

**SOLID SUPPORT ON THIOSALICYLATE BASED IONIC LIQUID FOR METAL
EXTRACTION**

by

Nursyahirah bt Mohd Safie

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JANUARY 2013

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL


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Approved by,



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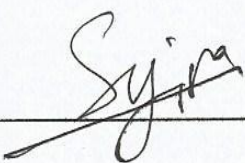
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TRONOH, PERAK

January 2013

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.



(Nursyahirah bt Mohd Safie)

ABSTRACT

Providing safe drinking water for human being has always been the subject of interests for many scientists. Since decades ago, serious efforts have been taken to solve the drinking water pollution issue especially those cases that involved the lethal effects on human. Cleaning water from heavy metal such as nickel, cadmium, lead and iron is always be very challenging since some conventional methods used such as solvent extraction method has harmful effects on environment. In this research the choice of having metal extraction using greener technology will be applied by using ionic liquid as the extraction agent. Octylpyridinium thiosalicylate ionic liquid are stable at high temperature will be the modified by syntheses process with silica as the absorbent material. The syntheses of ionic liquid will involve the process of quarternization, purification, drying and metathesis. The parameters that will be varied in order to get high efficiency of metal removal is the variation of silica loading. Analysis on the efficiency of this method will be evaluated through the results obtained from Atomic Absorption Spectrometer (AAS) reading.

ACKNOWLEDGEME

I would like to take this opportunity to express our sincere thanks and appreciation to the following person and organizations that have directly or indirectly given generous contributions towards the success of this project.

First and foremost, i would like to thanks our project supervisor, Ap Dr. Cecilia Devi Wilfred for her consistent guidance and advice throughout the preparation of this project. This project would not be able to be completed in time without her constant encouragement and guidance.

Besides, the support and tolerance by each of our family members and friends are much appreciated. Without their constant and encouragement and support, i would not have the total concentration on doing a good job.

Lastly, i also like to express my gratitude and thanks to University of Technology Malaysia for having such a complete and resourceful library. Without it, i would not be able to complete my project in time as much of my literature study and analysis are based on the sources and information gathered from the library.

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CHAPTER 1

INTRODUCTION

1.1. Project Background

Human survival is dependent on water as it has been ranked as second only to oxygen as essential for life because human can stay for a few days without drinking water. Human health will rely upon the quality of the water they took every day, thus the quality of water should be properly monitored. From the international standard, water that is used for human consumption should be clean from any concentration of chemical substance or heavy metal that may be hazardous to human health. There are 50 elements found on earth that can be classified as heavy metal whereas 17 of them are considered to be very toxic and relatively accessible. Toxicity levels depend on the type of metal, its biological role, and the type of organisms that are exposed to it. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters that lead to pollution and toxicity problem (Wan Ngah & Hanafiah, 2008). Toxicity effects of heavy metal are more sensitive in rapidly developing body system especially in the fetus, infants and young children. Excess level of lead taken from contaminated drinking water could slow down the physical and mental development in infants and children. Toxicity effects shown by childhood that were exposed to some metals include learning difficulties, memory impairment, damage to the nervous system, and behavioral problems such as aggressiveness and hyperactivity. Meanwhile, kidney problems and high blood pressure seems to occur in adult that drink heavy metal-contaminated water for many years. More alarming, irreversible brain damage could happen if high doses of heavy metals are accidentally (Haman & Bottcher, 1986).

In addition, drinking water also has its own parameter set in order to make sure the water is safe for drink. For example, the safety value of aluminum concentration in drinking water should be 0.2 mg/l (considered a safe maximum) and average concentration of copper is 1 mg/l (Haman & Bottcher, 1986). The main source of drinking water is the ground water; however pollution of these resources is widespread.

Besides, insufficient removal of toxic metal or heavy metal leads to contamination of water source(A Rajendran, 2010).

There are many methods have been applied for extraction of heavy metal (for example; iron, lead and chromium) such as co-precipitation, ion exchange, liquid-liquid extraction, solid phase extraction, solvent extraction and etc.(H Abdolmohammad-Zadeh, Galeh-Assadi, Shabkhizan, & Mousazadeh, 2011). Among the different extraction technologies, solid phase extraction is the widely used for extraction of liquid sample because it is easily automated, gives a rapid extraction process and useful for extraction since the absorbent and the size can be varies in many parameter.(Vidal, Riekkola, & Canals, 2012)

For the choice of solvent, a conventional organic solvent is not suitable since it can cause loss of organic diluent via volatilization which has harmful effect to the environment(de los Ríos et al., 2012).

In terms of absorbent materials such as organic resin, silica, titania, and alumina have been widely used as absorbent in solid phase extraction(H Abdolmohammad-Zadeh et al., 2011).

Therefore, ionic liquid is proposed as greener technology because of the unique property that gives them the capability to expand traditional laws of chemistry and modification of this absorption material is made in order to get the maximum selectivity and increase removal efficiency.

The focus of this research is to implement the more environmental friendly method as a replacement to the traditional method which uses organic solvent as the absorption material. Safer materials used in this study are ionic liquid (IL) and silica.

1.2. Problem statement

It is well known that ionic liquids are very promising in extracting metal ion. However, the application of ionic liquid to environment in solution phase is less practical and always time-consuming. In order to overcome this challenge, ionic liquid is bounded to solid support, in this case is silica. This is because, insoluble material is easier to handle compared to liquid and more environmentally cleaner. Other advantages are the complete separation of reagents and -products through simple filtration and it could be done in a faster way.

1.3. Objectives

The objectives of this research are:

1. To study the combinations of octyl pyridinium thiosalicylate with silica as absorbent material.
2. To apply the modified ILs for metal extraction- octyl pyridinium thiosalicylate.
3. To study the effects of varying the loading of silica on the metal extraction process.
4. To find the best amount of loading that gives high efficiency of metal extraction.

1.4. Scope of work

Based on the objective, we are going to synthesize octyl pyridinium thiosalicylate as our ionic liquid. Then this octyl pyridinium thiosalicylate will subject to NMR analysis (Nuclear Magnetic Resonance), Ion Chromatography analysis (Halide content testing) in order to characterize the ionic liquid. After the ionic liquid has been synthesized, it will be supported with silica which acts as a solid support for this ionic liquid. The loading of the silica will be varied on weight percent ratio.-SS: IL, 90:10, 80: 20, and 70: 30 in order to see the correlation of different silica loading to the metal extraction process.

1.5. Relevancy of project

This project can be conducted appropriately relevant considering the lack of comprehensive studies on ionic liquid, especially on modified ionic liquid which involve in removal and separation of metal from the wastewater.

1.6. Feasibility of project within time frame

This project should be finished within the given time frame if everything is running smoothly. Throughout the last 8 weeks of FYP II, the ionic liquids have been synthesized and several characterizations have been preceded. With remaining 2-3 weeks' time fame, the whole project should be able to be finished, hopefully earlier.

CHAPTER 2

LITERATURE REVIEW

2.1. Ionic liquids

The application of ILs has been widely spread in areas of chemistry such as organic and inorganic chemistry, analytical chemistry and electrochemistry (Sun & Armstrong, 2010). Significant increase in publications for the last decades showed high interests of the usage of ILs in analytical chemistry research. Basically the focus of the research was on extraction and separation.

Ionic liquid are liquid at or near the room temperature that have temperature below 100°C (Vioux, Viau, Volland, & Le Bideau, 2010). They are normally salts that typically consist of organic cations (e.g. imidazolium, pyridine, pyrrolidinium, phosphonium, and ammonium) and inorganic anions (de los Ríos et al., 2012). The constituents of ionic liquids are constrained by columbic forces, exhibiting practically no vapour pressure. This unique property gives them the capability to expand traditional laws of chemistry (A Rajendran, 2010).

The advantages of ionic liquid compared to other convention solvent are their negligible vapour pressure and highly thermal stability and their physic-chemical properties which can be tuned by modifying their structure of the component ions to obtain desired solvent properties (Ho, Canestraro, & Anderson, 2011).

Some unique properties of ionic liquids which make them can be easily modified are; it is highly polar, can be miscible with water and/or other organic solvents and also non-volatile at higher temperature.

2.2. Ionic liquid for metal removal

For metal extraction, new approach was proposed based on a method so-called as Task Specific Ionic Liquids (TSILs). Functionalised ILs provides particular properties of action for metal removal for example, Tricaprylmethylammonium salicylate [ILH]. In removing zinc from their aqueous solution, ILH was found to be better extractive agent compared to others ionic (ILH, ILB, ILA, ILD, ILC, ILI, ILF and ILE) The efficiency of removal zinc from their aqueous solution follows the order of, Tricaprylmethylammonium salicylate (ILH) > tetrapropylammonium salicylate (ILB) > tetrapropylammonium benzoate (ILA) > tetrabutylammonium benzoate (ILD) > tetrapropylammonium anthranilate (ILC) > tricaprylmethylammonium anthranilate (ILI) > tetrabutylammonium anthranilate (ILF) > ILH > tetrabutylammonium salicylate (ILE). For nickel removal, almost all ionic liquid employed were proved to extract nickel from their aqueous solution. (A. Rajendran et al., 2011)

Ionic liquid	% Removal of				
	Zn	Ni	Pb	Fe	Cu
ILA	54.5	60.0	82.4	88.4	11.7
ILB	65.8	52.7	70.6	40.4	26.1
ILC	43.4	63.0	88.2	40.4	34.9
ILD	48.8	66.0	44.1	82.6	11.7
ILE	12.9	68.0	85.3	94.2	11.7
ILF	43.1	84.7	72.1	86.5	34.9
ILG	19.3	53.4	73.5	82.6	29.09
ILH	93.3	66.6	88.2	46.1	44.6
ILI	43.4	54.1	44.1	63.4	47.5

Figure 1: Metal removal of ionic liquid

Thus, it is proved that ionic liquid can be used as extracting agent of metal removal from their aqueous solution.

2.3. Ionic liquid incorporating thiosalicylate for metal removal

The incorporation of thiosalicylate has been studied and used for metal extraction. For example, there are studies on ionic liquid incorporating thiosalicylate, (Tricaprylmethylammonium thiosalicylate [A336][TS]), for extraction of cadmium from ultrapure water and natural river water.

The results of the extraction follows the order Tricaprylmethylammonium thiosalicylate [A336][TS] > tricaprylmethylammonium hexanoate, [A336][Hex] > tricaprylmethylammonium benzoate, [A336][BA]. In ultrapure water, extraction efficiencies of >99.9% were obtained for [A336][TS], 16% for [A336][Hex] and 13% for [A336][BA]. For the elimination of cadmium from river water [A336][TS] showed an efficiency of >99.9%, [A336][Hex] 14% and [A336][BA] 11% as shown in figure 1.(Kogelnig et al., 2008)

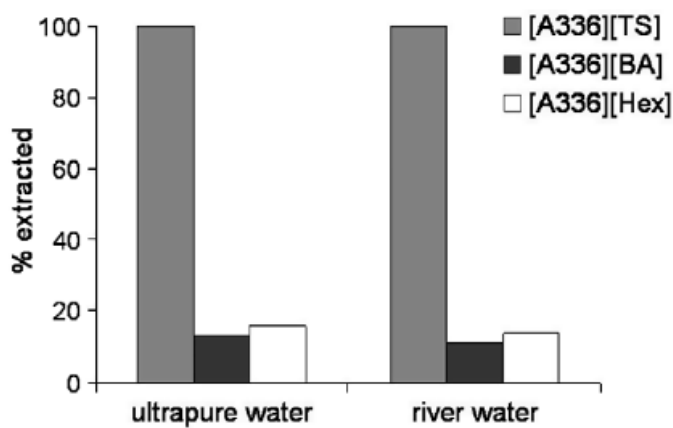


Figure 2 : Extraction efficiency of evaluated ionic liquids for the extraction of cadmium from ultrapure water and a natural river sample.

Besides, Octylpyridinium thiosalicylate [OPy]TS, have shown a great result too with almost 100% efficiency for metal removal as shown table below.(Wilfred, Mustafa, & Romeli, 2012).

Ion	Extraction efficiency (%)
Zinc	99.9
Nickel	100.0
Copper	99.9
Chromium	99.9

Table 1: Efficiency for metal removal by [OPy] TS

2.4. Solid support ionic liquid

There are many type of support that are being used in various concepts emerging from supported ionic liquids (SILs) including supported ionic liquid films (SILFs), supported ionic liquid catalysis/catalysts (SILC/SILCAs), solid catalysts with ILs (SCILs), solid catalysts with IL layer (SCILL), supported IL nanoparticles (SILnPs) and supported ionic liquid phase catalysts (SILPC)(Kuhlmann, Haumann, Jess, Seeberger, & Wasserscheid, 2009).

Throughout this project, only ionic-liquid phases (SILPs) will be focus on. Ionic-liquid phases (SILPs) which favorably combine the properties of ionic liquids (ILs) with the advantages of solid supports. This study was presented in 2009 as an alternative material for solid-phase extraction (SPE). Since then, the number of SILPs used as SPE materials has increased and the results are promising.(Fontanals, Borrull, & Marcé, 2012). SPE belongs to the group of absorptive-based extraction techniques, in which the sample is placed in contact with a suitable material.

SILP and SILC have same similarities in catalytic systems, such that an IL film is supported on a highly porous inert substrate (SiO₂ or Al₂O₃). But there is difference in preparation for both methods. In SILP method, IL is attaching to solid support by physisorbed IL (ILs did not undergo reaction with the support but it brought into contact by absorption) and SILC by covalently linked with ILs. (Selvam, Machoke, & Schwieger, 2012)

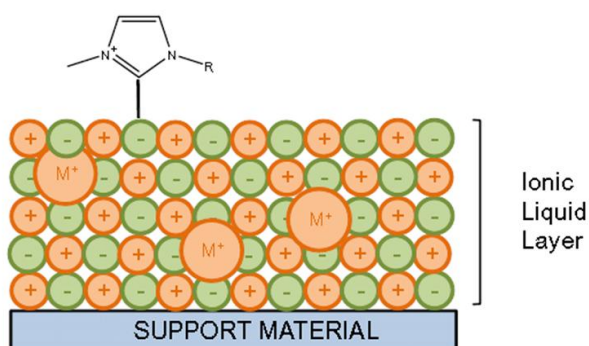


Figure 3: Physisorbed IL

The important factor in solid support ionic liquid is the absorbent. Therefore, the availability of different materials to carry out the extraction is essential.

The classic absorbents used in SPE are:

1. silica-based,
2. carbon-based sorbents, including graphitized carbon black (GCB) and porous graphitic carbon (PGC)
3. Porous polymeric sorbents, primarily polystyrene-divinylbenzene (PS-DVB).

Ionic liquid modified silica has been successfully used as absorbent for solid phase extraction of some organic compounds. The first study about IL-modified was N-Methylimidazolium modified silica, with chloride as counterion, was used to extract three tanshinone compounds from *Salvia Miltiorrhiza* Bunge. (Vidal et al., 2012).

In the case of metal ions, one study has been reported about the application of immobilized IL onto silica absorbent for separation of Cd ions. (H. Abdolmohammad-Zadeh, Galeh-Assadi, Shabkhizan, & Mousazadeh). The potential of ILs with the dual nature, thermal stability and designer property enables IL modified (SILP) new materials to be applicable for a wide range of analytes in studies where stability and tunable selectivity are required. (Vidal et al., 2012).

Besides, there are also studies on dispersing the ionic liquid as thin film on highly porous silica and it exhibits a significantly higher extraction performance due to their largest surface area. (Kuhlmann et al., 2009). Details on solid-phase extraction studies carried out with IL-modified silica materials can be seen in Table 1.

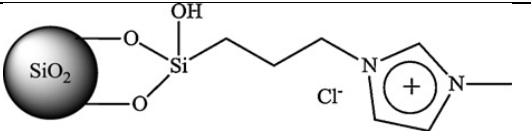
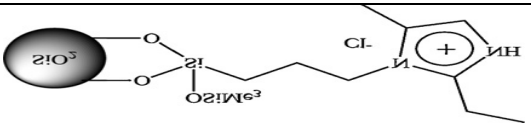
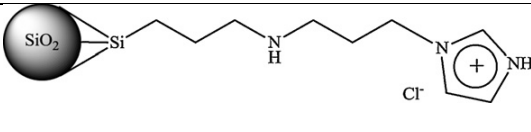
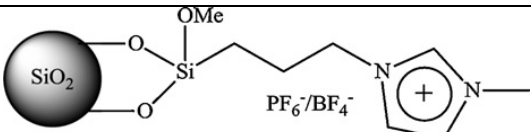
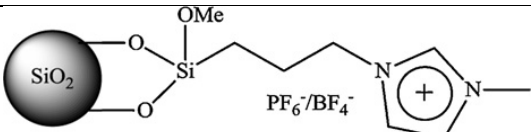
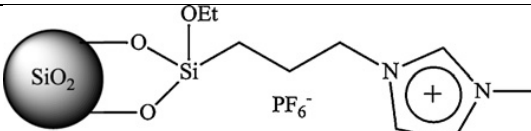
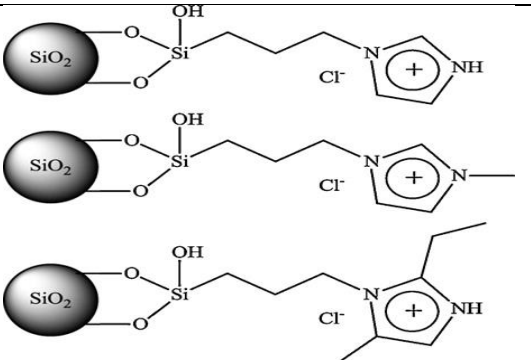
Ionic Liquid	Structure	Sample	Recoveries
<i>N</i> -Methylimidazolium chloride		Salvia Miltiorrhiza Bunge	87.2–91.5%
2-Ethyl-4-methylimidazolium chloride		Licorice and medicines	81.0–90.3%
Imidazolium chloride		Salvia Miltiorrhiza Bunge and ginseng drinks	87.5–90.6%
<i>N</i> -Methylimidazolium hexafluorophosphate/tetrafluoroborate		Soy-derived biodiesel	85.2–95.7%
<i>N</i> -Methylimidazolium hexafluorophosphate/tetrafluoroborate		Fish oil	93.5%
<i>N</i> -Methylimidazolium hexafluorophosphate		Environmental water and soil	Water: 53.8–118.2% Soil: 60.9–121.3%
Imidazolium chloride <i>N</i> -Methylimidazolium chloride 2-Ethyl-4-methylimidazolium chloride		Fermentation broth	91.9%

Table 2: Example of modified ionic liquid with their sample

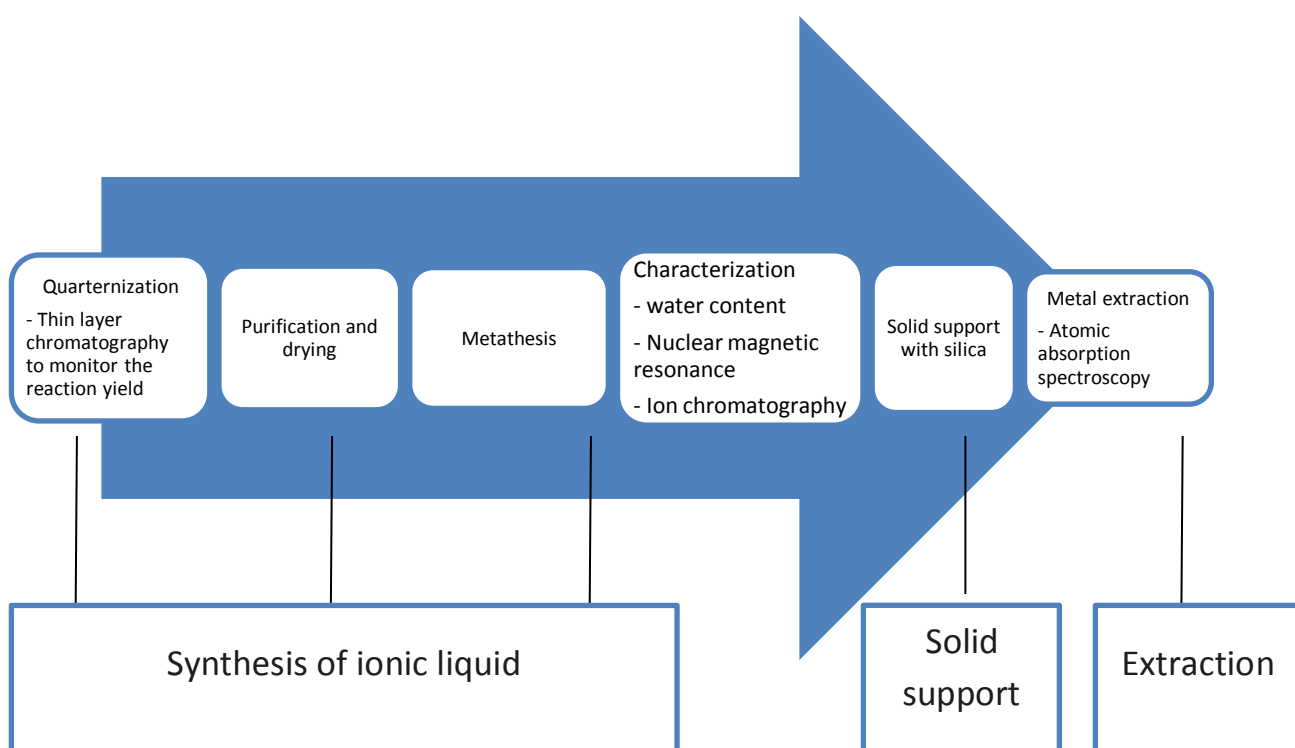
Therefore, in this project, we are focusing on producing an ionic liquid which incorporates thiosalicylate with pyridinium cation and supported with silica as absorbent material and apply for a metal removal.

CHAPTER 3

METHODOLOGY

Project Activities

Throughout the project, most of the activities are laboratory works. The whole process can be divided into several major steps as follows:

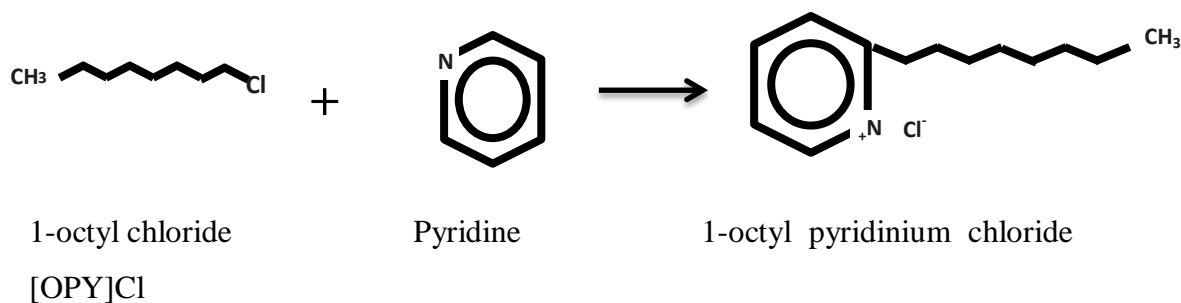


SYNTHESIS OF IONIC LIQUID

In order to produce thiosalicylate ILs, synthesis of halide ILs of pyridinium is the first step. For example, to produce octylpyridinium thiosalicylate, octyl chloride will react with pyridine to produce 1-octyl pyridinium chloride (in quarternization process). Then this product will react with sodium thiosalicylate in order to produce octylpyridinium thiosalicylate-in metathesis process.

3.1.Quartenization

Quartenization is the process of cation synthesizing. In this project pyridinium is mixed with 1 type of alkyl chloride which is 1-octyl chloride (1-chlorooctane).



Name	Structure	Mol. Weight	Density	Boiling point
Pyridine	C ₅ H ₅ N	79.09 g/mol	0.978 g/ml	115 °C
1-chlorooctane	C ₈ H ₁₇ Cl	148.67 g/mol	0.875 g/ml	183 °C
Sodium hydroxide	NaoH	39.99 g/mol	2.13 g/ml	1390 °C
Thiosalicylic acid	C ₇ H ₆ O ₂ S	154.19 g/mol	1.489 g/cm ³	163.5 °C

Table 3: Properties of reactants

3.1.1. Amount of reactant to produce 1-octyl pyridinium chloride

All the reactant we used pyridine as the limiting reactant and octyl chloride is an excess reactant in order to make sure the reaction is completely react. The reaction is 1:1 mole ratio (equivmolar).

	Pyridine	Octyl-chloride
Ratio	1	1
Mole	0.1	0.1
Mass (g)	7.909	14.867
Volume (ml)	8.08	17.00

Table 4: Amount of reactant to prepare 1-octyl pyridinium chloride

3.1.2. Quarternization procedure

1. A 100ml of three-neck round bottom flask was prepared by flush it with nitrogen to ensure the reaction is not is not under ambient air.
2. The amounts of reactant were prepared and the reactants are put in three-neck round bottom flask. The amounts of reactant are prepared as table above.

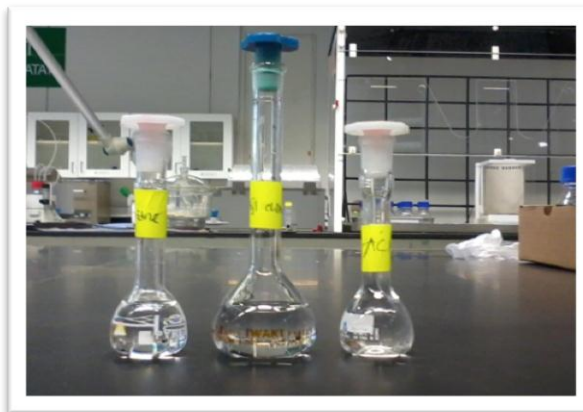


Figure 5: Reactant used to produce octyl pyridinium chloride

3. The solution is now heated under nitrogen atmosphere at temperature at 80 °C and range of 300-400 rpm.

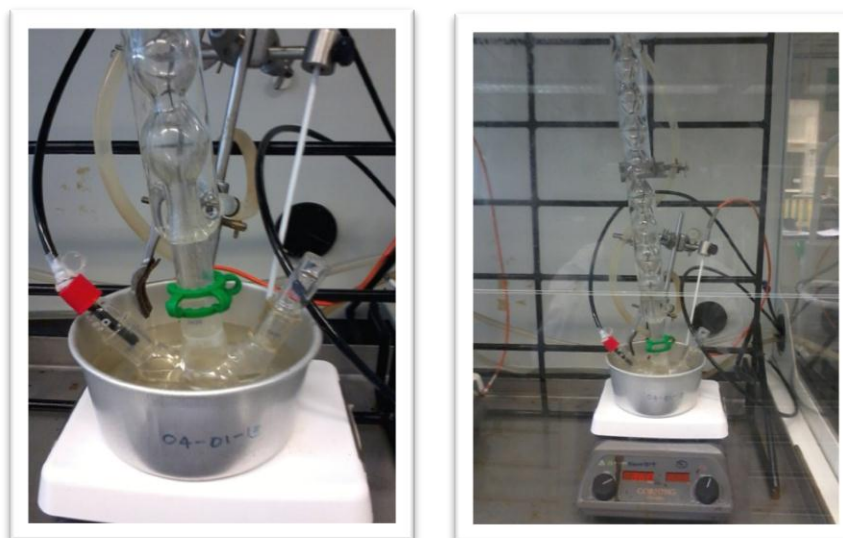


Figure 6: Solution heated under nitrogen line

- The reaction takes around 72 hours to complete and in order to make sure the reaction is complete; TLC (thin layer chromatography) analysis is used.

3.1.3. Thin layer chromatography

- A pencil line is drawn near the bottom of the plate. Any labeling on the plate is to show the original position of the drop
- Small drop of solution is placed on the paper (2drops). The drops consist of the reactant (pyridine and Octyl-chloride) and the product.
- When the spot mixture is dry, the paper is put in a shallow layer of solvent which is acetonitrile.

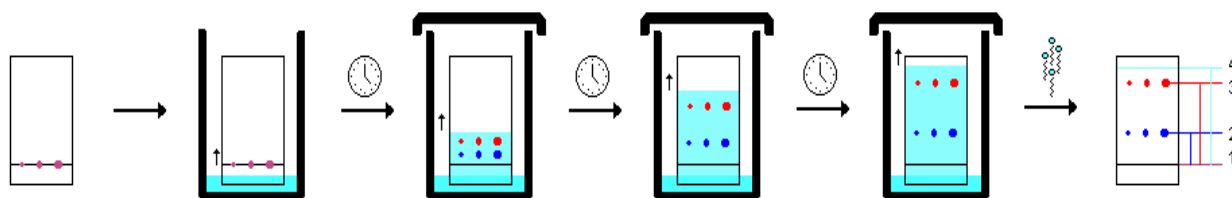


Figure 7: Thin layer chromatography

- Wait for a certain time, until see any dot on the paper. The dot of product must not reach the same line as reactant. Failure to get this result means longer quartenization time might be needed.

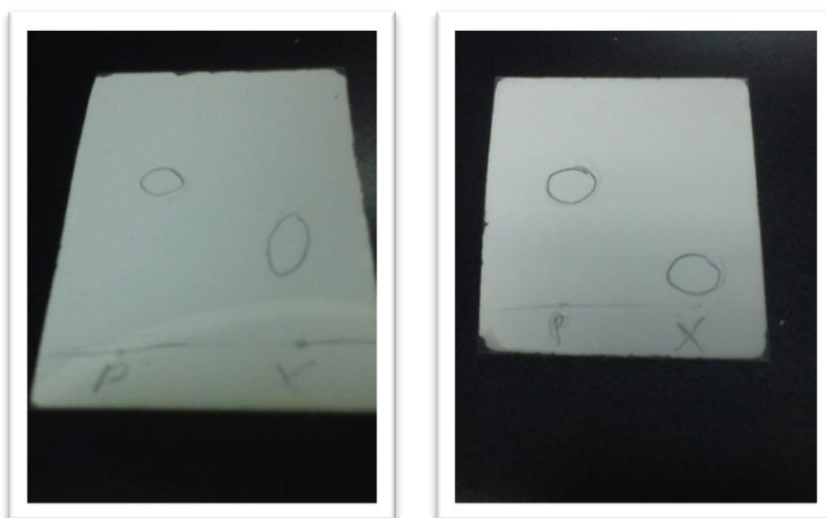


Figure 8: Thin layer chromatography result

3.2. Purification and drying

3.2.1. Extraction of residue

Purification is the process where the residue (if any) is removed from ionic liquid. This can be done by washing the ionic liquid with ethyl acetate in the separation funnel.

1. 20ml ethyl acetate is added to ionic liquid.
2. Stir the solution until 2 layers are form. The top layer of mixture is the IL and the bottom layer is the solvent that we want to remove.
3. Remove the solvent and wash again the ionic liquid for three times.

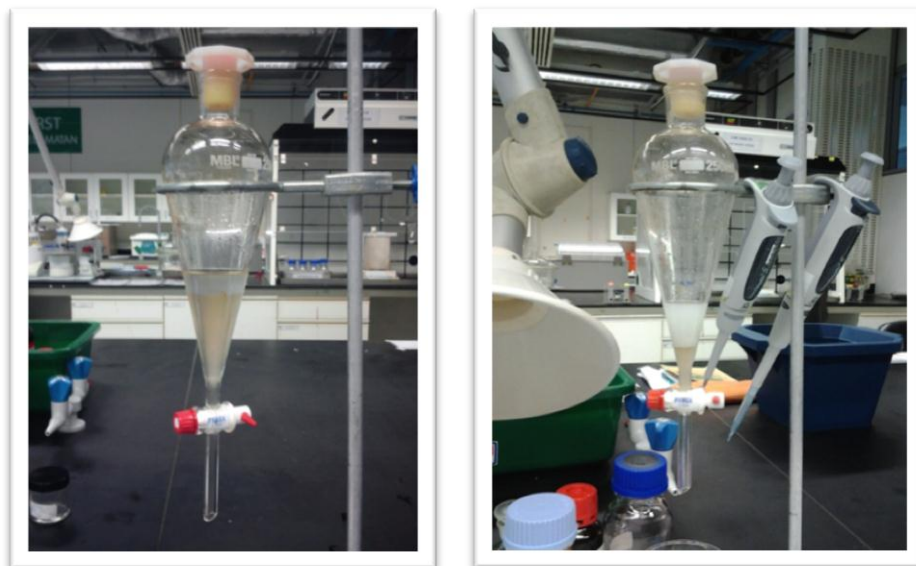


Figure 9: Two layers formed

3.2.2. Removal of acetonitrile

Acetonitrile which react as the intermediate solvent is removed from this process. This can be done by using rotary evaporator at 80°C. This is because; the boiling point of acetonitrile is 82 °C at 1 atm. Therefore, by heating it at 80°C, acetonitrile will vaporize and leave along the ionic liquid.

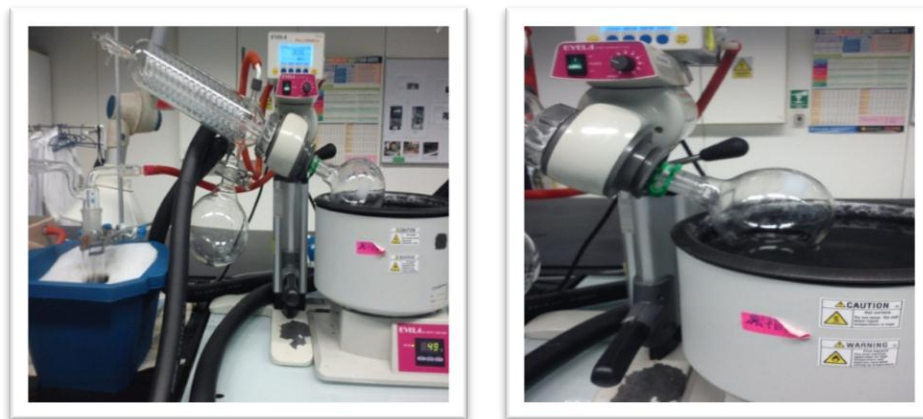


Figure 10: Rotary evaporator

3.2.3. Drying the ionic liquid

Pure ionic liquid is dried in the oven at 70 °C for 72 hours. The result of this synthesis is a viscous yellowish liquid.

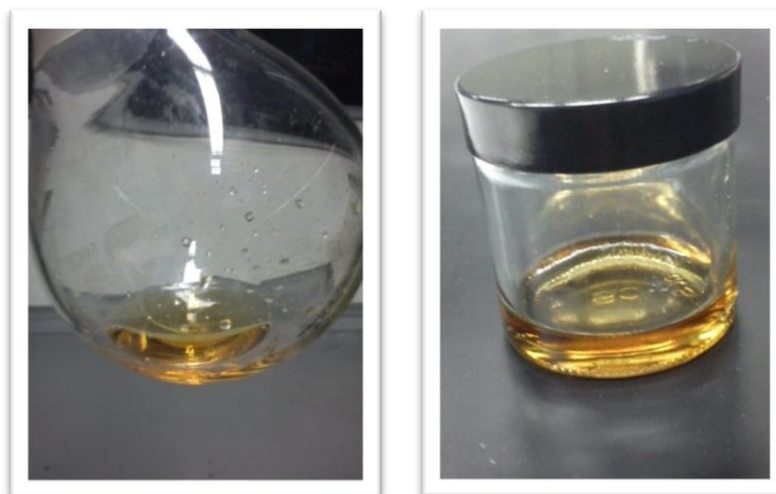
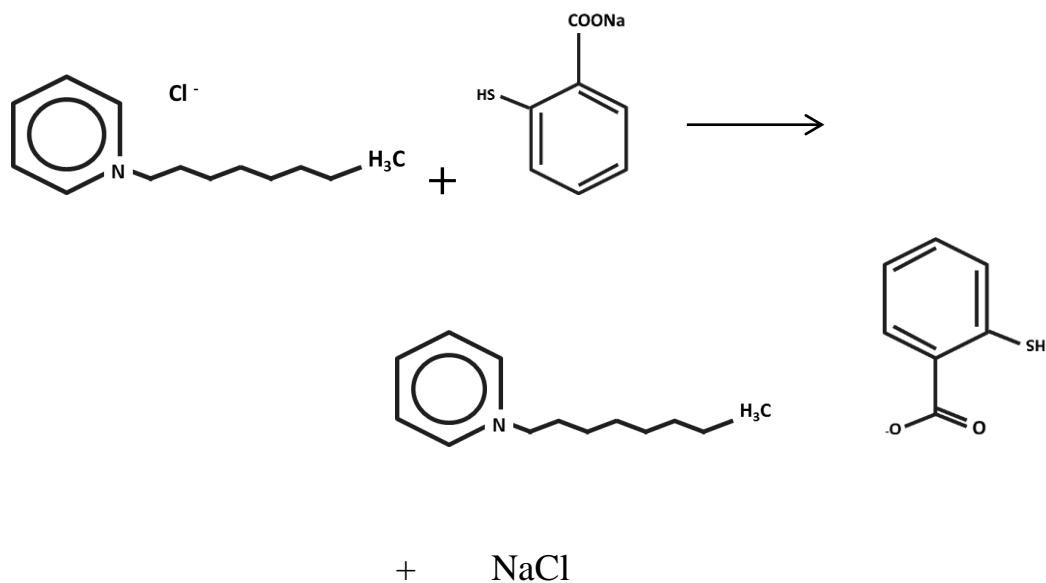


Figure 11: Viscous yellowish liquid.

3.3. Metathesis

Metathesis reaction is where the cations and anions exchange partners. In this process, halide is removed and will be replaced by cation.



3.3.1. Metathesis procedure

1. Sodium thiosalicylate is prepared through neutralization process.
2. In neutralization process, an equimolar amount of thiosalicylic acid and sodium hydroxide are diluted inside the distilled water at room temperature and ambient pressure. Thiosalicylic acid is poorly dissolve in water. Therefore, to make sure the thiosalicylic acid dissolve, sodium hydroxide is added simultaneously during the string process. Clear yellow solution will be formed after the neutralization process.



Figure 12: Clear yellow solution after neutralization process

3. After the neutralization reaction, tare the weight of the intermediate ionic liquids (from quarternization) and calculate the amount of mole. Subsequently, prepare equimolar amount of sodium thiosalicylate and mix it with the intermediate ionic liquid. Both the mixture is combined and stir at 500-600 rpm. This process required no heating but only stirring. The reaction takes 72 hours to complete react.
4. Since both synthesized ILs and sodium thiosalicylate are soluble in water, the water is removed via evaporation in rotary evaporator.
5. The salt (NACl) produced from the compound was removed using filtration by adding acetonitrile to it. Repeat the steps to 3 times in order to make sure all the NACl are removed. A clear yellow solution was formed after all the NACl are removed.

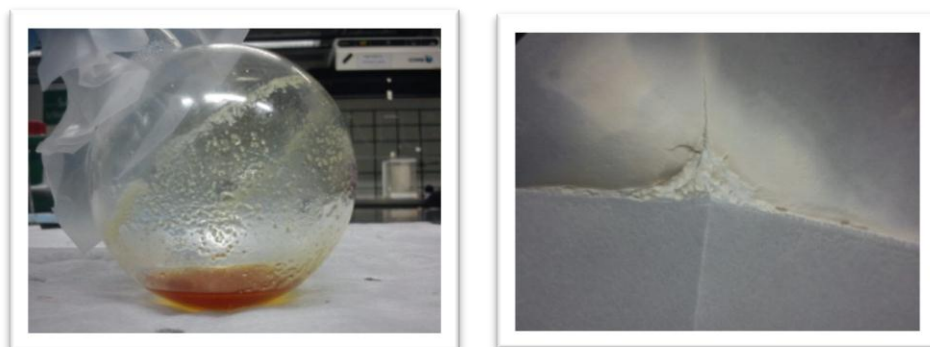


Figure 13: Salt (NaCl) produce after filtration

6. Then, the acetonitrile was removed by rotary evaporator until a viscous liquid are formed.

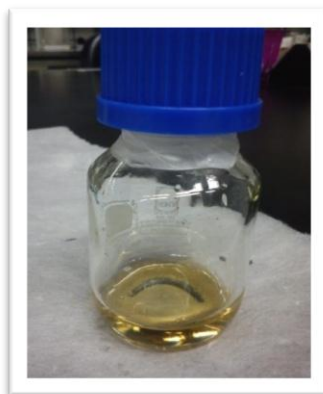


Figure 14: Octyl pyridinium thiosalicylate

CHARACTERIZATION

The ionic liquid will be subjected to several analyses in order to understand the detail structure and its behavior.

1. ^1H NMR : Nuclear magnetic resonance is to analyze whether ionic liquid is pure or not by weighing the hydrogen atom position in the spectrum and the number of these atoms through peaks integration
2. Water content: using Karl-Fisher equipment for all pure ILs due to its high effect on the density and viscosity.
3. Ion Chromatography: to measure the halide content in the compound.

SOLID SUPPORT IONIC LIQUID

Preparation of solid support (silica) (AK-12) adsorber using wet impregnation method.

1. Small amount of AK-12 was tested for solubility in methanol. AK-12 was added in small amounts to 2 gm of methanol. AK-12 dissolved properly. In alcohol, solution was transparent.
2. Commercial silica oxide was used as a support material.

3. Before impregnation Silica oxide (SiO_2) was calcined in 550°C for 12 hours. Before and after calcination SiO_2 was measured in order to check for weight loss. (Before-20 gm, After-19 gm) **3gm of SiO_2** was used as a support material
4. Required amounts of AK-12 for impregnation was 5 wt% - 0.1 g.
5. 0.1 g (5 wt%), was dissolved in 3 ml of methanol and left overnight by closing the caps of the containers.

Preparation of silica based ionic liquid

Silica based ionic liquid material was prepared by:

1. Dissolving the ionic liquid in the dichloromethane.
2. The appropriate amount of dried support is added to the solution depending on the loading that we want to vary.

Loading of silica	Loading of IL
10	90
20	80
30	70

Table 5: Loading of silica and ILs

3. The suspension is stir for 24 hours and the solvent use has to be removed. It can be done by dried it under an oven for overnight.
4. Make sure all the solvent are removed before proceed to the metal extraction.



90: 10



80:20



70: 30

METAL EXTRACTION

After the modified ionic liquid has been synthesis and support with silica, several samples of metal ions solutions are prepared.

1. Aqueous solution o metal ion Zn^{2+} , Ni^{2+} and Cu^{2+} were prepared in 10ppm
2. 0.35g of ionic the solid support ionic liquid was added to the metal ion solution.
3. Shake the solution 5-10 minutes to allow mixing. The solid support will
4. These mixtures were then, centrifuged at 4000r rpm for 10 minutes.
5. Allow the mixture to settle from the centrifuged for 1 hour.



Figure 15: Metal extraction

6. Takes 5ml from topside of each sample to prevent sedimentation and AAS was conducted in order to detect the remaining metal concentration in distilled water.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Ionic liquid

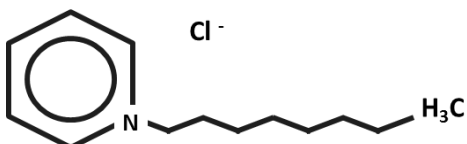
Octyl pyridinium chloride

Figure 16: Octyl pyridinium thiosalicylate

Properties	Remarks
Color	Brownish yellow
Molecular structure	C13H22ClN
Molecular weight	227.5 g/mol
Synthesis condition	80°C, 1 atm, 400 rpm stirring

Table 6: Properties of Octyl pyridinium chloride

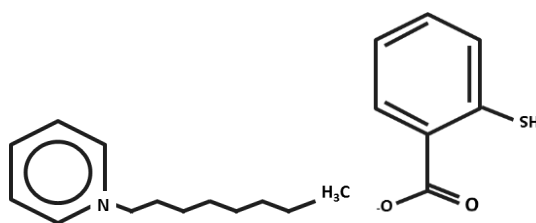
Octyl Pyridinium Thiosalicylate

Figure 17: Octyl pyridinium thiosalicylate

Properties	Remarks
color	Dark brown
Molecular structure	C20H27O2NS
Molecular weight	345.07 g/mol
Synthesis condition	25°C, 1 atm, 500 rpm stirring

Table 7: Properties of Octyl pyridinium thiosalicylate

4.2. Solid support ionic liquid



Solid support	Ionic Liquid
90	10



Solid support	Ionic Liquid
80	20



Solid Support	Ionic Liquid
70	30

4.3. Atomic Absorption Spectroscopy

All products of solid support ionic liquids have been tested at three different types of metals. The results of the metal extraction are measured with Atomic Absorption Spectroscopy (AAS) and fragmented down into specific metal as listed below:

4.3.1. Zinc (Zn^{2+})

The following graph showed the reading of concentration for metal standard. The concentration of sample will be based on the reading of these standards. The initial samples were all set at 10 ppm (high concentration).

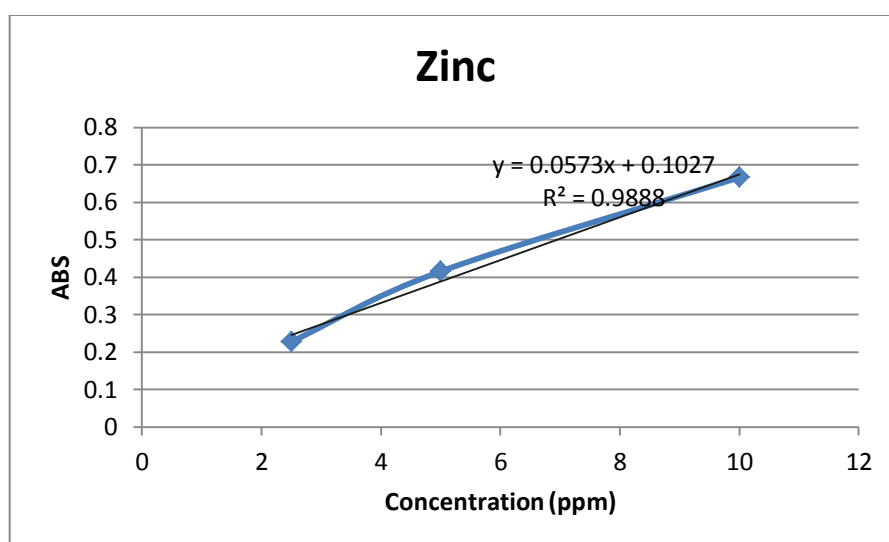


Figure 18: Graph ABS versus zinc concentration

Ratio Ionic liquid and solid support (IL : SS)	Initial concentration (ppm)	Final concentration (ppm)	Percent removal (%)
10 : 90	10	5.13	48.7
20 : 80	10	4.97	50.3
30 : 70	10	4.79	52.1

Table 8: Atomic Absorption Spectroscopy Result (zinc)

The table above is the result obtained from AAS (Atomic Absorption Spectroscopy). The differences can be seen, where combination of IL and solid support with the higher amount of IL gives a slightly higher percentage of Zinc removal of 52.1%. IL:SS combination with the ratio of 20:80 and 10:90 each demonstrated 50.3% and 48.7% Zinc removal. As seen in the pictures below, the usage of solid support although does not give satisfactory removal of the metal itself, but the advantage is remain. Solution shown in Figure 19 shows the cloudy mixtures of IL and metal extracts while Figure 20 shows the separation occurs good with the use of solid support compared to separation without solid support.



Figure 19: Metal extraction by ionic liquid

Figure 20: metal extraction by solid support ionic liquid

4.3.2. Copper (Cu^{2+})

The following graph showed the reading of concentration for metal standard. The concentration of sample will be based on the reading of these standards. The initial samples were all set at 10 ppm (high concentration).

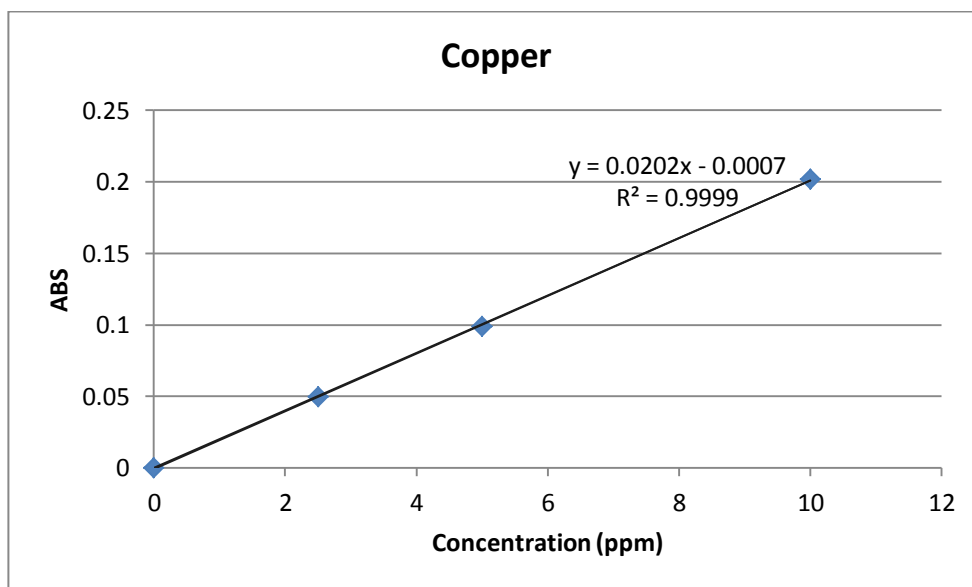


Figure 21: Graph ABS versus copper concentration

Ratio Ionic liquid and solid support (IL : SS)	Initial concentration (ppm)	Final concentration (ppm)	Percent removal (%)
10 : 90	10	7.35	26.6
20 : 80	10	7.78	22.2
30 : 70	10	7.86	21.4

Table 9: Atomic Absorption Spectroscopy Result (copper)

The table shows the result of copper removal by silica supported IL. A huge difference can be seen where not even half of coppers are extracted from the water. However, the higher the solid support, the higher the percent of removal. ABS result shows 26.6% of zinc was removed from the water when the IL was combined with silica at ratio of 10:90. Meanwhile, at ration of IL:SS (20:80), 22.2% copper removal was attained followed by 21.4% of copper removal for lower solid support amount at ratio of IL:SS (30:70).

4.3.3. Nickel (Ni^{2+})

The following graph showed the reading of concentration for metal standard. The concentration of sample will be based on the reading of these standards. The initial samples were all set at 10 ppm (high concentration).

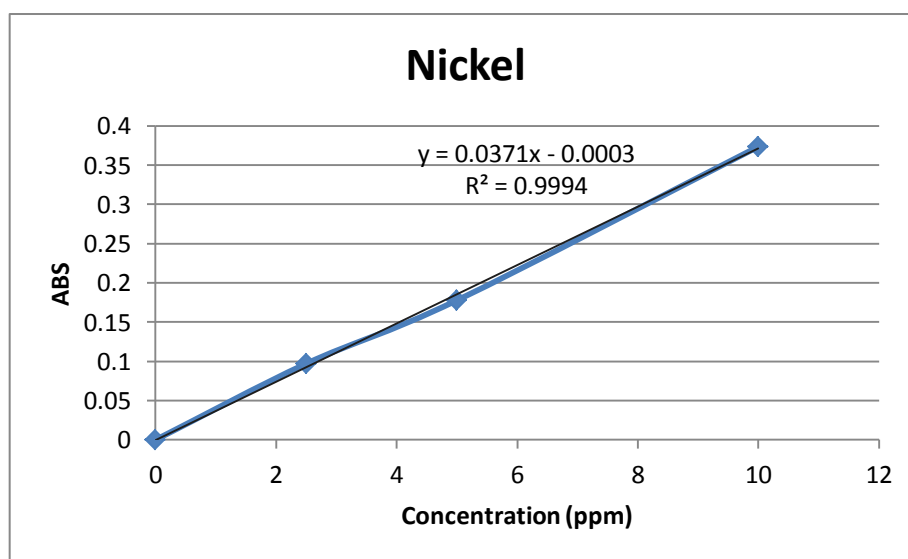


Figure 22: Graph ABS versus nickel concentration

Ratio Ionic liquid and solid support (IL : SS)	Initial concentration (ppm)	Final concentration (ppm)	Percent removal (%)
10 : 90	10	10	0
20 : 80	10	10	0
30 : 70	10	9.93	0.7

Table 10: Atomic Absorption Spectroscopy Result (nickel)

AAS reading for three different mixtures of Nickel immobilized through silica supported ILs showed shocking result which for two different IL: SS ratio of 10:90 and 20:80, no nickel removal exists. The combination of IL: SS has a very less efficiency in extracting nickel out of the water. Very least percentage of copper removal is achieved at ratio of IL: SS (30:70), with less than 1% of removal.

Silica supported IL seems to gives inconsistent removal for three different metal ions. The percentage Zinc removal from this method found to be the most satisfactory with average of 50% of removal from the original concentration. The result is followed by copper with average percentage of removal at 20% and nickel that has the negligible amount of reduction of less than 1%.

The same amount of silica bounded to IL does not have same effect for the zinc and copper extraction. Higher amount of silica with lower IL's loading gives better result for copper removal, while higher IL amount is needed for zinc and nickel removal.

The combination of IL: SS could have been varied to find the most optimum ratio for better extraction. This research should be carried with further with variation of parameters to get optimum result. The parameters could be the type of solid support used for separation, the mixing duration and the ratio of IL bounded to solid support. The need of solid support however is substantial to achieve better separation, thus provides a cleaner and easy handling procedure.

4.4. Characterization

4.4.1. Nuclear Magnetic Resonance

The ^1H NMR of the ionic liquid is summarized as picture below. The chemical shifts and its peak integration from the ^1H NMR confirmed the compound is octylpyridinium chloride. Chemical shifts between 8.2 and 9.5 ppm could be assigned to aromatic hydrogen atoms of thiosalicylate, whilst peaks between 0 to 5 ppm belongs to the pyridinium cation.

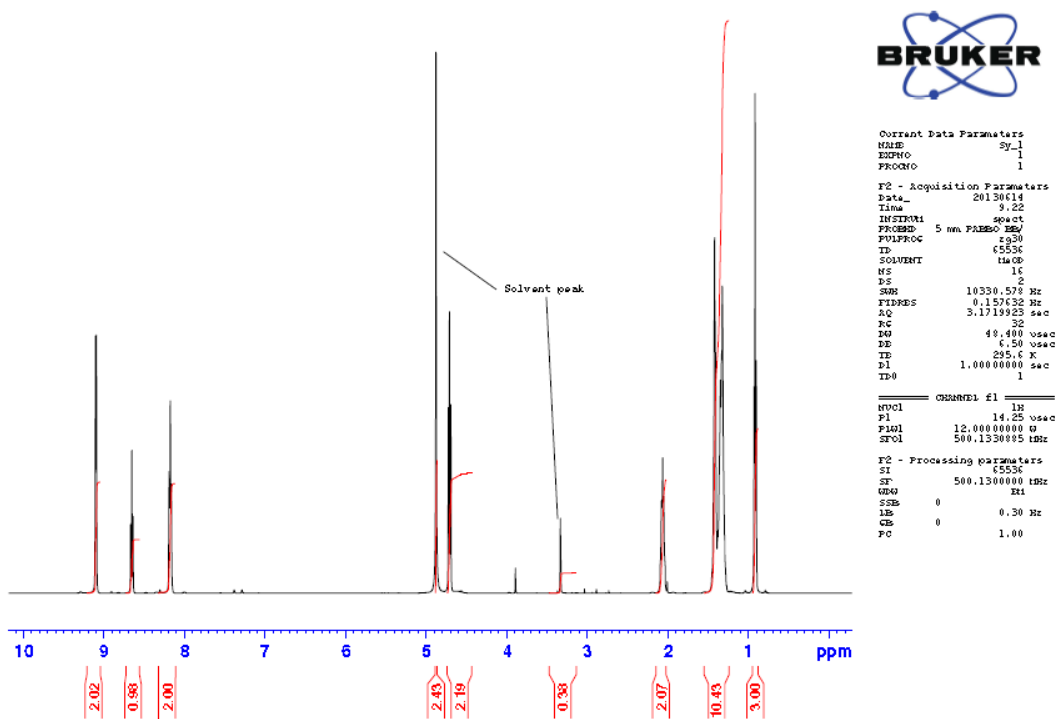


Figure 23: NMR-H Result

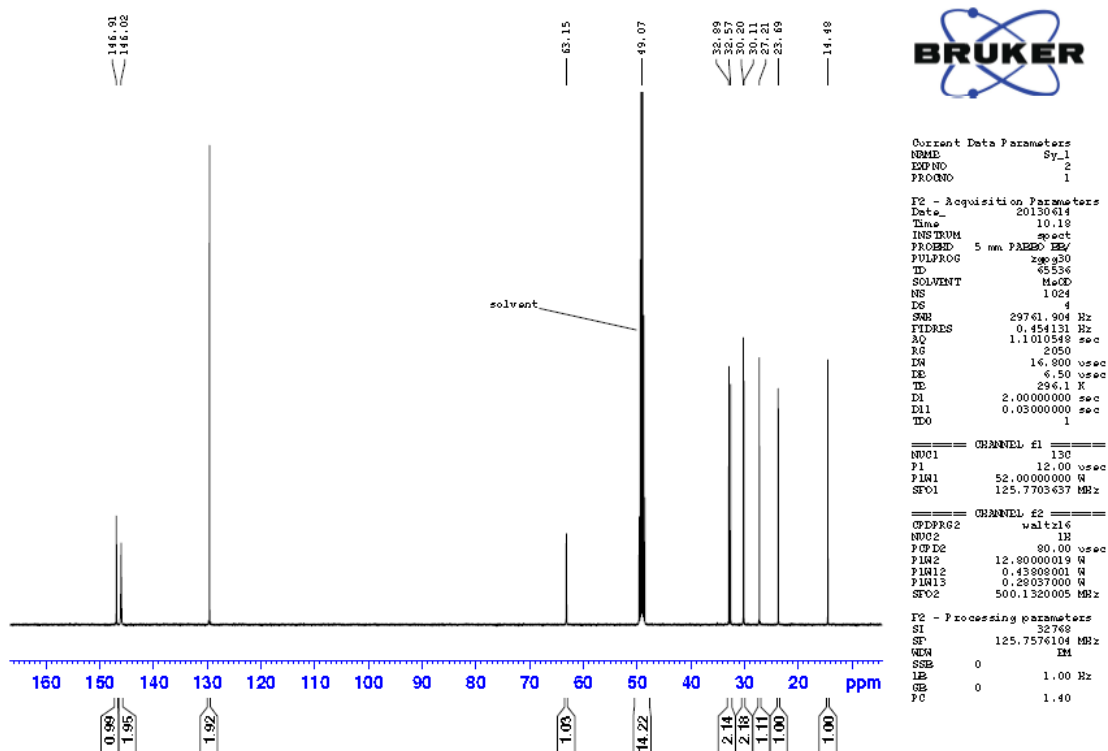


Figure 24: NMR-C Result

4.4.2. Water Content Measurement

Karl Fisher titration is a classic titration method to determine trace amounts of water in a sample. Therefore in this analysis, the sample is tested and the result is showed as below.

sample	Water percent (%)
1	0.01
2	0.08

Table 11: Water percent for IL

This result shows that the sample produced content only small amount of water which less than 1 %. Although the effect of the drying is visibly significant, the period should also be taken account. All ionic liquids have been through 96 hours of drying in order to reduce the water content to be less than 0.1%.

4.4.3. Ion Chromatography

Ion chromatography is aims to detect the halide content of the ionic liquids. The process allows the separation of ions and polar molecules based on their charge. The halide content of this compound is 13.092 ppm.

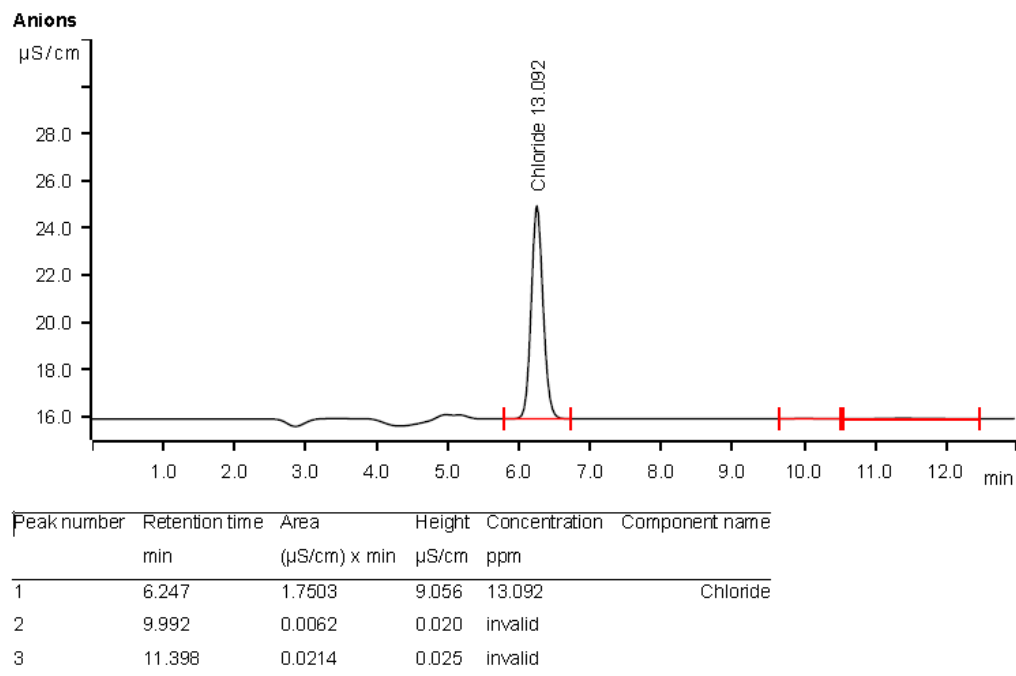


Figure 25: Ion chromatography result

CHAPTER 5

CONCLUSION

All three modified ionic liquids with different ratio ionic liquid and silica loading have been synthesized. Several analyzing methods such as Karl-Fisher water content analysis, H1 Nuclear Magnetic Resonance, and Ion Chromatography have been done. Karl-Fischer showed a good result to the ionic liquids by having less than 0.1% water content. The chemical shifts and peak integration from the H¹NMR analysis confirmed the compound is octylpyridinium thiosalicylate and the value halide content for this compound is less than 50 ppm.

In solid support view, silica supported IL seems to give inconsistent removal for three different metal ions. The percentage Zinc removal found to be the most satisfactory with average of 50% of removal from the original concentration. The result is followed by copper with average percentage of removal at 20% and nickel that has the negligible amount of reduction of less than 1%.

The same amount of silica bounded to IL also does not have same effect for the zinc and copper extraction. Higher amount of silica with lower IL's loading gives better result for copper removal, while higher IL amount is needed for zinc and nickel removal.

It is recommended for future FYP project to proceed on find the most optimum ratio of solid support and ionic liquid by increasing the loading silica and ionic liquid used. Last, find the best solid support that gives high efficiency of each of metal since silica did not give high efficiency for metal removal.

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