and will reflect light at slightly different angles. Left alone, diffusion alone is left to make the solution uniform and since sugar water is denser than pure water, diffusion also has to overcome gravity. Stirring increases the rate of diffusion and will increase the rate of dissolution.

Stirring will also increase the surface area. The top of a thick layer of sugar has moderate to decent access to the water that is doing the dissolving, but the bottom of that layer either does not have access to water at all or quickly becomes saturated and no further dissolution can occur. This is because the rate of diffusion in and out of the solid sugar layer will be extremely slow. Stirring drastically increases the available surface area of sugar to water thus will increase the dissolution rate of that sugar in water.

The difference of efficiency of removal between BMIMBF_4 and BMIMCl from the soil can be explained by relating with the relationship between molecular weight and bonding of cations and soil matter. In this case, BMIMBF_4 has lower molecular weight which is equal to 226 g/mol while BMIMCl is equal to 284g/mol. Higher molecular weight indicates the cations attached is more electronegative. With the occurrence of organic matter in the soil, more interactions can happen. In case of BMIM , besides the interaction of hydrogen bonding, van der Waals (longer side alkyl chain) will start to play an important role. This will effect to more complex leaching and harder removal of ionic liquids from the soil. (Buszewski *et al.*, 2009).

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Generally, the enhancement of ionic liquids removal using the methanol in soil washing experiments was more effective when solvent and speed of shaking are increased. The explanation of this phenomenon can be explained by relating the factors of dissolution rate of a solute in a solvent. In addition, the effect of soil's pH may also influence the efficiency of ILs removal from the soil. This is because the acidity of soil is closely related with soil's porosity and its organic carbon content, moderate acidity of soil indicates the transport of imidazolium cations of ILs is not immobilized. Different type of cations may also differ the result of ionic liquids removal. This is due to different cations may interact either weak or strong bond with organic matter in soil. The stronger the bond is (eg: van der Waals), thus the harder it is to remove ionic liquid molecules from the soil. Therefore, results from this study may be informative in the design of a field scale investigation and can also be improved.

5.2 Recommendations

Throughout this project, the author learnt that there are ways to improve this study. It is recommended that the experiment will employ different types of soil. These types may differ in terms of its porosity and TOC. This can make the author to examine and prove the effect of soil's porosity onto ionic liquids removal. Other than that, it is also recommended that different group of ionic liquids is to be used. This can lead to the study of alkyl groups' effects on the ionic liquids removal from the soil. Finally, other type of alcohol may also be used in this study to see the impacts of higher molecular weight of alcohol towards the efficiency of ionic liquids removal from soil.

Project Gantt Chart

Table 5.1: Project's Gantt chart for FYP I

Month	Feb 2010				Mar 2010				Apr 2010				May 2010			
Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Title Released																
First meeting and brief introduction about project																
Familiarization to Ionic Liquid																
Chemical Requisition Process																
Preliminary Research																
Study on Treatments for ionic liquids																
Mid Semester Break																
Submission of Progress Report																
Seminar																
Surfactant wash method																
Interim Report																
Oral Presentation																

Table 5.2: Gantt chart for FYP II

Month	Aug 2010				Sept 2010				Oct 2010				Nov 2010			
Week	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Research for methodology adjustment	■	■	■	■	■	■										
Progress Report 1 submission				■												
Preparation of sample					■	■	■	■	■	■						
HPLC analysis									■	■	■	■				
Seminar										■	■					
Poster exhibition										■						
Submission of dissertation (softbound)													■			
Oral presentation														■		
Submission of dissertation (hardbound)															■	

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