BENZYL IMIDAZOLIUM-BASED IONIC LIQUIDS FOR THE REMOVAL OF PHENOLS FROM NON-AQUEOUS SOLUTION

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BENZYL IMIDAZOLIUM-BASED IONIC LIQUIDS FOR THE REMOVAL OF PHENOLS FROM NON-AQUEOUS SOLUTION

ABSTRACT

Two types of method were studied to remove phenol from non-aqueous solution namely; liquid-liquid extraction (LLE) and adsorption technique in which hexane was used as the model oil. Three types of benzyl imidazolium-based room temperature ionic liquids (RTILs) were synthesized and used as extractants in LLE while silica-titania mixed oxide with RTILs were used as adsorbents in adsorption technique. In LLE technique, 1-allyl-3-benzylimidazolium chloride ([Abzim][Cl]) was used in the optimization of parameters including influence of phase volume ratio between IL and model oil, time, temperature, type of model oils and selectivity study. Based on three different types of substituents on benzyl imidazolium-based ILs, allyl substituent showed excellent phenol removal efficiency compared to vinyl and benzyl substituents. The ^{1}H NMR spectra revealed that the distance of chloride anion (Cl^-) from carbon C2 on imidazolium ring played a vital role in determining the performance of the ILs to form hydrogen bonding with phenol besides the presence of π-π interaction. The performance of [Abzim][Cl] was excellent even in synthetic oil where phenol (Ph), 2,4-dichlorophenol (2,4-DCP) and 2,4-dinitrophenol (2,4-DNP) can be removed even in the presence of other aromatic compounds such as fluorene and fluoranthene. On the other hand, silica-titania mixed oxide with monocationic and dicationic ILs were synthesized as adsorbents. These compounds then underwent preliminary study for removal of phenol via adsorption process. However, the result revealed that the performance of these adsorbents were not as good as RTILs as extractants in LLE. It can be concluded that the developed LLE method is the best method to remove phenols from oil compared to adsorption technique.

Keywords: Benzyl imidazolium-based ionic liquids, silica-titania, phenols, liquid-liquid extraction, adsorption.

CECAIR IONIK BERASASKAN BENZIL UNTUK PENYINGKIRAN FENOL DARIPADA LARUTAN TIDAK AKUEUS

ABSTRAK

Dua jenis teknik telah dikaji untuk penyingkiran fenol daripada larutan tidak akueus iaitu pengekstrakan cecair-cecair (LLE) dan teknik penjerapan di mana heksana telah dipilih sebagai model minyak. Tiga jenis cecair ionik suhu bilik (RTILs) berasaskan benzil imidazolium telah disintesis dan digunakan sebagai pengekstrak dalam LLE manakala campuran oksida silika-titania dengan cecair ionik telah digunakan sebagai penjerap dalam teknik penjerapan. Di dalam teknik LLE, 1-alil-3-benzilimidazolium klorida ([Abzim][Cl]) digunakan dalam pengoptimuman parameter termasuklah pengaruh nisbah isipadu fasa di antara IL dan model minyak, masa, suhu, jenis model minyak dan kajian selektiviti. Berdasarkan tiga jenis pengganti pada cecair ionik berasaskan benzil imidazolium, pengganti alil menunjukkan kecekapan penyingkiran fenol yang cemerlang berbanding pengganti vinil dan benzil. Spektrum ^{1}H NMR mendedahkan bahawa jarak anion klorida (Cl^-) daripada karbon C2 pada gelang imidazolium memainkan peranan penting dalam menentukan prestasi IL untuk membentuk ikatan hidrogen bersama fenol di samping interaksi π-π. Pencapaian [Abzim][Cl] cemerlang walaupun di dalam minyak sintetik di mana fenol (Ph), 2,4-diklorofenol (2,4-DCP) dan 2,4-dinitrofenol (2,4-DNP) boleh disingkirkan meskipun dalam kehadiran sebatian aromatik seperti fluorena dan fluoranthena. Di samping itu, campuran oksida silika-titania dengan IL monokation dan dwikation masing-masing telah disintesis sebagai penjerap. Sebatian ini kemudiannya melalui kajian awal untuk penyingkiran fenol melalui proses penjerapan. Walau bagaimanapun, keputusan mendedahkan bahawa pencapaian penjerap ini tidak sebaik RTILs sebagai pengekstrak dalam LLE. Ia boleh disimpulkan bahawa kaedah LLE yang dibangunkan adalah kaedah yang lebih baik untuk menyingkirkan fenol berbanding teknik penjerapan.

Kata kunci: cecair ionik berasaskan benzil imidazolium, silika-titania, fenol, pengekstrakan cecair-cecair, penjerapan.

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[Abzim][Cl] : 1-Allyl-3-benzylimidazolium chloride

[Bmim][Cl] : 1-Butyl-3-methylimidazolium chloride

[Bmim][NTf_2] : 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[Bzvim][Cl] : 1-Benzyl-3-vinylimidazolium chloride

[Dbzim][Cl] : 1,3-Dibenzylimidazolium chloride

[Dicat-BzIm][Cl] : 3,3'-(1,4-Phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) dichloride

^{13}C NMR : Carbon-13 nuclear magnetic resonance

^{1}H NMR : Proton nuclear Magnetic Resonance

2,4,6-TCP : 2,4,6-Trichlorophenol

2,4,6-TNP : 2,4,6-Trinitrophenol

2,4-DCP : 2,4-Dichlorophenol

2,4-DNP : 2,4-Dinitrophenol

2-CP : 2-Chlorophenol

2-NP : 2-Nitrophenol

3-CP : 3-Chlorophenol

4-CP : 4-Chlorophenol

4-NP : 4-Nitrophenol

BET : Brunauer-Emmett-Teller

$CDCl_3$: Deuterated chloroform

CH_3CN : Acetonitrile

C_f : Phenol concentration in the upper layer after reaction

C_o : Phenol concentration in the original model oil

DMSO-d_6 : Deuterated dimethyl sulfoxide

EDX : Energy dispersive X-ray

EtOH	:	Ethanol
FESEM	:	Field emission scanning electron microscopy
FT-IR	:	Fourier transform infrared
HCl	:	Hydrochloric acid
HPLC	:	High performance liquid chromatography
ILs	:	Ionic liquids
LLE	:	Liquid-liquid extraction
PAHs	:	Polycyclic aromatic hydrocarbons
Ph	:	Phenol
RTILs	:	Room temperature ionic liquids
SiO_2-TiO_2	:	Silica-titania mixed oxide
Si-Ti	:	Silica-titania
Si-Ti-AbzImCl	:	Silica-titania mixed oxide with [Abzim][Cl]
Si-Ti-Dicat-BzImCl	:	Silica-titania mixed oxide with [Dicat-BzIm][Cl]
Si-Ti-ILs	:	Silica-titania mixed oxide ionic liquids
TEOS	:	Tetraethoxysilane
TGA	:	Thermogravimetric analyses
TMS	:	Tetramethylsilane
TTIP	:	Titanium tetraisopropoxide
UV-Vis	:	Ultraviolet-Visible
v/v	:	Volume/volume
VOCs	:	Volatile organic compounds
wt%	:	Weight percentage
XRD	:	X-ray diffraction
δ	:	Chemical shift

CHAPTER 1: INTRODUCTION

1.1 Introduction

Phenol is a major industrial chemical where the major sources of phenolic compounds can be found in petroleum, coal liquefaction oil and coal tar (Guo *et al*., 2013; Jiao *et al*., 2015a). It is used industrially for the production of phenolic resins, bisphenol A, caprolactam, and other phenolic compounds. In addition, they have been widely employed in many industrial processes as synthesis intermediates or as raw materials in the manufacturing of wide classes of industrial products (Pera-Titus *et al*., 2004). Even though the petroleum industry has recognized the occurrence of phenolic compounds in various types of petroleum fractions as well as in crude oil, the presence of phenols could be problematic in some fraction of petroleum as they lead to corrosion and declining fuel properties of oil (Zhu *et al*., 2017). Therefore, the availability of phenols in coal tar and other petroleum origins has brought the attention of this study to extract these materials from those sources.

The traditional method employed to separate phenols from oil mixtures uses very strong alkaline solution and strong acid. This technique eventually produces extreme amounts of harmful wastewater (Jiao *et al*., 2015b; Pang *et al*., 2012). Therefore, an environmentally friendly and efficient method becomes necessary to exhaustively extract phenols from oil.

Recently, a new type of green solvent has emerged as an alternative reaction media to traditional organic solvents. Ionic liquids (ILs) can be broadly defined as ionic species that melt at or below 100 °C. Their structure typically consist of organic cations and either inorganic or organic anions (Mahlambi *et al*., 2009). Room temperature ionic liquids (RTILs) are a subset of ILs and they exist as liquids at room temperature (Hagiwara & Ito, 2000; Sun & Armstrong, 2010). ILs have caught considerable attention in the separation field due to their unique solvent properties (Lee, 2012; Wei *et al*., 2003; Welton, 1999).

Among the different kinds of materials that have been utilized for the removal of phenol from oil, ILs have shown great potential as an extractant due to their numerous advantages such as high polarity, high thermal stability, low melting point and liquidus over a wide range of temperature, low vapour pressure due to strong ion-ion interaction, less polluting and easily recyclable as well as the possibility of designing many ionic liquids with tailored properties due to the availability of a large number of organic cations and inorganic/organic anions which can form ionic liquid (Singh *et al*., 2014).

The choice of both cations and anions allows us to tweak the properties of the resulting ILs to obtain the desired solvent properties (Huddleston *et al*., 2001; Visser *et al*., 2000). In order to enhance the properties of ILs as extractants, their substituent alkyl group can be customized. In fact, increasing the chain length of the substituent groups on the cations modifies the viscosity, hydrophobicity, and melting point (Visser *et al*., 2000).

Thus, in order to effectively extract phenols from oil, two methods have been of interest in this study i.e. liquid-liquid extraction (LLE) and adsorption technique. LLE which is also known as solvent extraction is a process for separating components in solution between two immiscible liquid phases (Robbins & Cusack, 1999). There are some critical issues in LLE due to the consumption of enormous amount of traditional volatile organic compounds (VOCs). LLE which utilizes VOCs, generate contaminated solvents and therefore also create disposal issues to the environment (Vidal *et al*., 2005). Thus, in order to avoid the use of VOCs, ILs are seen as noble alternatives because they possess more fascinating properties and greener than VOCs. Moreover, ILs help to improve the selectivity and extractability of the required substances compared to typical solvents (Liu *et al*., 2005a).

Thus, in order to increase their extraction capability toward phenolic compounds, in this study, a series of benzyl imidazolium-based ILs with allyl, benzyl and vinyl substituents were synthesized. By employing substituents with double bonds and aromatic rings, phenols can be extracted by enhancing the π-π interaction. Due to the aromatic characteristic of phenolic compounds, the designation of ILs with aromatic and double bond moieties could open up a new frontier in the separation studies of phenolic compounds.

On the other hand, adsorption is one of the techniques available in separation study which involves the partitioning of chemical species between bulk phase and an interface via physical or chemical binding (Bajpai & Rajpoot, 1999). This surface phenomenon is renowned as an effective and economic method for separation analytical purposes (Crini, 2005). The search of new adsorbents is crucial in order to improve the performance in adsorption processes. The new adsorbent should meet the following criteria (Huang & Hu, 2008):

- It should achieve fast adsorption;
- It should have high adsorption capacity;
- Good recyclability;
- High surface area accessibility;
- It should consist of a stable and insoluble porous matrix with suitable active groups which can interact with analytes.

Among the available adsorbents, silica-titania mixed oxide composites have emerged as one of the most reliable adsorbent due to its large surface area, high thermal stability, high mechanical strength and good dispersibility (Hilonga *et al.*, 2009). Moreover, they are extensively used as catalysts (Miao *et al.*, 2011; Shi *et al.*, 2005), photocatalysts (Hou *et al.*, 2008; Wu *et al.*, 2014) and adsorbents (Enomoto *et al.*, 2002; Ismail *et al.*, 2016;

Londeree, 2002). The sol-gel method offers a convenient way for the production of silica-titania mixed oxides due to its lower temperature synthesis scheme (Miskam *et al*., 2013).

From the literature survey, this is the first attempt to employ adsorption process for the separation of phenols from oil. By considering the unique properties of ILs and the remarkable ability of silica-titania mixed oxides, the encapsulation of ILs onto the silica networks may lead to a new pathway in adsorption process where these materials possess a porous solid support with active sites to form chemical interaction with phenols.

1.2 Problem statement

As mentioned in Section 1.1, phenolic compounds have tremendous industrial applications. Therefore, it is significant to effectively extract phenols from oil due to this economic reason. Moreover, being oxygen-containing compounds, the presence of phenols in crude oil creates corrosion problem which consequently leads to operational issues. Their presence could also affects fuel properties such as viscosity, stability and heating value (Kim, 2015). Thus, appropriate methods should be investigated in order to separate phenols from oil. However, the traditional method applied in industry involved the use of an enormous amount of volatile solvent as well as strong acidic and alkaline media (Pang *et al*., 2012). Thus, realizing the fascinating properties of ILs, two methods have been selected to separate phenols i.e. LLE and adsorption technique by using imidazolium-based ILs. In order to enhance the extracting ability of these ILs on phenols, the alkenyl and benzyl chains were chosen respectively as a part of the ILs structure. This suggestion could improve the π-π interactions between the benzene ring of phenols and ILs and consequently, increase the percentage removal of phenols.

1.3 Scope of research

This research involved two types of extraction processes to remove phenol from model oil. The first process exploited ionic liquids as extractant to extract phenol via liquid-

liquid extraction where the ILs itself are liquid in nature. The ILs were initially synthesized and characterized by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR), Fourier transform infrared spectroscopy (FT-IR), carbon, hydrogen and nitrogen elemental analysis (CHN), thermogravimetric analysis (TGA), as well as density and viscosity measurement. Three benzyl imidazolium-based ILs with different aromatic and double bond substituents namely allyl, vinyl and benzyl were then employed as extractants for the removal of phenol from model oil. The removal process was evaluated by investigating the type of substituents on the IL cation, the phase volume ratio of model oil to IL, temperature, time, type of model oils and selectivity study.

The potential IL which is [Abzim][Cl] was then used for the synthesis of silica-titania mixed oxide with IL via sol-gel method for the removal of phenol through adsorption technique. Dicationic IL with more benzyl groups was also used for comparison study with [Abzim][Cl]. Both materials were subjected to the structural characterization by FT-IR spectroscopy, X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), field emission scanning microscopy (FESEM), surface area and porosity analysis and energy dispersive X-ray (EDX). The composites were then used as adsorbents for the removal of phenol from model oil and their performance was analyzed comprehensively.

1.4 Objective of research

The objectives of this study are:

- To synthesize and characterize benzyl imidazolium-based ILs by various characterization techniques.
- To evaluate the ability of benzyl imidazolium-based ILs as a solvent for the removal of phenols from model oil via liquid-liquid extraction.

- To synthesize and characterize silica-titania mixed oxide ILs by various characterization techniques.
- To study the ability of silica-titania mixed oxide ILs as an adsorbent for the removal of phenols from model oil via adsorption process.

CHAPTER 2: LITERATURE REVIEW

2.1 Phenols

Phenols are categorized as a class of aromatic organic compounds with related *o*-, *m*-, and *p*-cresol as their isomers (Jiao *et al*., 2015a). They are one of the constituents compounds found naturally in petroleum with various concentrations subjected on the different petroleum fractions (Anku *et al*., 2017; Zhu *et al*., 2017). These valuable compounds can also be derived from pyrolysis of low-rank coals as well as via gasification, carbonization and liquefaction process of coal tars (Schobert & Song, 2002). Other sources might include the product of pyrolysis of biomass-derived bio-petroleum as well as bio-oil (Li *et al*., 2010; Yaman, 2004).

Phenols have been widely employed in tremendous industrial processes as synthesis intermediates or raw materials in the manufacturing of herbicides, pesticides, insecticides, pharmaceuticals, and dyes (Nadavala *et al*., 2009; Pera-Titus *et al*., 2004). They can also be used as intermediates in the production of adhesive and the synthesis of polymers (Amen-Chen *et al*., 1997). Moreover its isomers such as *p*-cresol has been used to produce light-resistant antioxidants and dyes while *o*-cresol is used to synthesize epoxy resins and pharmaceutical products and *m*-cresol has been employed in the production of preservatives, disinfectants and explosive materials (Jiao *et al*., 2015a). Due to their enormous industrial uses, they have attracted the attention of researchers to develop methods of separating them from crude oil (Bhadra *et al*., 2016). Moreover, it is desirable to separate phenolic compounds from the oil mixture before further refining due to their relatively high concentration in coal tar. For this economic reason, separating phenols from neutral oils is beneficial due to their industrial applications. Thus, the presence of approximately 20% to 30% phenolic compounds in low-temperature coal tar distillates should then be fully utilized (Jiao *et al*., 2015a).

Apart from economic reasons and their industrial applications, phenols sometimes may cause certain problems in several petroleum fractions. Phenol contamination might occur in jet fuel which is one of the petroleum fractions where phenols are the major oxygen-containing compound and thus, they have become the source of corrosion (Zhu *et al*., 2017). In addition, they also contribute to the formation of surface deposition which in turn causes operational problems in the petroleum industry (Bhadra *et al*., 2016). Furthermore, the existence of phenols in bio-oils may results in deteriorating fuel properties which include high viscosity, instability and low heating value (Kim, 2015). Due to these reasons as well as the vast industrial uses of phenols, the separation of phenols from oil is crucial.

2.1.1 Phenol extraction from oil

Over the years, a vast number of studies has been focused on the separation of phenols from those coal and petroleum sources. The traditional method currently employed to separate phenols from oil mixtures is through the use of strongly alkaline and acidic chemicals. However, this method produces excessive amounts of phenol-containing wastewater (Jiao *et al*., 2015b; Pang *et al*., 2012).

Amen-Chen *et al*. (1997) have previously isolated phenols such as phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol from Eucalyptus wood pyrolysis tar via liquid-liquid extraction using alkali and organic solvents. Wood tar is a complex mixture of various compounds including phenols and in fact, before the rise of petrochemical industry, the wood carbonization for the extraction of chemicals such as acetone, methanol and phenols has been performed on an industrial scale. The drawback of this method is that under a low pH value, the extraction of the selected compounds was incomplete. Thus, a very high pH value was indeed needed for the complete isolation of phenols from the oil matrix by using a concentrated alkaline solution (Amen-Chen *et al*., 1997).

On the other hand, in 1998, separation of *m*-cresol has been carried out by means of liquid-liquid extraction by using a high-boiling solvent namely tetraethylene glycol with a co-solvent water and an anti-solvent hexane (Venter & Nieuwoudt, 1998). Even though an alternative approach was used by employing tetraethylene glycol with a high boiling point of 285 °C, but there was no process of recovery being mentioned in the literature.

Some studies have reported the use of solvents such as aqueous acetamide, methanol, isobutyl acetate and sodium phenolate in extraction of phenolic compounds from neutral oils. However, the problems aroused from these processes were the requirement to employ high solvent ratios as well as complex purification of the products (Nair *et al*., 1967; Venter & Nieuwoudt, 1998).

The reported method of separating phenols from oil was using very strong alkaline solution which is sodium hydroxide and forming a phenolate precipitate upon reacting with phenol. Subsequently, a strong acid such as sulphuric acid was used to neutralize the phenolate. Unfortunately, this method produces a great amount of phenol-containing waste water which in turn might enter the water stream (Jiao *et al*., 2015c).

Thus, knowing that the traditional processes are generally causing some environmental problems, an improvement of these processes is essential. The solution of this problem should meet the relevant criteria such as environmentally friendly and economically feasible (Alonso *et al*., 2008; Arce *et al*., 2006). Therefore, ionic liquids (ILs) are recently seen to be a novel candidate to fulfil those criteria. This is due to the fact that ILs possess more fascinating properties that they eventually outperform their conventional counterparts in separation technology (Cheng & Chu, 2006).

2.2 Ionic liquids

2.2.1 Introduction

In general, ionic liquids are a class of salts that melt at or below 100 °C. Meanwhile, room temperature ionic liquids (RTILs) are the subset of ILs, which exist as liquid at room temperature (Hagiwara & Ito, 2000; Sun & Armstrong, 2010). The term IL and RTIL will be used interchangeably in this study. Even though, there are no clear definition for the term ionic liquid found in the literature, however, the definition has evolved and at the present time it is used to describe a broad class of low-melting semi-organic salts which have considerable liquid range (Baker *et al*., 2005). In contrast to the other typical salts like NaCl, their ions are poorly coordinated and as a result they normally exist as liquid at ambient temperature (Buszewski & Studzińska, 2008). Historically, the first IL; ethylammonium nitrate ($[EtNH_3][NO_3]$) was discovered by Paul Walden in 1914 with a melting point of 13-14 ℃ (Plechkova & Seddon, 2008).

ILs are known as ionic species with structures typically consist of organic cations such as pyrrolidinium cations, quaternary ammonium cations, and heterocyclic aromatic compounds for example imidazolium and pyridinium cations with either inorganic or organic anions (Mahlambi *et al*., 2009). Figure 2.1 depicts some common anions and cations which constitute the structure of most ILs. As can be seen in the figure, the anions can be either inorganic or organic where the inorganic anions usually consist of halides (Cl^-, Br^-), tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) while the organic ions may include trifluoroethanoate ($[CF_3CO_2]^-$), bis[(trifluoromethyl)sulfonyl]imide ($[(CF_3SO_2)_2N]^-$), trifluoromethanesulfonate $[CF_3SO_3]^-$, and so on (Soukup-Hein *et al*., 2009). In addition, Figure 2.2 illustrates the combination of cations and anions to form some common ILs existing in the literature. Amazingly, there are currently a huge number of ILs being reported where the cation and anion pair can generate up to 10^8 different structure of ILs (Tan *et al*., 2012).

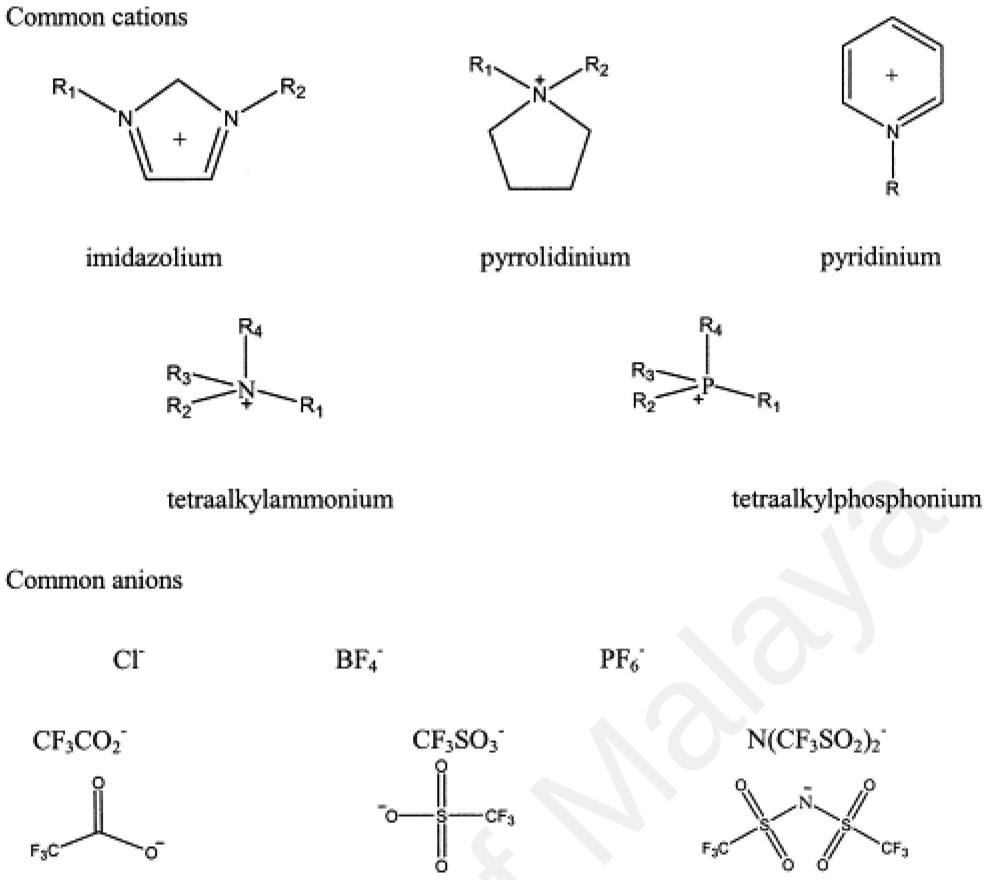
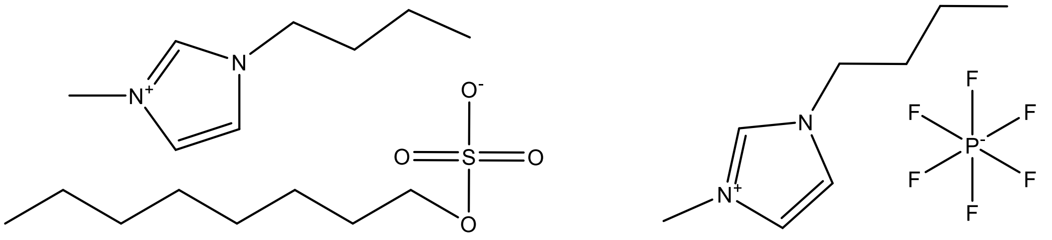
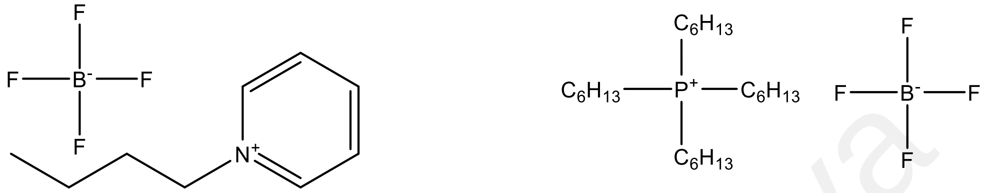


Figure 2.1: Structures of typical cations and anions of ILs (Sun & Armstrong, 2010)



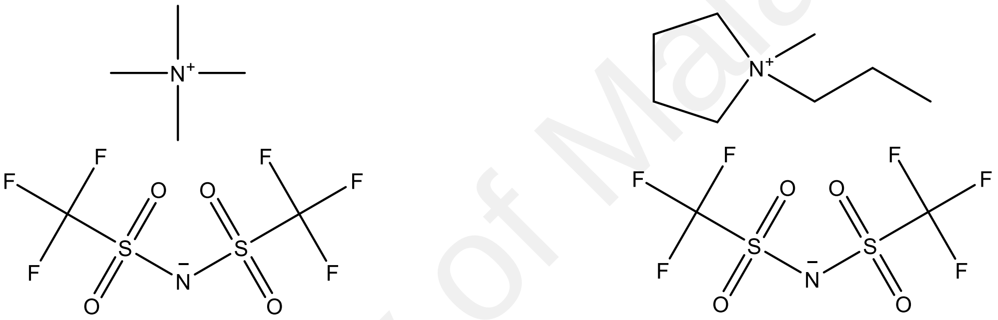
1-Butyl-3-methylimidazolium octyl sulphate

1-Butyl-3-methylimidazolium hexafluorophosphate



N-butylpyridinium tetrafluoroborate

Trihexyltetradecylphosphonium tetrafluoroborate



Tetramethylammonium bis(trifluoromethylsulfonyl)imide

N-methyl-N-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide

Figure 2.2: Example of typical ILs in the literature

Dicationic ILs on the other hand have been developed recently which consist of one dication and two monoanions. For example, the structures comprising two imidazolium- or pyrrolidinium-based monocations are bridged together via an alkyl chain to form a dication (Maton *et al*., 2013; Sun *et al*., 2009). The chain that bridge those cations can be a cyclic or aliphatic chain via either a rigid or a flexible spacer but alkyl chain is the most common (Masri *et al*., 2016). Figure 2.3 shows some typical structure of dicationic ILs.

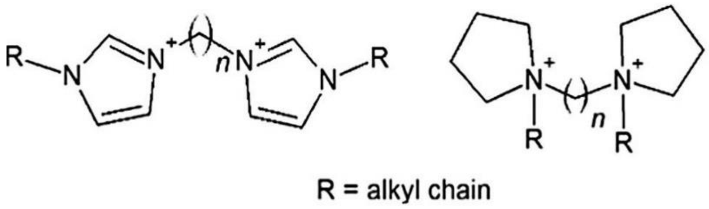


Figure 2.3: Typical structures of dicationic ILs (Masri *et al*., 2016)

Dicationic ILs have several advantages compared to monocationic ILs. Interestingly, they have a higher thermal stability and volatility over the monocationic ILs (Shirota *et al*., 2011). The higher thermal stability is attributed to the greater charge and intermolecular interactions, their higher molecular weight, higher density and higher shear viscosity (Maton *et al*., 2013). In recent time, dicationic ILs have been favoured due to their unique features such as their liquid densities are larger than those of monocationic ILs (Ishida & Shirota, 2013). They can be used as lubricants, separation media, solvents for high temperature uses, and catalyst for transesterification and esterification reactions. However, the knowledge in dicationic ILs in still scarce compared to monocationic ILs due to fewer reports on their study in the literature (Shirota *et al*., 2011).

2.2.2 The properties of ionic liquids

ILs have caught considerable attention in a wide field of analytical chemistry due to their excellent properties. A better understanding of the physical and chemical properties of the ILs is crucial in order to make use of their benefits towards the ideal applications.

One of the most fascinating attraction of ILs is their almost non-detectable vapour pressure. Due to their low-volatility and non-flammability properties, they have been acknowledged as ‘green’ materials. ILs have become the focus of recent researches as greener alternatives to replace traditional organic solvents. In fact, their tuneable structures enable them to be tailored for specific applications by appropriate modifications of their anion and cation combination thus, producing ILs with a multitude physical and chemical properties (Martín-Calero *et al.*, 2011). Due to those remarkable properties, ILs have been termed as “designer solvents” (Alonso *et al.*, 2008).

By having the ability to be tailored into specific functionality, the physicochemical properties of the ILs such as the viscosity and solubility can also be designed according to the desired purposes. This is because their viscosity is strongly influenced by the length of alkyl chain length of the cation as well as the type of ion pair species (Dzyuba & Bartsch, 2002; Kim *et al.*, 2004; Zarca *et al.*, 2015). As a matter of fact, ILs have higher viscosity value compared to water and other typical organic solvents. As of now, the viscosity values of most ILs at ambient temperature can reach up to two to three orders of magnitude larger than organic solvents. Some highly viscous ILs are favoured in certain applications but conversely, too high viscosity value can also cause some handling problems (Yu *et al.*, 2012). However, the experimental viscosity data in the literature is currently inadequate (Gardas & Coutinho, 2008). Thus, synthesizing ILs with an ideal viscosity required us to have a comprehensive understanding on how the structure of ILs influence their viscosity (Tokuda *et al.*, 2004). Table 2.1 shows the viscosity of some ILs as well as their other physical properties (Buszewski & Studzińska, 2008).

Table 2.1: Physico-chemical properties of some ILs

Ionic liquid	Density ($g\ mL^{-1}$)	Melting point (°C)	Viscosity (cP)
Ethylammonium nitrate	1.122	12.5	32.1
n-Propylammonium nitrate	1.157	4.0	66.6
Butylammonium thiocyanate	0.949	20.5	97.1
Tetra-*n*-heptylammonium chloride	0.882	-9	598
1-Butyl-3-methylimidazolium hexafluorophosphate	1.373	10	450
1-Butyl-3-methylimidazolium tetrafluoroborate	1.208	81	219
1-*n*-Decyl-3-methylimidazolium tetrafluoroborate	1.072	-25	928
1,3-Diethylimidazolium trifluoromethanesulfonate	1.330	23	53
1-Ethyl-3-methylimidazolium trifluoroacetate	1.285	-14	35
1-*n*-Hexyl-3-methylimidazolium hexafluorophosphate	1.304	-61	585
1-*n*-Octyl-3-methylimidazolium tetrafluoroborate	1.110	-79	439

Besides affecting the viscosity behaviour of ILs, the choice of the anion species also contributes to the solubility behaviour of ILs. Theoretically, halide, nitrate, trifluoroacetate and ethanoate-based ILs are soluble in water. However, ILs with tetrafluoroborate and trifluoromethanesulfonate are somehow partially immiscible in water depending on the alkyl chain length on the cation. Therefore, it can be concluded that the anion has a major influence towards their miscibility with water followed by the secondary effect of the cation species (Seddon *et al*., 2000). The ability to have various compatibility with water and other organic compounds has made ILs compounds to have interesting solvation properties (Erdmenger *et al*., 2008). This is because they have the ability to dissolve a large array of compounds in relatively small quantities separation (Cheng & Chu, 2006).

Other quality which makes ILs of being the only one of its kind is their high thermal stability. They have a wide liquid range and their temperature limit is normally specified by their thermal degradation temperature due to their non-boiling character. By having this special property, ILs have been employed in various high temperature applications (Maton *et al*., 2013).

Another intriguing property of ILs is that they can be recycled and reused after accomplishing specific tasks (Erdmenger *et al*., 2008). Moreover, ILs help to improve the selectivity and extractability of the required substances compared to typical solvents (Liu *et al*., 2005a).

In short, the uniqueness of ILs includes the possibility to synthesize an enormous number of different ILs, each with their own specific solvation properties by combining different cations and anions. They also make good solvents for a wide range of both inorganic and organic materials. Moreover, ILs have very low volatility, therefore they eliminate several contamination problems related to volatile organic solvents. The good solubility of gases such as O_2, benzene, nitrous oxide, ethylene, ethane, and carbon monoxide makes them an attractive solvent system for catalytic hydrogenations, carbonylations, hydroformylation, and aerobic oxidations. Furthermore, they are especially suitable as a reaction media for electrochemical due to the large electrochemical window. ILs tend to have good thermal stability and can be liquid over a range of 300 °C. Thus, this wide liquid range is a distinct advantage over VOCs that have a much narrower liquid range. In addition, ILs can be recycled. As a result, recovery and recycling of the catalyst are also possible with the ILs, thus keeping production of waste and loss of valuable catalysts to a minimum (Buszewski & Studzińska, 2008; Singh *et al*., 2012).

2.3 Applications of ILs

The properties of ILs mentioned from the previous sub-chapter make them interesting compounds for utilization in countless different applications. Owing to these advantages, ionic liquids have currently been applied as solvents in catalysis, chemical separation, organic synthesis and electrochemistry (Tshibangu *et al*., 2011).

A number of research studies have focused on the application of ILs in separation studies where ILs are used as the stationary phases in gas chromatography and as additives of the mobile phase in liquid chromatography (Han & Row, 2010; Soukup-Hein *et al*., 2009; Sun & Armstrong, 2010).

Recently, the applications of ionic liquids has been significantly extended in many areas. They have been utilized as catalysts in many chemical reactions . For example, Deng *et al*. (2001) employed 1-butylpyridinium chloride–aluminium (III) chloride as a green reaction medium in the esterification of alcohols with carboxylic acids. They reported excellent conversion and selectivies of the IL due to the immiscibility of the IL with esters (Deng *et al*., 2001).

Since ILs possess ionic conductivity, they have been employed as novel electrolytes in electrochemical processes and devices such as electric double layer capacitors, dye-sensitized solar cells, lithium secondary batteries and fuel cells (Erdmenger *et al*., 2008; Galiński *et al*., 2006).

Nowadays, ILs are already utilized in polymer science mainly as polymerization media in polymerization processes. However, application of ILs in polymer is not only limited to traditional polymerization solvent but ILs have also been used as the components in the polymeric matrixes such as polymer gels, as electrolytes in conducting polymer-based electrochemical devices as well as templates for porous polymers (Kubisa, 2004; Kubisa, 2009; Lu *et al*., 2009; Tshibangu *et al*., 2011).

On the other hand, the uses of ILs as extractants in LLE have progressively developed. A number of studies revealed that ILs have been successfully used to extract numerous compounds from aqueous or organic solutions. Recent study by Deng *et al.* (2011) reported the use of IL in its magnetised form as an extraction solvent for the separation of various phenolic compounds from aqueous solution. The study showed that magnetic IL demonstrated much higher extraction capacity than the non-functionalized RTILs under the same conditions (Deng *et al*., 2011). Moreover, studies have also been performed to test the ability of imidazolium-based ILs in replacing volatile organic solvents for LLE of selected endocrine-disrupting phenols from aqueous solutions. The effect of alkyl chain length of the ILs' cation as well as the anion effect was also investigated. It was found that the hydrophobic interactions and the hydrogen-bonding between ILs and the phenols are the main mechanism in the separation of phenols from aqueous solution (Fan *et al*., 2008). Furthermore, ILs have also been reported to be used as extractants of bioactive chemicals such as tocopherol homologues. The separation of tocopherols by 1-butyl-3-methylimidazolium chloride ([Bmim][Cl) was achieved via LLE by the hydrogen bonding interaction between the IL's anion and the hydroxyl group on the tocopherols (Yang *et al*., 2009).

In addition, the uses of ILs as an adsorbent in adsorption studies can also be highlighted in which some studies reported the ability of ILs as adsorbents for desulfurization of fuel oil (Huang *et al*., 2004; Khan *et al*., 2014; Liu *et al*., 2008). For instance, Khan *et al.* (2014) synthesized IL supported on metal-organic frameworks (MOFs) as an efficient adsorbent of benzothiophene where a significant improvement in the adsorption capacity was observed with the use of IL. Moreover, the idea of using IL as adsorbent has been extended in the extraction of toxic heavy metals. Ismaiel *et al*. (2013) used IL-modified palm shell activated carbon to extract mercury ions from aqueous solution through a batch-adsorption technique. The method showed a higher removal efficiency of mercury ions due to the presence of functionalized IL on the surface of modified activated carbon (Ismaiel *et al*., 2013). In addition, ILs have also been used as versatile adsorbents to extract organic pollutants from environmental samples. A number of studies displayed the excellent ability of ILs to extract organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and organophosphorus pesticides (OPPs) from aqueous media (Zhang *et al*., 2010; Zheng *et al*., 2014). From these findings, it can be concluded that ILs can be used as a greener and highly effective extractant in liquid–liquid extraction as well as a promising adsorbent in adsorption techniques. The remarkable potential of ILs should then be utilized in LLE and adsorption technique so as to improve the efficiency of these methods in separation study.

2.4 Liquid-liquid extraction

2.4.1 Introduction

Liquid-liquid extraction (LLE) which is also known as solvent extraction is a technique of matter transfer between two liquid phases. The operation involves extracting a desired analyte from a solution by simple dissolution process into another solvent in which the analyte is more soluble (Bendebane *et al*., 2013). In other words, an extraction occurs when the compound has favourable solubility in a particular solvent compared to the initial solvent where it exists (Mitra, 2003). LLE is a well-known technique and can be considered as the most widely used techniques in the preparation of samples in analytical chemistry. There are two bulk liquid phases involve namely the aqueous phase which is usually contains the dissolve analyte and the organic phase. Traditionally, one can perform this technique by agitating the aqueous and organic phases together in a separating funnel to disperse drops of one liquid in the other either by mechanical or manual agitation and then discontinuing agitation to allow drop coalescence and finally separating the bulk liquid phases from one another (Cantwell & Losier, 2002).

The application of LLE is very common in the industry. The typical uses of LLE in industry include separation of high boilers and low concentrated solutes from aqueous solutions (e.g., phenol), separation of systems with similar boiling points (e.g., separation of aromatics from aliphatic hydrocarbons), extraction of metal salts from wastewater (e.g., copper), separation of temperature-sensitive compounds (e.g., acrylates, biotechnology), extraction of organic compounds from salt solutions (e.g., caprolactam) and extraction of salts from polymer solutions (e.g., ketone resins, polyols) (Müller *et al*., 2000).

LLE offers a great deal of benefits which includes that the organic phase itself can be directly subjected to the quantitative analytical instrument such as liquid and gas chromatography after the extraction process. The direct injection of the organic phase into the analytical instrument help us to avoid the unnecessary step such as desorption of the analyte from the extract phase. Thus, it helps to avoid time-consuming procedure. Moreover, the vast information provided in the literature helps us to construct the LLE experiment quite well to improve the performance of other researchers work such as the selection of organic solvent, the type of reagents needed as well as the suitable optimum pH (Cantwell & Losier, 2002). Moreover, liquid-liquid extraction became a favourable method due to its large capacity and easy operation (Jiao *et al*., 2016).

Even though liquid-liquid extraction have been favoured for the past decades, however, LLE also possesses some drawbacks. The continuous use of large amounts of volatile organic solvents (VOCs) as liquid media for extraction process leads to environmental problems. The volatility and flammability of VOCs have drawn attention to the research community due to their harmful effects (Huddleston *et al*., 2001).

Moreover, the end result of using VOCs could generate contaminated solvents together with the problems associated to their disposal (Vidal *et al*., 2005). Apart from that, traditional VOCs are difficult to be recycled and thus, lead to higher consumption in separation works and eventually causing pressure in terms of cost perspective (Liu *et al*., 2015).

LLE is a progressively promising method in extracting phenols because it exhibits large capacity and easy accessibility. However, the recyclability and selectivity of the extraction agents has become the constraint (Jiao *et al*., 2015c). Thus, in order to avoid the reliance on flammable and toxic VOCs, the exploitation of a greener replacement is essential to be the best extraction agent. The employment of ILs as extractants in LLE could be an important alternative to diminish the environmental problems associated with VOCs as well as to improve the selectivity towards the specific analytes due to the intriguing properties of ILs as mentioned before.

2.4.2 The application of ILs as extractants in phenol separation

As reported in the literatures, ILs are very valuable in liquid-liquid extraction due to their undetectable vapour pressure (Liu *et al*., 2005a). Thus, ILs have been the choice as extracting agents in enormous number of studies because of their ability to promote environmentally benign separation processes in the development of extraction technology (Han & Row, 2010).

Recently, there has been a growing interest in manipulating ILs and other types of salts for the removal of phenolic compounds from oil. Hou *et al*. (2013) studied several imidazolium-based ILs with different cationic alkyl chain length to separate phenol from hexane model oil. The study proved that imidazolium IL with shorter alkyl chain length in particularly [Bmim][Cl] extracted phenol with a higher efficiency compared to its longer alkyl counterparts. The anions effect was also studied and the extraction efficiency using Cl^- surpassed Br^-, BF_4^-, and PF_6^- due to the higher electronegativity of Cl^- (Hou *et al*., 2013). Moreover, after the separation, the phenol could be recovered at 150 °C by evaporation and the restored ILs could be reused for four cycles with the same phenol extraction efficiency.

In addition, there is also an interesting study of phenols separation by other group of ILs instead of imidazolium-based ILs. Meng *et al*. (2013) synthesized six ethanolammonium-based ILs and subsequently studied their efficiencies to separate phenol and *o*-cresol from model coal tar of hexane and toluene. The study suggested that phenolic compounds in low temperature coal tar may be extracted by the protonated alcoholic amines ILs at ambient temperature with good recyclability even though the thermal stability of these ILs is not so high which is in the range of 140 °C - 180 °C considering their overall performance and cost (Meng *et al*., 2013).

The use of ILs as extractants has also been extended by using trimethylamine-based dicationic ILs to extract phenolic compounds from model oil. Interestingly, the study highlighted the high thermal stability of dicationic ILs which is between 215 °C - 260 °C and showed an excellent extraction ability of phenols. Moreover, a fast equilibrium time of only 5 minutes at room temperature could be achieved successfully. Under optimal conditions, the extraction performance was efficient even when applied in the real coal tar oil. The study succeeded to prove that dicationic ILs could extract phenols via the formation of hydrogen bonds as revealed by FT-IR analysis (Ji *et al*., 2018b).

An effort has also been performed to extract phenols by using imidazolium-based dicationic ILs. Ji *et al*. (2017) demonstrated the phenol separation from oil mixtures by three type of ILs. The authors claimed that the ILs can be used as extractants to replace traditional methods where there is no strong alkali or acid being used and consequently preventing the production of wastewater. In addition, they agreed with the unique properties of ILs such as non-volatile and high stability as well as the ability to be reused several times (Ji *et al*., 2017).

From the excellent study of ILs as extractants in phenol separation, it can be concluded that ILs have a very remarkable ability compared to other VOCs. Their low-volatility, with the ease of handling and high extraction ability for the solute have superseded their counterparts as novel reaction media in separation studies (Tokuda *et al*., 2004). Thus, it is the interest of this research to extend the study of phenol separation from oil by exploring the role of double bonds and benzyl groups on imidazolium-based ILs. The presence of these aryl and alkenyl chains on ILs structure could enhanced the ability of ILs to interact with benzene ring of phenols via strengthened π-π interactions. By considering the idea of this non-covalent interaction and the existing hydrogen bonding between phenols and ILs, it is expected that the synthesized benzyl imidazolium-based ILs could offer excellent extraction separation of phenols from the model oil.

2.5 Adsorption

2.5.1 Introduction

Adsorption technique is one of the technique extensively used in separation study in which the solute or analyte molecules known as adsorbate from the solution comes into contact with a solid which has a highly porous surface structure (adsorbent) and finally accumulating the surface of the adsorbent bound by physical or chemical interactions (Rashed, 2013). It is generally considered as a promising method in equilibrium separation process due to the ease of operation and does not produce harmful substances (Rafatullah *et al*., 2010). Adsorption process is strongly affected by the chemistry and surface morphology of the adsorbent (Senturk *et al*., 2009). Therefore, the selection of suitable adsorbents is fundamental. The selection depends on the analyte characteristics, the sample matrix and the analytical method (Żwir-Ferenc & Biziuk, 2006). Moreover, a good adsorbent should have strong affinity and high loading capacity.

2.5.2 Adsorbent

Adsorbents are the solid substances that collect and retain the solutes on their surface in an adsorption process. They can be classified into two groups; mainly natural adsorbents and synthetic adsorbents (Rashed, 2013). They may consists of natural materials such as zeolites, chitosan, clay or several waste products from industrial such as fly ash, oxides, red mud and sludge (Ahmaruzzaman, 2008). The appropriate choice of adsorbent is crucial in order to have an efficient adsorption process. The adsorbent should therefore meet certain criteria such as able to adsorb rapidly as well as high and reproducible percentage of the analytes. Adsorbents should also be porous with large surface areas. In addition, the solutes must be easily and completely eluted from the solid particles. They must be free from leachable impurities and exhibit stability toward the sample matrix. Finally, they should also have good surface contact with the sample solution, recyclable and economically feasible (Mitra, 2003).

A few type of adsorbents have been used for separation of phenol such as activated carbon, red mud and rubber seed coat (Senturk *et al.*, 2009). Among the vast kind of adsorbents available, silica-based adsorbents have attracted the attention in separation and extraction of numerous types of compounds due to their resistance to swelling and shrinking of the silica support compared to unmodified natural adsorbents. Moreover, they possess excellent thermal stability and higher removal efficiency (Liu *et al.*, 2010). Due to these features, it is of the interest of this research to explore the ability of silica-based materials to extract phenols from oil.

2.5.3 Silica-titania mixed oxide

One of the available adsorbents in separation studies are silica-titania mixed oxide, SiO_2-TiO_2 (Si-Ti) composites. Silica has been widely used as a host material for titania in many applications due to its ability to accommodate TiO_2 within its matrix. Furthermore, its availability, affordability and chemical stability has been favoured among the research community (Wu *et al*., 2014). However, as compared to silica, titania has been used extensively in separation science due to its greater mechanical strength and pH stability (Miskam *et al*., 2013). Titania has been used as a component in liquid solar cells, advanced photocatalysis and electroluminescent hybrid devices.

Thus, realising that by exploiting the good properties of both silica and titania could produce the best properties of composites, a growing number of studies has started to blend them into composites (Hilonga *et al*., 2009). SiO_2-TiO_2 mixed oxides are commonly used as catalysts, selective adsorbents, thin film coatings and photocatalysts (Mikushina *et al*., 2008; Shishmakov *et al*., 2012). The properties of these materials depend on their synthesis method and are affected by their structure, particle size and shape, phase composition, as well as pore size. Generally, compared with pure SiO_2 or TiO_2, SiO_2-TiO_2 mixed oxide composite has an improved mechanical strength, a higher thermal stability, and good dispersibility in resin and solvents (Hilonga *et al*., 2009).

There are many approaches to synthesize Si-Ti composite such as hydrothermal Si-Ti co-precipitation or post-synthetic grafting (Husing *et al*., 2002). However, the most frequently used method is the sol-gel technique because it offers a homogeneous distribution of the components on the atomic level where the nature of the active sites of SiO_2-TiO_2 mixed oxides is determined by the location of titania on the silica gel surface (Mikushina *et al*., 2008).

The sol-gel method has become one of the most popular options to synthesize mixed oxides materials due to its low temperature synthesis scheme. Initially, the sol-gel process is mainly used for the preparation of inorganic materials such as ceramics and glasses (Miskam *et al*., 2013).

A sol is a colloidal suspension of particles, while the term gel refers to the semi-rigid material formed when the colloidal particles link together in a liquid to form a network. The sol-gel precursors usually consist of metals or metalloids surrounded by various ligands, in which the most widely used are metal alkoxides. Aluminates, borates, silicates, and titanates are the examples that can be used to generate a sol-gel. On the other hand, a gel consisting of silica matrices is known as silica gel (Londeree, 2002).

The traditional synthesis of SiO_2-TiO_2 mixed is via the hydrolysis of a mixture of titanium and silicon alkoxides in an aqueous alcohol medium with the presence of an alkali or acid catalyst followed by the controlled drying of the hydrolysis product (Shishmakov *et al*., 2012). The main starting materials usually used in the sol-gel method are tetraethoxysilane (TEOS), titanium isopropoxide (TTIP) and ethanol (EtOH) (Vives & Meunier, 2008). TEOS is less sensitive to hydrolysis than the transition metal alkoxides. Thus, in the case of silicon alkoxides, acid or basic catalysts is used to enhance the hydrolysis and condensation reactions (Vives & Meunier, 2008).

2.5.4 Silica-titania mixed oxide as adsorbents

Silica-titania composites have been used vastly as adsorbents for adsorption of different kinds of compounds. For instance, Uchiyama *et al*. (2005) prepared a new type of photocatalytic adsorbent consisting of nanoscale titania and mesoporous silica for adsorption of acetaldehyde. The material showed rapid adsorption of acetaldehyde due to the high specific surface area of the mesoporous silica (Uchiyama *et al*., 2005).

On the other hand, silica-titania composite has also been applied to remove trace level of mercury from aqueous solutions. The study by Byrne and Mazyck (2009) claimed that the combination of silica and TiO_2 provides a macrosorbent with cation electrostatic attraction to achieve an excellent mercury removal by adsorption. Furthermore, it was suggested that this material is promising and should be established for the treatment of mercury loaded waters such as contaminated ground waters from industrial activity and so on (Byrne & Mazyck, 2009).

The application of silica-titania mesoporous materials as adsorbents have also been extended to the adsorption of dyes. Messina and Schulz (2006) studied the adsorption of two basic dyes, methylene blue and rhodamine B from aqueous solution onto silica-titania. The study revealed that the presence of TiO_2 increased the adsorption capacity due to the degradation of the dye molecule in contact with the TiO_2 particles in the adsorbent interior (Messina & Schulz, 2006).

Likewise, mesoporous titania-silica-phosphonate hybrid materials with different Si/Ti molar ratios have been synthesized to demonstrate their potential as adsorbents for the adsorption of CO_2 and the removal of heavy metal ions in waste water. The incorporation of silica has been claimed to improve the regularity of mesostructure as well as the increase of the specific surface area, pore volume and pore diameter (Lin *et al.*, 2011).

2.5.5 Silica-titania mixed oxide with ionic liquids

In the past few years, the interest of employing ILs in sol-gel methods has grown rapidly for the synthesis of well-defined porous structured materials (Choi *et al.*, 2006). The confinement of ILs in porous matrices helps to prevent the silica-titania skeletons from collapsing into compact mass while simultaneously the network prevents the ILs from flowing away (Singh *et al.*, 2014). Moreover, in the organic/inorganic hybrid adsorbents, the inorganic parts will act as adsorption substrate and provide large surface area. On the other hand, the organic parts will enhance the adsorption and selectivity to the inorganic substrates (Sakai *et al*., 2013).

Dai *et al*. (2000) demonstrated that the synthesis of silica-titania mixed oxide with IL eliminates the risky supercritical drying process and produces stable silica network (Dai *et al*., 2000). Moreover, it is believed that ILs play an important role as a template and eventually producing a high surface area of the composites. This is because in a study led by Marimuthu *et al*. (2014), the IL which is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf_2]) had been confined onto the Si–Ti mixed oxide gel surface and it had comparatively better stability as a template and possessed the ability to control the pore size distribution and overall morphology (Marimuthu *et al*., 2014).

In recent years, ionic liquid-modified silica materials have attracted significant interest as adsorbents. Wang *et al*. (2013) prepared a few imidazole-functionalized silica with variable position of methyl group on imidazolium ring for the adsorption of phenolic compounds from aqueous solutions. The adsorbents showed high adsorption activity and could be regenerated and reused several times by simple washings with hydrochloric acid and water (Wang *et al*., 2013). In addition, IL-functionalized silica materials have also been synthesized and applied for the extraction of organic acids, amines and aldehydes which are important compound families in atmospheric aerosol particles. The presence of sulfonic group and longer alkyl chain in the structure of the adsorbent provides an additional active site for the extraction (Vidal *et al*., 2012). Du *et al*. (2011) synthesized new supported ILs composed of the N-methylimidazolium and quinoline cations for the adsorption of ferulic acid, caffeic acid and salicylic acid. The adsorption efficiency was found to be excellent and superior compared to the traditional adsorbent macroporous resins with the ability to be reused three times (Du *et al*., 2011). It was also reported that imidazolium-based IL-functionalized silica was synthesized by grafting the N-methylimidazolium IL onto silica surface. The adsorbent exhibits high selectivity for 12 types of sulfonylurea herbicides in environmental water and soil samples, suggesting the superiority of the adsorbents in separation study (Fang *et al*., 2010).

Recently, silica-titania mixed oxide with IL has emerged as a highly selective adsorbents for the adsorption of organic pollutants. The latest study involving silica-titania mixed imidazolium-based IL shows that the composite was effectively used as adsorbent towards 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trichlorophenol (2,4,6-TCP) (Ismail *et al*., 2016). Furthermore, an investigation has been carried out to apply this kind of composite for the separation of chlorophenols from water samples prior to their HPLC-UV determination. The study synthesized a novel cyano functionalized silica-titania oxide sol–gel based IL via sol-gel immobilization of cyanopropyltriethoxysilane and benzyl imidazolium IL on the silica-titania mixed oxide surface. They discovered that the adsorption of chlorophenols toward Si-Ti composite was due to various kinds of interactions such as π-π interactions and hydrogen bonding between the anionic/cationic sites (Bakhshaei *et al*., 2016).

By considering the good properties of Si-Ti mixed oxides and the intriguing properties of ILs, it is fascinating to encapsulate ILs into the silica network for an improved surface morphology and better selectivity towards phenols. Upon having a better morphology compared to unmodified silica gel, it is expected that Si-Ti mixed oxides with IL could be applied as adsorbents in the separation of phenol from the oil by displaying the ultimate properties of silica-titania as well as the combination of unique criteria of ILs. From the literature study, there is still no report on the employment of silica-based materials to separate phenol from oil. Therefore, it is of interest of this research to explore these promising materials to separate phenols from model oil by taking into account the stability and porosity of silica-titania solid support as well as the ability of ILs to be a selective material for phenols extraction.

Thus, in this work, the Si-Ti mixed oxide gel adsorbent was synthesized via sol-gel method where [Abzim][Cl] was encapsulated in a silica gel matrix. [Abzim][Cl] was chosen due to its efficiency to remove phenol via LLE compared to the other two ILs. Another IL which is dicationic IL was also synthesized in order to compare their performance in phenols separation. [Dicat-BzIm][Cl] was used due to its greater number of benzyl substituents compared to [Abzim][Cl].

CHAPTER 3: RESEARCH METHODOLOGY

3.1 Chemicals, materials and reagents

The chemicals and reagents used in this research are listed in Table 3.1. All chemicals were used as received without further purification. Ultrapure water was used throughout this research.

Table 3.1: Chemicals and reagents used for synthesis and analysis

Chemical	Grade	Supplier
1-Benzylimidazole	99%	Aldrich
Allyl chloride	98%	Aldrich
1-Vinylimidazole	≥99%	Aldrich
Benzyl chloride	For synthesis	Merck
Acetonitrile (CH_3CN)	For synthesis	Merck
n-Hexane	For liquid chromatography	Merck
n-Heptane	For analysis	Friedemann and Schmidt
Petroleum ether	For analysis	Friedemann and Schmidt
Cyclohexane	For analysis	Fisher Scientific
Crystallized phenol (Ph)	99%	Scharlau
2-Nitrophenol (2-NP)	98%	Sigma-Aldrich
4-Nitrophenol (4-NP)	≥99%	Sigma-Aldrich
2-Chlorophenol (2-CP)	≥99%	Sigma-Aldrich
2,4,6-Trichlorophenol (2,4,6-TCP)	98%	Sigma-Aldrich
2,4-Dinitrophenol (2,4-DNP)	Analytical standard	Sigma-Aldrich
2,4-Dichlorophenol (2,4-DCP)	Analytical standard	Sigma-Aldrich
2,4,6-Trinitrophenol (2,4,6-TNP)	Analytical standard	R&M Chemicals
3-Chlorophenol (3-CP)	Analytical standard	Merck
4-Chlorophenol (4-CP)	Analytical standard	Merck
Toluene	Analytical standard	Merck
Xylene	Analytical standard	Merck
Fluoranthene	Analytical standard	Sigma-Aldrich
Fluorene	Analytical standard	Sigma-Aldrich
Ethyl acetate	For analysis	Merck
Titanium tetraisopropoxide (TTIP)	97%	Sigma-Aldrich
Tetraethoxysilane (TEOS)	98%	Sigma-Aldrich
Hydrochloric acid (HCl)	37%	Fisher Scientific
Ethanol (EtOH)	99.7%	R&M Chemicals
α,α-dichloro-*p*-xylene	98%	Sigma-Aldrich

3.2 Instrumentations

3.2.1 Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared (FT-IR) spectra were recorded by Perkin-Elmer Spectrum 400 FTIR spectrometer (Waltham, MA, USA) at room temperature equipped with a diamond attenuated total reflectance attachment. All spectra were recorded with characteristic peaks in the range of 450–4000 cm^{-1}.

3.2.2 Proton and carbon-13 nuclear magnetic resonance (^{1}H and ^{13}C NMR)

The proton nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR spectra were recorded by JEOL 400 MHz FT-NMR spectrometer (Japan). All the samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference for the calibration of proton chemical shift.

3.2.3 Elemental analysis (CHN analysis and EDX spectroscopy)

Elemental analysis (CHN) were performed using Pelkin-Elmer 2400 Series II Elemental Analyser (US) and Hitachi SU8200 field emission scanning electronic microscope (FESEM) (Tokyo, Japan) equipped with Oxford Instruments XMX1011 energy dispersive X-ray (EDX) spectrometry (Abingdon, UK).

3.2.4 Density measurement

The densities of all products were obtained from automatic density meter Rudolph Research Analytical DDM 2910 (Hackettstown, NJ, USA) at 25 °C.

3.2.5 Viscosity measurement

The viscosities were measured using Anton Paar Physica MCR 301 rheometer (Graz, Austria) at 25 °C.

3.2.6 X-ray Diffraction (XRD)

X-ray diffraction (XRD) patterns were taken using Cu Kα irradiation with a PANalytical Empyrean X-ray diffractometer (Frimley, UK) (voltage, 40 kV; current, 40 mA) in the scanning range of 10º to 90º.

3.2.7 Field emission scanning electron microscopy (FESEM)

The surface morphology of the materials were determined by using Hitachi SU8200 field emission scanning electronic microscope (Tokyo, Japan) equipped with Oxford Instruments XMX1011 energy dispersive X-ray (EDX) spectrometry (Abingdon, UK).

3.2.8 Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were conducted using Perkin Elmer TGA 4000 (Waltham, MA, USA). The samples were heated at a constant rate of 20 ℃/min within the temperature range of 30 ℃ to 900 ℃ under a stream of nitrogen atmosphere.

3.2.9 Brunauer-Emmett-Teller (BET)

The surface area and pore size distribution of the sol-gel hybrid were measured by nitrogen adsorption-desorption isotherms at 77 K in Micromeritics ASAP2020 (USA) using Brunauer-Emmett-Teller (BET) desorption methods.

3.2.10 Ultraviolet-visible (UV-Vis) spectroscopy

Electronic spectra were recorded by UV Visible spectrophotometer Shimadzu UV 265 (Tokyo, Japan) in the range of 200-800 nm using a 1 cm quartz cell.

3.2.11 High performance liquid chromatography (HPLC)

A HPLC system consisting of a Shimadzu (Tokyo, Japan) LC-20AT pump, SPD-M20A diode array detector, SIL-20A HT auto sampler and CTO-10AS VP column oven was used for the separation and quantification of the analytes. The separation of phenols and polyaromatic compounds (PAHs) was conducted using a C-18 reverse phase column

(250 mm x 4.6 mm; particle size 5 μm) hypersil gold, Thermo Science USA. A mobile phase of methanol:water (80:20, v/v) was used at a flow rate of 1.0 mL min^{-1}. The injection volume was 10 μL.

3.3 Synthesis

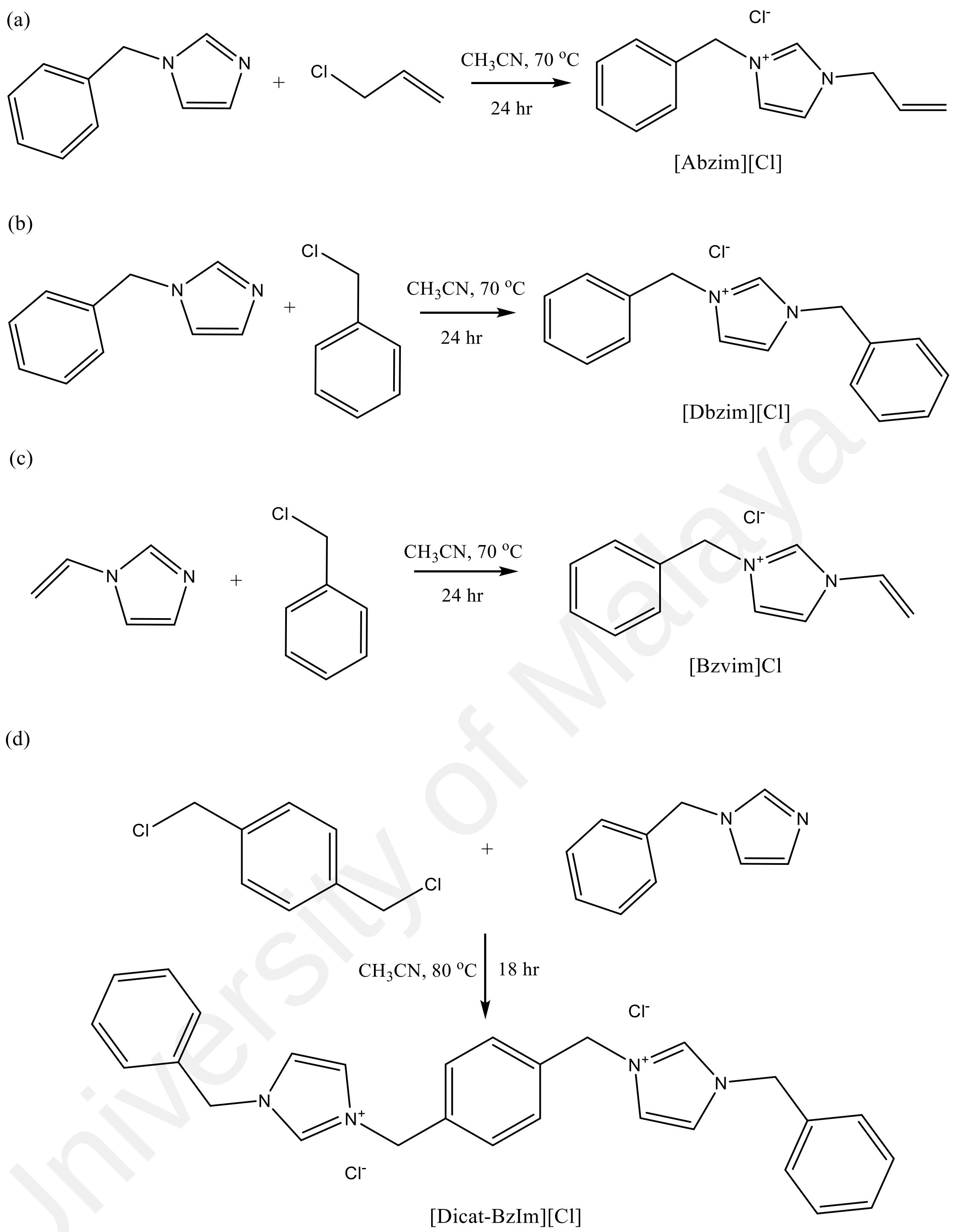
3.3.1 Synthesis of ILs

Allyl chloride (0.10 mol, 7.652 g) was added dropwise over a period of 30 minutes to a round-bottomed flask containing 1-benzylimidazole (0.05 mol, 7.910 g) in 20 mL CH_3CN under continuous stirring. The mixture was then stirred for about 1 hour and subsequently refluxed at 70 °C for 24 hours till light brown liquid forms. Excess reactants and solvent were removed by rotary evaporation. The crude product was then diluted in an appropriate volume of water and washed three times with 15 mL ethyl acetate in a separating funnel. Finally, excess water was removed by rotary evaporation and dried under vacuum at 70 °C overnight to yield [Abzim][Cl].

The same method was used to synthesize [Dbzim][Cl] with 1-benzylimidazole (0.05 mol, 7.910 g) and benzyl chloride (0.10 mol, 12.658 g). On the other hand, 1-vinylimidazole (0.05 mol, 4.706 g) and benzyl chloride (0.10 mol, 12.658 g) were used to synthesize [Bzvim][Cl].

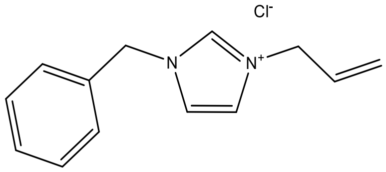
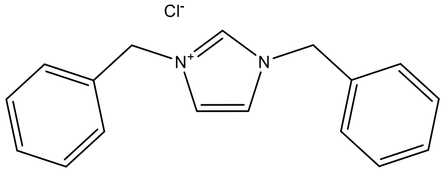
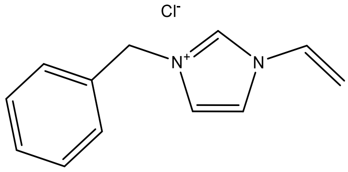
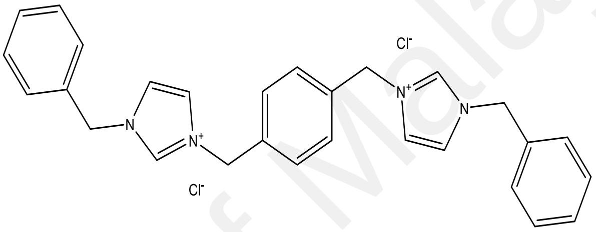
[Dicat-BzIm][Cl]) was prepared by separately reacting α,α-dichloro-*p*-xylene (0.016 mol, 2.801 g) with 1-benzylimidazole (0.033 mol, 5.206 g) in 10 mL CH_3CN at 80 °C for 18 hours under magnetic stirring. The resulting product was then washed repeatedly with ethyl acetate to remove any residues, and then vacuum dried at 80 °C.

All synthesized ILs were stored in a desiccator due to their hygroscopic property. The synthetic route used to prepare the ILs is illustrated in Scheme 3.1. The name and structure for all ILs are tabulated in Table 3.2.



Scheme 3.1: Synthetic route of ILs preparation

Table 3.2: Name and structure of benzyl imidazolium-based ILs

IL	Structure	Abbreviation
1-Allyl-3-benzylimidazolium chloride		[Abzim][Cl]
1,3-Dibenzylimidazolium chloride		[Dbzim][Cl]
1-Benzyl-3-vinylimidazolium chloride		[Bzvim][Cl]
3,3'-(1,4-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) dichloride		[Dicat-BzIm][Cl]

3.3.2 Synthesis of Si-Ti-ILs

The Si-Ti-ILs were synthesized according to the literature with some modifications (Marimuthu *et al.*, 2014). The molar ratio of TEOS:EtOH:HCl:TTIP for the preparation of Si-Ti-AbzImCl was 1:8:0.05:1. Firstly, TEOS was partially hydrolyzed in EtOH with the presence of 0.1 M aqueous HCl for about 1 hour of stirring. Then, the solution of TTIP in EtOH (TTIP:EtOH = 1:20 molar ratio) was added into the reaction mixture and a clear aqueous sol was obtained after 30 minutes under vigorous stirring. [Abzim][Cl] was then added into the sol. The reaction was stirred for another 30 minutes until a homogeneous mixture appeared. The weight percentage of [Abzim][Cl] to TEOS was varied such as 25 wt%, 50 wt% 75 wt% and 100 wt%. After that, the sols were left for 24 hour at room temperature and subsequently dried in an oven at 80 °C to remove the solvents used. The dried gel was finally grounded into powder using mortar and pestle. Si-Ti-DicatBzImCl was prepared using the same method by using [Dicat-BzIm][Cl] as the precursor. The unmodified Si-Ti mixed oxide was also prepared as a reference material.

3.4 Liquid-liquid extraction of phenols by ILs

3.4.1 Solubility study of IL in model oil

A preliminary study was carried out in order to investigate the solubility of IL in the model oil. A specific amount of IL was charged in a capped glass vial and then pure hexane was added to the IL. Figure 3.1 shows the two immiscible phases of [Abzim][Cl] and the model oil. The IL forms the bottom layer while the model oil forms the top layer. The vial was then placed in a shaker at room temperature. The vial was shaken for 30 minutes and then allowed to settle. The upper hexane layer was decanted and analyzed by UV-Vis spectroscopy and ^{1}H NMR spectroscopy. For UV-Vis analysis, pure IL was dissolved in water to a concentration of 0.10 g/L and its spectrum was then recorded. The spectrum of final hexane phase was also recorded. For ^{1}H NMR analysis, pure hexane and final hexane phase were dissolved in $CDCl_3$ while the ionic liquid phase after extraction was dissolved in DMSO-d_6. Their NMR spectra were recorded and analyzed accordingly.

Figure 3.1: Golden brown [Abzim][Cl] at the bottom while colourless model oil on the top

In order to indicate the solubility data of IL in hexane and toluene, a quantitative analysis was also conducted where [Abzim][Cl] underwent the LLE. The procedure involved the mixing of 0.1 mL [Abzim][Cl] with 4 mL hexane under the optimized conditions. The calibration curve in Figure 3.2 was set up by preparing various concentrations of standard solution of [Abzim][Cl] in water. A standard solution of [Abzim][Cl]with a concentration of 500 ppm was also prepared as a reference. After the LLE procedure, the hexane layer was decanted out and the [Abzim][Cl] layer was diluted with water until its concentration reached 500 ppm. This sample was then analyzed by UV-Vis spectrophotometer where the maximum absorption of [Abzim][Cl] appeared at wavelength, λ = 256 nm. The sample was prepared in triplicate. The solubilities of [Abzim][Cl] in hexane and toluene were determined by the difference of absorbance between the reference sample and the [Abzim][Cl] sample after extraction.

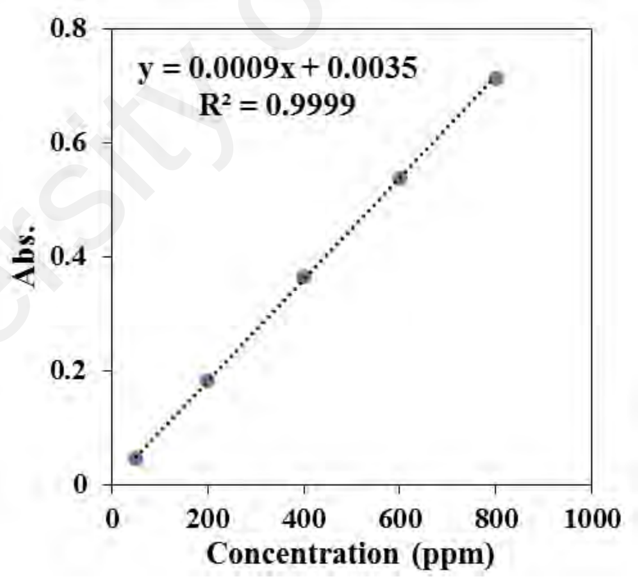


Figure 3.2: Calibration curve for various [Abzim][Cl] standard solutions

3.4.2 Preparation of model oil and synthetic oil

Each phenolic compound as well as xylene and toluene was dissolved in hexane to obtain a standard stock solution with a concentration of 100 ppm. All stock solutions were stored in the refrigerator. Working solutions were prepared daily by diluting the standard stock solutions with hexane.

In order to study the extractive performance of the ionic liquid in real samples, synthetic oil was prepared to simulate real oil (Erdmann *et al*., 1996). In this study, 2,4-DCP, 2,4-DNP and phenol were chosen as representatives for phenolic compounds while two types of polyaromatic hydrocarbons (PAHs), fluorene and fluoranthene were chosen to represent the aromatic compounds. 50 ppm of 2,4-DCP, 2 ppm of 2,4-DNP, 5 ppm of phenol, 0.5 ppm of fluorene and 1 ppm of fluoranthene were completely dissolved in hexane and then diluted to 25 mL in a volumetric flask. Concentrations of PAHs and phenols were varied accordingly to resemble their different compositions in real oil.

3.4.3 Separation process in model oil

First, 0.05 mL of IL was charged in a tightly sealed vial and 4.0 mL of model oil with phenol (Ph) concentration of 5 ppm was added to the IL. The vial was then placed on a shaker (180 rpm) at room temperature. After shaking for 30 minutes and allowing it to settle, the upper hexane layer was decanted and the phenol content was analyzed by UV-Vis spectroscopy. Concentrations of the phenol in hexane before and after the extraction were determined by UV-Vis spectrophotometer in which maximum absorption of phenol in hexane appeared at wavelength, $\lambda_{max} = 271$ nm. In order to determine the concentration of phenol, various concentrations of standard solution of phenol were prepared and measured to obtain a calibration curve. Removal efficiency was calculated by using Equation 3.1 as shown below:

$$\% Removal = \frac{C_o - C_f}{C_o} \times 100\% \qquad \textbf{Equation 3.1}$$

where C_o and C_f represents the phenol concentration in the original model oil and the upper layer after reaction respectively. Seven parameters were studied in order to perform better extractions:

(a) *Effect of structure of ILs*

The effect of structure of ILs was studied at room temperature by varying the cations with different substituents (vinyl, allyl and benzyl). The phenol concentration was fixed at 5 ppm in 4 mL of model oil with ILs volume of 0.05 mL. The IL with the best performance was used in the succeeding optimization procedure.

(b) *Effect of phase volume ratio of model oil to IL*

The volume ratio between the model oil and IL was varied at different intervals such as 20, 40, 80, 120, 160, 200, 320 and 500. The meaning of volume ratio = 20 is in which the volume of model oil used is 4 mL while the amount of IL is 0.2 mL. The phenol concentration was fixed at 5 ppm in 4 mL of model oil with [Abzim][Cl] volume of 0.1 mL.

(c) *Effect of contact time*

The effect of contact time was studied at different time intervals from 10, 20, 30, 40, 50 to 60 minutes with 5 ppm phenol concentration in 4 mL of model oil with [Abzim][Cl] volume of 0.1 mL.

(d) *Effect of temperature*

The effect of temperature on the phenol removal efficiency was studied comprehensively at temperatures 25 °C, 30 °C, 40 °C, 50 °C and 60 °C for 30 minutes. The phenol concentration was fixed at 5 ppm in 4 mL of model oil with [Abzim][Cl] volume of 0.1 mL.

(e) *Type of model oils*

The type of model oil was varied by using petroleum ether, cyclohexane and heptane. The phase volume ratio of model oil to [Abzim][Cl] was fixed at 40 and conducted at 25 °C for 30 minutes.

(f) *Selectivity study*

Different phenolic compounds consisting of nitro- and chloro- substituents such as 2-CP, 3-CP, 4-CP, 2,4-DCP, 2,4,6-TCP, 2-NP, 4-NP, 2,4-DNP and 2,4,6-TNP as well as two aromatic compounds such as xylene and toluene were used as analytes in investigating the influence of various phenol substituents on the removal efficiency of IL. The phase volume ratio of model oil to [Abzim][Cl] was fixed at 40 and carried out at 25 °C for 30 minutes with the maximum absorption of each analytes was measured individually by UV-Vis spectrophotometry as shown in Table 3.3.

Table 3.3: Wavelength of phenols and aromatic compounds measured by UV-Vis

Compound	Wavelength (nm)
2-NP	270
4-NP	284
2,4-DNP	256
2,4,6-TNP	229
2-CP	281
3-CP	274
4-CP	224
2,4-DCP	284
2,4,6-TCP	296
Toluene	262
Xylene	274

(g) *Recyclability study*

The recyclability of [Abzim][Cl] was investigated by recovering it after the first extraction and then reused for subsequent cycles. Ethyl acetate was used as extraction solvent to recycle IL. The recyclability steps involved the mixing of ethyl acetate with [Abzim][Cl] for 30 minutes on a shaker at room temperature. The ethyl acetate layer was then decanted and the process was repeated three times to ensure the recycled IL is free from impurities. The same processes were repeated for each cycle.

3.4.4 Separation process in synthetic oil

The separation process of phenolic compounds in synthetic oil was performed under optimized conditions. A specific amount of IL and synthetic oil was charged in a capped glass vial. After shaking for a set amount of time and allowing it to settle, the upper synthetic oil layer was decanted and filtered using a PTFE syringe filter (13 mm, 0.22 µm pore size). The filtrate was transferred into a vial and subsequently injected into the HPLC system for analysis. The detection for phenol was found at a retention time of 3.56 min and wavelength of 272 nm; 2,4-DCP at 4.37 min and 286 nm; fluorene at 6.91 min and 262 nm ; fluoranthene at 8.34 min and 286 nm; and 2,4-DNP at 9.37 min and 267 nm. The % removal of phenolic compounds was determined by the difference in chromatograms peak area of the synthetic oil before and after extraction.

3.5 Adsorption study of phenol by Si-Ti-ILs

Sorption experiments were carried out by the following batch method: in each experiment 20 mg of 25 wt%, 50 wt%, 75 wt% and 100 wt% Si-Ti-AbzImCl were mixed individually with 10 mL of model oil with a phenol concentration of 10 ppm in a tightly sealed vial. The vials were shaken mechanically (180 rpm) at room temperature. After shaking for 30 minutes and allowing it to settle the adsorbent was separated by filtration and the residual concentration was determined by UV-Vis spectroscopy at λ_{max} at 271 nm. The process was repeated for Si-Ti-DicatBzimCl (25 wt%, 50 wt%, 75 wt% and 100 wt%) and unmodified Si-Ti mixed oxide as a reference material.

CHAPTER 4: LIQUID-LIQUID EXTRACTION OF PHENOL BY IONIC LIQUIDS

4.1 Yield of product and general characterization

In this work, a series of benzyl imidazolium-based ILs with different benzyl and double bond substituents have been prepared by a facile method. The synthesis involved the quaternization of imidazole (vinyl imidazole and benzyl imidazole) precursors to alkyl halide (benzyl chloride and allyl chloride). They were analyzed with respect to the influence of the various substituents on the ILs structure. The molecular weight (g mol^{-1}), yield (%) and the appearance of the three ILs are tabulated in Table 4.1.

Table 4.1: Molecular weight, yield and appearance of benzyl imidazolium-based ILs

RTIL	Molecular weight (g mol^{-1})	Yield (%)	Appearance
[Abzim][Cl]	234.73	97.29	Light golden brown liquid
[Dbzim][Cl]	284.79	98.15	Pale yellow viscous liquid
[Bzvim][Cl]	220.70	98.17	Dark brown viscous liquid

All the ILs were successfully synthesized with an excellent yield of approximately 98%. [Abzim][Cl] appeared as a light golden brown-coloured liquid at room temperature while [Dbzim][Cl] existed as a pale yellow-coloured liquid and [Bzvim][Cl] showed a darker brown-coloured liquid.

The solubility of these ILs in polar and non-polar solvents were also investigated. These ILs are very miscible in water and other polar solvents, whereas they are immiscible in non-polar solvents. This behaviour may be attributed by their polar protonated imidazolium rings as well as their hydrophilic chloride anions (Cl$^-$). The solubility of the ILs in common solvents is shown in Table 4.2.

Table 4.2: Solubility of benzyl imidazolium-based RTILs in polar and non-polar solvents

Solvent	Polarity	RTIL		
		[Abzim][Cl]	[Dbzim][Cl]	[Bzvim][Cl]
Water Methanol Dimethyl sulfoxide	Polar	Miscible	Miscible	Miscible
Hexane Toluene Xylene Chloroform Cyclohexane Petroleum ether	Non-polar	Immiscible	Immiscible	Immiscible

4.2 Characterization of benzyl imidazolium-based ILs

The three benzyl imidazolium-based ILs were characterized using various analytical instruments namely ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, FT-IR spectroscopy, CHN elemental analysis, and TGA analysis. Their physicochemical properties such as density and viscosity were also measured at room temperature.

4.2.1 ^{1}H NMR spectroscopy

The synthesized ILs were firstly characterized by using ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopy is a powerful tool to evaluate the chemical composition of those synthesized ILs (Weingärtner, 2013). Figure 4.1 shows the ^{1}H NMR spectrum of [Abzim][Cl]. There are 8 signals of unsymmetrical hydrogen from a total number of 15 hydrogen atoms. Three important signals related to the imidazolium ring protons of H5, H4 and H2 were observed at 7.78 ppm, 7.90 ppm, and 9.55 ppm respectively. In the aliphatic region, a doublet at 4.87 ppm was observed due to the presence of methylene hydrogens of the allylic moiety. The two allylic protons labelled as H15 were resonated as a doublet of doublet at around 5.26 ppm to 5.35 ppm. The other allylic proton labelled as H14 was found resonated at δ 6.04 ppm as a multiplet due to the splitting from the neighbouring protons of H15 and H13. The singlet peak appeared at δ 5.48 ppm was attributed to the hydrogen of methylene group attached between the phenylene ring and the imidazolium ring. As for the aromatic protons, their signals were apparently observed at downfield region of 7.34 ppm to 7.46 ppm as a multiplet.

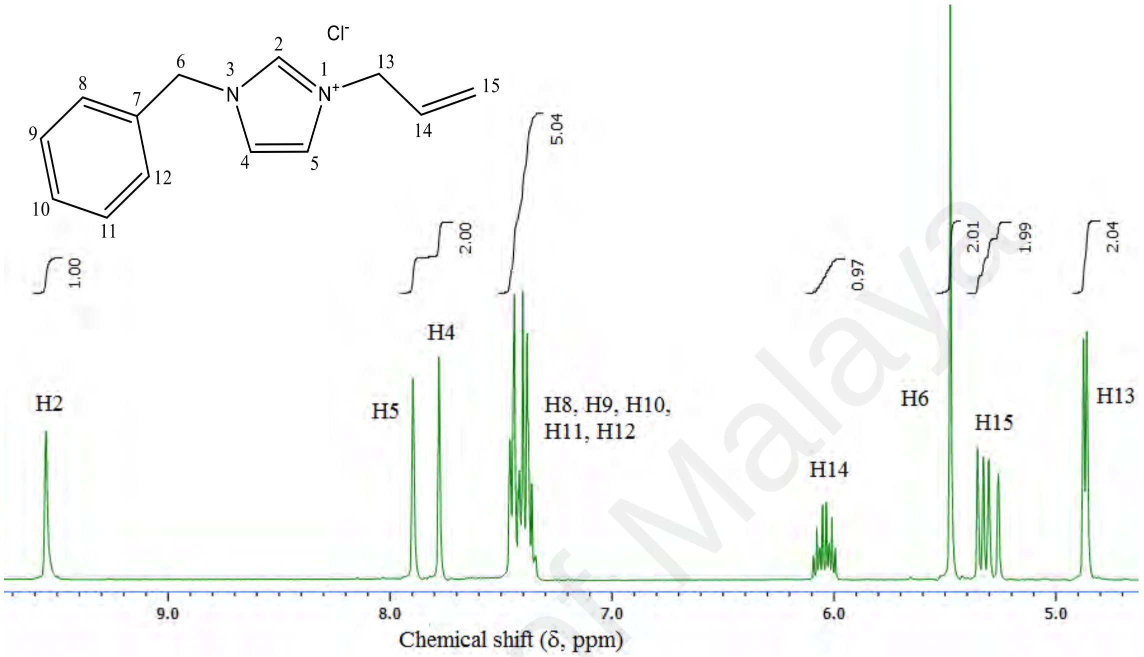


Figure 4.1: ^{1}H NMR spectrum of [Abzim][Cl]

On the other hand, the NMR spectrum of [Dbzim][Cl] in Figure 4.2 shows only 4 peaks of unsymmetrical proton atoms. This is due to the fact that the IL itself is a symmetric compound and thus, showed only 4 peaks where some of the protons existed in the same chemical environment. As for example, proton H6 and H13 are chemically equivalent. Therefore, they exhibited the same chemical shift and hence, appeared at a single value of δ.

According to the spectrum, only one singlet peak was observed at the aliphatic region which belonged to the methylene hydrogens H6 and H13 attached to the benzyl rings at 5.43 ppm. The chemical shift at around 7.32 ppm to 7.42 ppm was due to the aromatic protons. Lastly, the singlet peaks at 7.85 ppm and 9.64 ppm were corresponded to the H4 / H5 and H2 protons on the imidazolium ring respectively. It should be noted that the integral value for all the protons except for proton H2 was doubled due to the symmetric structure of the IL.

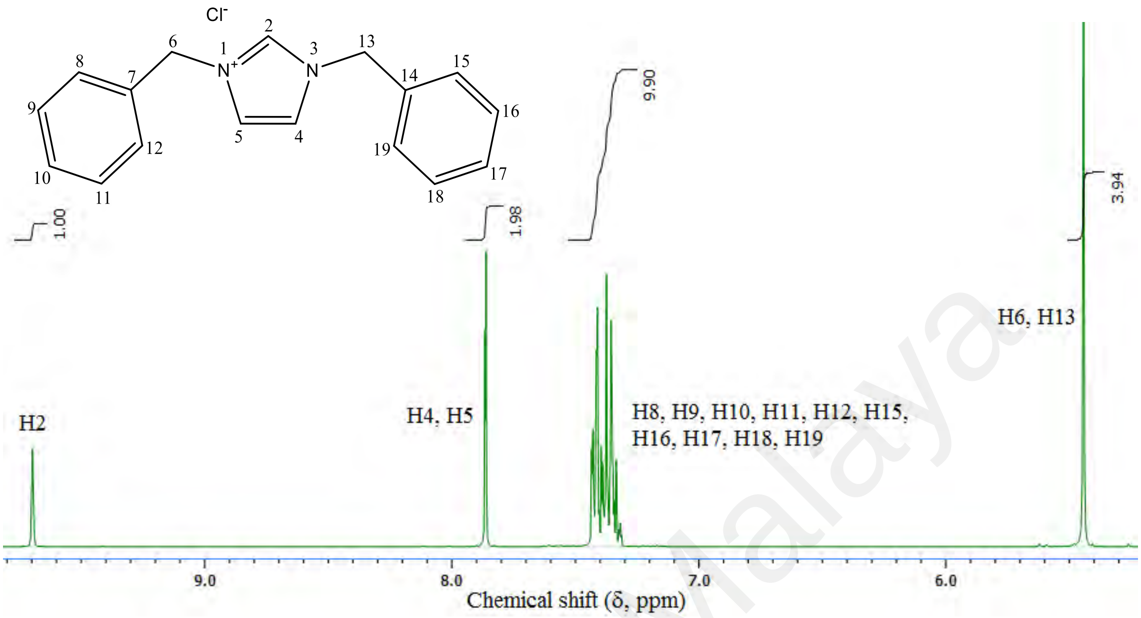


Figure 4.2: ^{1}H NMR spectrum of [Dbzim][Cl]

The ^{1}H NMR spectrum of [Bzvim][Cl] in Figure 4.3 recorded 8 signals of unsymmetrical protons. Two sets of doublet of doublets peak were observed at 5.36 ppm to 5.38 ppm and 5.97 ppm to 6.00 ppm due to the vinylic hydrogen atoms labelled as H7. Another vinyl proton; H6 resonated at a higher chemical shift of 7.31 ppm also as a set of doublet of doublets due to the splitting from the neighbouring allylic protons. The signal appeared as a singlet peak at 5.47 ppm was due to the methylene protons of benzyl ring. Aromatic protons were found to resonate at around 7.35 ppm to 7.47 ppm while imidazolium protons labelled as H4, H5 and H2 appeared at 7.97 ppm, 8.26 ppm and 9.92 ppm respectively.

It is also important to note that the chemical shift of proton H2 for all the ILs was observed at a more downfield region compared to H4 and H5. The presence of chloride causes a downfield shift for the H2 proton signal (Seddon *et al.*, 2000). This is due to the existence of a significant interionic force mainly a hydrogen bond between the proton H2 and the chloride anion (Cl^-) compared to the other two protons (Dong *et al*., 2006; Remsing *et al*., 2007; Wulf *et al*., 2007). The interaction between proton H2 with Cl^- will be further discussed in the next sub chapter. The complete ^1H NMR spectral data of the three ILs was tabulated in Table 4.3.

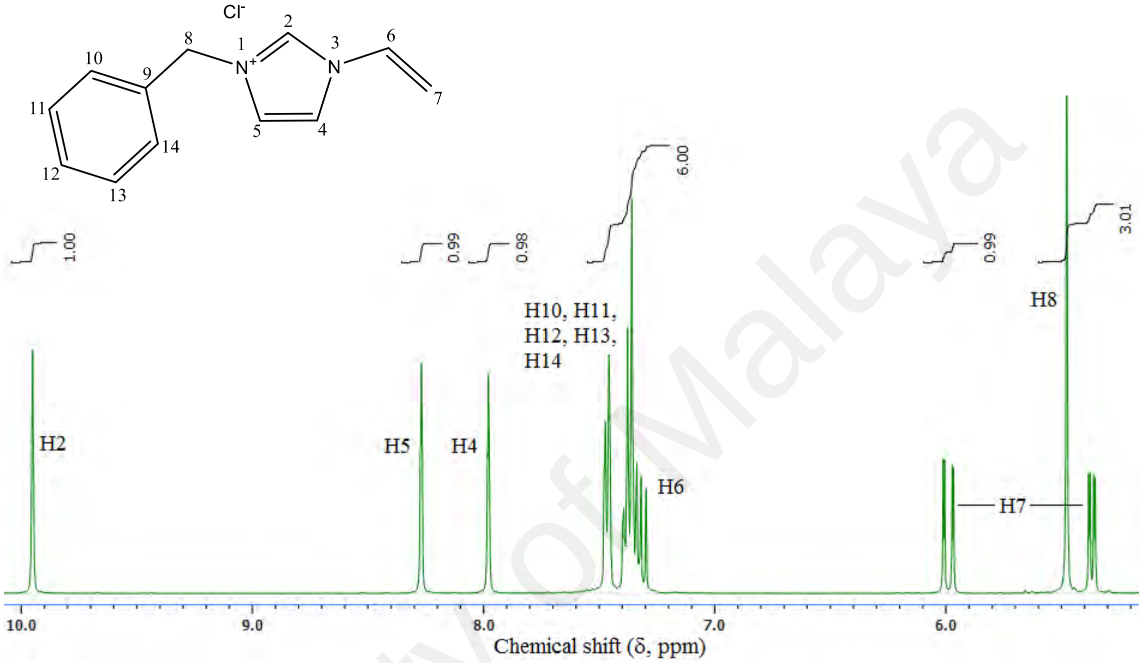


Figure 4.3: ^1H NMR spectrum of [Bzvim][Cl]

Table 4.3: Chemical shift (δ, ppm) of ILs

IL	Proton	Chemical shift (δ, ppm)	Multiplicity
[Abzim][Cl]	H2	9.55	Singlet
	H4	7.90	Singlet
	H5	7.78	Singlet
	H6	5.48	Singlet
	H7 - H12	7.34 - 7.46	Multiplet
	H13	4.87	Doublet
	H14	6.04	Multiplet
	H15	5.26 - 5.35 (J_{H-H} = 10.25 Hz, 17.08 Hz)	Doublet of doublets
[Dbzim][Cl]	H2	9.64	Singlet
	H4, H5	7.85	Singlet
	H6, H13	5.43	Singlet
	H8 - H12, H15 - H19	7.32 - 7.42	Multiplet
[Bzvim][Cl]	H2	9.92	Singlet
	H4	7.97	Singlet
	H5	8.26	Singlet
	H6	7.31 (J_{H-H} = 8.70 Hz, 16.03 Hz)	Doublet of doublets
	H7	5.36 - 5.38, 5.97 - 6.00 (J_{H-H} = 2.75 Hz, 8.70 Hz, 2.29 Hz, 15.57 Hz)	Doublet of doublets
	H8	5.47	Singlet
	H10 – H14	7.35 - 7.47	Multiplet

The spectra of all ILs show that the approximate ratios of the integration lines are consistent with the ratios of the number of hydrogen atoms. Furthermore, there are no additional peaks existing in the ^{1}H NMR spectra of all ILs. Based on the spectral data, all the ILs obtained were free from impurities and thus, indicating that all ILs have been synthesized successfully with high purity.

4.2.2 ^{13}C NMR spectroscopy

^{13}C NMR spectroscopy was carried out in order to determine the number of non-equivalent carbon atoms and subsequently help to elucidate the chemical structure of the synthesized ILs in terms of the types of carbon atoms such as methyl, methylene or aromatic carbons. Figure 4.4 shows the ^{13}C NMR spectrum of [Abzim][Cl]. It can be seen that there are 10 non-equivalent carbon peaks from a total of 13 carbon atoms. The signals at 51.48 ppm and 52.35 ppm were due to the methylene carbons (C6, C13) of the allylic side chain and phenylene ring respectively. The allylic carbons C15 and C14 exhibited a greater chemical shift of 120.88 ppm and 123.19 ppm respectively compared to the methylene carbons due to the sp^2 hybridization of the carbons. The aromatic carbons resonated at 123.39 ppm, 128.93 ppm, 129.25 ppm and 129.50 ppm and finally, the imidazolium carbons (C2, C4, C5) found at 132.28 ppm, 135.53 ppm and 136.87 ppm.

On the other hand, the spectrum of [Dbzim][Cl] shows 7 carbon peaks from a total of 17 carbons in Figure 4.5. Two important signals related to the imidazolium ring (C2, C4, C5) were observed at 135.44 ppm and 136.93 ppm. The signals appeared at 123.39 ppm, 128.95 ppm, 129.29 ppm and 129.53 ppm attributable to the aromatic carbons. The methylene carbon (C6, C13) was observed at 52.46 ppm. It is important to note that this IL is symmetric in structure and thus, some carbons share the same chemical shift such as C4 and C5, C6 and C13 as well as the aromatic carbons.

Figure 4.6 shows the spectrum of [Bzvim][Cl] with 10 non-equivalent carbon peaks from a total of 12 carbons. The imidazolium carbons (C2, C4, C5) were detected at 129.51 ppm, 135.07 ppm and 136.17 ppm. The peak at 123.79 ppm, 129.09 ppm, 129.36 ppm and 129.43 ppm were due to the resonance of aromatic carbons. The methylene carbon of the benzyl ring (C8) resonated at 52.63 ppm while the carbon at the vinyl side (C6) appeared at 120.06 ppm. The other vinyl carbon (C7) was found at 109.32 ppm. The complete ^{13}C NMR data was tabulated in Table 4.4.

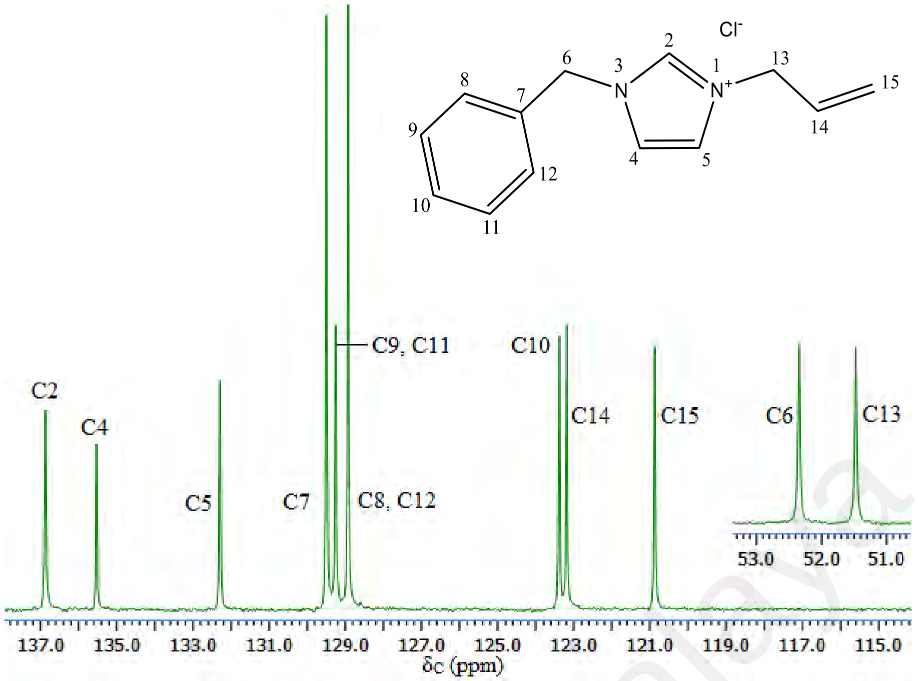


Figure 4.4: ^{13}C NMR spectrum of [Abzim][Cl]

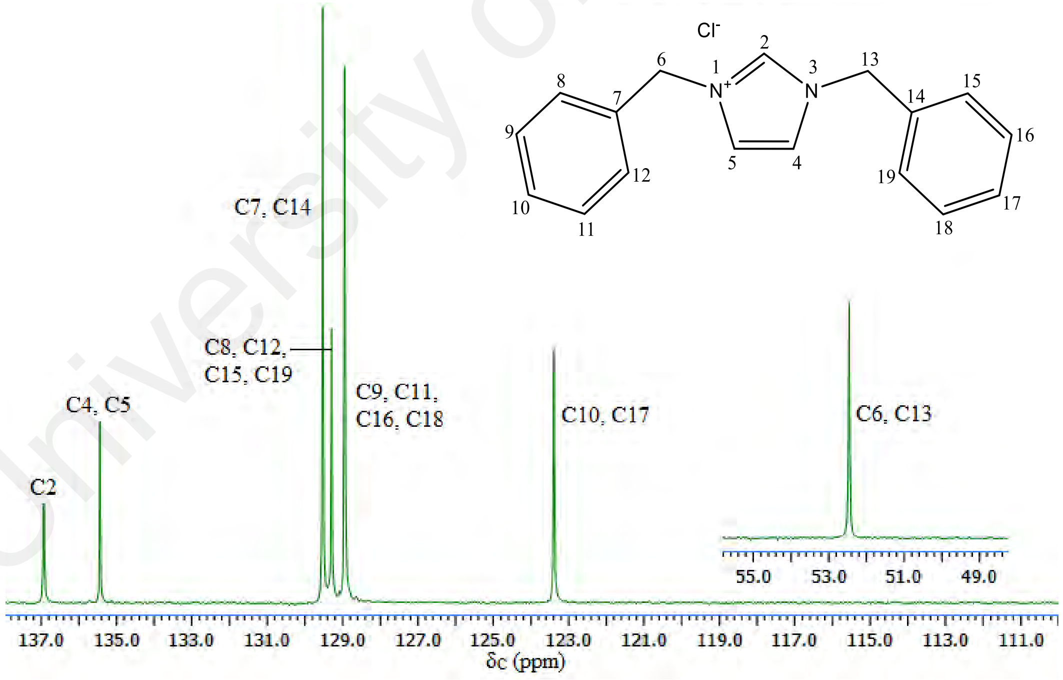


Figure 4.5: ^{13}C NMR spectrum of [Dbzim][Cl]

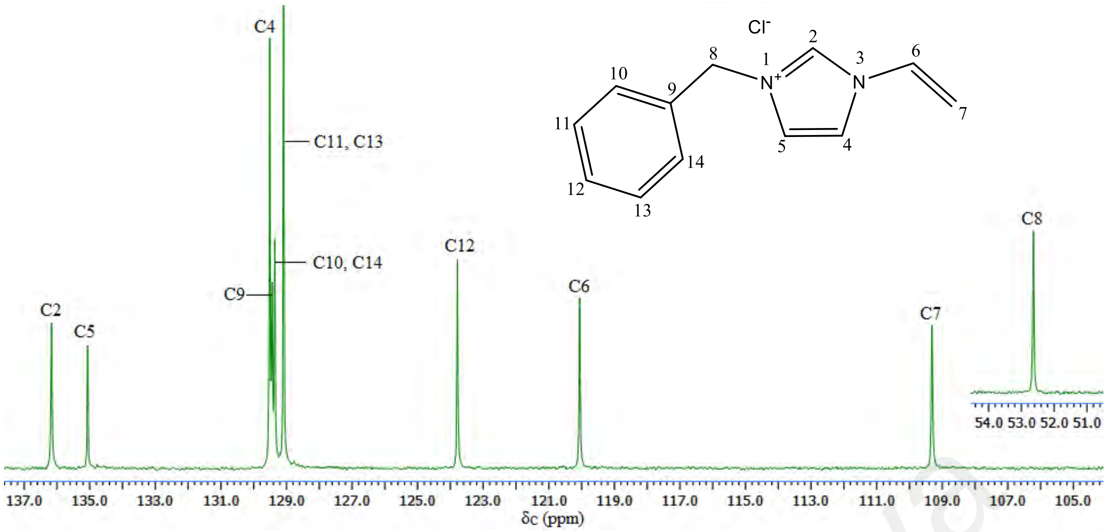


Figure 4.6: ^{13}C NMR spectrum of [Bzvim][Cl]

Table 4.4: Chemical shift (δ_C, ppm) of ILs

IL	Carbon	Chemical shift (δ_C, ppm)
[Abzim][[Cl]	C2	136.87
	C4	135.53
	C5	132.28
	C6	52.35
	C7	129.50
	C9, C11	129.25
	C8, C12	128.93
	C10	123.39
	C13	51.48
	C14	123.19
	C15	120.88
[Dbzim][Cl]	C2	136.93
	C4, C5	135.44
	C6, C13	52.46
	C7, C14	129.53
	C8, C12, C15, C19	129.29
	C9, C11, C16, C18	128.95
	C10, C17	123.39
[Bzvim][Cl]	C2	136.17
	C4	129.51
	C5	135.07
	C6	120.06
	C7	109.32
	C8	52.63
	C9	129.43
	C10, C14	129.36
	C11, C13	129.09
	C12	123.79

4.2.3 FT-IR analysis

In order to further confirm the structure of the synthesized ILs, FT-IR spectra of the ILs were studied. As can be seen in Figure 4.7, the vibrational bands of sp^2 hybridized C-H were observed in the range of above 3000 cm^{-1} for all the ILs. Broad peaks at approximately 3380 cm^{-1} were due to the quaternary amine salt formation (Dharaskar *et al*., 2016). The C=N absorption bands for the imidazolium rings appeared at around 1559-1548 cm^{-1} (Qiao *et al*., 2006; Zheng *et al*., 2014). The stretching bands for aromatic rings usually appear outside the usual range of C=C for alkenes. Thus, the absorption bands at approximately 1497 cm^{-1} were evidence of the C=C ring stretch of the benzyl groups (Qiao *et al*., 2006). The ILs also exhibited significant bands at wavenumber 1450 cm^{-1} which corresponded to the characteristic bending absorption of methylene groups. The intense vibrational frequencies at 1150 cm^{-1} confirmed the presence of C-N stretching. From the analysis, it can be concluded that all the ILs possessed almost identical vibrational bands with the presence of similar functional groups. The significant vibrations of the cations are tabulated in Table 4.5.

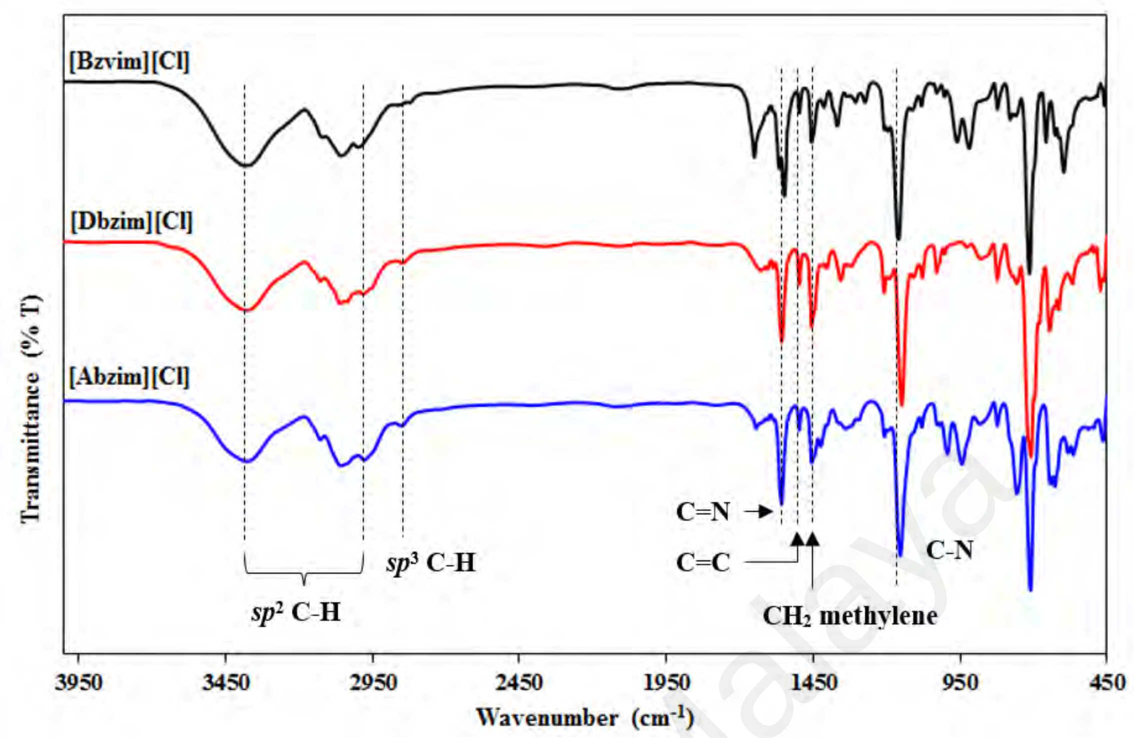


Figure 4.7: FT-IR spectra of ILs

Table 4.5: Characteristic FT-IR bands of ILs

Functional groups	Wavenumber (cm^{-1})		
	[Abzim]Cl	[Dbzim]Cl	[Bzvim]Cl
Quaternary amine	3383	3382	3383
sp^2 C-H (vinyl)	3128	3126	3120
sp^2 C-H (aromatic)	3055	3054	3056
sp^2 C-H (imidazolium ring)	2978	2982	2999
sp^3 C-H	2851	2848	2861
C=N	1559	1557	1548
C=C (aromatic)	1498	1497	1498
CH_2 (methylene)	1452	1455	1454
C-N	1154	1149	1160

4.2.4 CHN elemental analysis

The elemental analysis results for all ILs are tabulated in Table 4.6. It can be seen that the percentage of C, H and N atoms obtained from the analysis were almost accurate with the calculated theoretical percentage. Based on the result, it is concluded that the prepared ILs were successfully synthesized.

Table 4.6: The percentage of C, H, and N of ILs

RTIL	Results	C (%)	H (%)	N (%)
[Abzim][Cl]	Calculated	66.52	6.44	11.93
	Found	65.34	6.87	11.70
[Dbzim][Cl]	Calculated	71.70	6.02	9.84
	Found	69.93	6.41	9.53
[Bzvim][Cl]	Calculated	65.31	5.94	12.69
	Found	64.78	5.45	12.63

4.2.5 Thermal analysis

Thermogravimetric analyses were conducted to determine the thermal stabilities of the ILs. A good thermal stability of the ILs is important for many applications particularly in a harsh environment. As can be seen in Figure 4.8, a three-stage decomposition process was observed in the heating profiles of the ILs except for [Dbzim][Cl]. The first stages of weight loss at temperature around 50 ℃ to 120 ℃ in all the thermograms can be referred as the volatilization of adsorbed water molecules which might be present due to the hygroscopic properties of the ILs. The higher weight loss at temperature 190 ℃ to 400 ℃ was attributed to the degradation process of the organic contents and from this observation, it can be concluded that all these ILs are thermally stable up to approximately 200 ℃. The trend of the decomposition temperature (T_d) follow the order of allyl > benzyl > vinyl as tabulated in Table 4.7. This phenomenon can be explained in terms of the structure of the substituents where [Abzim][Cl] has a longer chain compared to [Bzvim][Cl] and consequently, increasing its T_d. On the other hand, [Dbzim][Cl] has a larger steric hindrance compared to [Abzim][Cl] which contributed to its lower thermal stability (Dou *et al*., 2012). As for [Bzvim][Cl], it has a shorter alkyl length compared to allyl and benzyl substituents which requires less heat energy in order to decompose it completely. This trend was also observed in a previous study by Makhoukhi *et al*. (2016)

workers where the stability of IL improved as the chain length increased (Makhoukhi *et al*., 2016). Lastly, a relatively low weight decomposition at the final stage was due to the thermal degradation of the residue formed during the second stage. The thermograms of all ILs are shown in Figure 4.8 and the thermal decomposition temperatures are tabulated in Table 4.7.

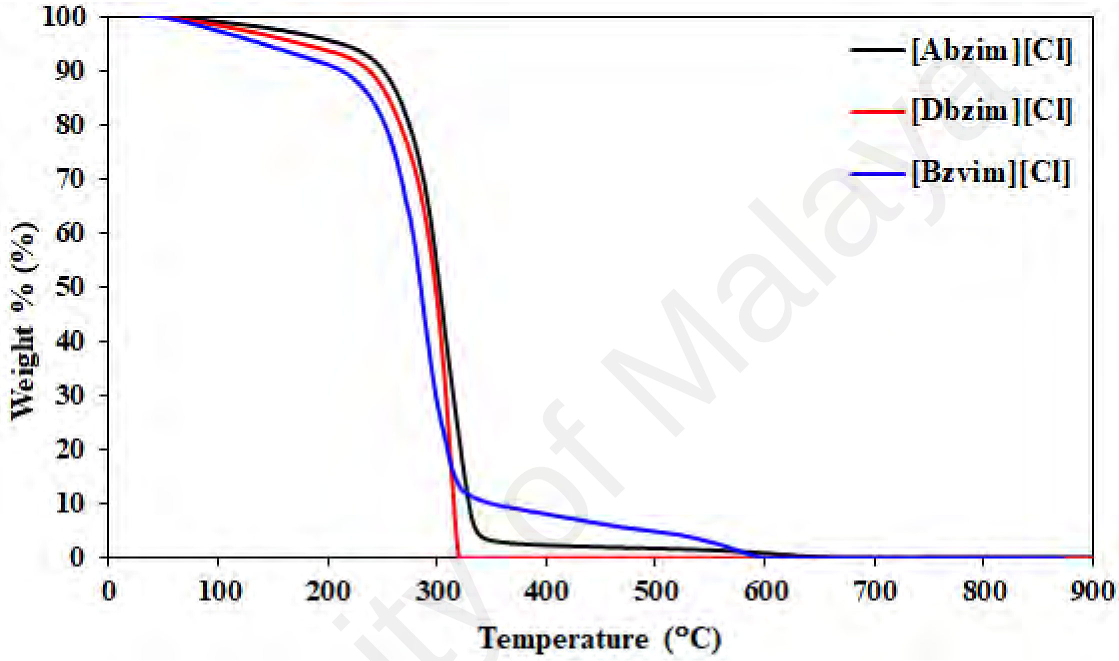


Figure 4.8: TGA curve of ILs

Table 4.7: Thermal decomposition of ILs

ILs	Temperature (°C)	Assignment
[Abzim][Cl]	54.82 – 115.56	Water loss / moisture
	215.69 – 407.69	Decomposition of IL
	543.58 – 683.66	Carbon residue
[Dbzim][Cl]	54.00 – 110.00	Water loss / moisture
	200.04 – 342.00	Decomposition of IL
[Bzvim][Cl]	47.70 – 121.07	Water loss / moisture
	189.71 – 382.14	Decomposition of IL
	382.14 – 696.43	Carbon residue

4.2.6 Density and viscosity measurement

Some physical properties of the ILs particularly their density and viscosity were also investigated. This measurement was done in order to explore the behaviour of their physical properties when different substituents were employed. Viscosity and density are fundamental properties of ILs which is vital to be studied because these properties give a broad information on how the structure of ILs affects the mass transfer rate in liquid-liquid extraction. Moreover, these properties may be adjusted by varying the cation-anion combination depending on the application needed (Santos *et al*., 2014; Tokuda *et al*., 2005). In this study, the cationic structures of ILs were adjusted by changing the alkyl group with benzyl, allyl and vinyl group without tuning the structure of anions.

Generally, ILs are denser than water and other organic solvents (Singh & Kumar, 2008). The density of the ILs are tabulated in Table 4.8 where their densities varied in the range of 1.1578 to 1.1948 g cm^{-3}.

Viscosity is one of the crucial physical properties of ionic liquids. It is important to note that the viscosity for most ILs is higher compared to traditional organic solvents (Yu *et al*., 2012) .Usually, a less viscous IL is favourable to be used as a solvent in order to increase the mass transfer rates (Gardas & Coutinho, 2008). From the result obtained in Table 4.8, it can be seen that IL with two benzyl substituents exhibits the highest viscosity value compared to ILs with only one benzyl. The trend in viscosity follows the order of benzyl > vinyl > allyl. Higher viscosity was observed in [Dbzim]Cl due to the increase in van der Waals interaction between the larger volume of benzyl groups (Dharaskar *et al*., 2013; Shah *et al*., 2015). This is consistent with the previous report where the viscosity of the IL increased when methyl substituent was replaced with benzyl ring (Mahurin *et al*., 2011). On the other hand, [Abzim][Cl] and [Bzvim][Cl] showed an unusual trend where vinyl substituted IL is more viscous than the allyl. This phenomenon might be arising due to the flexibility of the allyl compared to vinyl which help to compensate the van der Waals effect (Yu *et al*., 2012).

Table 4.8: Density and viscosity of ILs at 25 °C

RTILs	Density, ρ (g cm^{-3})	Viscosity, η (Pa.s)
[Abzim][Cl]	1.1578	3.26
[Dbzim][Cl]	1.1871	1395.30
[Bzvim][Cl]	1.1948	39.90

4.3 The application of ILs in liquid-liquid extraction

The synthesized ILs were then applied as an extractant for the removal of phenols from model oil of hexane via liquid-liquid extraction. Existing in liquid form at room temperature, the potential of these ILs has been utilized in this study with the fact that the designation of new ILs with aromatic and double bond moieties could open up a new frontier in the separation studies of phenolic compounds. In this part, the solubility of IL in model oil of hexane and toluene which represent the aliphatic and aromatic compounds respectively will be investigated before further analysis. Then, the optimization study was carried out with several parameters such as the effect of IL substituents, the phase volume ratio of IL and model oil, phase contact time, temperature, and selectivity study.

4.3.1 Solubility study of IL in model oil

The idea behind this study is to use hydrophilic benzyl imidazolium-based ILs as an extractant for the removal of phenolic compounds from model oil. However, there exists a concern where these ILs may have a certain solubility in the model oil and eventually contaminate it. Moreover, the solubility of ILs in the oil may cause the loss of its efficiency as an extractant (Dharaskar *et al*., 2013). This matter suggest that the solubility of benzyl imidazolium-based ILs should be investigated in order to validate the potential mutual solubility between the ILs and oil. Therefore, a preliminary study was carried out to determine the solubility of [Abzim][Cl] in hexane and then was analyzed by UV-Vis analysis and ^{1}H NMR spectroscopy.

For UV-Vis analysis, the absorption of pure IL was used as a reference and compared with the absorption of the final hexane phase. As can be seen in Figure 4.9, the maximum absorption of [Abzim][Cl] appeared at λ_{max} = 256 nm. There was no [Abzim][Cl] absorption found in the final hexane phase after extraction. Thus, it can be concluded that the IL does not contaminate the model oil.

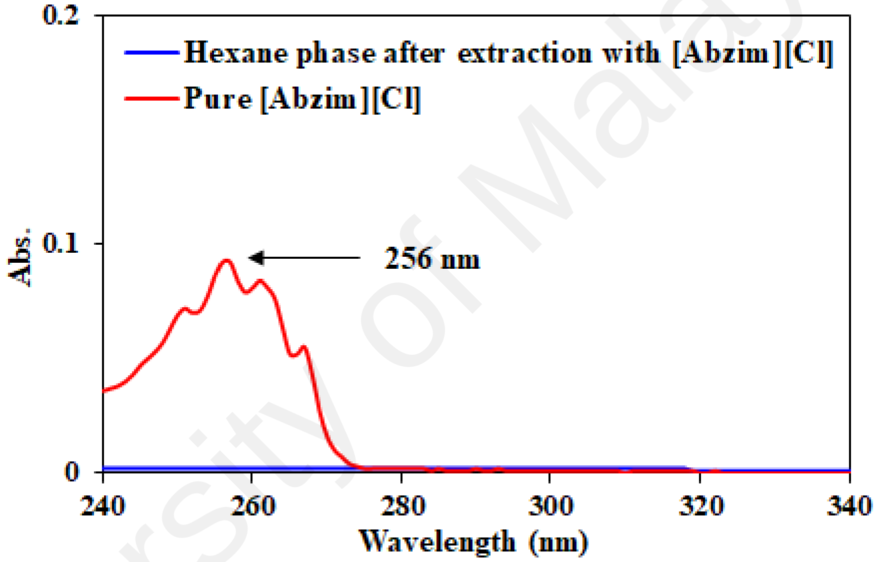


Figure 4.9: UV-Vis spectrum of final hexane phase and pure [Abzim][Cl]

The insolubility of [Abzim][Cl] in hexane was also proved by ^{1}H NMR spectroscopy. Figure 4.10 (a) shows the spectrum of pure hexane as a reference to the spectrum of final hexane phase after extraction in Figure 4.10 (b) which showed no evidence of any IL contamination. The NMR spectrum of [Abzim][Cl] after extraction in Figure 4.10 (c) was also recorded as a reference and there was no hexane chemical shift observed. Thus, it can be concluded that the IL is not soluble in the model oil.

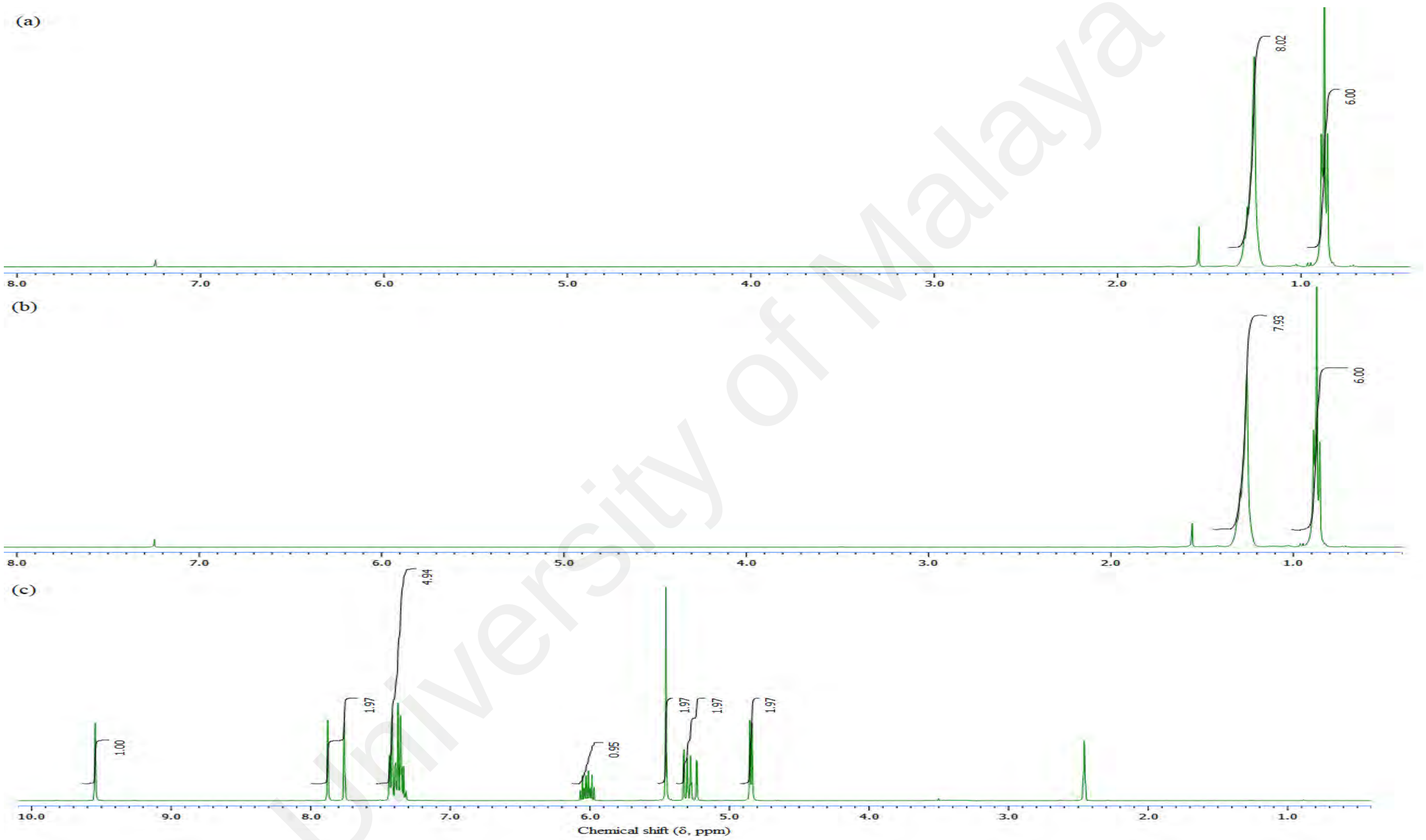


Figure 4.10: ^{1}H NMR spectra of (a) pure hexane phase, (b) final hexane phase and (c) [Abzim][Cl] after extraction

A quantitative analysis was also carried out in order to determine the solubility of [Abzim][Cl] in hexane. It was found that the solubility of [Abzim][Cl] in hexane is (0.0022±0.0001) wt%. This very low figure confirmed that [Abzim][Cl] is very hydrophilic and have no tendency to interact with non-polar solvent.

Apart from the IL contamination in hexane, there is also an arising issue in which aromatic compounds are used as the model oil instead of aliphatic compounds since the IL itself possesses aromaticity in its structure. This is because there are usually some amount of aromatic compounds such as benzene, toluene and xylene exist in the oil that maybe interact with the IL. Thus, the solubility of [Abzim][Cl] in aromatic compounds should also be investigated in order to prove the possibility of IL contamination in aromatic compounds as well. The solubility of [Abzim][Cl] in toluene is (0.0032±0.0004) wt%. The results prove that the solubilities of the IL in hexane and toluene are very low which indicates that the IL has good properties and it is important for its application.

4.3.2 Effect of structure of ILs

The influences of various cation substituents (benzyl, vinyl and allyl groups) on the performance of the IL in the removal of phenol were investigated. It has been reported that changing the alkyl substituents have significant effect on the removal efficiency.

Fig. 4.11 shows the phenol removal efficiency for the three RTILs. [Abzim][Cl] managed to remove 78.33% phenol from the model oil while [Dbzim][Cl] and [Bzvim][Cl] were able to remove 73.17% and 63.83% phenol respectively. The substituent groups of the RTIL from the best to the worst performing follows the order of allyl > benzyl > vinyl. There are two explanations for how the substituents affect the phenol removal performance.

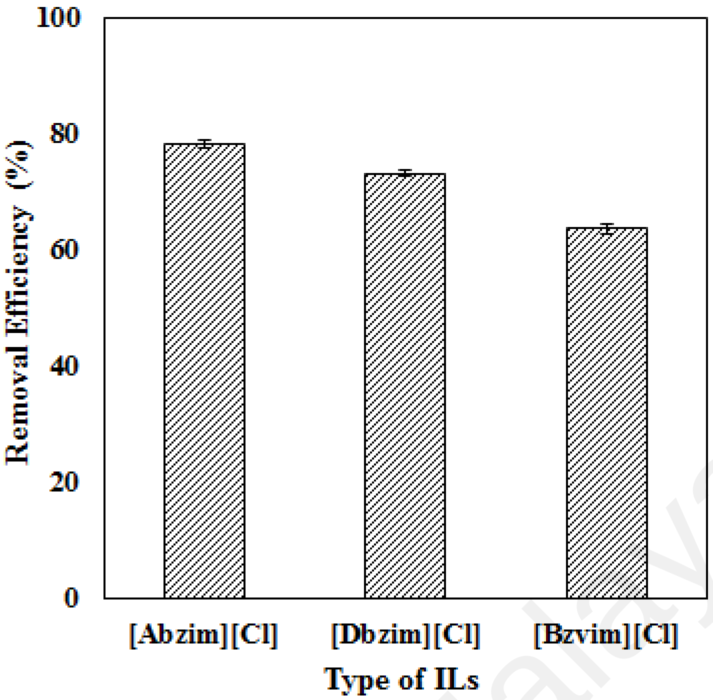


Figure 4.11: Effect of ILs structure on the phenol removal efficiency

The first explanation is related to the ability of the IL to form hydrogen bonds with phenol. The main mechanism involves the chloride ion (Cl^-) of the IL which acts as the electron donor to the hydroxyl group on the phenol. The Cl^- ion has a higher probability to come in contact with the phenol, therefore causing a higher degree of hydrogen bonding to occur in the system. Thus, freely moving Cl^- anions are favourable in order to have a high removal efficiency of phenol. It is important to note that the distance of Cl^- from the imidazolium ring in IL is governed by the interionic force between the anion itself and the hydrogen on the imidazolium ring attached to the C(2) carbon (Hunt *et al*., 2015; Remsing *et al*., 2007). The numberings of the ring atoms for the imidazolium structures are depicted in Figure 4.12. The strength of the C(2)-H bond can be seen from the ^1H NMR chemical shift value (δ, ppm) of the ILs. The higher the C(2)-H chemical shift, the stronger its interaction with the anion thus lowering the probability of the anion to form H-bond with phenol (Suarez *et al*., 1998; Wulf *et al*., 2007). By comparing the ^1H NMR spectra of all synthesized ILs, it can be seen that the C(2)-H of [Abzim][Cl] had the least chemical shift (δ, ppm). Thus, it can be concluded that the Cl^- of [Abzim][Cl] can move rather freely to form stronger hydrogen bonds with phenol compared to the other two ILs. The chemical shift of C(2)-H for the three RTILs are tabulated in Table 4.9.

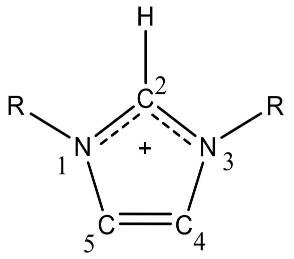


Figure 4.12: The numberings of the ring atoms of imidazolium ring

Table 4.9: Chemical shift of carbon C(2) proton

RTILs	Chemical shift of carbon C(2) proton δ, ppm
[Abzim][Cl]	9.55
[Dbzim][Cl]	9.64
[Bzvim][Cl]	9.92

The second explanation of how various substituents on ILs affect its performance can be attributed to the alkyl chain length on the imidazolium ring. According to literature, the longer the N-alkyl side chains, the weaker the intramolecular hydrogen bonding between the C(2)-H and the anions (Dong *et al*., 2006). As a consequence, the ability of longer alkyl chain ILs to remove phenol increases. This phenomenon can be observed in [Bzvim][Cl] whose vinyl side chain is shorter than the allyl group on [Abzim][Cl], resulting in lower interaction to form hydrogen bonds with phenol due to the close distance between the cation and Cl^- (Guo *et al*., 2013; Jiao *et al*., 2015b). The ability of [Abzim][Cl] to remove phenol from the model oil surpassed that of [Dbzim][Cl] due to the larger volume occupied by the benzyl group compared to that of the allyl substituent. The large volume of the substituent also increased the molecular volume of [Dbzim][Cl], thus affecting the distance between the charge centres of the anion and the cation. As a result, the steric hindrance caused by bigger benzyl group hindered the ability of the chloride ion to form H-bond with phenol. Therefore, it should be noted that there is an optimum distance between the chloride ion and cation to form hydrogen bond with phenol (Guo *et al.*, 2013; Jiao *et al.*, 2015b; Jiao *et al.*, 2015c). [Abzim][Cl] was used in the succeeding optimization step due to its higher extraction of phenol.

4.3.3 Effect of phase volume ratio

The phase volume ratio is an important factor for the extraction process. In order to determine the effect of phase volume ratio of the model oil and IL on the phenol removal efficiency, an experiment was conducted using [Abzim][Cl] at 25 °C for 30 min. Hexane-to-[Abzim][Cl] volume ratios of 20 (4 mL/0.2 mL) to 500 (4 mL/0.008 mL) were investigated as shows in Figure 4.13. It can be seen that the percentage removal of phenol dropped significantly with increasing phase volume ratio. The decrease in removal efficiency could be due to the much greater volume of oil phase compared to IL phase used in this extraction, thus reducing the active site of H-bond. The right volume of IL is crucial because insufficient volume of IL may lead to lower analyte recovery (Lai *et al.*, 2014). The performance of [Abzim][Cl] in removing phenol achieved 99.46% when a phase volume ratio of 20 was used. It is also observed that the removal efficiency remained sufficiently high at 95.24% even when a higher volume ratio such as 40 (4 mL/0.1 mL) was used. Therefore, taking into account the economic efficiency, a volume ratio of 4:0.1 of model oil to IL was selected as the optimal value and used in succeeding steps in order to decrease the usage of IL in this extraction.

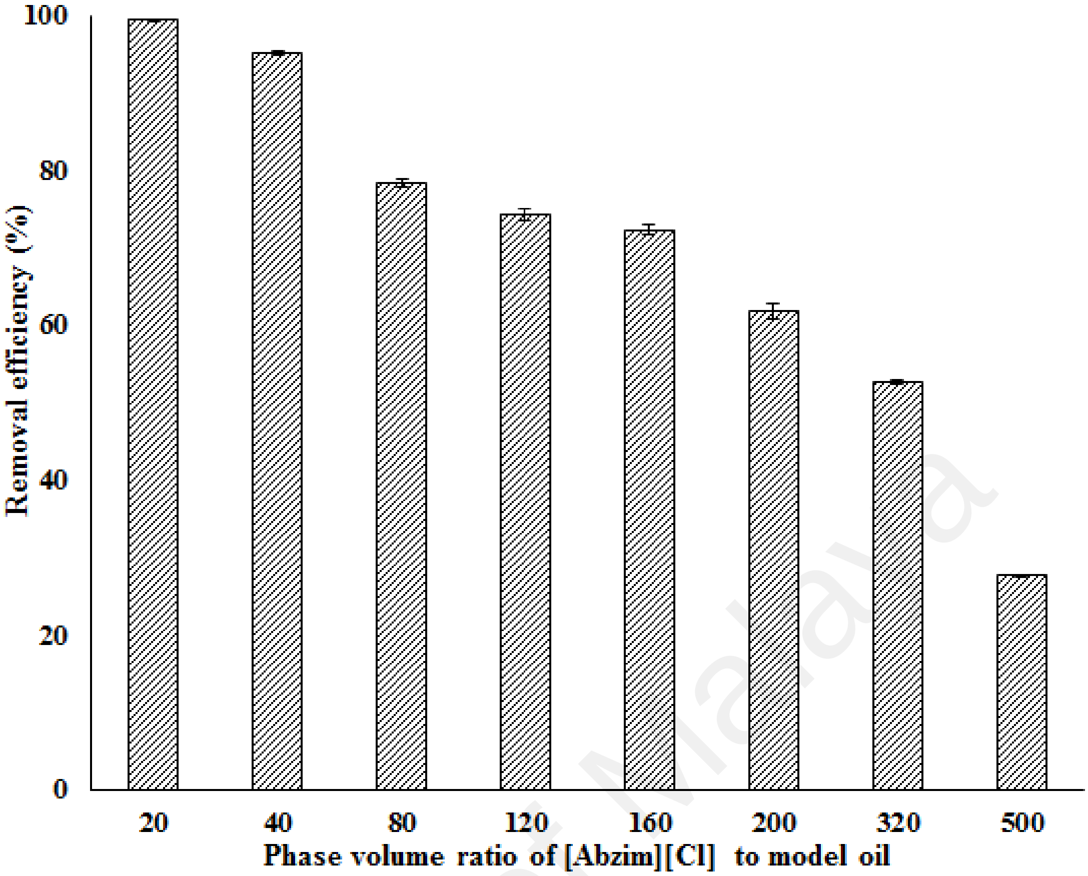


Figure 4.13: Effect of phase volume ratio of [Abzim][Cl] to model oil

4.3.4 Effect of phase contact time

The phase contact time is another important parameter in the extraction process because the mass transfer of analyte between two immiscible phases requires some time to reach equilibrium (Deng *et al*., 2011). The effect of contact time was investigated comprehensively from 10 min to 60 min at a volume ratio of 40 and reaction temperature at 25 °C. From Figure 4.14 (a), the removal efficiency increased sharply for the first 30 min since more H-bond sites were available at this time interval. Moreover, the short equilibrium time of phenol was achieved between the oil and IL phases suggested that there was a rapid mass transfer of phenol as well as a strong complexation between phenol and IL (Ji *et al*., 2018a; Meng *et al*., 2013; Yao *et al*., 2017). The percentage removal of phenol reached a plateau after 30 min indicating the system has achieved equilibrium within this duration. Therefore, a period of 30 min was employed as the optimum time for phenol extraction.

4.3.5 Effect of temperature

The effect of temperature on the phenol removal efficiency was studied thoroughly at temperatures 25 °C to 60 °C at a volume ratio of 40 and contact time of 30 min. Figure 4.14 (b) shows the temperature dependence of the phenol removal efficiencies. It can be deduced that increasing the reaction temperature decreased the phenol removal efficiencies. The percentage removal decreased gradually from 25 °C to 30 °C and then exhibited a more significant decrease at elevated temperature up to 60 °C. The slight effect of temperature on the phenol removal might be due to the fact that the formation of hydrogen bonding between IL and phenol involved an exothermic process. Thus, a high temperature condition would disturbed the complexation of extractant and phenol which subsequently lead to negative performance (Meng *et al.*, 2013). Therefore, from the results obtained, the extraction procedure is best operated at room temperature.

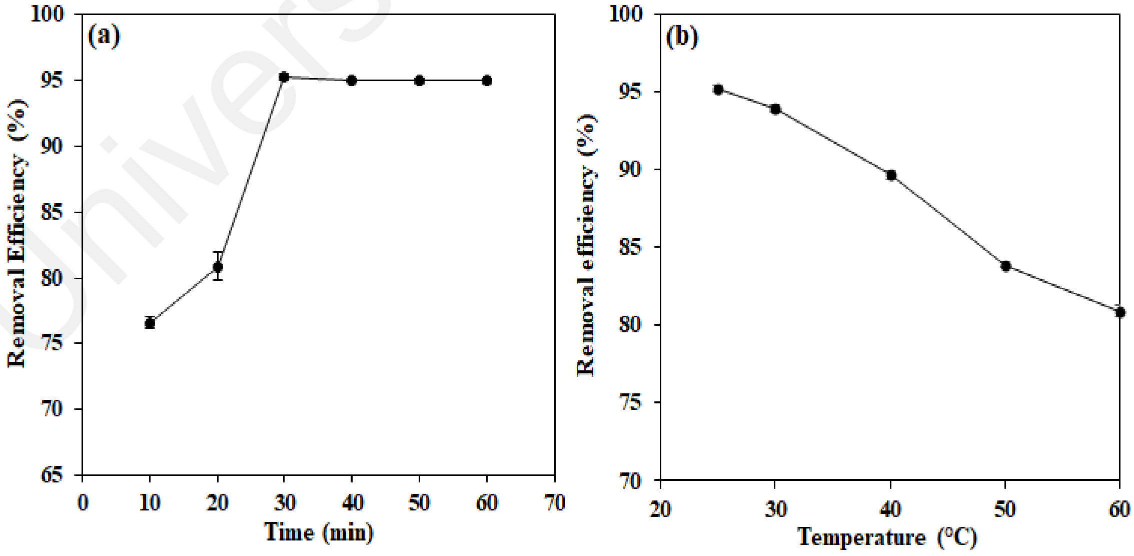


Figure 4.14: (a) The effect of time on the phenol removal efficiency, (b) The effect of temperature on phenol removal efficiency

4.3.6 Types of model oil

In order to study the effectiveness of [Abzim][Cl] in removing phenols from oil, n-heptane, cyclohexane and petroleum ether were selected as the model oils as they represent non-aqueous environments. Figure 4.15 shows that [Abzim][Cl] managed to remove approximately 85 % phenol from all the model oils used. Thus, it can be concluded that [Abzim][Cl] is a suitable solvent to use for liquid-liquid extraction in non-aqueous media.

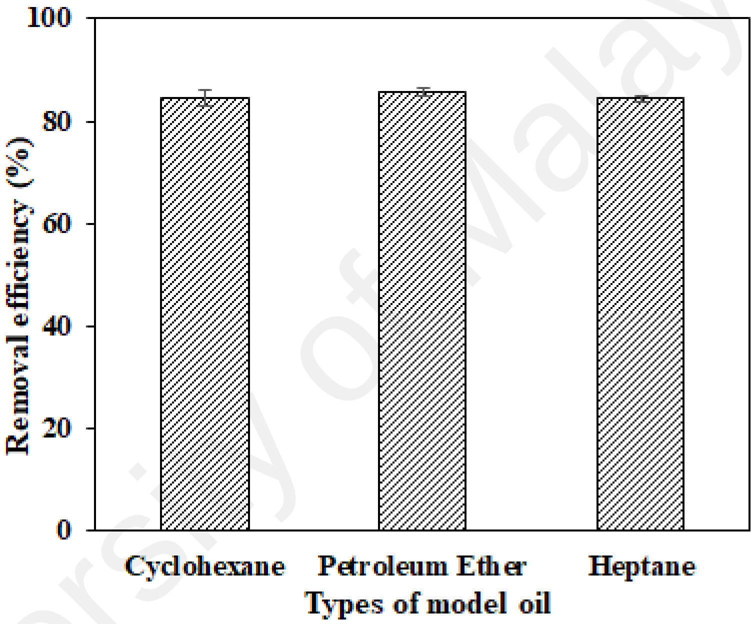


Figure 4.15: Effect of types of model oil on phenol removal efficiency

4.3.7 Selectivity study

Nine phenolic compounds with different nitro and chlorine substituents as well as two other aromatic compounds; namely xylene and toluene were used as analytes in investigating the influence of various phenol substituents on the removal efficiency of IL. The % removal efficiency increased in the order of Ph > 4-CP > 3-CP > 2CP > 2,4-DCP > 2,4,6-TCP for chlorinated phenols while for nitrophenols, it increased in the order of 4-NP > 2,4-DNP > 2,4,6-TNP under the same experimental conditions. Higher removal efficiencies were observed for phenols containing lesser amounts of the hydrophobic substituents chlorine and nitro. This is because hydrophilic interaction is favourable for the reaction between IL and phenols. As an example, 2,4,6-TCP has the lowest % removal from the oil and this is attributed to the higher number of chlorine substituents (Ahmaruzzaman, 2008; Deng *et al*., 2011; Egorov *et al*., 2008; Fan *et al*., 2008).

There are usually aromatic compounds other than phenols found in oils such as toluene, xylene, biphenyl and naphthalene (Erdmann *et al*., 1996). Thus, it is important to study the selectivity of IL towards those compounds. In this study, there was no extraction of toluene and xylene from the model oil by the IL. This is because there are no available sites where H-bond can form between IL and aromatic compounds which is vital for the extraction. The reaction mechanism is further discussed in Section 4.3.8. Thus, it can be concluded that the synthesized IL is only selective towards phenolic compounds and not towards other aromatic compounds that may be present in the oil.

4.3.8 Reaction mechanism

The ILs enable the separation of phenol from the model oil via dissolution of phenol from the oil phase into the ILs phase. According to literature, there are two significant interactions that govern the ability of ILs to extract phenol. The first is the formation of hydrogen bonds in which the chloride ion acts as the electron donor to the hydroxyl group in the phenol structure. The high electronegativity of chloride ion favours hydrogen bonding and thus, plays a crucial role in the extraction process. The second driving force for the removal of phenol by imidazolium-based IL is the π-π conjugation between the imidazolium ring and the benzene ring of phenol (Fan *et al*., 2014). Moreover, additional π-π interaction is contributed by the presence of benzyl and allyl substituents.

The formation of hydrogen bond between phenol and [Abzim][Cl] were analyzed from the FT-IR and ^{1}H NMR spectra. FT-IR is an important tool in determining the presence of hydrogen bonding (Guo *et al*., 2013; Jiao *et al*., 2015b; Jiao *et al*., 2015c). In order to confirm the presence of H-bonding, 1:1 mole ratio of [Abzim][Cl]and phenol were prepared and analyzed. The OH vibrational frequency of pure phenol could be observed at wavenumber of 3217 cm^{-1} as shown in Figure 4.16 (a). However, after extraction using [Abzim][Cl], this peak shifted to a higher frequency of 3371 cm^{-1} as can be observed in Figure 4.16 (c). This change in the absorption peak is mainly due to the migration of the electron cloud in oxygen atom on the phenol to a higher wavenumber (Jiao *et al*., 2015d).

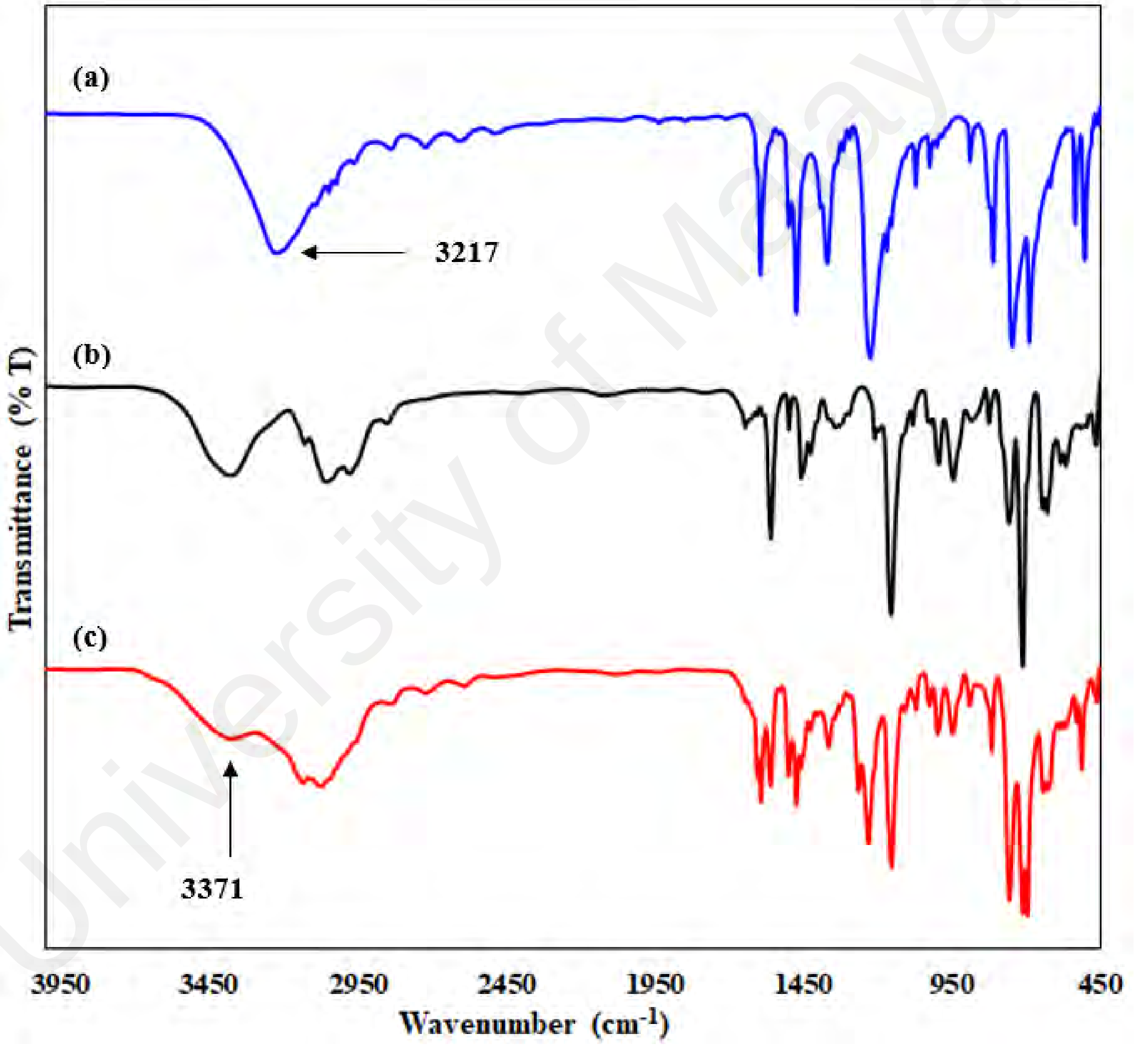


Figure 4.16: FT-IR spectra of (a) [Abzim][Cl]-Phenol, (b) [Abzim][Cl] and (c) Phenol

In addition, a ^1H NMR analysis was also employed in order to confirm the formation of hydrogen bond between [Abzim][Cl] and phenol. NMR spectrometry is one of the useful tools to identify the chemical modifications of compounds because some differences in the chemical shifts of the protons are observed in the spectrum. From Figure 4.17, it can be deduced that a hydrogen bond was formed due to the shifting of OH chemical shift on phenol from 9.2920 ppm to 9.4760 ppm after extraction with [Abzim][Cl]. Moreover, the sharp peak of OH on the pure phenol spectrum also broadened.

Interestingly, the role of aromatic moieties and unsaturated substituents in strengthening π-π interaction of ILs with phenyl ring of phenol can be proven from their ^{1}H NMR spectrum. This is because cationic imidazolium ring modified with unsaturated substituents such as benzyl and allyl groups could attract aromatic compounds more efficiently compared to their alkyl counterparts (Zhang *et al*., 2016). Table 4.10 shows the chemical shift changes (Δδ, ppm) for [Abzim][Cl] after extraction of phenol. The numbering on the proton atoms has been changed for a better understanding of the NMR spectrum. The allylic protons of [Abzim][Cl]-Phenol mixture (**H1**, **H2** and **H3**) experienced a downfield shift suggesting that there was a strong interaction between the IL and phenol. Moreover, greater chemical shift changes are observed on aromatic protons of [Abzim][Cl] (**H7**, **H8** and **H9**) confirming the ability of aromatic moieties in strengthening the π-π interaction and on imidazolium protons of [Abzim][Cl] namely **H10** and **H11** proving that imidazolium ring could also form π-π stacking with phenol. Figure 4.18 illustrates the π-π interaction of aromatic benzene ring of phenol with aromatic and allylic moieties of [Abzim][Cl] as well as H-bonding of Cl^- with hydroxyl group of phenol.

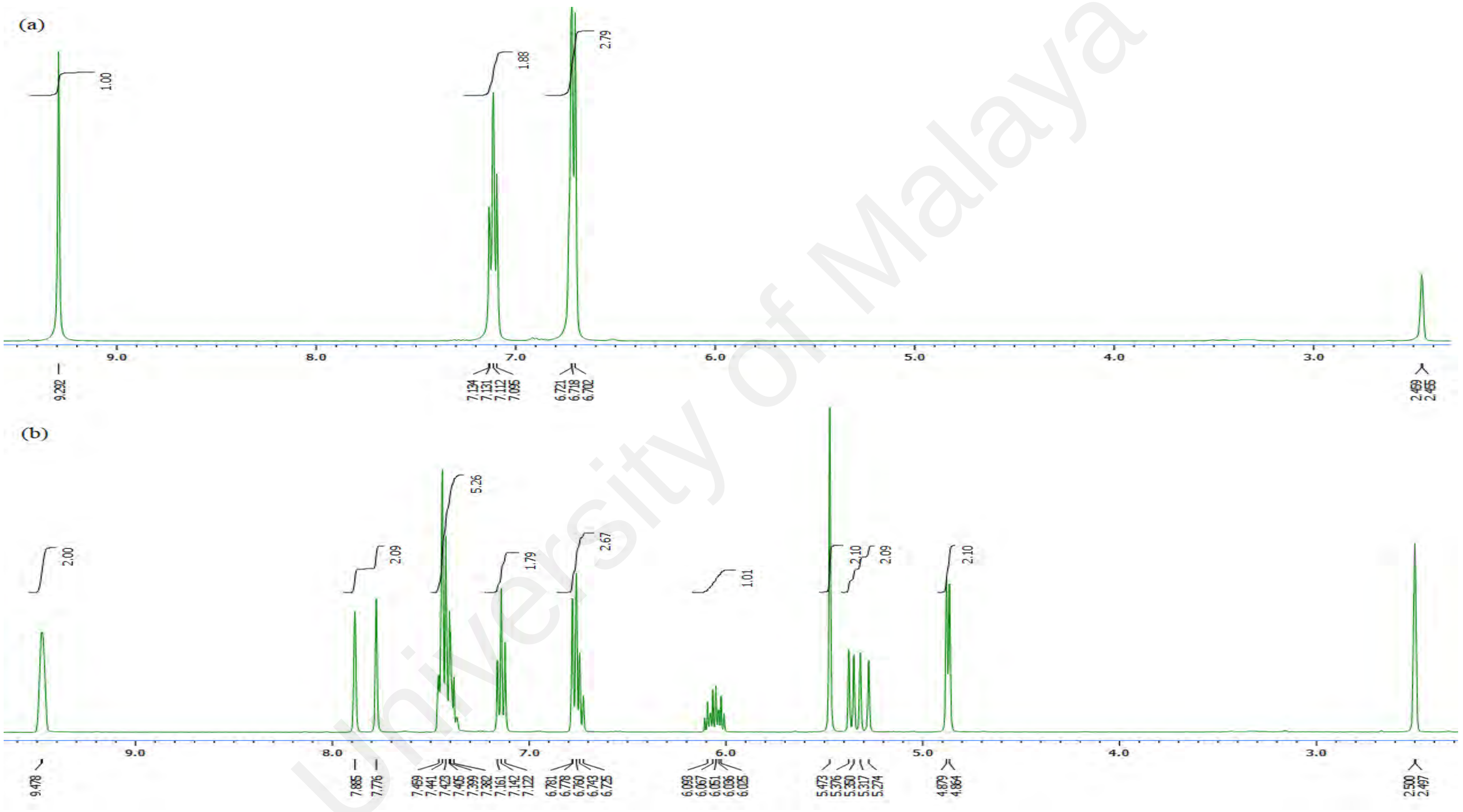


Figure 4.17: ^{1}H NMR spectra of (a) pure phenol and (b) [Abzim]Cl-Phenol

Table 4.10: The chemical shift changes (Δδ, ppm) of [Abzim][Cl]-Phenol mixture

Proton	δ, ppm			Δδ, ppm
	[Abzim]Cl	Phenol	[Abzim]Cl-Phenol	
H1	**5.2805**	**-**	**5.2955**	**+ 0.0150**
H2	**5.3400**	**-**	**5.3630**	**+ 0.0230**
H3	**6.0430**	**-**	**6.0590**	**+ 0.0160**
H4	4.8685	-	4.8715	+ 0.0030
H5	9.5500	-	9.4760	- 0.0740
H6	5.4760	-	5.4730	- 0.0300
H7	**7.3725**	**-**	**7.3935**	**+ 0.0210**
H8	**7.4100**	**-**	**7.4230**	**+ 0.0130**
H9	**7.4945**	**-**	**7.4500**	**- 0.0445**
H10	**7.8970**	**-**	**7.7760**	**- 0.1210**
H11	**7.7800**	**-**	**7.8850**	**+ 0.1050**
Ha	-	9.2920	9.4760	+ 0.1840
Hb	-	6.7020	6.7340	+ 0.0320
Hc	-	6.7195	6.7730	+ 0.0535
Hd	-	7.1120	7.1420	+ 0.0300

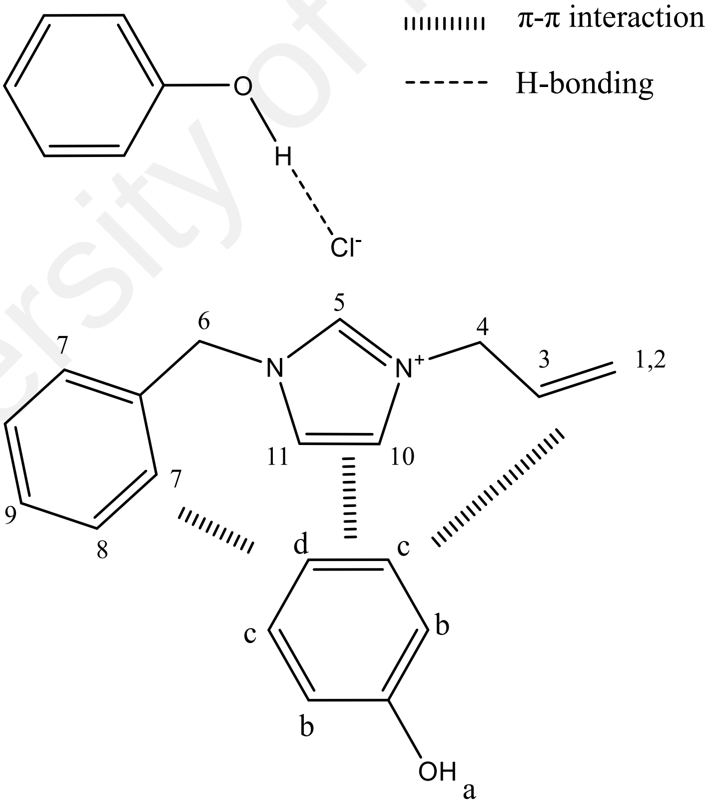


Figure 4.18: The π-π interaction of aromatic benzene ring on phenol with aromatic and allylic moiety of [Abzim]Cl as well as H-bonding of Cl- with hydroxyl group on phenol

4.3.9 Recyclability study

To test the recyclability of [Abzim][Cl], it is recovered after the first extraction and then reused for subsequent cycles. Ethyl acetate was used as an efficient back-extraction agent to recycle ILs due to the significant solubility difference between IL and phenol in ethyl acetate. Upon addition of ethyl acetate to IL layer, the phenol reached equilibrium in ethyl acetate after shaking for 30 min. The ethyl acetate layer was then decanted and the process was repeated three times to ensure the recycled IL is free from impurities. The phenol removal efficiencies were finally calculated to evaluate the extraction ability of the recycled IL. Figure 4.19 shows that the recycled IL can be reused several times and the phenol removal performance remains constant after 5 cycles. However, the efficiencies dropped gradually after 6th cycles but the efficiency is still maintained at approximately 90%.

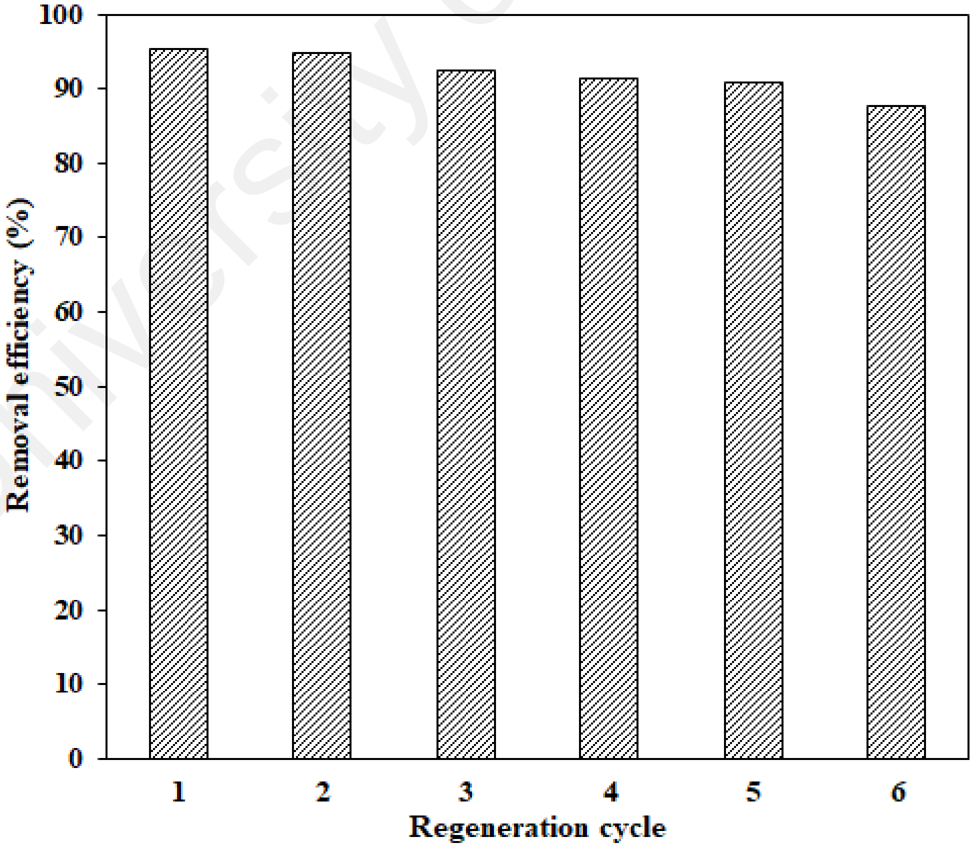


Figure 4.19: Phenol removal efficiency versus regeneration cycle of IL

To confirm the structure of the recycled IL, ^{1}H NMR and FT-IR analyses were carried out. In Figure 4.20, the characteristic absorption peaks of the recycled [Abzim][Cl] were identical to that of pure [Abzim][Cl]. This data proved that the IL was stable after the regeneration process and no new compounds were formed in the extraction process. In addition, the identity of the recycled [Abzim][Cl] was also confirmed by the ^{1}H NMR spectrum as shown in Figure 4.21. The spectrum of the recycled IL does not display any significant changes in terms of its δ value compared to the original one indicating that this IL can be completely regenerated without any changes in its structure.

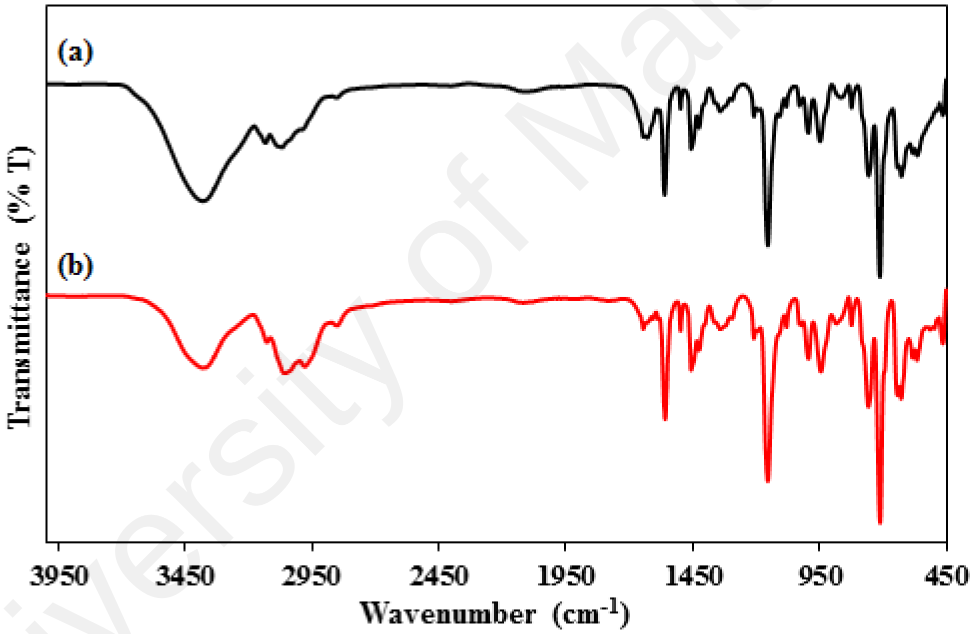


Figure 4.20: (a) FT-IR spectra of recycled [Abzim][Cl], (b) pure [Abzim][Cl]

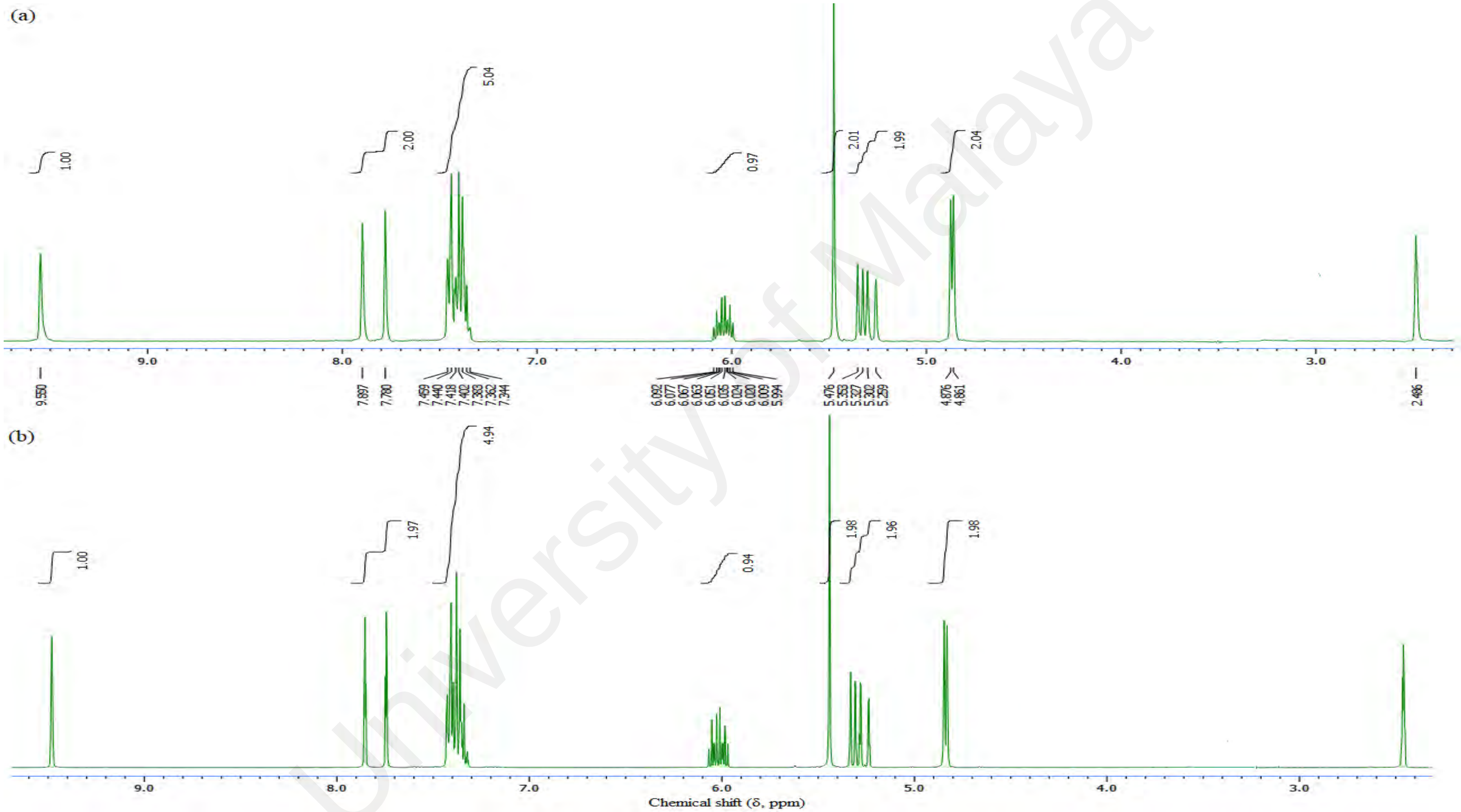


Figure 4.21: ^{1}H NMR spectra of (a) pure [Abzim][Cl] and (b) recycled [Abzim][Cl]

4.3.10 Extraction of phenols in synthetic oil

The objective of using synthetic oil compared to model oil is to study the performance of IL in a more complex environment. This is because synthetic oil consists of different kind of phenol derivatives as well as other benzylic compounds that might reduce the efficiency of the ILs. Thus, by conducting the extraction of phenols in synthetic oil, the effectiveness of the ILs can be acquired thoroughly.

The calculated HPLC chromatogram peak area of the synthetic oil before and after the extraction showed that [Abzim][Cl] was able to remove about 87.72% of phenol, 64.77% of 2,4-DNP and 63.47% of 2,4-DCP. This result proved that the performance of [Abzim][Cl] is excellent even in the presence of different types of phenolic compounds and polyaromatic hydrocarbons (PAHs). The % removal of fluorene and fluoranthene was found to be negligible. Thus, it can be concluded that benzyl imidazolium-based ionic liquid is only selective towards phenolic compounds and not selective to polyaromatic hydrocarbons. Figure 4.22 illustrates the HPLC chromatogram of the synthetic oil before and after extraction.

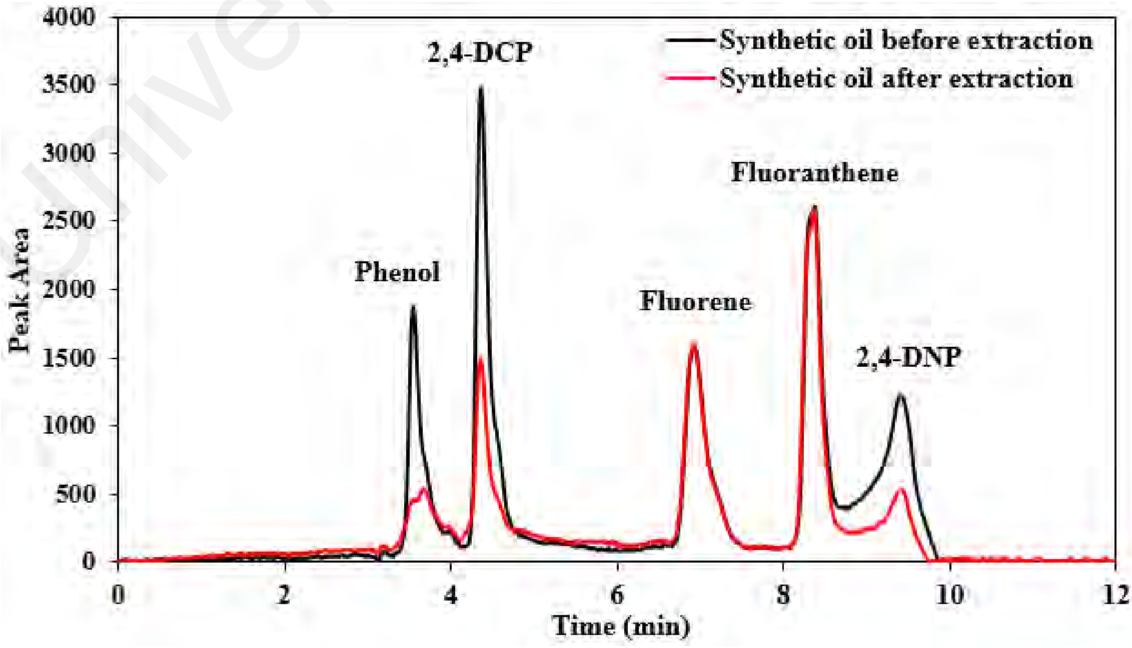


Figure 4.22: HPLC chromatogram of synthetic oil before and after extraction

CHAPTER 5: ADSORPTION OF PHENOLS BY SILICA TITANIA MIXED OXIDE IONIC LIQUIDS

5.1 Synthesis of silica titania mixed oxide ILs (Si-Ti-ILs)

In this chapter, the synthesis and characterization of Si-Ti-ILs were discussed thoroughly. The idea behind this study is to immobilize the liquid IL obtained from Chapter 4 which is [Abzim][Cl], via physical confinement in a silica gel matrix so that this solidified IL can be applied as an adsorbent for the removal of phenol. The IL was encapsulated through a sol-gel process where the amount of [Abzim][Cl] loading was varied at 25 wt%, 50 wt%, 75 wt% and 100 wt%. Finally, these Si-Ti-AbzImCl composites were used in the preliminary adsorption study to remove phenol from model oil.

In addition, a dicationic IL ([Dicat-BzIm][Cl]) with more benzyl substituents than [Abzim][Cl] was also synthesized and then encapsulated into silica gel. The performance of both Si-Ti-ILs as adsorbents were studied and compared. The objective of using dicationic IL is to study whether the amount of benzyl substituents affects the removal efficiency of phenol.

5.1.1 Synthesis and characterization of 3,3'-(1,4-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) dichloride ([Dicat-BzIm][Cl])

[Dicat-BzIm][Cl] was synthesized according to the method in section 3.3.1. The yield obtained for the synthesis of [Dicat-BzIm][Cl] was a white viscous liquid with a percentage yield of 85%. It was found that it was hydrophilic, possessing good solubility in polar solvents generally water and methanol but insoluble in non-polar solvents mainly hexane, diethyl ether and ethyl acetate. The IL was then characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and CHN elemental analyses.

5.1.1.1 ^{1}H NMR spectroscopy

Figure 5.1 shows the ^{1}H NMR spectrum of [Dicat-BzIm][Cl] and the chemical shifts for all the protons are tabulated in Table 5.1. The spectrum shows only 6 signals of unsymmetrical protons out of the total of 28 protons due to its symmetrical structure. Therefore, the protons existed in the same chemical environment would appeared at the same chemical shifts with the integral value would multiplied as well. The aliphatic region at δ 5.45 and 5.46 ppm was assigned as methylene protons; H6 and H13 respectively. The multiplet peaks in the range of 7.32 ppm to 7.48 ppm corresponded to the aromatic protons of benzene rings (H8 to H12 and H15 to H16). On the other hand, the imidazolium protons labelled as H4 and H5 appeared at 7.86 ppm and 7.87 ppm as doublet peaks respectively while H2 emerged as singlet peak at 9.75 ppm. As can be seen in the spectrum and table, it can be concluded that the IL has been successfully synthesized where the approximate ratios of the integration lines are consistent with the ratios of the number of hydrogen atoms. Moreover, there are no additional peaks existing in the ^{1}H NMR spectrum indicating that the product is pure.

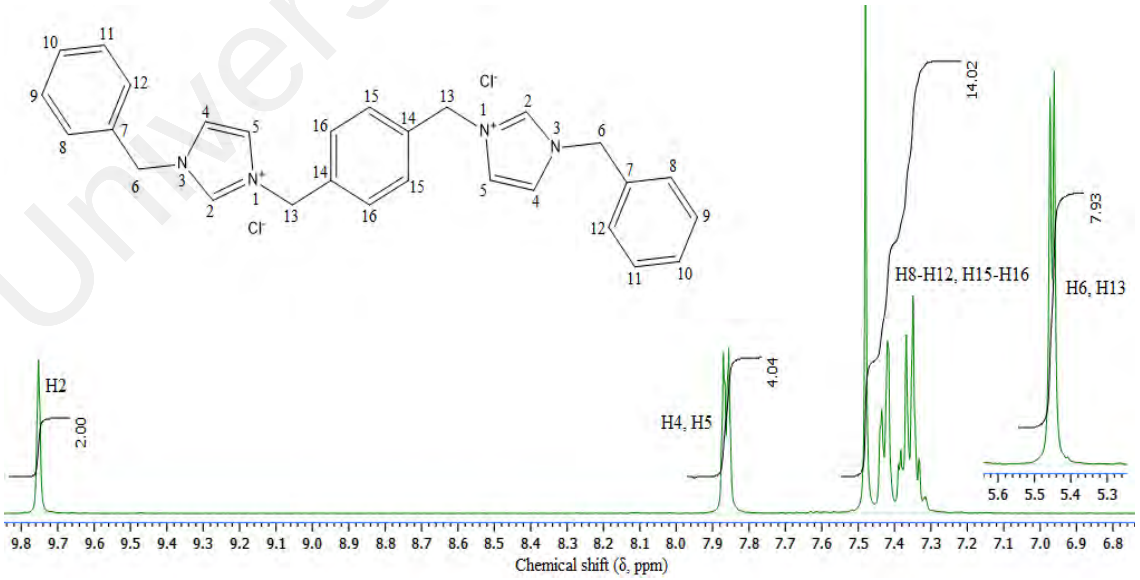


Figure 5.11: ^{1}H NMR spectrum of [Dicat-BzIm][Cl]

Table 5.1: Chemical shift (δ, ppm) of [Dicat-BzIm][Cl]

IL	Proton	Chemical shift (δ, ppm)	Multiplicity
[Dicat-BzIm][Cl]	H2	9.75	Singlet
	H4, H5	7.86-7.87	Doublet
	H8-H12,H15-H16	7.32-7.48	Multiplet
	H13	5.46	Singlet
	H6	5.45	Singlet

5.1.1.2 ^{13}C NMR spectroscopy

Figure 5.2 shows the ^{13}C NMR spectrum of [Dicat-BzIm][Cl]. It can be seen that there are 10 non-equivalent carbon peaks from a total of 28 carbon atoms. The assignment for all carbons are shown in the figure and tabulated in Table 5.2. The methylene carbons C6 and C13 appeared at 52.58 ppm and 53.02 ppm respectively. Aromatic carbons mainly C7 to C12 and C14 to C16 can be found in the range of 123.09 ppm to 129.65 ppm. On the other hand, imidazolium ring carbons C2, C4 and C5 emerged in the higher chemical shift of 134.18 ppm to 136.55 ppm.

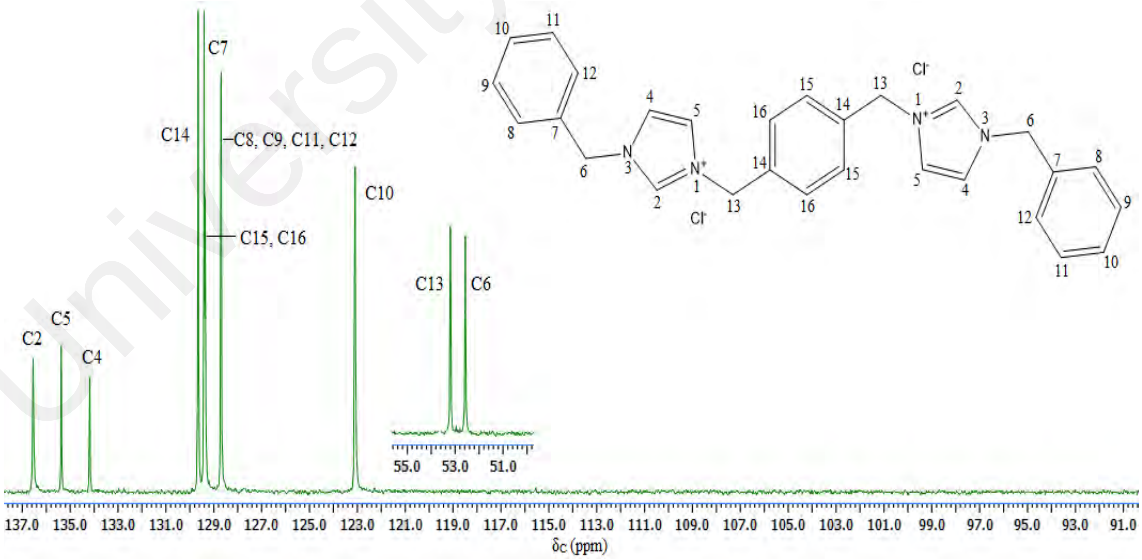


Figure 5.2: ^{13}C NMR spectrum of [Dicat-BzIm][Cl]

Table 5.2: Chemical shift (δ_C, ppm) of [Dicat-BzIm][Cl]

IL	Carbon	Chemical shift (δ_C, ppm)
[Dicat-BzIm][Cl]	C2	136.55
	C5	135.37
	C4	134.18
	C14	129.65
	C7	129.41
	C15, C16	129.36
	C8, C9, C11, C12	128.69
	C10	123.09
	C13	53.02
	C6	52.58

5.1.1.3 FT-IR spectroscopy

FT-IR analysis was carried out in order to further confirm the structure of [Dicat-BzIm][Cl]. Figure 5.3 shows the FT-IR spectrum for [Dicat-BzIm][Cl]. The spectrum shows some significant absorption peaks related to imidazolium rings at wavenumber 3384 cm^{-1}, 3017 cm^{-1}, 1556 cm^{-1}, 1496 cm^{-1} and 1150 cm^{-1} which corresponded to quaternary amine salt, *sp*^{2} C-H, C=N, C=C and C-N vibrations respectively. The complete vibrational frequency of each functional groups is tabulated in Table 5.3.

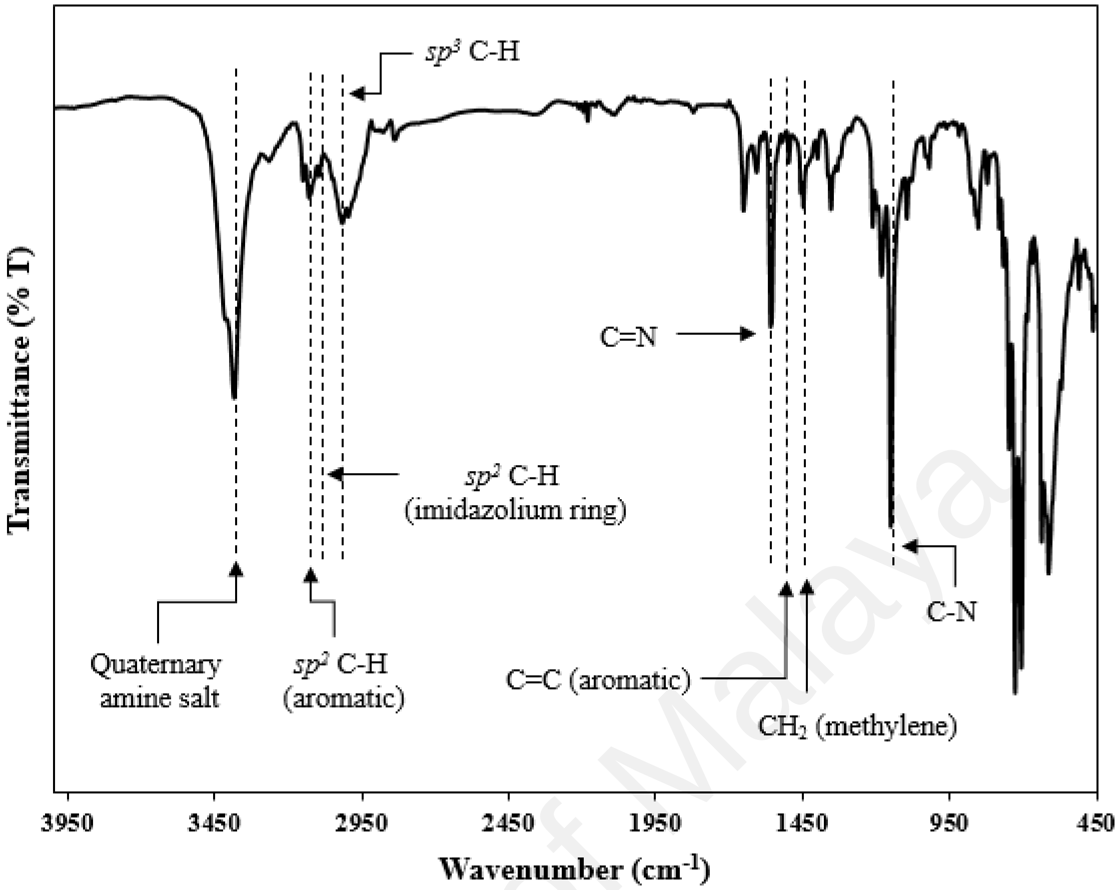


Figure 5.3: FT-IR spectrum of [Dicat-BzIm][Cl]

Table 5.3: Characteristic FT-IR bands of [Dicat-BzIm][Cl]

Functional groups	Wavenumber (cm^{-1})
Quaternary amine	3384
sp^2 C-H (aromatic)	3128
sp^2 C-H (imidazolium ring)	3017
sp^3 C-H	2997
C=N	1556
C=C (aromatic)	1496
CH_2 (methylene)	1446
C-N	1150

5.1.1.4 Elemental analysis

The elemental analysis result is tabulated in Table 5.4. The result shows that the percentage of C, H and N atoms obtained from the analysis were almost accurate with the calculated theoretical percentage where the difference was only about 1%. Based on the result, it is concluded that the prepared IL was successfully synthesized.

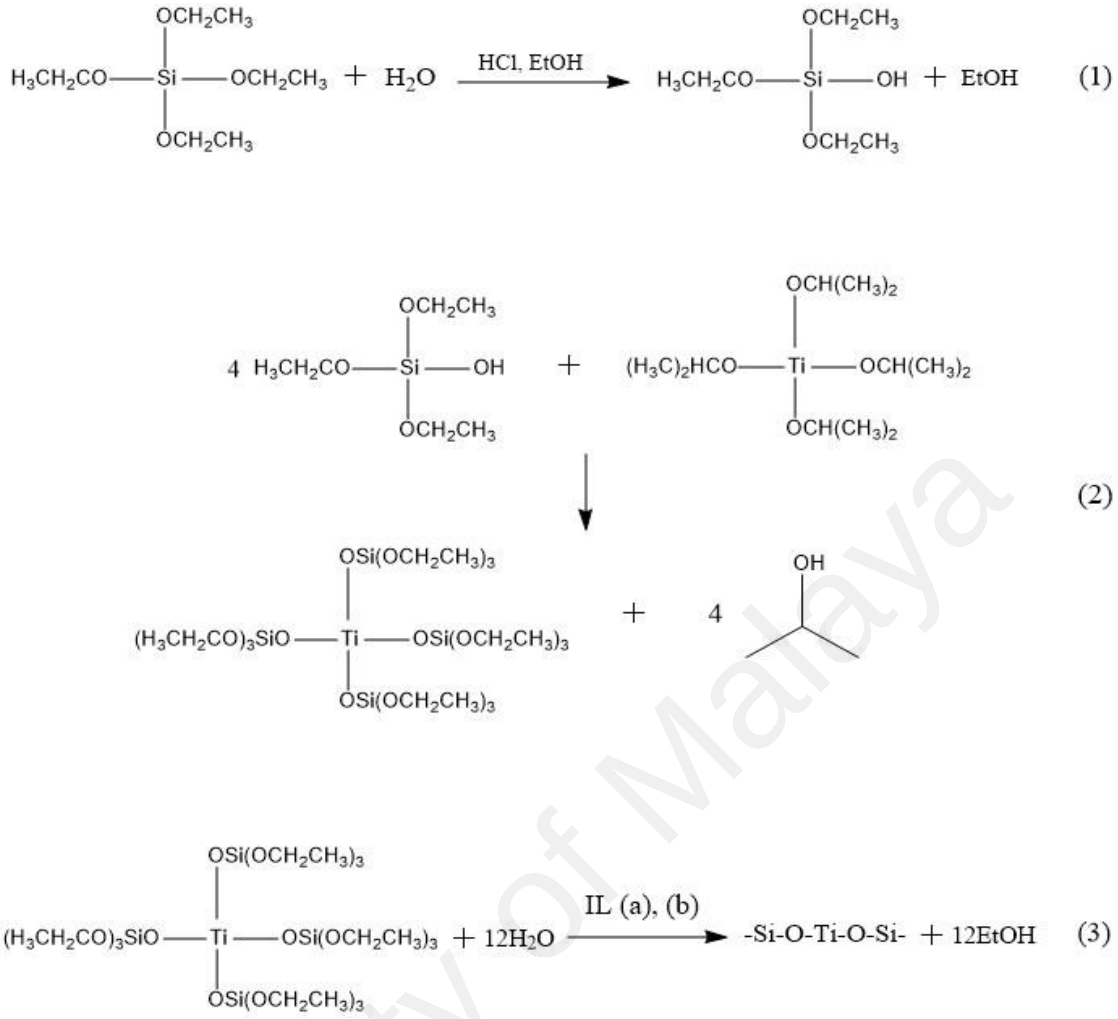
Table 5.4: The percentage of C, H, and N of [Dicat-BzIm][Cl]

Result	C (%)	H (%)	N (%)
Calculated	68.43	5.74	11.40
Found	69.63	5.92	12.01

In order to prepare solid adsorbents for adsorption of phenol, the synthesized ILs was encapsulated in a silica gel matrix to form Si-Ti mixed oxide gel adsorbent. The transformation involved a sol-gel method where [Abzim][Cl] represents a monocationic IL while [Dicat-BzIm][Cl] a dicationic IL.

5.1.2 Mechanism and reactions of Si-Ti-ILs

The Si-Ti-IL sol-gel was formed through the hydrolysis of TEOS by acidic catalyst where EtOH was used as the solvent to mix the starting materials as shown in Scheme 5.1 (1). Subsequently, the mixture underwent partial hydrolysis with TTIP (Scheme 5.1 (2)) and further polycondensation with IL produced a larger silica matrix where IL was encapsulated in the matrix pores (Scheme 5.1 (3)). The mechanism of sol solution via the sol-gel method is summarized in Scheme 5.1.



Scheme 5.1: Formation of Si-Ti-AbzImCl and Si-Ti-DicatBzImCl by sol-gel reactions where IL (a) is [Abzim][Cl] and (b) is [Dicat-BzIm][Cl]. Step (1) represents the hydrolysis of TEOS, step (2) involves partial hydrolysis with TTIP and step (3) polycondensation of silica matrix with the encapsulation of IL

5.2 Characterization of silica titania mixed oxide ILs

5.2.1 Fourier transform infrared analysis

FT-IR analysis was used to determine the significant functional groups found in the Si-Ti-ILs composites because of its ability to provide information on the molecular vibrations (Shi & Deng, 2005). The main feature in all of the Si-Ti composites spectra as shown in Figure 5.4 was the presence of Si-OH vibration as well as the bending vibration of trapped water molecules at approximately 3400 cm^{-1} (Amarasekara & Owereh, 2010; Miao *et al.*, 2011; Qiao *et al.*, 2006). Other characteristic peaks available on all spectra at

1620 cm^{-1} and 1020 cm^{-1} were attributable to the bending vibration of surface adsorbed water and the asymmetric stretching vibrations of Si-O-Si bond respectively (Mikushina *et al*., 2008; Murashkevich *et al*., 2008). The bending vibrations of Si-OH bond were found at ~ 920 cm^{-1} as a strong peak. This band can also be assigned as the Si-O-Ti bond as reported by the other works (Husing *et al*., 2002; Vives & Meunier, 2008). The fact that all these bands appeared in the IL-loading Si-Ti composites proved that both ILs were successfully encapsulated into the silica framework.

Upon modification with both ILs, some new peaks appeared at ~ 2900 cm^{-1}, 1560 cm^{-1}, 1497 cm^{-1}, 1450 cm^{-1} and 1150 cm^{-1} indicating the confinement of ILs onto the silica pores. The band at ~ 2900 cm^{-1} proved the presence of sp^3 C-H group and this peak became clearly obvious with the increasing amount of ILs. A significant C=N absorption of imidazolium ring as well as C=C vibration were observed at 1560 cm^{-1} and 1497 cm^{-1} respectively (Amarasekara & Owereh, 2010; Bakhshaei *et al*., 2016; Miao *et al*., 2011). The C-H bending vibrations appeared at 1450 cm^{-1} while C-N absorptions were observed at 1150 cm^{-1}. All these peaks intensified and became stronger as the amount of ILs was increased suggesting the ILs have occupied the silica pores (Chen *et al*., 2007).

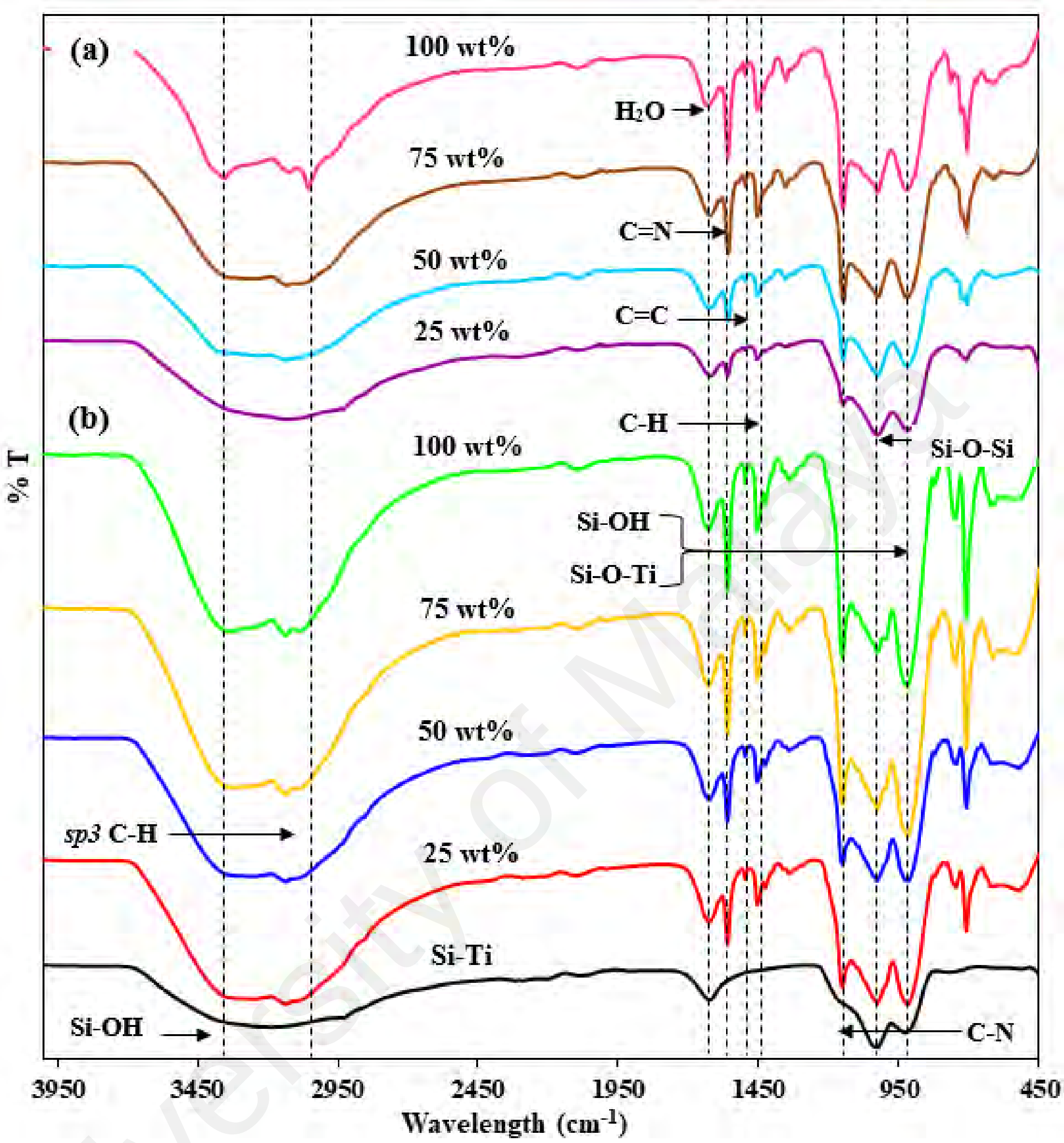


Figure 5.4: FT-IR spectra of (a) Si-Ti-DiCat-BzImCl and (b) Si-Ti-AbzImCl

5.2.2 X-ray diffraction analysis

The XRD patterns of Si-Ti composites are presented in Figure 5.5. The XRD characterization of Si-Ti, Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl showed a broad peak within the range $2\theta = 15^o - 35^o$ which indicates that the composites are amorphous. However, 75 wt% Si-Ti-Dicat-BzImCl showed some sharp peak at $2\theta = 25^o$ and the peak intensified with the increasing amount of IL to 100 wt%. This behaviour proved that the dicationic IL has been physically confined into the pores of silica in which the dicationic

IL itself exhibited some crystallinity. On the other hand, the Si-Ti-AbzImCl composites maintained their amorphous phase indicating that [Abzim][Cl] itself does not possess the crystalline behaviour.

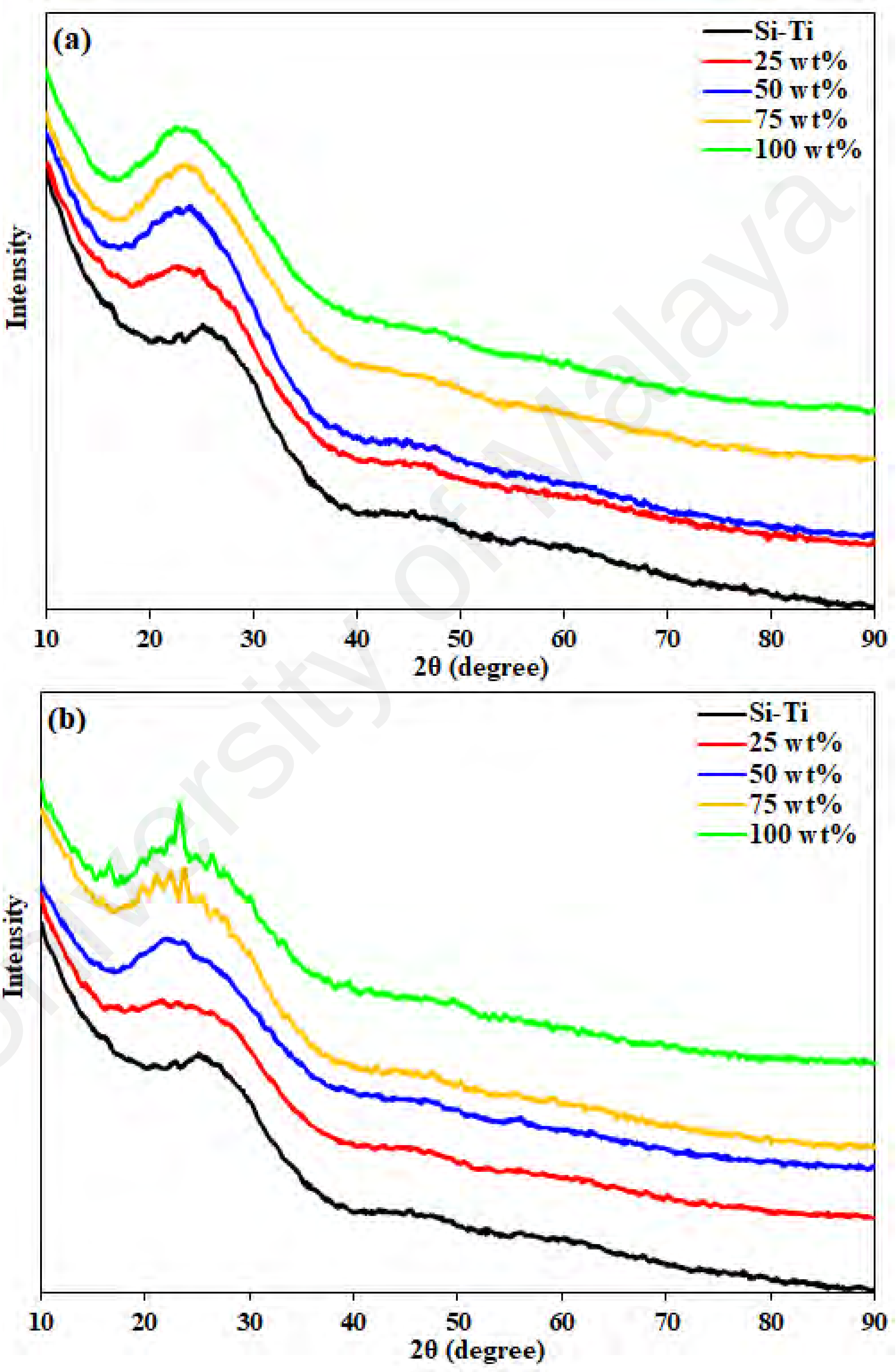


Figure 5.5: XRD patterns of (a) Si-Ti-AbzImCl and (b) Si-Ti-Dicat-BzImCl

5.2.3 Energy dispersive x-ray analysis

The elemental analysis was carried out by using EDX analysis where the presence of these elements; silicon, titanium, oxygen, carbon, nitrogen and chlorine can be identified. Table 5.5 reveals the percentage of those elements in the Si-Ti composites as well as confirming the existence of ILs. The results show that only Si, Ti and O were present in the pure Si-Ti. The percentage of Si and Ti were around 6% – 17% and 2% – 26% respectively for all Si-Ti composites. On the other hand, the presence of C, N and Cl were about 18% – 40%, 5% – 13% and 1% – 8% respectively, confirming the encapsulation of ILs onto the Si-Ti matrix. The data also provide the amount of confined ILs in which the percentage of carbon increased progressively from 25 wt% to 100 wt% of ILs loading. Furthermore, the successful immobilization of ILs onto the Si-Ti matrix can also be observed from the composition of nitrogen indicating the presence of imidazole ring of ILs.

Table 5.5: EDX analysis of Si-Ti composites

Sample	Element					
	Si	Ti	O	C	N	Cl
Si-Ti	17.57	24.30	58.14	-	-	-
25 wt% Si-Ti-AbzImCl	11.99	14.88	48.05	18.19	4.99	1.90
50 wt% Si-Ti-AbzImCl	10.25	26.77	31.69	23.75	5.98	1.56
75 wt% Si-Ti-AbzImCl	9.36	8.53	33.03	33.85	11.02	4.21
100 wt% Si-Ti-AbzImCl	8.46	13.53	24.21	35.68	10.01	8.1
25 wt% Si-Ti-Dicat-BzImCl	10.53	8.78	52.97	18.5	7.8	1.42
50 wt% Si-Ti-Dicat-BzImCl	6.94	11.11	28.90	38.43	11.75	2.87
75 wt% Si-Ti-Dicat-BzImCl	6.07	7.25	28.82	40.06	12.47	5.32
100 wt% Si-Ti-Dicat-BzImCl	6.67	2.39	34.60	40.82	13.56	1.96

5.2.4 Surface morphological analysis

The surface morphology of all the Si-Ti composites were carried out by field emission scanning electron microscopy (FESEM) analysis. Figure 5.6 illustrates the FESEM images for Si-Ti, 25 wt% to 100 wt% Si-Ti-AbzImCl and 25 wt% to 100 wt% Si-Ti-Dicat-BzImCl where the changes of morphology before and after the modification of ILs to the silica framework can be observed clearly. As can be seen in the figure, the unmodified Si-Ti exhibited an irregular and rough surface. However, upon modification with both ILs, the particles started to aggregate together to form a bigger agglomeration and their surface became smoother. The smooth surface was a result of the filling of the silica pores by ILs (Ismail *et al.*, 2016). Moreover, the particles agglomeration became more intensified as the amount of ILs increased and the agglomeration was seen more dominant for silica containing dicationic IL. This phenomenon appeared as expected due to the aggregation of the bulky benzyl groups of dicationic IL in the pores compared to monocationic IL. In addition, the progressively increasing particles agglomeration was a result of the greater amount of ILs filling in the pores. So, the changes in the surface morphology confirmed the successful attachment of both ILs in all the Si-Ti composites. It is therefore important to conclude that ILs have a huge impact on the surface morphology of Si-Ti materials.

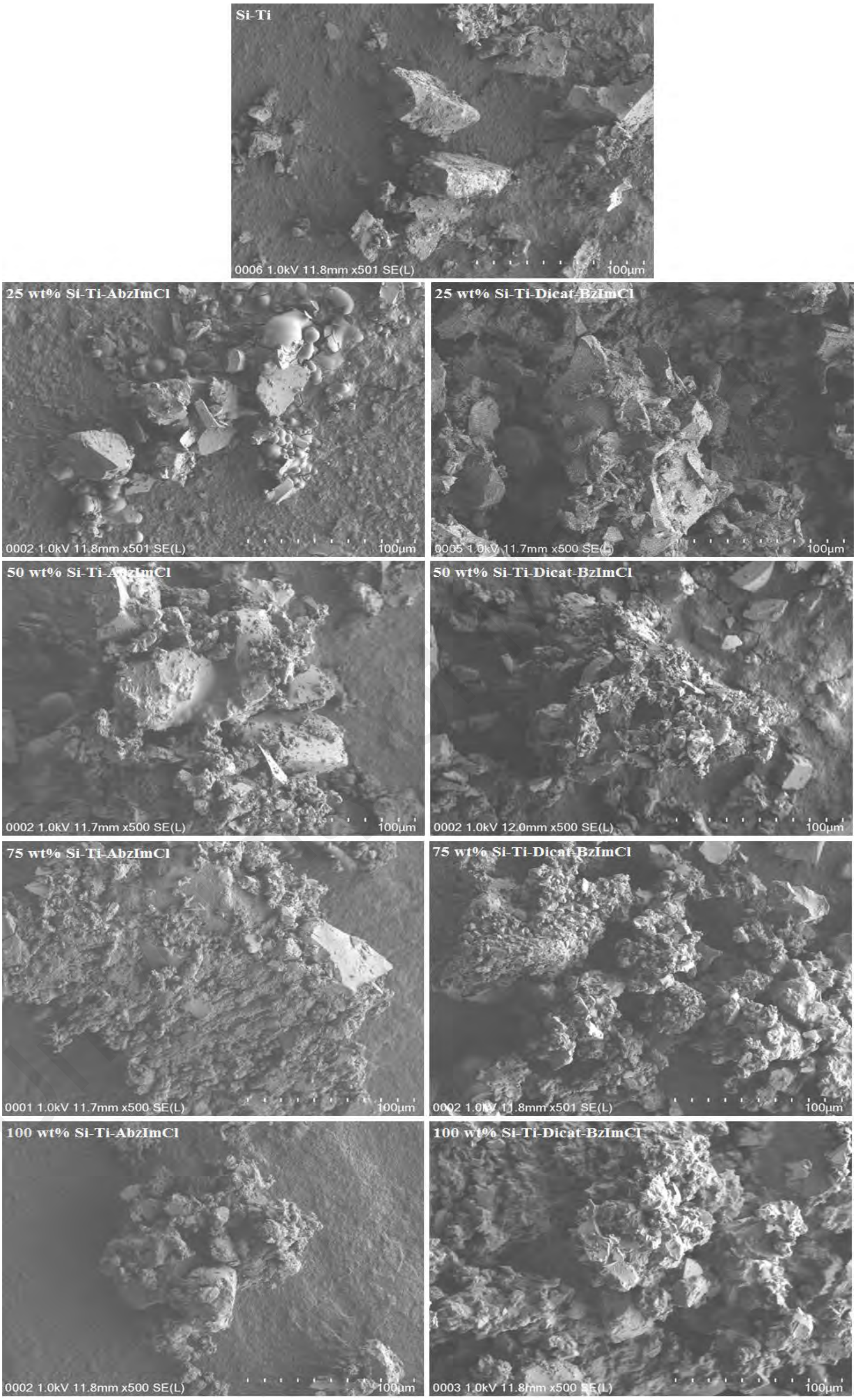


Figure 5.6: FESEM of Si-Ti and Si-Ti-IL composite

5.2.5 N_2 adsorption-desorption analysis

The surface analysis of the Si-Ti-ILs was determined by the N_2 adsorption-desorption and BET analysis. N_2 adsorption measurement helps to determine the surface area and the porosity of the Si-Ti-ILs. As can be seen in Figure 5.7, Si-Ti showed a type IV isotherm indicating a typical mesoporous structure (Ismail *et al.*, 2016). On the other hand, the isotherms for Si-Ti composites loading with 25 wt% and 50 wt% [Abzim][Cl] exhibited the tendency to change from type IV to type I isotherms which is a typical phenomenon observed in compounds with pore sizes situated between the mesoporous to microporous structures (Bakhshaei *et al.*, 2016; Wahab, 2004). Upon increasing the IL loading to 75 wt% and 100 wt%, the materials showed type I isotherms indicating the formation of microporous structures (Marimuthu *et al.*, 2014). The Si-Ti-Dicat-BzImCl isotherms with IL loading of 25 wt% to 100 wt% belonged to type IV in nature with the tendency to change to Type I.

The pore sizes related to all the materials are consistent with the IUPAC definition where the classification of the pore size of adsorbents includes; micropores (diameter < 2 nm), mesopores (2-50 nm) and macropores (> 50 nm) (Zhang *et al.*, 2009). Based on Table 5.6, all the materials exhibited the mesoporous structures except for 75 wt% and 100 wt% Si-Ti-AbzImCl which possessed the microporous structures. The trend in BJH pore size as calculated from Barret-Joyner-Halenda model revealed that the size increased upon the addition of both ILs up to 50 wt%. This phenomenon was consistent with other reported data (Ismail *et al.*, 2016; Liu *et al.*, 2005b; Shi *et al.*, 2005). The enlargement of the pore diameter might be due to the stacking arrangement of the ILs cation and anion when the amount of confined ILs in the silica skeleton increased (Marimuthu *et al.*, 2014). However, the size then decreased greatly after loading up to 100 wt% of [Abzim][Cl]. This behaviour suggested that [Abzim][Cl] may be well confined in the pores of silica gel. On the other hand, the pore size for Si-Ti-Dicat-BzImCl subsequently decreased with further addition of IL from 75 wt% to 100 wt%. This result suggested that the optimum amount of confined dicationic IL is 50 wt% and the silica skeleton was not significantly affected by the variations of IL content from 75 wt% to 100 wt%. This phenomenon is also observed in other report (Zhang *et al*., 2009).

On the other hand, the BET surface area of Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl decreased greatly from 318.42 m^2/g to approximately 0.9 m^2/g – 3.0 m^2/g as a result of the confinement of both ILs. This result was well supported with the other reported work (Zou *et al*., 2010). The pore volume of the composites also decreased greatly after modification with both ILs from 0.17 cm^3/g to approximately 0.0007 cm^3/g – 0.0025 cm^3/g.

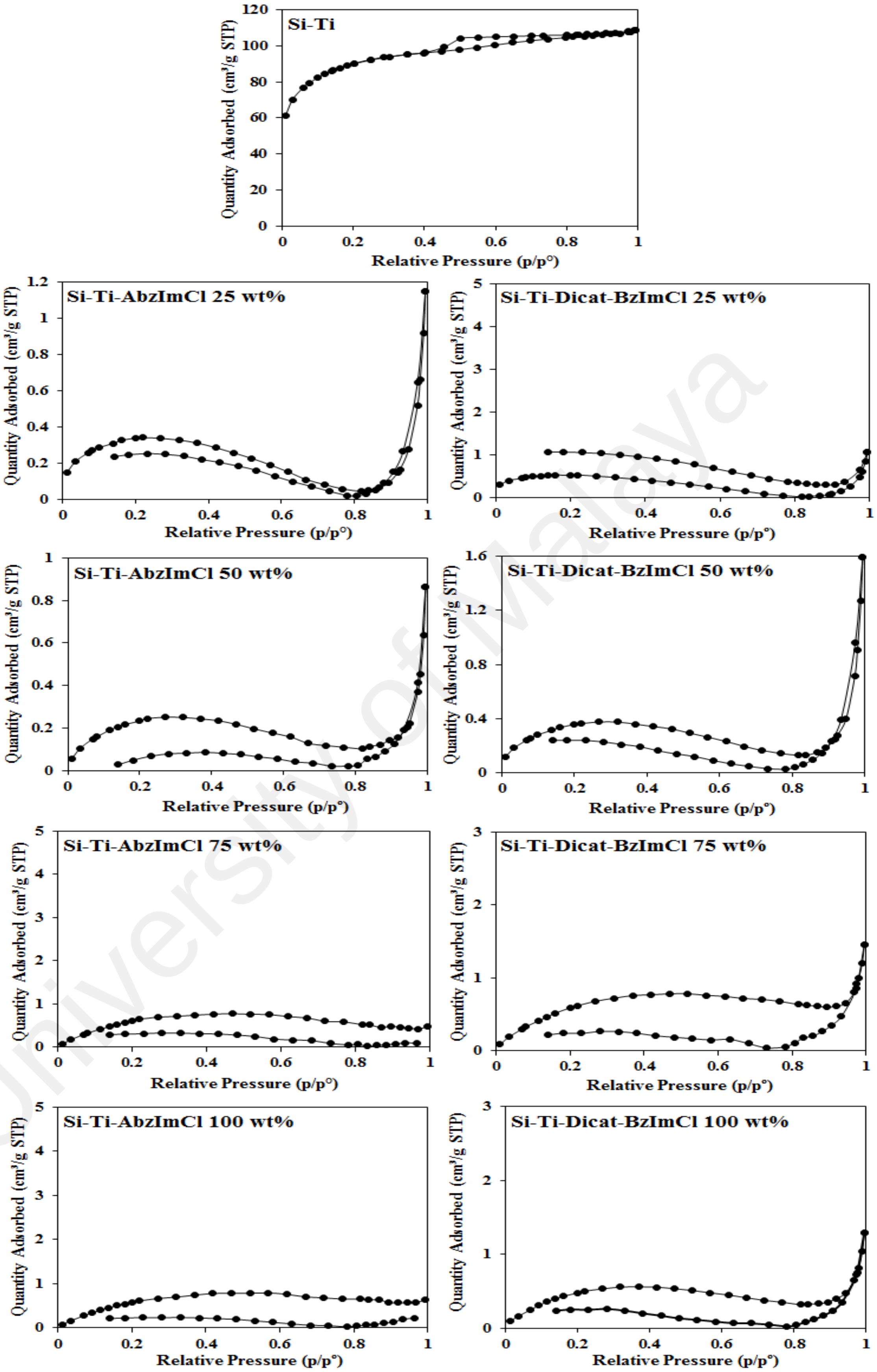


Figure 5.7: N_2 adsorption-desorption isotherms of Si-Ti composites with [Abzim][Cl] and [Dicat-Bzim][Cl] loading from 25 to 100 wt%

Table 5.6: Pore structure of Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl with various loading

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Si-Ti	318.42	0.17	2.11
25 wt% Si-Ti-AbzImCl	1.26	0.0018	5.62
50 wt% Si-Ti-AbzImCl	0.96	0.0013	5.60
75 wt% Si-Ti-AbzImCl	3.14	0.0007	0.93
100 wt% Si-Ti-AbzImCl	2.97	0.0010	1.34
25 wt% Si-Ti-Dicat-BzImCl	1.91	0.0017	3.47
50 wt% Si-Ti-Dicat-BzImCl	1.40	0.0025	7.06
75 wt% Si-Ti-Dicat-BzImCl	2.91	0.0022	3.09
100 wt% Si-Ti-Dicat-BzImCl	2.24	0.0020	3.57

5.2.6 TGA

The thermal stability of the Si-Ti composites was studied by TGA. Figure 5.8 (a) illustrates the TGA curves for 25 wt% to 100 wt% Si-Ti-AbzImCl while Figure 5.8 (b) represents the curves for 25 wt% to 100 wt% Si-Ti-Dicat-BzImCl which were compared with unmodified Si-Ti as the reference. The Si-Ti thermogram shows only one-step decomposition while upon modification with both ILs, the thermograms show three-stage decomposition process. The initial weight losses at 30 °C – 200 °C for Si-Ti, Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl were due to the physically absorbed water as well as the dehydration of alcohol existing in the gel (Bakhshaei *et al*., 2016; Farag *et al*., 2008; Liu *et al*., 2005b). As there was no further weight loss observed for Si-Ti after 400 °C, it can be assumed that a phase transition from amorphous to crystal has occurred in the sample (Marimuthu *et al*., 2014).

A significant weight loss in the subsequent stages at the temperature range of 200 °C – 450 °C observed in IL-loaded Si-Ti was attributed to the degradation of the ILs. It is also worth noting that the more ILs was incorporated into the silica skeleton, the higher was the weight loss percentage of the thermograms of the composites. This result proved that the incorporation of increasing amount of ILs into the silica gel was successful. This phenomenon was supported by the other preceding work (Fang *et al*., 2010). Moreover, the incorporation of ILs into the silica gel greatly improved the thermal stability (Marimuthu *et al*., 2014). The final stages of decomposition with smaller percentage of weight losses were assigned for the oxidation of the carbon residue (Ismail *et al*., 2016; Marimuthu *et al*., 2014). The exact thermal decomposition temperatures of the Si-Ti composites were tabulated in Table 5.7.

Table 5.7: Thermal decomposition of Si-Ti, Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl composites

Sample	Temperature (°C)	Assignment
Si-Ti	31.02 – 400.00	Water & alcohol dehydration
25 wt% Si-Ti-AbzImCl	30.00 – 219.41	Water & alcohol dehydration
	219.41 – 482.20	[Abzim][Cl] decomposition
	482.20 – 694.32	Carbon residue oxidation
50 wt% Si-Ti-AbzImCl	29.67 – 196.79	Water & alcohol dehydration
	196.79 – 449.11	[Abzim][Cl] decomposition
	449.11– 710.77	Carbon residue oxidation
75 wt% Si-Ti-AbzImCl	29.68 – 191.83	Water & alcohol dehydration
	191.83 – 462.07	[Abzim][Cl] decomposition
	462.07 – 688.95	Carbon residue oxidation
100 wt% Si-Ti-AbzImCl	29.65 – 189.54	Water & alcohol dehydration
	189.54 – 426.08	[Abzim][Cl] decomposition
	426.08 – 664.32	Carbon residue oxidation
25 wt% Si-Ti-Dicat-BzImCl	30.84 – 228.21	Water & alcohol dehydration
	228.21 – 433.88	[Dicat-Bzim][Cl] decomposition
	433.88 – 858.18	Carbon residue oxidation
50 wt% Si-Ti-Dicat-BzImCl	29.66 – 210.04	Water & alcohol dehydration
	210.04 – 428.45	[Dicat-Bzim][Cl] decomposition
	428.45 – 852.12	Carbon residue oxidation
75 wt% Si-Ti-Dicat-BzImCl	31.51 – 200.56	Water & alcohol dehydration
	200.56 – 416.79	[Dicat-Bzim][Cl] decomposition
	416.79 – 857.23	Carbon residue oxidation
100 wt% Si-Ti-Dicat-BzImCl	31.16 – 208.04	Water & alcohol dehydration
	208.04 – 427.03	[Dicat-Bzim][Cl] decomposition
	427.03 – 856.60	Carbon residue oxidation

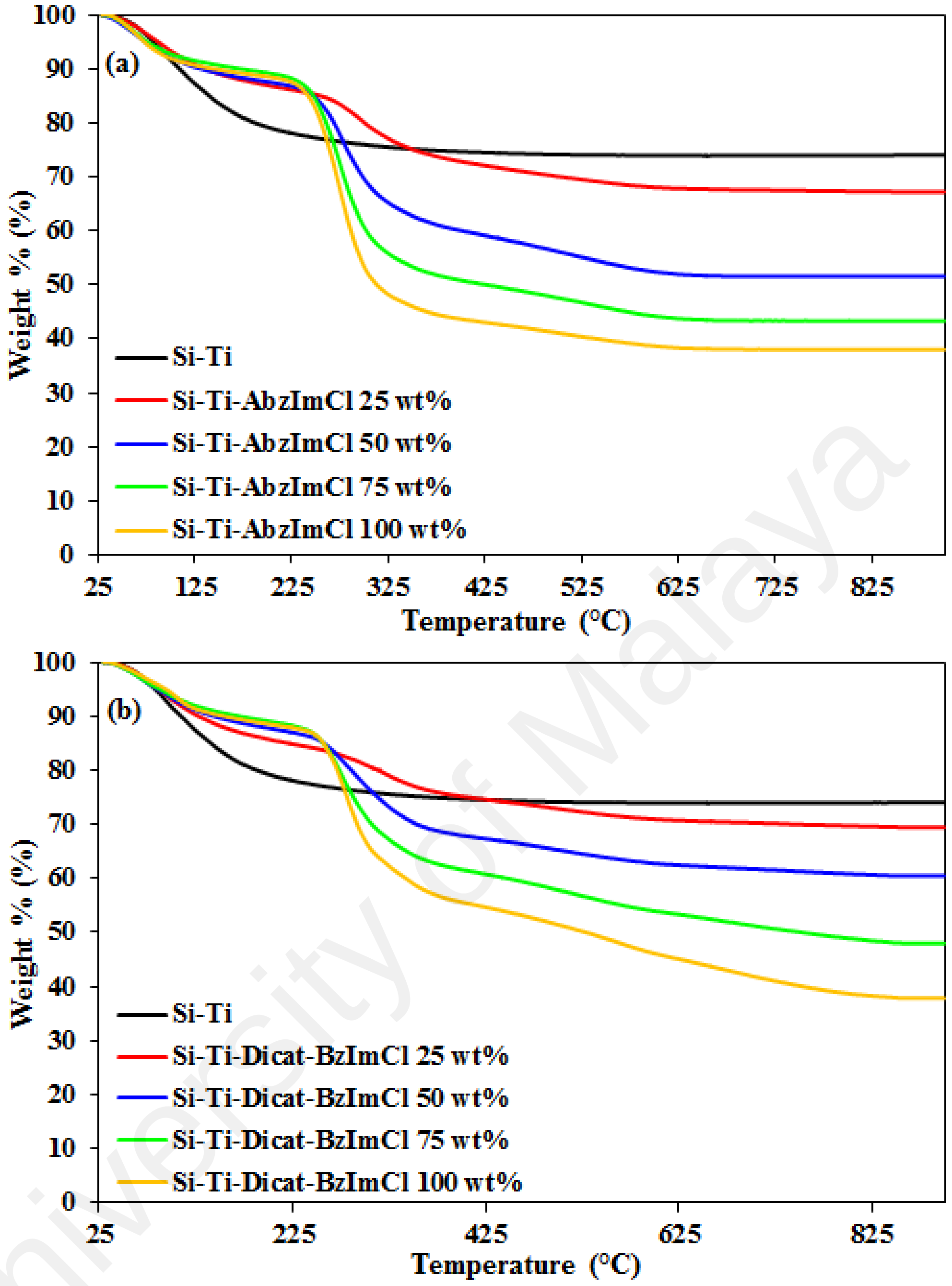


Figure 5.8: The TGA curves of (a) Si-Ti-AbzImCl and (b) Si-Ti-Dicat-BzImCl

5.3 Adsorption study

The synthesized ILs confined in silica-gel were then applied as adsorbents in removing phenol from model oil. Figure 5.9 illustrates the removal efficiency of various loading of [Abzim][Cl] and [Dicat-BzIm][Cl] in removing phenol from hexane. Unmodified Si-Ti was also studied as the reference material. It can be seen that the percentage removal of phenol by Si-Ti-AbzImCl increased gradually from 3.46% to 9.68% with increasing loading of [Abzim][Cl] from 0 wt% to 25 wt%. Upon increasing the amount of [Abzim][Cl] to 50 wt% and 75 wt%, the efficiency increased to 10.69 wt% and 15.67 wt% respectively. At 100 wt% of IL loading, the removal of phenol reached 24.74%. This result revealed that the encapsulation of IL to the silica matrix improves the efficiency of unmodified Si-Ti mixed oxide in extracting phenol from model oil. This result is also supported by previous report where the modified Si-Ti-mixed oxide imidazolium-based IL was successfully used as adsorbent to remove other phenol derivatives from aqueous medium (Ismail *et al.*, 2016). This is due to the possibility of the interaction between phenol and [Abzim][Cl] inside the sol-gel pores which enable these Si-Ti composites to attract phenol during the adsorption process. The main mechanism might include the formation of H-bonding between the Cl^- anion of the IL and hydroxyl group of the phenol as comprehensively described in Section 4.3.7. In addition, the possibility of π-π interaction between the benzene ring of phenol with the imidazolium and benzyl rings as well as double bond on allyl site of IL may have occurred. After the adsorption process, the phenol analyte remained inside the Si-Ti mixed oxide pores due to these possible interactions. The possible mechanism between phenol and Si-Ti-AbzImCl was illustrated in Figure 5.10. The fact that the removal efficiency increases upon increasing the amount of IL loading shows the important function of IL as adsorbent. The addition of higher IL content improves the performance of Si-Ti sol-gel in attracting more phenol.

On the other hand, the performance of Si-Ti-Dicat-BzImCl composites was different from Si-Ti-AbzImCl. Upon addition of 25 wt% of [Dicat-BzIm][Cl], Si-Ti mixed oxide enable to remove about 13.68% phenol. However, upon increasing the amount of IL to 50 wt%, the efficiency decreased to 5.08%. The performance continued to drop to 3.85% and 3.98% after 75 wt% and 100 wt% modification respectively. These results indicate that the optimum [Dicat-BzIm][Cl] loading on Si-Ti sol-gel is 25 wt% and further loading will not improve its performance. The poor performance might be due to the fact that

[Dicat-BzIm][Cl] consists of a very large structure of 3 benzyl rings and occupying the space in the silica pores, eventually leaving a very small space for phenol attachment site. Thus, the possibility of attracting more phenol by using a greater amount of benzyl groups compared to only 1 benzyl substituent was not possible due to the restriction in pore spaces. The performance dropped once the optimum loading of [Dicat-BzIm][Cl] exceeded due to the possibility of blocking pores by the IL itself and subsequently, restricting the phenol from entering the pores. Thus, as a result of poor space in the pores, some phenol cannot be retained in the silica networks and hence, reducing the efficiency. Thus, from this study, it can be concluded that Si-Ti-AbzImCl as a monocationic IL is a better adsorbent compared to dicationic Si-Ti-Dicat-BzImCl.

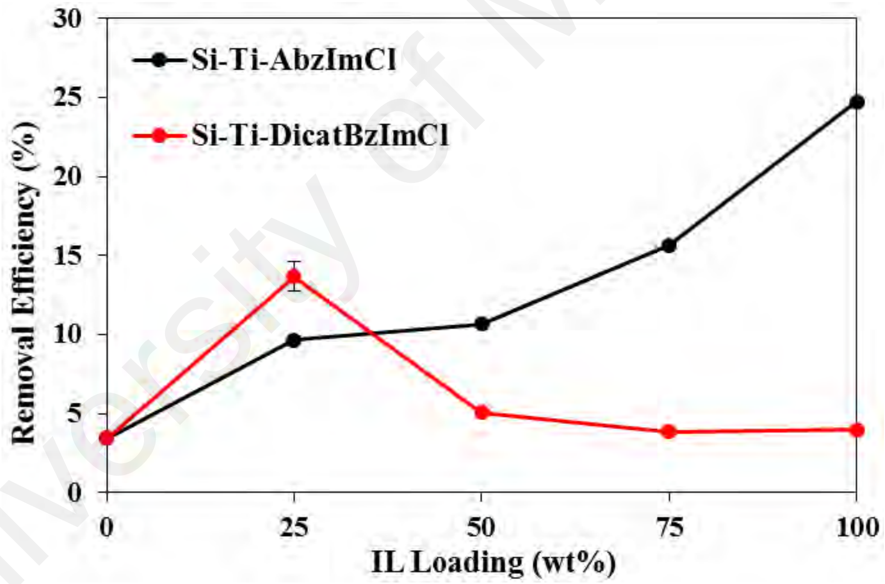


Figure 5.9: The removal efficiency of phenol by different loading of Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl

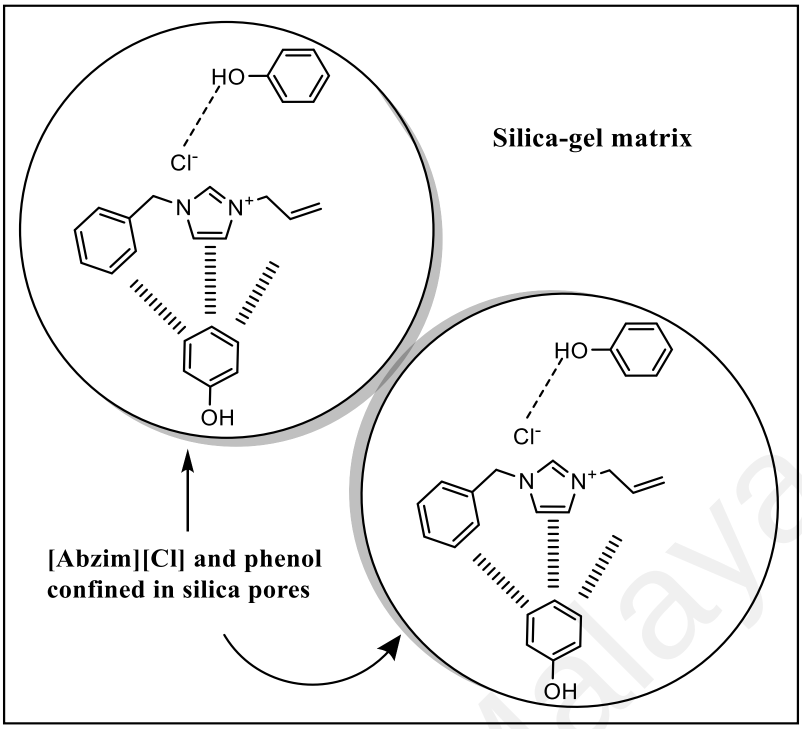


Figure 5.10: The possible mechanism involved for phenol extraction by Si-Ti-AbzImCl

Even though the performance of Si-Ti-AbzImCl is superior than Si-Ti-Dicat-BzImCl, however, the performance of [Abzim][Cl] as an extractant in LLE for phenol removal is more excellent compared to Si-Ti-AbzImCl in adsorption study. The percentage removal of phenol via LLE can be achieved up to 99.46% while via adsorption only 24.74%. Due to the poor performance of Si-Ti composites, the optimization of the adsorption technique was not carried out but another study was performed to investigate the reason. This is because the low percentage removal of phenol by certain amount of Si-Ti composites was not economic and not practical and thus, the optimization part was discarded. A study was subsequently carried out by interacting Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl in hexane respectively and their absorptions were examined by UV-Vis spectroscopy. It was discovered that these two materials appeared in the UV-Vis spectrum indicating that leaching occurred in the hexane. As can be seen in Figure 5.11, both hexane samples of Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl showed maximum absorptions at wavelength, λ_{max} = 225 nm. The UV-Vis data revealed the reason of the poor performance of these two composites where it was found out that these materials leached out to the hexane phase and thus, were not suitable in removing phenol from hexane. Therefore, the cause of the low percentage removal of phenol by Si-Ti composites can be concluded by the contamination of these materials into the hexane phase where this phenomenon was not discovered in LLE study.

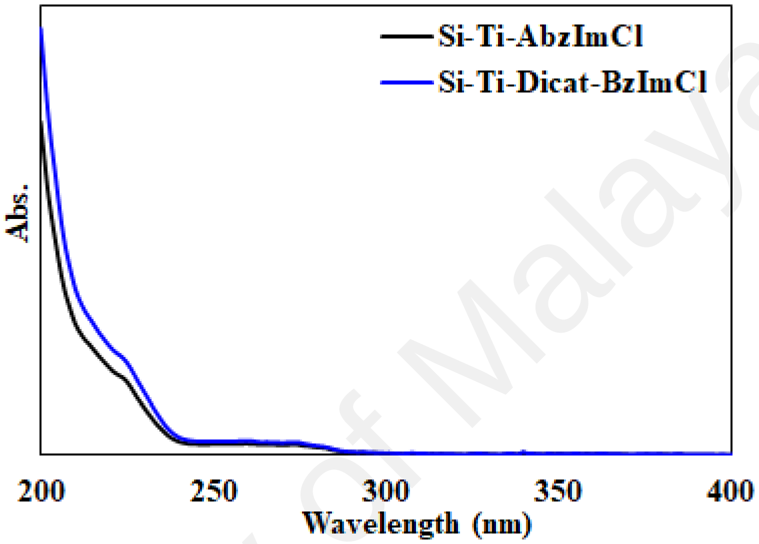


Figure 5.11: Absorption of hexane after interacting with Si-Ti-AbzImCl and Si-Ti-Dicat-BzImCl

CHAPTER 6: CONCLUSION AND FUTURE RECOMMENDATIONS

6.1 Conclusion

Three benzyl imidazolium-based ILs with different aromatic and double bond substituents used as extractants for the removal of phenol via LLE from oil have been successfully synthesized and characterized comprehensively. The characterization results justified the synthesis of those pure ILs.

For the LLE procedure, [Abzim][Cl] outperformed the other two ILs with percentage removal of phenol achieving 95.24% under optimized conditions. The presence of benzyl and double bond groups significantly improve the ability of ILs to remove phenol via hydrogen bonding and enhanced π-π interaction of aromatic moieties. As revealed by the ^{1}H NMR of [Abzim][Cl]-Phenol mixture, the benzene ring on phenol interacts with both allylic and benzylic substituents of [Abzim][Cl] as well as the imidazolium ring. Thus, it can be concluded that [Abzim][Cl] form strong bonds with phenol under optimized conditions with good recyclability up to 6 cycles without significant loss in mass. This study also revealed that the long double bond group on the benzyl imidazolium IL allow strong interaction with the phenol due to the freely moving chloride anion forming hydrogen bonds with phenol compared to the shorter double bond due to the tightly-attached chloride anion to the C(2)-H on imidazolium ring.

On the other hand, the Si-Ti-AbzImCl and Si-Ti-DicatBzImCl composites were successfully synthesized via sol-gel method and characterized accordingly. The characterization results clarified that both ILs were successfully encapsulated onto Si-Ti mixed oxide matrix and influenced the structure and surface morphology of the composites. However, upon employing these composites as adsorbents for the removal of phenol from model oil via adsorption, the percentage removal for Si-Ti-AbzImCl only achieved 24.74% while Si-Ti-DicatBzImCl only managed to obtain 13.68%. Thus, it can be concluded that the most relevant method to remove phenol from oil is via LLE due to the nature of the oil and liquid ILs.

6.2 Future recommendations

In this study, it was found that benzyl imidazolium-based ILs are potential alternative extraction medium for separating phenols from oil. However, it is expected that ILs might be capable of extracting various other compounds found in oil by tuning the cationic part of the ILs. Thus, it would be interesting to investigate the effects of other substituent groups of the ILs in order to have active site for specific target analytes. Moreover, the effect of anionic part of the ILs is not included in this study. It is known that the anion pair plays an important role in determining the solubility and polarity of ILs in other media. Therefore, future investigations should focus on the role of the anionic pair in influencing the performance of ILs as extractants and adsorbents.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

List of publication

1. Sidek, N., Manan, N. S., & Mohamad, S. (2017). Efficient removal of phenolic compounds from model oil using benzyl imidazolium-based ionic liquids. *Journal of Molecular Liquids*, 240, 794-802.

List of conferences

1. Removal of Phenolic Compounds Using Benzyl Imidazolium-based Ionic Liquids. The 29th Malaysian Analytical Chemistry Symposium, (2016), Malaysia.
2. Removal of Phenolic Compounds Using Benzyl Imidazolium-based Ionic Liquids. 16th Asia Pacific International Symposium on Microscale Separations and Analysis, (2016), Malaysia.