APPLICATION OF IMIDAZOLIUM-BASED IONIC LIQUID AS BULK LIQUID MEMBRANE IN PHENOL REMOVAL

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ABSTRACT

Performance of imidazolium-based ionic liquid membranes [Bmim][PF_6], [Bmim][NTf_2] and [Bmim][FAP] on phenol removal was evaluated under room temperature by using batch bulk liquid membrane system. The results showed that all ionic liquids tested formed stable membranes and exhibited better solvent recoveries in comparison to organic membrane solvent, dichloromethane with [Bmim][NTf_2] showing the highest extraction and stripping efficiencies of 94.18% and 73.39%, respectively after 300 min experiment due to its relatively higher hydrogen bond basicity strength and adequate hydrophobicity. Following the finding, [Bmim][NTf_2] was further analyzed to determine the effect of the feed phase pH, feed concentration, NaOH concentration and stirring speeds on liquid membrane behavior and performance. Based on the experimental results, a phenol transport mechanism which is similar to that of organic liquid membranes was proposed for [Bmim][NTf_2] based liquid membrane. [Bmim][NTf_2] possessed similar behavior as organic membrane solvent whereby it favoured molecular phenol extraction to phenolate anion. Besides, high phenol dissolution capacity of this ionic liquid also prevented membrane saturation even in high phenol concentration solution treatment.

An optimization study on the significant parameters using Central Composite Design showed that maximum extraction and stripping efficiencies of 96.21% and 98.10% were achieved under the conditions of feed phase pH ≈6.5, 300ppm phenol concentration, 0.5M NaOH concentration, 135rpm membrane stirring speed and 255rpm aqueous stirring speed. This study has proven that [Bmim][NTf_2] is a better choice than kerosene and dichloromethane.

ABSTRAK

Prestasi membran cair ionik imidaozlium berdasarkan [Bmim][PF_6], [Bmim][NTf_2] dan [Bmim][FAP] untuk penyingkiran fenol dinilai pada suhu bilik dengan sistem membran cair pukal secara kelompok. Kajian menunjukkan bahawa semua cecair ionik yang diuji membentuk membran yang stabil dan mempunyai pemulihan yang lebih baik berbanding dengan membran cair organik diklorometana. Didapati bahawa [Bmim][NTf_2] adalah membran cair ionik terbaik antara cecair ionik yang diuji di mana ia memberi 94.18% kecekapan ekstraksi dan 73.39% kecekapan *stripping* selepas 300 minit. Ini disebabkan oleh sifat-sifat [Bmim][NTf_2] yang menunjukkan ikatan hidrogen kebesan tertinggi dan hidrofobik di antara cecair-cecair ionik tersebut. Dengan itu, [Bmim][NTf_2] dipilih untuk mengkaji pengaruh pH, konsentrasi fenol, konsentrasi NaOH dan kelajuan pengadukan terhadap perilaku and prestasi membran cair ionik. Keputusan eksperimen menunjukkan bahawa membrane cair ionik [Bmim][NTf_2] mempunyai mekanisma pengangkutan fenol yang seiras dengan membran cair organik. [Bmim][NTf_2] menunjuk perilaku yang sama seperti membran cair organik di mana ia lebih cenderung untuk mengekstrak fenol dalam bentuk molekul berbanding dengan bentuk ion. [Bmim][NTf_2] juga dapat digunakan untuk mengekstrak fenol dalam larutan berkonsentrasi tinggi tanpa ketepuan membran kerana kapasiti ekstrasi fenolnya yang tinggi. Kajian pengoptimuman berdasarkan *Central Composite Design* menunjukkan bahawa 96.21% kecekapan ekstraksi dan 98.10% kecekapan *stripping* dapat dicapai di bawah keadaan pH pada larutan suapan ≈6.5, konsentrasi fenol 300ppm, konsentrasi NaOH 0.5M, pengadukan fasa membran dengan kelajuan 135rpm dan 255rpm untuk pengadukan fasa cecair. Ini menunjukkan bahawa [Bmim][NTf_2] memberi prestasi membrane cair yang lebih baik berbanding dengan kerosene dan diklorometana.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Mass transfer interfacial area (m^2)
A_1'	Absorbance for phenol
A_2'	Absorbance for sodium phenolate
α	Coded membrane stirring speed
ANOVA	Analysis of Variance
β	Coded aqueous stirring speed
BF_4^-	Tetrafluoroborate
BILM	Bulk ionic liquid membrane
Bmim	1-butyl-3-methylimidazolium
BOLM	Bulk organic liquid membrane
Br^-	Bromide
BR_4^-	Tetraalkylbromide
$C(CN_3)^-$	Tricyanomethanide
C_1	Solute concentration in the donor phase (mg/L)
C_1'	Solute concentration in the donor phase in equilibrium with the acceptor phase (mg/L)
$C_6H_5O^-$	Phenolate anion
C_6H_5OH	Phenol
C_6H_5ONa	Sodium phenolate
CCD	Central composite design
C_f	Phenol concentration in the feed phase (mg/L)
C_f'	Phenol concentration in the feed phase (interface) in equilibrium with the membrane phase (mg/L)
C_f^*	Equilibrium phenol concentration in the feed phase (mg/L)
$C_{f,0}$	Initial phenol concentration in the feed phase (mg/L)
$C_{f,t}$	Concentration of phenol in the feed phase at time t (mg/L)
$CF_3CO_2^-$	Trifluoroacetate
$CF_3SO_3^-$	Trifluoromethanesulfonate
$CH_3CO_2^-$	Acetate
$CH_3SO_2^-$	Sulfinate
Cl^-	Chloride
C_m	Phenol concentration in the membrane phase (mg/L)
C_m'	Phenol concentration in the membrane phase (interface) in equilibrium with the stripping phase (mg/L)
C_m^*	Equilibrium phenol concentration in the membrane phase (mg/L)
$C_{m,t}$	Phenol concentration in the membrane phase at time t (mg/L)
C_s	Phenol concentration in the stripping phase (mg/L)
C_s^*	Equilibrium phenol concentration in the stripping phase (mg/L)
C_s^{Ph}	Concentration of sodium phenolate in stripping phase (mg/L)
$C_{s,t}$	Concentration of phenol in the stripping phase at time t (mg/L)

D	Diffusion coefficient (m^2/s)
D_1	Distribution coefficient of phenol between membrane/feed phase
D_2	Distribution coefficient of phenol between stripping/membrane phase
DCA^-	Dicyanamide
DF	Dilution factor
DMSO	Dimethyl sulfoxide
e	Cumulative amount of phenol loss due to sampling (mg)
Emim	1-ethyl-3-methylimidazolium
FAP^-	Tris(perfluoroalkyl)trifluorophosphate/ Tris(pentafluoroethyl)trifluorophosphate
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
HF	Hydrogen fluoride
Hmim	1-hexyl-3-methylimidazolium
I^-	Iodide
J	Mass transfer rate by mass (mg/min)
k	Mass transfer coefficient (minute basis) (m/min)
k'	Mass transfer coefficient (m/s)
k_1	Extraction kinetics (m/min)
k_{-1}	Back extraction kinetics (m/min)
K	Transport kinetics (min^{-1})
K_1	Extraction kinetics (min^{-1})
K_{-1}	Back extraction kinetics (min^{-1})
K_2	Stripping kinetics (min^{-1})
K_{-2}	Back stripping kinetics (min^{-1})
k_B	Boltzmann constant (1.38×10^{-23} m^2kg/s^2K)
L	Liter ($0.001m^3$)
L	Characteristic length/diffusion path (m)
LD_{50}	Median lethal dose
M	Molarity (mol/L)
MIBK	Methyl isobutyl ketone
min	Minute (60s)
μ	Viscosity (Pa.s or kg/ms)
N	Normality
N_3^-	Azide
NaCl	Sodium chloride
NaOH	Sodium hydroxide
N_f	Mass of phenol in the feed phase (mg)
$N_{f,0}$	Initial mass of phenol in the feed phase (mg)
$N_{f,t}$	Mass of phenol in the feed phase at time t (mg)
$N_{IL,0}$	Mass of ionic liquid before the experiment (g)
$N_{IL,r}$	Mass of ionic liquid after the regeneration process (g)
N_m	Mass of phenol in the membrane phase (mg)
NO_3^-	Nitrate

N_s	Mass of molecular phenol in the stripping phase (mg)
$N_{s,t}$	Mass of phenol in the stripping phase at time t (mg)
NTf_2^-	Bis(trifluoromethylsulfonyl)imide
Omim	1-octyl-3-methylimidazolium
PF_6^-	Hexafluorophosphate
π	3.14159…
PIB	Polyisobutylene
pK_a	Dissociation constant
ppm	Parts per million
r	Radius of the particle (m)
rpm	Revolution per minute
RSO_4^-	Alkylsulfate
Sh	Sherwood number
T	Temperature (K)
TBME	Tert-butyl methyl ether
TBP	Tributyl phosphate
TOA	Trioctylamine
TOMAC	Tri-octylmethylammonium chloride
TOPO	Trioctylphosphine Oxide
V	Volume of the phases (L)
wt	By weight
Y_1	Extraction efficiency (%)
Y_2	Overall phenol recovery (%)

General Subscripts and Superscripts

0	Initial
aq	Aqueous phase
f	Feed phase
IL	Ionic liquid
m	Membrane phase
s	Stripping phase
t	At the time of
*	Equilibrium

LIST OF APPENDICES

CHAPTER 1: INTRODUCTION

1.1 Background

Phenol is an organic compound which is normally present in the industrial effluents originating from petrochemical, coal processing and refinery operations. It is highly toxic and has a considerable effect on human health with a deadly dose of 1g (Busca *et al.*, 2008). Phenol is readily absorbed by various ways such as inhalation, ingestion, eyes and skin contact. According to World Health Organization (1994), phenol causes severe effects such as gastrointestinal irritation, methaemoglobinaemia, neurological effect, cardiovascular shock, coma and even death. Besides human health, toxicity of phenol is also a major concern to aquatic lives as it forms carcinogenic chloro-phenol compounds in the presence of chlorine in water (Sirianuntapiboon *et al.*, 1999). Its high solubility in water causes disruption to aquatic ecosystem balance as the toxicity threshold and LD_{50} for the aquatic lives such as bacteria (64mg/L), crustaceans and fishes (3-7mg/L) are low (World-Health-Organization, 1994). Therefore, a careful handling of phenol is necessary to minimize release into the water body.

Large applications of phenol in industries have increased the possibilities of its release to the environment. Typical phenol concentration in the effluents is in several thousand parts per million (ppm) which is critically above the threshold value of the aquatic lives. Hence, to ensure the aquatic ecosystem balance is well maintained, Department of Environment Malaysia (2009) has implemented two standards for phenol concentration in the treated effluents, namely standard A (0.001ppm, near water uptake source) and standard B (1ppm, away from water uptake source). Several treatment methods for the effective removal of phenol have been suggested, the common ones

being activated carbon adsorption, liquid-liquid extraction, chemical oxidation, biological treatment and liquid membranes (Busca *et al.*, 2008; Ng *et al.*, 2010).

Liquid membrane technique is the focus in this study. In comparison to the more familiar liquid-liquid extraction, the extraction process in liquid membranes is free from equilibrium limitation, thus providing a maximum driving force in the transport process (Frankenfeld and Li, 1987; Yang *et al.*, 2003; Nabieyan *et al.*, 2007). Recent studies on phenol removal using liquid membranes show that the highest achievable phenol extraction efficiency is more than 99%, depending on the types of liquid membranes, as summarized in Section 2.2.3. However, most of the liquid membranes applied for phenol removal utilize organic membrane solvents which are normally volatile, flammable and toxic. These properties often cause the loss of membrane solvent, membrane instability and consequently restrict the applications of liquid membranes in larger scale.

In contrast, ionic liquids emerge as alternatives to the organic membrane solvents. Ionic liquids are a group of salts that consist of organic cations and organic/inorganic polyatomic anions. They can be referred as molten salts that have lower melting point (<373K) (Jodry and Mikami, 2005; Keskin *et al.*, 2007; Holbrey and Rogers, 2008). Due to their salt properties, they have negligible volatility and are less flammable, as will be discussed in Sections 2.3.2.1 and 2.3.2.2. Besides that, they are tunable as their properties are strongly dependent on the combination between the cations and anions (Section 2.3.2.3).

Preliminary studies on the applications of imidazolium-based ionic liquids on phenol removal were conducted by researchers via liquid-liquid extraction (Khachatryan *et al.*, 2005; Li *et al.*, 2005; Vidal *et al.*, 2005; Fan *et al.*, 2008). These ionic liquids which are based on the anions of tetrafluoroborate, $[BF_4^-]$ and hexafluorophosphate, $[PF_6^-]$ showed better phenol extraction efficiency than that of organic solvents. However, these ionic liquids are not suitable to be further utilized as they have low moisture stability which tend to degrade and form toxic and corrosive gases such as hydrogen fluoride (HF) under moist environment (Swatloski *et al.*, 2003; Jodry and Mikami, 2005; Keskin *et al.*, 2007; Wagner and Hilgers, 2008).

Besides that, the studies on the applications of these ionic liquids as liquid membranes also showed that unstable membranes were obtained when the aqueous phase was in contact with them (Fortunato *et al.*, 2004; 2005a; Matsumoto *et al.*, 2007). Imidazolium-based ionic liquids with anion $[PF_6^-]$ showed the formation of water microenvironment path during the experiments due to their significant water solubility. This reduces the selectivity of ionic liquid membrane on the transport of water soluble compounds such as tritiated water, NaCl, amino acid, amino acid esters (Fortunato *et al.*, 2004; 2005a) and Penicillin G (Matsumoto *et al.*, 2007) as these compounds were transported through the membrane by the microenvironment path rather than the solubility in the membrane. Consequently, these ionic liquid membranes fail.

The above published works lead to an idea that these ionic liquids have potential as extraction solvents for phenol removal, but they face a major problem on the loss of membrane operability when they are in contact with aqueous phase. This questions the suitability of ionic liquids as alternatives to organic solvents in liquid membrane systems. In this study, technical feasibilities of ionic liquids as stable liquid membranes on phenol removal from aqueous solution are investigated experimentally by utilizing other types of imidazolium-based ionic liquids which are more hydrophobic and have

less water solubility. The feasibility analysis covers the extraction efficiency, stripping efficiency, membrane stability and ionic liquid recovery.

1.2 Research Objectives

The goal of this study is to evaluate the technical feasibilities of imidazolium-based ionic liquids as alternatives to organic membrane solvents for phenol removal from aqueous solution. Among the objectives of the research are:

i. To determine the suitability of imidazolium-based ionic liquids as carriers or diluents in liquid membrane system.
ii. To determine the technical feasibilities for different types of imidazolium-based ionic liquids as liquid membranes on phenol removal in terms of extraction efficiency, stripping efficiency, membrane stability, reusability and ionic liquid recovery.
iii. To determine the best ionic liquid as liquid membrane.
iv. To study the effect of feed phase pH, feed concentration, NaOH concentration and stirring speeds on the behavior and performance of bulk ionic liquid membrane.
v. To optimize the significant parameters using Response Surface Methodology so as to achieve the best phenol extraction and stripping efficiencies for bulk ionic liquid membrane.
vi. To compare the performance between ionic liquid membrane and organic liquid membrane.
vii. To propose the extraction and stripping mechanisms and the transport kinetics modeling for bulk ionic liquid membrane based on experimental data.

1.3 Research Approach

The research was conducted mainly by primary research based on the procedures as shown below:

Literature review: Based on the literature review conducted, imidazolium-based ionic liquids were considered as the published physical properties data on them were adequate. Hence, ionic liquids were screened based on the criteria such as high hydrophobicity, low mutual solubility with water, high moisture stability and low toxicity in accordance to the objectives of the research.

Methodology: The research was initiated by studying the behavior of ionic liquids as carriers and diluents via liquid-liquid extraction. Based on the results, bulk ionic liquid membrane study was conducted experimentally and the effects of some major parameters were investigated. The concentrations of phenol/phenolate in the samples were analyzed by UV-Vis spectrophotometer.

Data analysis and interpretation: The performance of bulk ionic liquid membrane was evaluated based on extraction efficiency, stripping efficiency, membrane stability and ionic liquid recovery. The behavior of the best ionic liquid membrane was further analyzed under different operating conditions of feed phase pH, feed concentration, NaOH concentration and stirring speeds. Based on the experimental results, transport mechanism of phenol in bulk ionic liquid membrane was proposed. Lastly, the technical feasibility of the ionic liquid membrane is justified through comparison of optimum efficiencies with organic liquid membranes.

1.4 Structure of Thesis

The thesis consists of 6 chapters.

Chapter 1 provides the background of the study, research objectives, research approach and the structure of the thesis is included.

Chapter 2 contains the literature review. The first section of this chapter is the introduction of phenol which discusses the properties of phenol, its applications and production, toxicity, concentration in industrial wastewaters, environmental regulation and the conventional treatment methods. Besides, this chapter also explains about liquid membranes such as the types of liquid membranes, transport mechanisms in liquid membranes and their applications in phenol removal. Furthermore, properties of the ionic liquids and recent studies on the ionic liquid membranes are included and lastly, screening and selection of ionic liquids and liquid membrane system are covered in this chapter.

Chapter 3 describes the experimental procedures of liquid-liquid extraction, bulk liquid membrane test and regeneration of ionic liquids. Besides, analytical methods such as preparation of calibration curves, dilution of samples and phenol concentration analysis are also elaborated. In addition, the chemicals and reagents used, experimental set-up and analytical equipment are also introduced in this chapter.

Chapter 4 presents the results and discussion on the role of ionic liquids as diluents and carriers via liquid-liquid extraction process. Based on the result obtained, the performances of bulk ionic liquid membrane on phenol removal under different operating conditions are discussed. In addition, a comparison between the optimum performance of the ionic liquid membrane and the organic liquid membranes is conducted in this chapter

Chapter 5 discusses on the transport kinetics modeling of phenol in bulk ionic liquid membrane system. Extraction and stripping mechanisms are proposed in the forms of theoretical and mathematical models based on the experimental data and the literature review. Possible model simplification and the validity of the model are discussed.

Chapter 6 covers the conclusions of this study and some recommendations for future studies.

CHAPTER 2: LITERATURE REVIEW

This chapter consists of four subchapters which discusses the properties, the hazardous nature of phenol, the types of liquid membranes and their applications on phenol removal, properties of ionic liquids and their applications as liquid membranes on organic compounds removal. Last part of this chapter discusses the selections of liquid membrane and ionic liquids which meet the objectives of this study in parallel with the literature review.

2.1 Phenol

Phenol, C_6H_5OH (CAS No. 108-95-2) is an organic substance which is normally present in the industrial effluents. It is an aromatic compound which has a –OH functional group attached to the benzene ring. Phenol is also known as benzophenol, carbolic acid, hydrobenzene, phenic acid, phenlic alcohol, phenyl hydroxide etc. (World-Health-Organization, 1994; United-States-Department-of-Labors, n.d). The molecular structure of phenol is as shown in Figure 2.1.

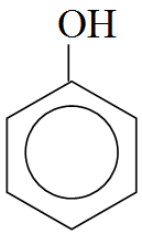


Figure 2.1: Molecular structure of phenol

2.1.1 Physical and Chemical Properties

Phenol is a hygroscopic white crystalline solid at room temperature and under atmospheric pressure. It has a characteristic of sweet, medicinal and tar like odour (Zidi *et al.*, 2010; United-States-Department-of-Labors, n.d) which causes off-flavour in drinking and food processing water. Some important physical properties of phenol are as shown in Table 2.1.

Table 2.1 shows that phenol is a weak acid with pK_a value range of 9.89-10. It has weaker tendency to undergo ionization and to lose H^+ from its hydroxyl group compared to other strong acids such as HCl and H_2SO_4. However, under high pH condition where low H^+ concentration is available, phenol readily loses its H^+ via acid-base equilibrium. For example, phenol dissociates and reacts with strong base such as NaOH to form sodium phenolate, a water soluble salt (Frankenfeld and Li, 1987; Le *et al.*, 2002; Park and Chung, 2003; Xiao *et al.*, 2006; Shen *et al.*, 2009; Zidi *et al.*, 2010).

Table 2.1: Physical properties of phenol

Physical properties	**Value**
Molecular Weight, g/mol	94.11[a,d,f]
Specific Gravity	1.07[a,f]
Melting Point, K	316[f] 313.9[a,d]
Boiling Point, K	454.75[a,d,f]
Vapour pressure, kPa	0.04 (293K)[a] 0.047 (298K)[f]
Solubility in water, g/100mL	6.7 – 9.3[a,d-e]
Solubility in organic solvent	Soluble in most of the organic solvents but insoluble in petroleum ether [a,d,f]
Dissociation constant, pK_a	9.89-10 [b-e]

(Source: [a]World-Health-Organization, 1994; [b]Vidal *et al.*, 2005; [c]Venkateswaran and Palanivelu, 2006; [d]Busca *et al.*, 2008; [e]Zidi *et al.*, 2010; [f]United-States-Department-of-Labors, n.d)

Besides acid-base reaction, the increment of the reactivity of the benzene ring contributed by –OH group increases the tendency of the ring towards electrophilic substitutions. The examples are the reaction with bromine and nitric acid (Clark, 2004). Moreover, as alcohol, phenol is combustible to produce carbon dioxide and water (Busca *et al*., 2008). However, the high carbon content and stable aromatic ring of phenol will make it difficult to combust completely in air as the oxygen content is low. Furthermore, phenol readily undergoes chlorination through the activation properties of hydroxyl group that is attached to the benzene ring to form chlorophenol (Sirianuntapiboon *et al*., 1999).

2.1.2 Production and Applications of Phenol

According to the China Chemical Reporter (2006), there is an increase in the demand of phenol from year 2004 to 2005 whereby the world's phenol production capacity is undergoing 7.6% increment at 9.044 million tonne, and it is believed that the demand will further increase in the future.

It has wide applications in industries such as manufacturing of phenolic resin, cyclohexanone, xylenols, alkylphenols, chlorophenols, aniline, polyphenoxy and polysulphone polymers, polyester, polyester polyols, insecticides, herbicides, dye, textile, paints, fertilizers and surfactants (World-Health-Organization, 1994; Busca *et al.*, 2008; United-States-Department-of-Labors, n.d). Besides that, phenol is being utilized as extracting solvent and additive in disinfectant for shaving soap preparation, as well as antiseptic in veterinary medicine, peptizing agent, blocking agent and reagent in chemical analysis.

2.1.3 Toxicity of Phenol

Phenol is toxic to human and aquatic lives even in small amount due to its carcinogenic effect to living things. It is readily absorbed into human body in various ways such as inhalation, ingestion, eye or skin contact. The effect depends on the exposed dosage and methods. Some of the effects are skin and eyes burn, gastrointestinal irritation, protein denaturing, tissue erosion, painless blanching, paralysis on nervous system, deep necrosis, cardiac dysrhythmias, respiratory distress, metabolic acidosis, damage on kidney, liver and pancreas, renal failure, dark urine, methaemoglobinaemia, neurological effect, cardiovascular shock, convulsion, cyanosis, coma and finally death (World-Health-Organization, 1994; Canadian Environmental Protection Act, 1999 (as cited in Busca *et al.*, 2008); United-States-Department-of-Labors, n.d). The deadly dose by ingestion for human is 1g.

Toxicity of phenol also presents major threats to aquatic lives and thus making it a substance that must be removed from the water body. From Table 2.1, phenol has high solubility in water which is in a range of 6.7-9.3g/100mL. In comparison to this value, the toxicity threshold and LD_{50} for aquatic lives are much lower. According to World Health Organization (1994), the threshold value for bacteria is 64mg/L and same magnitude for protozoa and fungi while the LD_{50} for higher water organisms such as crustaceans and fishes are in between 3-7mg/L. From this data, it is clear that minor concentration of phenol results in adverse effect to the aquatic ecosystem. Therefore, careful handling of phenol is necessary to minimize release into the water body.

2.1.4 Phenol Concentration in Wastewater and Environmental Regulations

The release of phenol to the environment happens in two ways, i.e. air and water. The release of phenol into the air is normally contributed to activities such as cigarette smoke, residential wood burning and degradation of benzene under influence of light (World-Health-Organization, 1994). The release of phenol into water body is more significant as compared to air. Large application of phenol in the industries increases the release of phenol to the environment via wastewaters and process effluents in a concentration ranging from several ppm to several thousand ppm, as shown in Table 2.2.

Table 2.2: Sources of phenol effluents and their concentrations

Sources of industrial effluents	**Concentration, ppm**
Refinery	6-500[b,c]
Coal Processing	9-6800[b,c]
Coking operation	28-3900[b,c]
Petrochemicals	2.8-1220[b,c]
Plastic industries	0.1-1600[b,c]
Pharmaceutical	0.1-1600[b,c]
Pulp and paper industries	0.1-1600[b,c]
Phenol production	>2000[a]
Wood product	0.1-1600[b,c]
Paint industries	0.1-1600[b,c]
Oily and process water/wash effluent	10-200[a]

(Source: [a]Nanoti *et al.*, 1997; [b]González-Muñoz *et al.*, 2003; [c]Busca *et al.*, 2008)

The table shows that the concentrations of phenol in the industrial effluents are much higher in comparison to the threshold value for aquatic lives. Department of Environment Malaysia (2009) has formulated two standards, namely standard A (0.001ppm, near water uptake source) and standard B (1ppm, away from water uptake source) for the phenol concentration in the discharged effluents in order to maintain the aquatic ecosystem balance. Hence, an efficient method has to be applied in order to achieve the discharge limit.

2.1.5 Conventional Phenol Removal Method

Generally, phenol treatment methods can be categorized into 3 groups: a) physicochemical which include extraction, liquid membranes and absorption/adsorption processes; b) biochemical which include activated sludge, bio-membrane and bio-contact processes; and c) chemical oxidation. Some of the common methods are activated carbon adsorption, liquid-liquid extraction, chemical oxidation, biological treatment and liquid membranes. A brief overview for each treatment method is discussed in the following sections.

2.1.5.1 Activated Carbon Adsorption

Activated carbon adsorption is an efficient method to adsorb colour, odor, suspended solids and organic compounds from wastewater as it has large interfacial area due to its microporous nature which provides high adsorption capacity. This process is mainly governed by physisorption mechanism whereby phenol is removed from water by adsorption onto the surface of activated carbon. The work of Sirianuntapiboon *et al.* (1999) showed that 99% of phenol can be removed by activated carbon-sequence batch reactor after 2 weeks operation. Using different configurations and operating periods, Qadeer and Rehan (2002) and Mukherjee *et al.* (2007) achieved high efficiency on phenol adsorption too.

Despite its high adsorption capacity, activated carbon carries several disadvantages. Activated carbon can act as a breeding ground for microorganisms, which means disinfection of water is necessary before the treatment proper (National-Research-Council, 1980). Besides that, another post-disinfection is required to remove undesired products that are yielded from the reaction between the activated carbon and the aqueous disinfectant. The utilization of fine powdered activated carbon also tends to

create colloidal issue whereby the colloids in the aqueous phase become contaminants and this reduces carbon's recovery in the system (Sirianuntapiboon *et al.*, 1999; López-Montilla *et al.*, 2005). Furthermore, activated carbon easily loses its adsorbent capacity due to irreversible chemisorption of phenol and thermal degradation of carbon during high energy thermal regeneration process (Burghoff *et al.*, 2008; Busca *et al.*, 2008).

2.1.5.2 Liquid-liquid Extraction

Liquid-liquid extraction is a technique applied to strip down the targeted solute, phenol using an extracting organic solvent. The extraction process is based on equilibrium distribution of phenol between the solvent and the aqueous phase. Phenol extracted by the solvent is then recovered using a stripping agent in a stripping column which allows solvent reuse.

Even though this process provides fast extraction, it carries several disadvantages such as high operating cost, large quantity of solvent usage, solvent loss issue (Yamini *et al.*, 2002; Yang *et al.*, 2003; Venkatesan and Begum, 2009) and organic carryover in the aqueous phase which contributes to pollutions (Cichy *et al.*, 2005; Burghoff *et al.*, 2008; Shen *et al.*, 2009). Besides that, equilibrium approach in the extraction process results in smaller driving force when treating low phenol concentration wastewater which limits the maximum extractable amount of phenol in single stage (Yang *et al.*, 2003). Other disadvantages mentioned by researchers are emulsification problem, high alkaline consumption, and circulation of extractant that leads to accumulation of phenol (González-Muñoz *et al.*, 2003; Yang *et al.*, 2003; Cichy *et al.*, 2005; Jiang and Guo, 2007; Reis *et al.*, 2007; Burghoff *et al.*, 2008; Shen *et al.*, 2009).

In order to enhance phenol extraction efficiency and minimize the negative impacts, several modifications have been suggested. Firstly, the enhancement of extraction efficiency via increasing interfacial area through microemulsion extraction was studied by López-Montilla *et al.* (2005). Besides that, minimization on equilibrium approach was conducted by Shen *et al.* (2006), who utilized three phase extraction system. Shen *et al.* (2006) showed that high separation factor above 80 for p-nitrophenol and phenol could be achieved by regulating pH of the system and the types of solvents. Furthermore, Jiang and Guo (2007) studied the extraction-evaporation system where the solvent was recovered from phenol by evaporation rather than the normal stripping process. This potentially helps to reduce usage of stripping agent while maintaining the purity of the recycled solvent and phenol dissolving capacity. With that, the issue of phenol accumulation in the solvent was minimized. Phenol extraction efficiency is also enhanced through the utilization of carrier such as Cyanex923, TOPO, TOA, TBP as additives in the solvents (Urtiaga and Ortiz, 1997; González-Muñoz *et al.*, 2003; Cichy *et al.*, 2005; Reis *et al.*, 2007; Shen *et al.*, 2009; Zidi *et al.*, 2010). However, enhancement by the addition of carrier became less effective when solvent of high phenol dissolving capacity such as 1-decanol was used (González-Muñoz *et al.*, 2003).

2.1.5.3 Chemical Oxidation

Wastewater with high phenol concentration can be detoxified by chemical oxidation method. It is also known as decomposition/destruction method whereby phenol is oxidized and converted into other products which are less toxic, such as maleic acid, fumaric acid and possibly CO_2 and water (Idris and Saed, 2002; Busca *et al.*, 2008). Some examples of this method are: wet air oxidation, wet oxidation (ozone,

hydrogen peroxide, horseradish peroxidase), electro-oxidation, anodic oxidation and photocatalytic oxidation (Idris and Saed, 2002; Busca *et al.*, 2008). According to Busca *et al*. (2008), this method is very efficient when the phenol concentration is excessively low to be incinerated and toxic to be biodegraded. However, high capital cost and high operating conditions often restrict wide application of this treatment method in the industries (Idris and Saed, 2002; Jiang and Guo, 2007; Busca *et al.*, 2008). Besides that, a risk of incomplete oxidation exists for this method which could result in more toxic intermediate products like iron sludge and also chlorinated organic that require further treatments (Noyes, 1991; Idris and Saed, 2002; Busca *et al.*, 2008).

2.1.5.4 Biological Treatment

Biological treatment of phenol occurs through the digestion of phenolic compounds by bacteria in the wastewater. Common example of biological treatment is activated sludge system which is simple in design and is considered to be of low cost, but requires large amount of land area for sludge disposal (Nanoti *et al.*, 1997). Despite its toxicity, phenol can be degraded by biological processes as some microbes are proven to be capable of degrading phenol (Busca *et al.*, 2008). However, this method shows low flexibility as it can only handle wastewater with low phenol concentration. At high phenol concentration, microbial growth is inhibited (Shen *et al.*, 2006; Burghoff *et al.*, 2008; Busca *et al.*, 2008). Hence, careful handling is critical so as to prevent shock loading for this method.

2.1.5.5 Liquid Membranes

Liquid membrane techniques are chosen as the separation method in this study as they have shown good potential for phenol removal from wastewaters. Liquid membranes are semi-permeable liquids which are capable of selectively transporting certain targeted solutes. Several types of liquid membrane configurations are available such as bulk liquid membrane, supported liquid membrane and emulsion liquid membrane. The details of these liquid membranes are discussed in Section 2.2.

2.2 Liquid Membranes

Liquid membranes are defined as liquids that serve as semi-permeable media. They form an immiscible barrier between the feed phase and the stripping phase and are capable of transporting certain solutes selectively depending on the difference in solubility and diffusivity of the solutes in the membrane (Kaur and Vohra, 2010; Vladimir, 2010). With the same concept applied in liquid-liquid extraction, liquid membranes combine the extraction process and stripping process into a single process.

Liquid membranes provide several advantages over other separation methods, such as low capital and operating cost, high efficiency, technical simplicity, kinetic-dependent transport which eliminates the equilibrium limitation of liquid-liquid extraction and providing maximum driving force in the transport process (Frankenfeld and Li, 1987; Le *et al.*, 2002; Yamini *et al.*, 2002; Yang *et al.*, 2003; Ma *et al.*, 2004; Nabieyan *et al.*, 2007; Muthuraman *et al.*, 2009). Generally, there are three types of liquid membranes, i.e. bulk liquid membrane, emulsion liquid membrane, and supported liquid membrane. An overview on their configurations, advantages and disadvantages are discussed in Section 2.2.1.

2.2.1 Types of Liquid Membranes

2.2.1.1 Bulk Liquid Membrane

Bulk liquid membrane has the simplest design whereby the bulk feed and stripping phases are separated into two different compartments by a liquid layer (membrane phase) which is immiscible with the phases, as shown in Figure 2.2. Configuration of bulk liquid membrane depends on the density of the liquid membrane and the contacting phases. The membrane serves as a bottom layer when it has higher density than the contacting phases and vice versa, as shown in Figure 2.2.

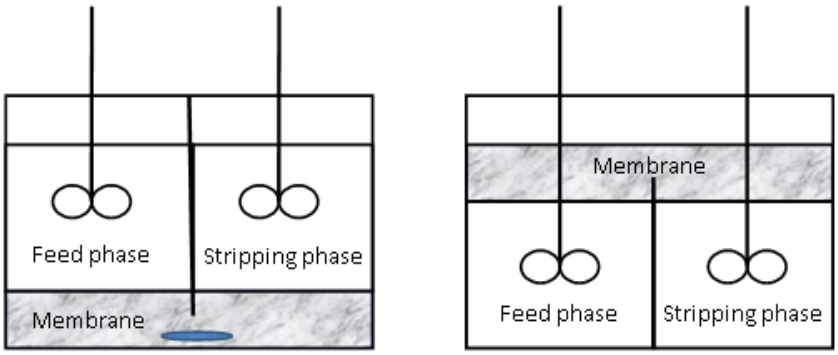


Figure 2.2: Schematic diagram for bulk liquid membrane

Bulk liquid membrane provides several advantages such as simplicity, possibility of identification of concentration in all three phases through experiment and visual observation of interfaces and phases (Schlosser and Sabolová, 1999; Cichy *et al.*, 2005). Kaur and Vohra (2010) claimed that bulk liquid membrane is an effective tool to study the system parameters affecting the transport process of solutes through the membrane. Its simple configuration means that it is free from membrane instability and this often contributes to wide applications among researchers to study the transport kinetics and mechanisms of the solutes in liquid membrane (Schlosser and Sabolová, 1999; Ma *et al.*, 2004; Cichy *et al.*, 2005; Gawronski and Religa, 2007). Besides that, its constant surface area to volume ratio, long diffusion time and high requirement of

membrane solvent volume allow it to be used for the study of the change of membrane properties with time during transport process (Fortunato *et al.*, 2004; 2005a). A number of solutes transport studies have been conducted in bulk liquid membrane system such as butyric acid (Schlosser and Sabolová, 1999), amino acids (Ma *et al.*, 2004; Fortunato *et al.*, 2005a), acetic acid and propionic acid (Kaur and Vohra, 2010), toluene (Chakraborty and Bart, 2007), phenol (Cichy *et al*., 2005), iodine (Nabieyan *et al*., 2007), lignosulfonate (Chakrabarty *et al*., 2009), dye (Muthuraman and Palanivelu, 2005), bismuth (Yamini *et al*., 2002), copper (Yang *et al*., 2003) and chromium (Gawronski and Religa, 2007; Muthuraman *et al.*, 2009).

The main disadvantage of bulk liquid membrane is its low mass transfer rate; the diffusion rate of solute through the membrane phase often becomes the limiting step for this system. This is mainly due to its high membrane thickness and low membrane surface area to volume ratio (Kamiński and Kwapiński, 2000) which further reduce its potential for practical applications. However, the concept of bulk liquid membrane is still applied to different types of membrane processes that utilize lower amount of membrane solvent. Some examples are hybrid liquid membrane, hollow fibre liquid membrane, membrane contactor system and contained liquid membrane (Yang *et al.*, 2003; Vladimir, 2010).

2.2.1.2 Emulsion Liquid Membrane

Emulsion liquid membrane is invented by Li (1968) with the purpose of increasing the mass transfer area between feed phase and membrane phase. Unlike bulk liquid membrane, this process involves complex procedures such as emulsification and demulsification. The membrane phase consists of carrier/extractant, diluent and surfactant. As shown in Figure 2.3, the membrane phase which is immiscible with the

feed phase and the stripping phase acts as a thin shell that traps the stripping agent within it by an emulsification/homogenization process. The emulsion is then further dispersed into the feed phase for the extraction process whereby the selected solutes permeate through the membrane and stripped down in the stripping phase.

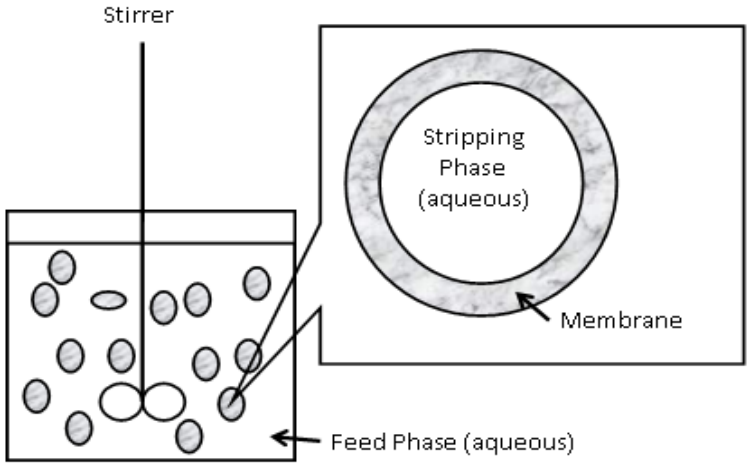


Figure 2.3: Schematic diagram for emulsion liquid membrane

Emulsion liquid membrane has the highest membrane surface area per unit volume among the liquid membrane systems (Kamiński and Kwapiński, 2000). Thus, high mass transfer rate can be obtained as a result of its high surface area and thin diffusion path. This liquid membrane has been studied for the separation of organic compounds (Nanoti *et al.*, 1997; Matsumoto *et al.*, 1998; Lin *et al.*, 2002; Correia and de Carvalho, 2003; Park and Chung, 2003; Manzak and Tutkun, 2005; Park *et al.*, 2006; Reis *et al.*, 2007; Mortaheb *et al.*, 2008; Venkatesan and Begum, 2009; Ng *et al.*, 2010), dyes (Djenouhat *et al*., 2008), metal ions (Gasser *et al.*, 2008; Hasan *et al.*, 2009), inorganic species, hydrocarbon separations, biochemical/biomedical applications, and fine particles preparation (Chakraborty *et al*., 2010). It has also been applied in various industries such as recovery of zinc from textile wastewater, nickel recovery from spent galvanic solution, recovery of uranium and copper, disposal of heavy metals in metallurgical/incineration plants, phenol removal, cyanide removal, ammonium removal,

hydrometallurgy and biochemical applications (Frankenfeld and Li, 1987; Kamiński and Kwapiński, 2000; Chakraborty *et al.*, 2010).

Emulsion instability is the main drawback for this system (Yang *et al.*, 2003; Djenouhat *et al.*, 2008; Chakraborty *et al.*, 2010). This is commonly caused by the mechanical swelling and osmotic pressure between the feed phase and the stripping phase (Venkatesan and Begum, 2009). Mechanical swelling causes the rupture of emulsion as a result of agitation process while osmotic swelling is caused by the difference in osmotic pressure between the feed and stripping phases which triggers the transport of water between the phases and increases the internal volume of emulsion. These cause the emulsion to swell, break down and consequently fail the membrane process. Generally, emulsion stability is dependent on various conditions such as the composition ratio of carrier: diluents: surfactant. It is also dependent on feed phase pH, emulsification speed and time, stirring speed, stripping phase concentration and the volume ratio of feed: membrane: stripping phase (Frankenfeld and Li, 1987; Lin *et al.*, 2002; Correia and de Carvalho, 2003; Park and Chung, 2003; Manzak and Tutkun, 2005; Park *et al.*, 2006; Djenouhat *et al.*, 2008; Gasser *et al.*, 2008; Mortaheb *et al.*, 2008; Hasan *et al.*, 2009; Venkatesan and Begum, 2009; Chakraborty *et al.*, 2010; Ng *et al.*, 2010).

2.2.1.3 Supported Liquid Membrane

Supported liquid membrane is the third type of liquid membranes. In this configuration, the membrane solvent is impregnated and immobilized into the pores of a thin microporous support and sandwiched between the feed phase and the stripping phase, acting as a physical barrier which separates the phases, as shown in Figure 2.4 (Yang *et al.*, 2003; Dzygiel and Wieczorek, 2010; Vladimir, 2010). The selected solutes

in the feed phase are transported to the stripping phase through the membrane solvent inside the pores of the support due to the solubility and diffusion coefficient of the solutes in the membrane solvent (Dzygiel and Wieczorek, 2010; Poole and Poole, 2010).

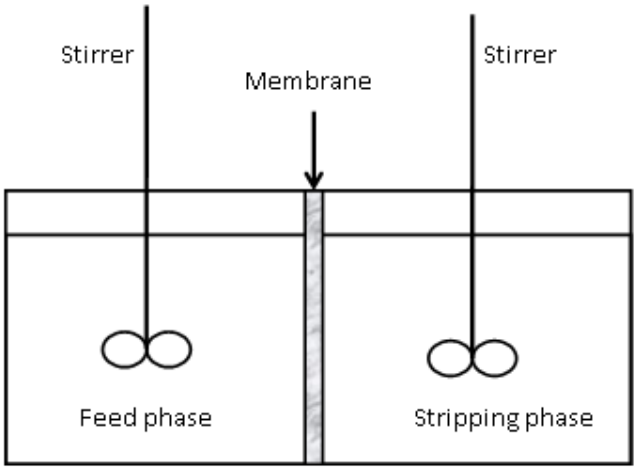


Figure 2.4: Schematic diagram for supported liquid membrane

In comparison to bulk liquid membrane, supported liquid membrane provides higher membrane surface area to volume ratio (Kamiński and Kwapiński, 2000), mainly due to its thin membrane layer which provides shorter transport path and thus higher mass transfer rate. Relatively low quantity of membrane solvent is required in supported liquid membrane and thus draws attention to the studies of separation of phenol (Garea *et al.*, 1993; Le *et al.*, 2002; Jaber *et al.*, 2005; Venkateswaran and Palanivelu, 2006; Zidi *et al.*, 2010), hydrocarbons (Matsumoto *et al*., 2005), penicillin G (Matsumoto *et al*., 2007), transesterification products (Hernández-Fernández *et al.*, 2007) and metal ions (Yang *et al.*, 2003; Venkateswaran and Palanivelu, 2005). Besides that, it has also been widely studied in several fields, such as gas separation, analytical methods, biotechnology, environmental science, separation of stereoisomers, pharmaceutical and hydrometallurgy (Kamiński and Kwapiński, 2000; Dzygiel and Wieczorek, 2010).

However, large commercial application of supported liquid membrane is scarce due to its instability and lifetime usage. According to Dżygiel and Wieczorek (2010) and Vladimir (2010), this is mainly caused by the chemical stability of the membrane solvent and the mechanical stability of the support whereby these mechanisms are mainly attribute to the loss of membrane solvent via dissolution to adjacent phases and emulsion formation (Zha *et al.*, 1995; Kemperman *et al.*, 1998; Kamiński and Kwapiński, 2000; Zheng *et al.*, 2009; Poole and Poole, 2010). Besides that, other degradation mechanisms such as wetting of pores, osmotic pressure gradient and blockage of membrane pores by precipitation of a carrier complex are also proposed to be the causes for instability (Dzygiel and Wieczorek, 2010). These mechanisms cause gradual decline of mass transfer rate with time and thus prohibits long-term operation of the membrane.

In order to overcome the above mentioned problems, investigations to enhance the performance and stability of supported liquid membrane are carried out, such as utilization of polymeric top layer on membrane (Kemperman *et al*., 1998), ultra-thin gates with alkyl chain with hydrophobic barrier (Le *et al*., 2002), functionalized polymers (Jaber *et al*., 2005), utilization of vegetable oils as membrane solvents (Venkateswaran and Palanivelu, 2006) and different types of membrane supports (Zidi *et al*., 2010). Besides that, Dżygiel and Wieczorek (2010) summarized that the stability of supported liquid membrane can be enhanced by maintaining proper operating parameters such as membrane thickness, stirring speed, types of carrier and concentration, feed concentration, operating temperature and pore size of the support. Recently, a review of ionic liquids as membrane solvents by Poole and Poole (2010) also showed that ionic liquids can improve the stability of supported liquid membrane by reducing membrane losses via evaporation while providing liquid membranes of higher mechanical stability. A detail discussion is conducted in Section 2.3.4.4.

2.2.2 Transport Mechanisms in Liquid Membranes

Transport mechanisms in liquid membranes are normally based on solution diffusion model which depends on the chemical potential difference of the solutes between the phases. Generally, the mass transfer mechanisms can be divided into two categories, i.e. simple permeation and facilitated transport.

2.2.2.1 Simple Permeation

Simple permeation is merely dependent on the solubility of the solute in the membrane phase. According to Frankenfeld and Li (1987), Chakraborty *et al.* (2010), Dżygiel and Wieczorek (2010) and Vladimir (2010), the mass transfer process starts by the partitioning of high concentration neutral solute from the feed phase into the membrane phase according to their solubility difference. The solute transports through the membrane phase and eventually dissolves into the stripping phase, depending on the solubility difference and concentration gradient between the phases. Permeation stops when equilibrium concentration is achieved between all phases. As an enhancement, a stripping agent is utilized which reacts with the solute to form a membrane insoluble compound that suppresses the activity of the solute in the stripping phase. This is found to maintain the concentration gradient and increases the permeation rate. Figure 2.5 explains this mechanism.

This process has been applied mainly for the separation of neutral organic compounds such as ammonia, hydrogen sulfide, phenol and amino acids (Frankenfeld and Li, 1987; Vladimir, 2010). Besides that, it has also been applied in the laboratory studies for the separation of iodine (Nabieyan *et al*., 2007), hydrocarbons (Matsumoto *et al*., 2005), transesterification products (Hernández-Fernández *et al.*, 2007) and phenolic compounds (Nanoti *et al.*, 1997; Le *et al.*, 2002; Lin *et al.*, 2002; Correia and de

Carvalho, 2003; González-Muñoz *et al.*, 2003; Park and Chung, 2003; Park *et al.*, 2006; Venkateswaran and Palanivelu, 2006; Chakraborty *et al.*, 2010; Ng *et al.*, 2010).

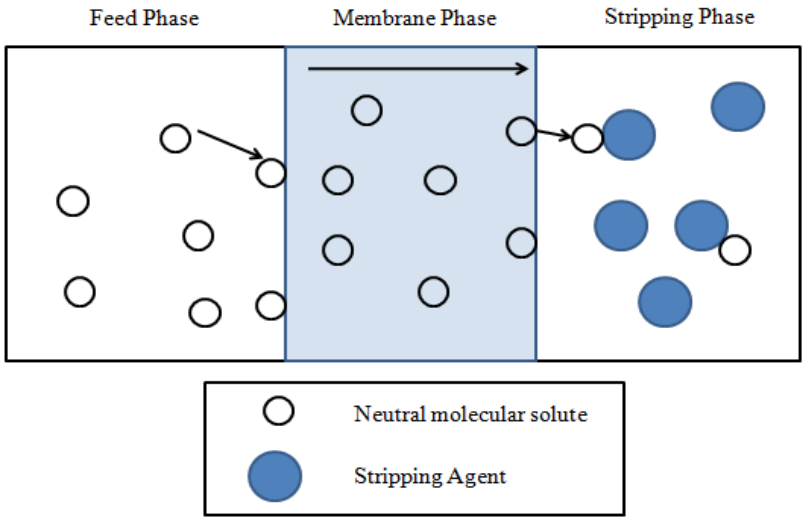


Figure 2.5: Simple permeation in liquid membrane

2.2.2.2 Facilitated Transport

Facilitated transport is another type of transport mechanism in liquid membranes. This transport process is facilitated by a carrier which serves as a "vehicle" to transport the solute from the feed phase to the stripping phase. This is normally applied on the separation of charged compounds which are usually insoluble in the membrane. The mechanism on the facilitated transport has been discussed by Frankenfeld and Li (1987), Chakraborty *et al.* (2010), Dżygiel and Wieczorek (2010) and Vladimir (2010). As shown in Figure 2.6, the charged ion reacts with the carrier on the feed/membrane interface and forms neutral complex that is soluble in the membrane phase. The neutral complex is then transported through the membrane to reach the membrane/stripping interface. Due to the condition in the stripping phase, the neutral complex undergoes another reaction whereby it separates into carrier and charged ion. The charged ion

reacts with the stripping agent to form a compound that is insoluble in the membrane phase. Simultaneously, the carrier is replenished and is ready for another transport.

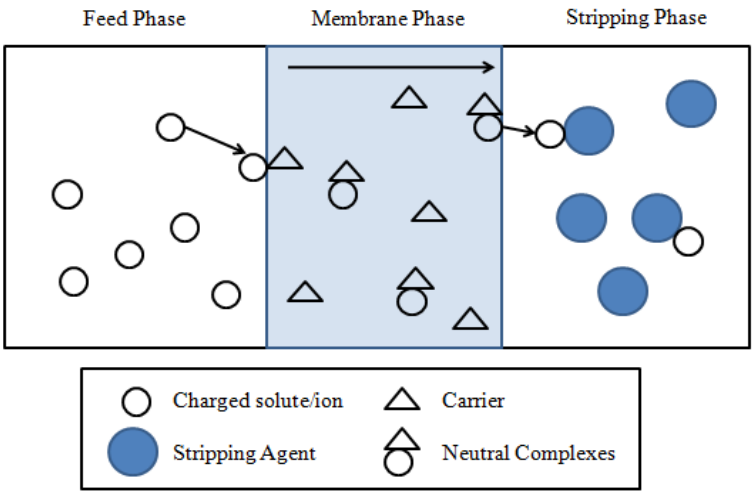


Figure 2.6: Facilitated transport in liquid membrane

Facilitated transport is often applied in the separation of metal ions (Frankenfeld and Li, 1987; Yamini *et al.*, 2002; Yang *et al.*, 2003; Venkateswaran and Palanivelu, 2005; Gawronski and Religa, 2007; Gasser *et al.*, 2008; Hasan *et al.*, 2009; Muthuraman *et al.*, 2009; Chakraborty *et al.*, 2010; Dzygiel and Wieczorek, 2010). However, it has also been applied in the separation of organic compounds such as dyes (Muthuraman and Palanivelu, 2005), hydrocarbons (Chakraborty and Bart, 2007), penicillin G (Matsumoto *et al*., 2007), benzimidazole (Venkatesan and Begum, 2009), lignosulfonate (Chakrabarty *et al*., 2009), acids (Matsumoto *et al.*, 1998; Schlosser and Sabolová, 1999; Kubisová *et al.*, 2004; Ma *et al.*, 2004; Manzak and Tutkun, 2005; Chakraborty *et al.*, 2010; Dzygiel and Wieczorek, 2010; Kaur and Vohra, 2010), and also phenol (Garea *et al.*, 1993; Cichy *et al.*, 2005; Jaber *et al.*, 2005; Reis *et al.*, 2007; Shen *et al.*, 2009; Chakraborty *et al.*, 2010; Ng *et al.*, 2010; Vladimir, 2010; Zidi *et al.*, 2010).

2.2.3 Applications of Liquid Membranes on Phenol Removal

2.2.3.1 Bulk Liquid Membrane

Efficiency of phenol removal by bulk liquid membrane is less studied. However, this type of liquid membrane is commonly utilized as a method to study the behavior and properties of the membrane during experiment and the transport mechanism of the system. Cichy *et al.* (2005) used bulk liquid membrane to study the effect of different carriers, namely TOA, Amberlite LA-2 and Cyanex923 on the transport of phenol in terms of mass transfer flux and transport mechanism. The study showed that purified Cyanex923 is the best carrier for enhancing the extraction rate of phenol, though the enhancement of stripping rate is low.

2.2.3.2 Emulsion Liquid Membrane

Emulsion liquid membrane has been widely studied in the field of phenol removal. As discussed in Section 2.2.1.2, emulsion liquid membrane is a complicated process and the phenol removal efficiency is strongly dependent on the stability of the emulsions.

Several studies were conducted by researchers to enhance phenol removal efficiency and to conserve emulsion stability. The major factors that affect phenol removal efficiency and emulsion stability are the operating parameters, as mentioned in Section 2.2.1.2. Optimization on these operating parameters for membrane properties are widely studied by researchers, as shown in Table 2.3. Generally, phenol removal efficiency of at least 95% with good emulsion stability can be achieved in the laboratory scale experiments.

Table 2.3: Optimum membrane properties for emulsion liquid membrane on phenol removal and emulsion stability

Parameters/ References	**Lin *et al.* (2002)**	**Correia and de Carvalho. (2003)**	**Park and Chung (2003)**	**Park *et al.* (2006)**	**Reis *et al.* (2007)**	**Mortaheb *et al.* (2008)**	**Ng *et al.* (2010)**
Diluent	Kerosene	ShellSol T	Kerosene	Soltrol 220	ShellSol T	Petroleum solvent	Kerosene
Carrier	-	-	-	-	Cyanex 923	-	Cyanex 923
Surfactant	SPAN 80	Polyamine ECA4360	SO-10, Arlacel83	SPAN 80	Polyamine ECA4360	synthesize surfactant	SPAN 80
Membrane: Internal Ratio	-	10:x	1:1	0.46:1	2:1	2:1	5:1
Membrane: External Ratio	1:10	x:1	1:5	1:3	1:10	1:10	1:2
Emulsification Speed	4000rpm	1000rpm	1200rpm	-	7000rpm	15000rpm	8000rpm
Surfactant Concentration	5%	2% wt	SO-10 5% wt, Arlacel83 7% wt	5% w/v	2% wt	3% wt	2% v/v
Emulsification Time	20 min	15 min	10 min	-	15 min	20 min	5 min
Carrier Concentration	-	-	-	-	2% wt	-	0% v/v
Internal Agent Concentration	0.5% wt	0.5M	3% wt	0.5N	0.5M	1% wt	0.5M
Extraction Time		2-10 min	10 min	10min	3-6 min	4 min	4 min
Extraction Efficiency	98%	>99%	99.55%	96.18%	98%	>95%	98.33%
Emulsion Leakage	-	-	<1.5%	-	1.2	<1%	1.25%

(Source: Ng *et al.*, 2010)

In addition to the efforts to optimize the various parameters, several modifications are also conducted to increase the membrane stability. Study on new surfactants was conducted by Park and Chung (2003) and Mortaheb *et al.* (2008). Mortaheb *et al.* (2008) showed that the new synthesized surfactant provided better phenol removal efficiency in comparison to conventional surfactant Span80 whereby it reduced the emulsion leakage effectively from 92% (Span80) to 1.1% (synthesized surfactant). Besides that, the conversion of membrane phase to non-Newtonian fluid through the addition of PIB also resulted in better emulsion stability (Park *et al.*, 2006). However, this effect was insignificant in the work of Mortaheb *et al.* (2008) as the synthesized surfactant used possessed similar structure with PIB. Furthermore,

mechanical swelling was found to be reduced effectively by modifications such as immobilization of emulsion into hollow fiber contactor (Nanoti *et al*., 1997), ultrasonic emulsification (Park and Chung, 2003), and uniform shearing process using Taylor Vortex Column (Park *et al.*, 2006).

2.2.3.3 Supported Liquid Membrane

The discussion in this sub-section is limited to supported liquid membrane of flat geometry. Generally, supported liquid membrane has lower phenol removal efficiency in comparison to emulsion liquid membrane under the same permeation duration whereby the best removal efficiency was found to be in range of 50-100% under different separation time, as shown in the work of Garea *et al.*, (1993), Le *et al*. (2002), Jaber *et al*. (2005), Venkateswaran and Palanivelu (2006) and Zidi *et al*. (2010). According to them, phenol removal efficiency and permeation rate are strongly dependent on the choice of membrane support and impregnated solvents. For example, the work of Venkateswaran and Palanivelu (2006) showed that palm oil provided higher permeability in comparison to other types of membrane solvents such as TOA-kerosene, Aliquat 336, and Dibenso-18-crown-6. In addition, modifications on the membrane support by functionalized polyorganosiloxane with various amino alcohols and ethers (Jaber *et al*., 2005) and the utilization of carrier-membrane mixture such as Cyanex923 (Garea *et al*., 1993) and TBP (Zidi *et al*., 2010) are found to improve the phenol extraction efficiency.

Despite phenol removal efficiency enhancement, the problem of membrane instability was also noticed in the work of Jaber *et al*. (2005) whereby phenol removal efficiency was reduced from 100% to 70% after two weeks of continuous run. This concludes that membrane stability is important in governing the feasibility of phenol removal using supported liquid membrane. The instability behaviour of supported liquid membrane on phenol transport was studied by Zha *et al.* (1995) and Zheng *et al*. (2009). Their works showed that the loss of membrane solvent via emulsion formation was the main factor that contributed to instability and this process was governed by hydrodynamic condition, interfacial tension between the membrane and aqueous phase and salinity of the aqueous phases.

In addition, some efforts have been carried out to enhance membrane stability. Le *et al*. (2002) found that the increment of the hydrophobicity of the membrane by modification of gold-coated alumina membrane using 1-octadecanethiol effectively reduced membrane solvent loss. Besides that, the work of Venkateswaran and Palanivelu (2006) also found that the utilization of high viscosity vegetable oil as the membrane phase increased membrane stability whereby polytetrafluoroethylene-palm oil membrane showed its reusability in 10 consecutive experiments without drop in permeability.

Literature survey shows that liquid membranes possess several advantages over other separation methods. Nevertheless, conventional liquid membrane modules carry the setbacks of long term stabilities and performance issues mainly due to the use of volatile organic membrane solvents such as alkanes and chloroalkanes. Several enhancement efforts on membrane stability, as discussed in Section 2.2.3, are restricted to lab scale operation. As such, search of a more stable membrane solvent is still necessary. In this study, ionic liquids are proposed as the new membrane solvents.

2.3 Ionic Liquids

Ionic liquids are salts that have melting point of less than 373K. They are referred as low melting point molten salts. However, unlike normal inorganic salts, ionic liquids normally behave as liquid with a combination of organic cations and inorganic polyatomic anions. The mismatched association of large size difference between the cations and the anions causes low lattice energy and low melting point (Huddleston *et al.*, 2001; Freire *et al.*, 2007; Keskin *et al.*, 2007; Holbrey and Rogers, 2008; Poole and Poole, 2010).

Among many types of ionic liquids, room temperature ionic liquids draw most attention from researchers for study in various fields such as catalysis, synthesis, electrochemical applications and separations (Jodry and Mikami, 2005; Keskin *et al.*, 2007; Berthod *et al.*, 2008; Wasserschield and Welton, 2008; Poole and Poole, 2010).

2.3.1 Types of Ionic Liquids

As can be expected, in the synthesizing of ionic liquids, there are large number of possible combinations between the cations and the anions. The typical cations and anions available in market are as shown in Table 2.4 and Table 2.5. In this study, dialkylimidazolium cations are singled out as more physical properties data are available to explain the behavior of ionic liquids, in particular, for the selection of suitable types of ionic liquids as liquid membranes.

Table 2.4: Common types of cations for ionic liquids

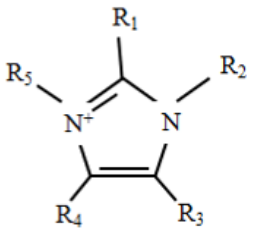
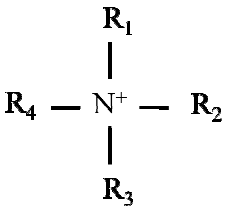
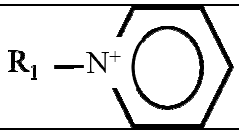
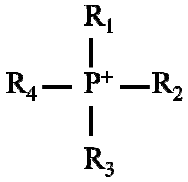
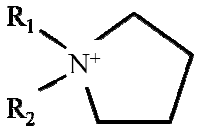
Cations	Structure	Remarks
Imidazolium		R can be hydrogen, alkyl chain or other substitutes
Ammonium		R can be hydrogen, alkyl chain or other substitutes
Pyridinium		R can be hydrogen, alkyl chain or other substitutes
Phosphonium		R can be hydrogen, alkyl chain or other substitutes
Pyrrolidinium		R can be hydrogen, alkyl chain or other substitutes

Table 2.5: Common types of anions for ionic liquids

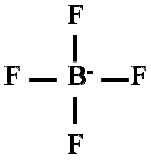
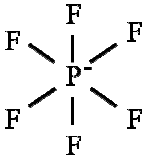
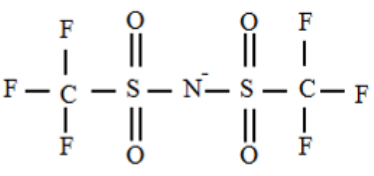
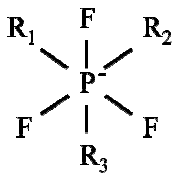
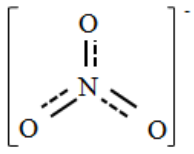
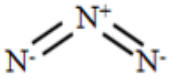
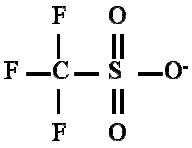
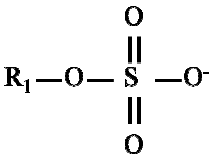
Anions	Structure	Remarks
Chloride, Cl-		-
Bromide, Br-		-
Tetrafluoroborate, BF_4^-		-
Hexafluorophosphate, PF_6^-		-
Bis(trifluoromethylsulfonyl)imide, NTf_2^-		-

Table 2.5, continued

Anions	Structure	Remarks
Tris(perfluoroalkyl) trifluorophosphate, FAP^-		R can be hydrogen, alkyl chain or other substitutes
Nitrate, NO_3^-		-
Azide, N_3^-		-
Trifluoromethanesulfonate, $CF_3SO_3^-$		-
Alkylsulfate, RSO_4^-		R can be hydrogen, alkyl chain or other substitutes

2.3.2 General Properties of Imidazolium-based Ionic Liquids

In the field of separation, the unique properties of imidazolium-based ionic liquids present attraction as alternatives to volatile organic solvents which are normally toxic, flammable and volatile. In comparison to organic solvents, imidazolium-based ionic liquids show low vapour pressure, are thermally stable and tunable according to the utilization purpose.

2.3.2.1 Vapour Pressure

Imidazolium-based ionic liquids consist entirely of ions. Therefore, they behave as salts and their high coulombic force and strong ionic bonding causing them a very low vapour pressure. This behaviour shows potency to replace conventional separation solvents as the loss of solvents via evaporation can be prevented. In a recent study,

imidazolium-based ionic liquids were found to be distillable under high temperature in vacuum condition (Earle *et al*., 2006). However, the vapour pressure present in the atmospheric condition is normally very low and often negligible in comparison to that of the organic solvents, as shown in Table 2.6.

Table 2.6: Vapour pressure of typical organic solvents and ionic liquids

Solvent	**Vapour pressure, kPa (T, K)**
Kerosene	0.1 (293)[e]
n-hexane	17.3 (293)[e]
Chloroform	21.1 (293)[e]
Dichloromethane	46.5 (293)[e]
1,2-dichloroethane	8.1 (293)[e]
Dichlorobutane	0.5 (293)[d]
Tetrachloromethane	12.1 (293)[d]
[Bmim][NTf_2]	1.22×10^{-5} (457.66)[a]
[Bmim][PF_6]	10^{-14} (298)[b]
[Emim][NTf_2]	1.2×10^{-8} (298)[c]
[Bmim][DCA]	2×10^{-9} (298)[c]

(Source: [a]Paulechka *et al.*, 2005; [b]Kabo *et al.*, 2004, (as cited in Keskin *et al.*, 2007); [c]Berthod *et al.*, 2008; [d]Oxford-University, n.d; [e]ScienceLab, n.d)

2.3.2.2 Thermal Stability

Imidazolium-based ionic liquids are less flammable as compared to conventional organic solvents (Fox *et al*., 2008). These ionic liquids are generally thermally stable with high decomposition temperature, depending on their salt structures (Ngo *et al*., 2000, as cited in Huddleston *et al.*, 2001) and nucleophilicity of the anions (Jodry and Mikami, 2005; Earle *et al.*, 2006; Holbrey and Rogers, 2008). Their low melting point and high decomposition temperature means that these ionic liquids provide wide liquidus range, as shown in Table 2.7. This stable nature provides better and safer means for chemicals handling such as for storage and high temperature operations.

Table 2.7: Melting point and decomposition temperature of typical imidazolium-based ionic liquids

Ionic liquids	Melting point, (K)	Decomposition temperature, (K)
[Bmim][Cl]	314 - 346	527
[Bmim][I]	201-215	538
[Bmim][BF_4]	192-223	676
[Bmim][PF_6]	277 – 285	622 – 633
[Bmim][NTf_2]	248 – 275	667 - 712
[Hmim][Cl]	198	526
[Hmim][BF_4]	191	-
[Hmim][PF_6]	212	649-690
[Omim][Cl]	273	516
[Omim][BF_4]	194	-
[Omim][PF_6]	203 – 233	647 - 649
[Omim][NTf_2]	187	>573

(Source: Huddleston *et al.*, 2001; Berthod *et al.*, 2008; Merck, 2009; Poole and Poole, 2010)

2.3.2.3 Tunable

The properties of ionic liquids can be fine-tuned by altering the types of cations and anions to fulfil the specific function for certain process. The physical properties of imidazolium-based ionic liquids are strongly affected by the cations, such as the length and types of substituent chains attached to the imidazolium ring and also the types of anions. Examples of physical properties which depend on the types of cations and anions of the ionic liquids are summarized in Table 2.8. The effect of cations and anions on the major properties of the ionic liquids such as water miscibility, mutual solubility, moisture stability, viscosity and toxicity are discussed in Section 2.3.3.

Table 2.8: The influence on the physical properties of imidazolium-based ionic liquids by the cations and anions

Cation	**Anion**
Viscosity	Viscosity
Surface tension	Surface tension
Density	Density
Melting point	Melting point
Hydrogen bond acidity/basicity	Hydrogen bond acidity/basicity
Water miscibility	Water miscibility
Mutual solubility	Mutual solubility
Thermal stability	Thermal stability
-	Moisture stability

(Source: Huddleston *et al.*, 2001; Fortunato *et al.*, 2004; Ignat'ev *et al.*, 2005; Jodry and Mikami, 2005; Vidal *et al.*, 2005; Rakita, 2006; Freire *et al.*, 2007; Keskin *et al.*, 2007; Berthod *et al.*, 2008; Fox *et al.*, 2008; Wasserschield and Welton, 2008; Cuadrado-Prado *et al.*, 2009; Ranke *et al.*, 2009; Zhao *et al.*, 2009; Poole and Poole, 2010)

2.3.3 Properties of Imidazolium-based Ionic Liquids as Liquid Membranes

The advantages demonstrated by imidazolium-based ionic liquids, such as having low vapour pressure, being thermally stable and tunable, have provided the opportunity for the replacement of organic membrane solvents which are normally known to have high volatility, flammability and toxicity. Besides, some other important parameters to be considered in the selection of suitable ionic liquids as membrane solvents are water miscibility, mutual solubility, moisture stability, viscosity and toxicity.

2.3.3.1 Water Miscibility

The miscibility of ionic liquid with water is the most important parameter in the selection of ionic liquid membrane. This criterion is governed by the combinations between the cations and the anions. Generally, the types of anions strongly affect the

miscibility of an ionic liquid with water. As shown in Table 2.9, the anions of [NTf_2^-], [FAP^-], [PF_6^-], [$C(CN_3)^-$] and [BR_4^-] tend to form ionic liquids that are immiscible with water while the ionic liquids with the anions of halides, [NO_3^-], [$CH_3SO_2^-$], [$CH_3CO_2^-$] and [$CF_3CO_2^-$] are miscible and soluble in water.

Table 2.9: Water miscibility of imidazolium-based ionic liquids with different types of anions

Immiscible	**Miscible**	**Special case**
PF_6^-	$Halide^-$	BF_4^-
NTf_2^-	NO_3^-	$CF_3SO_3^-$
FAP^-	$CH_3SO_2^-$	-
$C(CN_3)^-$	$CH_3CO_2^-$	-
BR_4^-	$CF_3CO_2^-$	-

(Source: Ignat'ev *et al.*, 2005; Jodry and Mikami, 2005; Rakita, 2006; Freire *et al.*, 2007; Donata *et al.*, n.d (as cited in Keskin *et al.*, 2007); Berthod *et al.*, 2008; Zhao *et al.*, 2009; Seddon *et al.*, 2000 (as cited in Poole and Poole, 2010))

Besides that, water miscibilities of the ionic liquids are also governed by the cations in certain circumstances, as shown in Table 2.9. For the anions of [BF_4^-] and [$CF_3SO_3^-$], the types of side chains and the length of alkyl side chain attached to the imidazolium cation strongly govern the water miscibility. The work of Vidal *et al.* (2005) and Cuadrado-Prado *et al.* (2009) showed that imidazolium-based ionic liquid with [BF_4^-] anion was found to be miscible with water when the length of cation's alkyl side chain was less than 6 (hexyl). However, this ionic liquid became partially miscible with water when the length of alkyl side chain was 6 and immiscible with water when the length was 8 (octyl). The increment in the length of cation's alkyl side chain decreases water miscibility of an ionic liquid. In addition, cations with polar functional group side chains are also found to increase the water miscibility, regardless of the hydrophobicity of the anion (Jodry and Mikami, 2005).

In this study, the ionic liquid membrane is to contact with aqueous phase. Hence, hydrophobic ionic liquids that are immiscible with water are chosen.

2.3.3.2 Mutual Solubility of Ionic Liquids with Water

In order to yield a stable ionic liquid membrane, hydrophobicity of the ionic liquid must be as high as possible such that the loss of membrane via dissolution can be prevented when it contacts with bulk aqueous phase. Besides that, the mutual solubility between the ionic liquid and water has to be minimized. Table 2.10 illustrates the solubilities of imidazolium-based ionic liquids in water.

From Table 2.10, it is found that organic membrane solvents have a wide range of solubility in water, ranging from negligible solubility (kerosene, n-hexane, tetrachloromethane) to significant solubility (chloroform, dichloromethane, dichloroethane). In contrast, all imidazolium-based ionic liquids have higher solubilities in water in comparison to kerosene, n-hexane and tetrachloromethane while they are comparable to chloroform, dichloromethane and dichloroethane, depending on their cationic and anionic combinations. The data in Table 2.10 also shows that the types of anions and the length of cation's alkyl side chain play significant roles in determining ionic liquid's solubility in water. According to Freire *et al.* (2007) and Freire *et al.* (2008) (as cited by Poole and Poole, 2010), the increment on the length of cation's alkyl side chain decreases the entropy of ionic liquid's dissolution in water. Thus, the solubility of the ionic liquid in water decreases. In terms of anion effect, ionic liquid's solubility in water decreases by the decrement of cation-anion strength (Freire *et al*., 2007). For example, hydrophobic anion [PF_6^-] and [NTf_2^-] gave lower solubilities in water at the same length of cation's alkyl side chain in comparison to [BF_4^-], as shown in Table 2.10.

Table 2.10: Solubilities of hydrophobic imidazolium-based ionic liquids and organic solvents in water

Ionic liquids	**Solubility, g/g**	**Temperature (K)**
[Emim][NTf_2]	0.0182 [c,d,e]	298
[Bmim][PF_6]	0.0194 [b,c,d,e]	296-298
[Bmim][NTf_2]	0.0071 [c,d,e]	298
[Hmim][BF_4]	Partial Soluble	-
[Hmim][PF_6]	0.0076 [c,d,e]	298
[Hmim][NTf_2]	0.0024 [c,d,e]	298
[Omim][BF_4]	0.0182 [e]	298
[Omim][PF_6]	0.0022 [b,c,d] 0.0024-0.0070 [e]	296-298 298
[Omim][NTf_2]	0.0011 [c,d,e]	298
Organic solvents	**Solubility, g/g**	**Temperature (K)**
Kerosene	Insoluble	-
n-Hexane	0.00014 [a]	288
Chloroform	0.0082 [a]	293
Dichloromethane	0.02 [a]	293
Dichloroethane	0.009 [a]	273
Tetrachloromethane	0.0008 [a]	293

(Source: [a]Liley *et al.*, 1997; [b]Fortunato *et al.*, 2004; [c]Freire *et al.*, 2007; [d]Ranke *et al.*, 2009; [e]Poole and Poole, 2010)

In addition, the solubility of water in ionic liquids is also important. Studies have shown that significant water content can be present in a hydrophobic ionic liquid. The equilibrium water content in hydrophobic ionic liquids are as shown in Table 2.11.

It is clear from Table 2.11 that most of the hydrophobic imidazolium-based ionic liquids have higher water content than organic solvents. The cation has significant effect on the water solubility in ionic liquids whereby the longer the length of alkyl side chain is, the lower the water solubility in the ionic liquid. According to Cuadrado-Prado *et al.* (2009), an increase in the length of alkyl side chain reduces the anchorage site for water molecules adsorption and thus reduces the water content. Besides that, Freire *et al.* (2007) claimed that the water content of an ionic liquid can be reduced by replacing hydrogen atom at C_2 position in imidazolium ring with a methyl group. Such modification reduces the hydrogen bond acidity of imidazolium cation with water and the relative strength between the cation and the anion. Thus, the strength of hydrogen bond with water is reduced (Freire *et al*., 2007). In term of anion effect, higher relative

cation-anion strength also increases the water solubility in the ionic liquids, as reported in the work of Freire *et al*. (2007).

Table 2.11: Water contents in hydrophobic imidazolium-based ionic liquids and organic solvents

Ionic liquids	**Water content, ppm**	**Water content range, ppm**	**Temperature (K)**
[Emim][NTf_2]	13798[e] 13706-19400[f]	13706-19400	298
[Bmim][PF_6]	11700[a] 21091-21136[b] 22600[c] 17095[e] 17222-23000[f]	11700-23000	296-298
[Bmim][NTf_2]	3280[a] 10730[e] 11031-14800[f]	3280-14800	298
[Hmim][PF_6]	8837[a] 13259[e] 13201[f]	8837-13259	298
[Hmim][NTf_2]	10670[c] 8448[e] 8368-10500[f]	8368-10670	298
[Hmim][FAP]	2030[c]	2030	NA
[Omim][BF_4]	40217-108000[f]	40217-108000	298
[Omim][PF_6]	6666[a] 13160-13218[b] 10845[e] 10845-13000[f]	6666-13218	296-298
[Omim][NTf_2]	6815[e] 7080-8700[f]	6815-8700	298
Organic solvent	**Water Content, ppm**		
Kerosene	40-80[d]		294
n-hexane	100[g]		293
Chloroform	560[g]		293
Dichloromethane	2400[g]		293

(Source: [a]Huddleston *et al.*, 2001; [b]Fortunato *et al.*, 2004; [c]Ignat'ev *et al.*, 2005; [d]EESIFLO, 2006; [e]Freire *et al.*, 2007; [f]Poole and Poole, 2010; [g]LSU(Louisiana-State-University-Macromolecular-Studies-Group), n.d)

Mutual solubility of ionic liquids with water can be a nuisance in liquid membrane operation, especially for long duration supported liquid membrane and bulk liquid membrane. High ionic liquid's solubility in water tends to raise solvent loss via dissolution and increases environmental pollution risk. Besides that, significant amount

of water content in the ionic liquid may cause loss on the selectivity of ionic liquid membrane processes through the formation of water microenvironment within the membrane. This is discussed in Sections 2.3.4.2 and 2.3.4.4.

2.3.3.3 Moisture Stability

As the ionic liquid membrane comes into contact with the aqueous phase in this study, moisture stability of the ionic liquid becomes one of the important criteria that must be considered. Generally, most of the ionic liquids are hygroscopic whereby they tend to absorb/adsorb water molecules from the surrounding as discussed in Section 2.3.3.2. Water molecules that are adsorbed/ absorbed may result in moisture instability issues. Rakita (2006) and Keskin *et al.* (2007) stated that moisture stability of an ionic liquid is dependent on the types of anions used. In some cases, undesired reactions may occur in the presence of water. For example, [BF_4^-] and [PF_6^-] ionic liquids have potential to hydrolyze with the water adsorbed and produce high corrosive and toxic HF gas (Swatloski *et al.*, 2003; Jodry and Mikami, 2005; Keskin *et al.*, 2007; Wagner and Hilgers, 2008). In contrast, the anion of [NTf_2^-] and [FAP^-] form stable hydrophobic ionic liquids which resist hydrolysis (Ignat'ev *et al.*, 2005; Keskin *et al.*, 2007; Wagner and Hilgers, 2008; Zhao *et al.*, 2009).

2.3.3.4 Viscosity

Viscosity is another parameter that plays an important role in mass transfer process. The diffusion coefficient and mass transfer coefficient of a substance are generally inversely proportional to the viscosity of the transport medium, as shown in Equation (2.1) and Equation (2.2) (Bird *et al*., 1964):

$$D = \frac{k_B T}{6\pi\mu r} \tag{2.1}$$

$$k' = \frac{Sh.D}{L} \tag{2.2}$$

Table 2.12 shows that all of the hydrophobic imidazolium-based ionic liquids are much viscous than organic liquid membranes. From the table, it is found that the range of viscosity for an ionic liquid is dependent on the length of cation's alkyl side chain and the types of anions. The longer the length of cation's alkyl side chain, the more viscous the ionic liquid. In terms of anion effect, [PF_6^-] anion yields higher viscosity ionic liquid in comparison to other anions such as [BF_4^-], [NTf_2^-] and [FAP^-] when the same type of cation is used. Anion is found to be more crucial in affecting the viscosity of an ionic liquid. For the same type of cation, an ionic liquid with lower viscosity can be obtained by utilizing a smaller anion that reduces the surface area for van der Waals interaction between the cation and the anion (Park and Kazlauskas, 2003; Jodry and Mikami, 2005; Poole and Poole, 2010). However, the increment of viscosity is not proportional to the size of anion (Ignat'ev *et al.*, 2005; Mantz and Trulove, 2008). Instead, several explanations on the geometry and symmetry of the anion are claimed to contribute more effects on the viscosity of an ionic liquid. (Huddleston *et al.*, 2001; Jodry and Mikami, 2005).

Table 2.12: Viscosities of hydrophobic imidazolium-based ionic liquids and organic solvents

Ionic liquids	**Viscosity, mPa.s**	**Viscosity range**	**Temperature, K**
[Emim][NTf_2]	28[e] 18[g] 31-34[h] 37[j]	18-37	298
[Emim][FAP]	75[i]	75	293
[Bmim][PF_6]	397-450[b] 250[c] 207[e] 400[g] 173-450[h] 450[j]	173-450	298
[Bmim][NTf_2]	27-69[b] 52[e] 51[f] 80[g] 47-69[h] 52[j]	27-80	298
[Bmim][FAP]	93[i]	93	293
[Hmim][PF_6]	452-585[b] 711[d] 496[f] 800[g] 585[h,j]	452-800	293-298
[Hmim][NTf_2]	61[d] 68[h] 71[j]	61-71	293-298
[Hmim][FAP]	115[d] 116[i]	115-116	293
[Omim][BF_4]	440[g] 439[j]	439-440	298
[Omim][PF_6]	506-682[b] 575[c] 810[g] 682[h,j]	506-810	298
[Omim][NTf_2]	93[h] 87[j]	87-93	298
Organic solvents	**Viscosity, mPa.s**		
Kerosene	2.3[a]		298
n-hexane	0.32[a]		298
Chloroform	0.55[a]		298
Dichloromethane	0.45[a]		298
Dichloroethane	0.80[a]		298
Tetrachloromethane	0.95[a]		298

(Source: [a]Liley *et al.*, 1997; [b]Huddleston *et al.*, 2001; [c]Fortunato *et al.*, 2004; [d]Ignat'ev *et al.*, 2005; [e]Jodry and Mikami, 2005; [f]Harris *et al.*, 2007; [g]Berthod *et al.*, 2008; [h]Mantz and Trulove, 2008; [i]Merck, 2009; [j]Poole and Poole, 2010)

Despite their higher relative viscosity than organic solvents, the reduction in the viscosity of ionic liquids are observed in the presence of impurities and the increment in temperature (Huddleston *et al.*, 2001; Fortunato *et al.*, 2004; Jodry and Mikami, 2005; Chakraborty and Bart, 2007; Harris *et al.*, 2007; Mantz and Trulove, 2008). However, the enhancement on the mass transfer coefficient normally requires higher energy consumption and yet a better mass transfer process is not guaranteed. Hence, it is better to utilize a low viscosity ionic liquid by choosing a proper cation-anion combination. In this case, short cation's alkyl side chain with the anions of [NTf_2^-] and [FAP^-] are good choices.

2.3.3.5 Toxicity

As the number of combinations between the cations and the anions is unlimited, a complete ecological assessment for ionic liquids is currently unavailable. However, based on data currently available, some trends on the toxicity of the ionic liquids can be summarized.

Generally, it is found that the side chain of the cation has the most significant effect on the toxicity of an ionic liquid. The increment on the length of cation's alkyl side chain increases the toxicity of the ionic liquid and this is valid for most types of cations such as imidazolium, pyridinium and quarternary ammonium (Jodry and Mikami, 2005; Keskin *et al.*, 2007; Stolte *et al.*, 2007; Pham *et al.*, 2008; Romero *et al.*, 2008; Wagner and Hilgers, 2008; Pham *et al.*, 2010). The review by Pham *et al*. (2010) concluded that increment in the length of cation's alkyl side chain increased the toxicity of an ionic liquid in all aspects, i.e. inhibitory of enzyme and antibacterial activity, cytotoxicity, phototoxicty, toxic towards algae and invertebrates.

On the other hand, it is found that different types of cations have different degrees of toxicity on different types of organisms and aquatic plants. This is mainly dependent on the lipophilicity of the cation whereby increase of lipophilicity causes higher toxicity as a result of membrane perturbation and disruption into the cell lipid bilayer (Stolte *et al.*, 2007; Pham *et al.*, 2010). A summary of the toxicity contributed by different cations is as shown in Table 2.13 with scale from 1 (more toxic) to 5 (less toxic). Based on the table, no obvious trend was observed to determine the best cation with the least toxicity for all types of organisms. However, it is reported that the toxicity of an ionic liquid can be reduced by substituting the side chain in the cation with polar functional group such as polar ethers, hydroxyl and nitrile functional groups (Stolte *et al.*, 2007; Pham *et al.*, 2010) or by introducing an electronegative atom on the alkyl side chain (Pretti *et al*., 2009).

Table 2.13: Toxicity of imidazolium-based ionic liquids with different types of cations to different organisms

Organisms	**Imidazolium**	**Pyridinium**	**Pyrrolidinium**	**Phosphonium**	**Ammonium**
P. subcapitata	2[b] 3[c]	1[b] 2[c]	- 4[c]	- -	- 1[c]
S. vacuolatus	2[a] -	1,3[a] 1[d]	4[a] -	- -	5[a] 5[d]
Enzyme level	2[d]	1[d]	-	3[d]	-
Fungi	-	1[d]	-	-	1[d]
V. fischeri	2[a] 1[d]	1[a] 2[d]	5[a] -	- -	5[a] 3[d]
HeLa cells	2[d]	3[d]	-	1[d]	4[d]
Lemna Minor	4[a] 1[d]	1,5[a] 1[d]	3[a] -	- -	2[a] 3[d]
D. magna	3[c] 1[d]	2[c] 2[d]	4[c] -	- -	1[c] 3[d]
D. rerio	5[d]	5[d]	5[d]	-	1[d]

(Source: [a]Stolte *et al.*, 2007; [b]Pham *et al.*, 2008; [c]Pretti *et al.*, 2009; [d]Pham *et al.*, 2010)

On the other hand, most of the anions of ionic liquids result in less toxic effect and the impact is much weaker as compared to cations' moiety (Stolte *et al.*, 2007; Romero *et al.*, 2008; Wagner and Hilgers, 2008; Matzke *et al.*, 2009; Pham *et al.*, 2010). However, it is found that the anion of [NTf_2^-] contributes part of the toxicity (Stolte *et al.*, 2007; Matzke *et al.*, 2009; Pretti *et al.*, 2009; Pham *et al.*, 2010), but the effect is claimed to be smaller as compared to that contributed by the length of cation's alkyl side chain (Pham *et al*., 2010). The degree of toxicity for this anion is dependent on the types of organisms and environments. For example, [NTf_2^-] anion is found to be toxic on *Triticum aestivum, Vibrio fischeri, Pseudokirchneriella subcapitata* and *Scendesmus vacuolatus,* (Stolte *et al.*, 2007; Matzke *et al.*, 2009; Pretti *et al.*, 2009), but harmless to *Lemna minor* (Stolte *et al*., 2007). Furthermore, the study of Matzke *et al.* and Stolte *et al.* (as cited in Pham *et al.*, 2010) also showed that the toxicity of [NTf_2^-] remains debatable as contradictory results were reported. It can either be toxic or non-toxic for both *Vibrio fischeri and Lemna minor* under different situations.

From the review, it is clear that the toxicity of an imidazolium-based ionic liquid is strongly dependent on the length of cation's alkyl side chain. As the anion effect is currently unclear, selection of ionic liquid will be based on the effect of cation only whereby shorter alkyl side chain is preferred.

2.3.4 Recent Studies of Imidazolium-based Ionic Liquids as Liquid Membranes

The applications of imidazolium-based ionic liquids as separation solvents have been investigated and in liquid membrane application, imidazolium-based ionic liquids with the anions of [BF_4^-] and [PF_6^-] are frequently utilized. This sub-section covers the utilization of these ionic liquids on the separation of organic compounds/phenol through liquid-liquid extraction and liquid membrane processes.

2.3.4.1 Liquid-liquid Extraction

Phenol and phenolic compounds can be extracted by imidazolium-based ionic liquids with the anions of [PF_6^-] and [BF_4^-]. Table 2.14 summarizes the distribution coefficients of phenol between ionic liquids/ organic solvents with water. From the table, ionic liquids show higher distribution coefficient than toluene, n-heptane, n-hexane, petrolsol 15/20, petrolsol D15/20 and methyl cyclohexane. Furthermore, they are comparable to 1-octanol, 1-decanol, MIBK, diisopropyl ether, rosin amine and butyl acetate.

Different types of ionic liquids show different phenol distribution coefficients. From Table 2.14, for the same types of anion, the increment on the length of alkyl side chain for dialkylimidazolium cation increases phenol distribution coefficient. According to Fan *et al*. (2008), the increment on the hydrophobicity of an ionic liquid increases the interaction strength between phenol and the ionic liquid and thus increased phenol distribution coefficient. Besides, types of anions have a significant effect in dictating the distribution coefficient of phenol. Some examples are as shown in Table 2.14 whereby phenol distribution coefficient for [BF_4^-] anion is always higher than [PF_6^-] anion for the same types of cations. This phenomenon was explained by Fan *et al.* (2008) in that the hydrogen bonding strength between phenol and the anion for [BF_4^-] was stronger and hence resulted in a higher phenol distribution coefficient.

Table 2.14: Distribution coefficients of phenol between ionic liquids/organic solvents and water at 293-298K

Ionic liquids	**Distribution coefficient**
[Bmim][BF_4]	13.9[e]
[Hmim][BF_4]	20.4[f]
[Omim][BF_4]	36[d] 37[f]
[Dmim][BF_4]	46[d]
[Bmim][PF_6]	11.3[b,f] 20[c]
[Hmim][PF_6]	16.7[f] 18[d]
[Omim][PF_6]	12[d] 23.2[f]
[Bmim][NTf_2]	16.9[e]
1,6-bis(3-methylimidazolium-1-yl)hexane bis(triflic)imide	17.5[e]
1,8-bis(3-methylimidazolium-1-yl)octane bis(triflic)imide	17.2[e]
1,10-bis(3-methylimidazolium-1-yl)decane bis(triflic)imide	16.7[e]
1,12-bis(3-methylimidazolium-1-yl)dodecane bis(triflic)imide	17.0[e]
Organic solvents	**Distribution coefficient**
1-octanol	30[c]
Diisopropyl ether	20[c]
Rosin amine	31[c]
Butyl acetate	50[c]
n-hexane	0.11[a]
n-heptane	0.11[a]
Petrolsol D15/20	0.11[a]
Methyl cyclohexane	0.15[a]
Petrolsol 15/20	0.2[a]
Toluene	1.5[a]
1-decanol	14[a]
MIBK	29[a]

(Source: [a]González-Muñoz *et al.*, 2003; [b]Khachatryan *et al.*, 2005; [c]Li *et al.*, 2005; [d]Vidal *et al.*, 2005; [e]Liu *et al.*, 2006; [f]Fan *et al.*, 2008)

Among the operating parameters, temperature and volume ratio were found to have less effect on the distribution coefficient of phenol in ionic liquids. Vidal *et al.* (2005) and Fan *et al.* (2008) claimed that the distribution coefficients of phenol in ionic liquids were independent with temperature. From this point, Li *et al.* (2005) even suggested that the distribution coefficients of phenol in the ionic liquids were lower at high temperature as phenol solubility in water was increased under this condition. This

reduces the amount of phenol that will dissolve into the ionic liquids. In term of volume ratio, the volume ratio for aqueous/ionic liquid of 5-50 was found to slightly reduce the distribution coefficients of phenol in [Hmim][PF_6] from 18.3-15.9 (Fan *et al*., 2008).

In comparison to temperature and volume ratio, pH of the system showed stronger effect in governing the distribution coefficients of phenol in ionic liquids. The work of Khachatryan *et al*. (2005), Vidal *et al.* (2005) and Fan *et al.* (2008) showed that the distribution coefficients were reasonably high and stable when the pH of the system was less than the pK_a value of phenol, or more precise, less than 7. Beyond this pH, the distribution coefficients were found to reduce steeply.

Furthermore, the reusability of the ionic liquids has also been studied. Fan *et al.* (2008) regenerated the ionic liquids by stripping down the phenol in the ionic liquids using 0.1M NaOH solution. The ionic liquids were further washed with water to neutralize its pH and were dried under vacuum at 348K for days. Similar procedures were also proposed by Wei *et al.* (2003) and Vidal *et al.* (2005) and their studies showed that the capacity and extraction efficiency for the recycled ionic liquids were maintained with a small efficiency deviations.

2.3.4.2 Bulk Ionic Liquid Membrane

Separations of several organic compounds through bulk ionic liquid membrane have been studied but this does not include phenol removal. Charkraborty and Bart (2007) utilized ionic liquids for the separation of toluene from heptane while the study on the separation of organic molecules of 1,4-dioxane, 1-propanol, 1-butanol, cyclohexanol, cyclohexanone, morpholine and methylmorpholine was conducted by Branco *et al*. (2008), using imidazolium cations with different types of side chains and anions.

Bulk ionic liquid membrane is a slow process as it has long diffusion path and high viscosity. The work of Chakraborty and Bart (2007) showed that the best toluene extraction efficiency using [Omim][Cl] in 100 hours was only 30% with a low stripping rate as a result of high viscous ionic liquid. However, the utilization of Ag^+ carrier in adequate concentration was found to improve the efficiency. Besides that, an optimum stirring speed and the increment on the operating temperature were found to enhance the extraction and stripping rates as well. Outside of the operating parameters, the work of Branco *et al.* (2008) found that polar side chain substitution on the cation increased the affinity of all solutes, but this also contributed to a drawback for the reduction on the membrane selectivity.

In addition, bulk ionic liquid membrane was also applied to study the influence of water content on the transport of solutes such as tritiated water, thymol blue (Fortunato *et al*., 2004), amino acids and amino acid esters (Fortunato *et al*., 2005a). Their works clarified that significant water content in the imidazolium-based ionic liquids with the anion of [PF_6^-] created water microenvironment in the ionic liquid membrane and this further marked a loss of membrane selectivity. According to Fortunato *et al*. (2004; 2005a), transport of these solutes were governed by the partition coefficients of the solutes in the ionic liquids initially. However, similar diffusion coefficients were obtained for the transport of tritiated water in different types of ionic liquids when the 75% water saturation was achieved in the ionic liquid membranes tested (Fortunato *et al*., 2004). Similar trend was also observed in the work of Fortunato *et al*. (2005a) for the transport of proline benzyl ester and phenylglycerine methyl ester. This justifies that the transport mechanisms of the solutes in ionic liquid membranes were switched from distribution coefficient dominant to water microenvironment dominant when the water content was saturated in the ionic liquids, as a result for contacting with aqueous phase.

However, the water microenvironment did not eliminate the transport selectivity of ionic liquid membranes entirely. Larger solute such as thymol blue was still found to be transported according to the distribution coefficient between the ionic liquids tested and the aqueous phase with less effect from water microenvironment (Fortunato *et al*., 2004).

2.3.4.3 Ionic Liquid Membrane Emulsion

The research and published literature on the utilization of imidazolium-based ionic liquids as solvent/diluent or carrier in emulsion liquid membrane are limited. The application of these ionic liquids is not favorable mainly due to their high viscosities in comparison to the conventional membrane solvents. The work of Ng *et al*. (2009) showed that the emulsification of ionic liquid membrane was almost impossible when [Bmim][PF_6] was utilized as membrane diluent while the effect of [Bmim][PF_6] on phenol removal was not observed significantly when it was applied as a carrier.

In comparison to imidazolium-based ionic liquids, ammonium based ionic liquids are preferred in emulsion liquid membrane due to their lower density and, in addition, they are miscible with most of the conventional light density membrane solvents. Tri-octylmethylammonium chloride (TOMAC) has been widely studied as a carrier in emulsion liquid membrane, such as the extraction of amino acids (Matsumoto *et al*., 1998), citric acid (Manzak and Tutkun, 2005) and benzimidazole (Venkatesan and Begum, 2009). This ionic liquid tends to form complexes with the targeted solutes by anion exchange mechanism and the solutes can be stripped down by a stripping agent which contains the anion [Cl^-] of the ionic liquid (Matsumoto *et al.*, 1998; Venkatesan and Begum, 2009). Thus, separation of solutes and the regeneration of TOMAC carrier can be achieved simultaneously.

2.3.4.4 Supported Ionic Liquid Membrane

Today, none of the phenol removal study is conducted by supported ionic liquid membrane. Instead, supported ionic liquid membrane is widely applied for catalysis separation and gas separation (Keskin *et al.*, 2007; Wasserschield and Welton, 2008; Poole and Poole, 2010). Besides, separations of other organic compounds such as aromatic hydrocarbons (Matsumoto *et al*., 2005) and trans-esterification reaction products (Hernández-Fernández *et al.*, 2007; de los Ríos *et al.*, 2008a; 2008b; 2009a) have also been studied using different types of anions and imidazolium cations with different length of cation's alkyl side chain. Selective transport was observed for the separation of these compounds by supported ionic liquid membrane. From their works, it was suggested that the permeability of a solute through the supported ionic liquid membrane was mainly governed by the nature of the solute and the ionic liquid used (Matsumoto *et al.*, 2005; Hernández-Fernández *et al.*, 2007; de los Ríos *et al.*, 2008a; 2008b; 2009a). In most of the studies mentioned, the permeabilities of the solutes were increased as hydrophobic ionic liquid of higher hydrophobicity was used. However, in term of selectivity, a less hydrophobic ionic liquid was preferred as it introduced greater difference in the mass transfer resistance between the solutes due to their solubility difference in the ionic liquids. Thus, selective transport can be achieved by adjusting the hydrophobicity and the types of cations/anions of the ionic liquids, depending on the nature of solutes to be separated (Matsumoto *et al.*, 2005; Hernández-Fernández *et al.*, 2007; de los Ríos *et al.*, 2008a; 2008b; 2009a).

Despite the above, the loss of membrane selectivity is observed when imidazolium-based ionic liquid membrane is in contact with an aqueous phase. In this case, the significant mutual solubility of the ionic liquid with water causes a different transport mechanism. This was observed by Matsumoto *et al.* (2007) for the separation of Penicillin G where they found that uphill transport was not achieved by [Bmim][PF_6]

supported ionic liquid membrane. Instead, the loss of pH in the feed phase and the stripping phase was observed and the equilibrium concentrations of Penicillin G in feed and stripping phases were the same after the experiment. This indicated that Penicillin G was transported through the phases via water microenvironment. Besides that, the formation of water microenvironment in supported ionic liquid membrane was also observed in the works of Fortunato *et al*. (2004; 2005a) for the transport of tritiated water, NaCl, amino acids and amino acid esters using imidazolium cations with the anion of [PF_6^-]. Their works showed that the transport dependencies of these compounds were shifted from the affinity of solutes towards the ionic liquids to the mobility of dynamic water microenvironment when the water content was saturated in the ionic liquid membrane. Thus, membrane selectivity was lost.

In contrast, it is found that supported ionic liquid membranes retained their stability for the studies that are summarized above even though they show different behaviours in the transport of solutes. Although it was shown that membrane selectivity was lost when the ionic liquid membrane contacted with aqueous phase, the work of Fortunato *et al*. (2005b) showed that there was no observable loss of [Bmim][PF_6] from the membrane pores. They claimed that hydrodynamic condition had less effect on the loss of ionic liquid from the pores. The ionic liquid detected in the aqueous phase originated mainly from the excess rinsing of ionic liquid that remained on the surface of the support during the impregnation process, as agreed by de los Ríos *et al*. (2007; 2009b).

The above argument is not applicable to every case since the nature of contact phase with ionic liquids (de los Ríos *et al.*, 2009b) and the impregnation method have strong influence on the membrane stability (Hernández-Fernández *et al.*, 2009). For the separations of hydrocarbons and trans-esterification reaction products, polar ionic liquid membranes were contacted with non-polar organic solvents, namely heptane, hexadecane (Matsumoto *et al*., 2005) and hexane (Hernández-Fernández *et al.*, 2007; de los Ríos *et al.*, 2008a; 2008b; 2009a). The immiscibility between the polar ionic liquids with non-polar organic solvents compromises the stability of the membrane. On the other hand, the work of de los Ríos *et al.* (2009b) on [Bmim][BF_4] based supported ionic liquid membrane showed that [Bmim][BF_4] was completely lost from the membrane support when it contacted with DMSO, a solvent that is miscible with it. This argument was also agreed by Hernández-Fernández *et al*. (2009) which claimed that the miscibility of an ionic liquid with the contact phase affected the loss of the ionic liquid from the membrane. In contrast, [Bmim][BF_4] was retained in the membrane support (87% -99%) when it was made to contact with TBME and n-hexane which have low polarity and immiscible with [Bmim][BF_4] (de los Ríos *et al.*, 2009b).

Besides that, the impregnation method also has a strong influence on the membrane stability. According to Hernández-Fernández *et al*. (2009), vacuum impregnation method works well for low viscosity ionic liquids such as [Bmim][NTf_2] and [Bmim][BF_4] while pressure method is suitable for high viscosity ionic liquids such as [Bmim][Cl] and [Bmim][PF_6] as they require additional force to overcome the high capillary force needed to penetrate into the membrane support. Generally, higher amount of ionic liquid immobilization with higher stability can be obtained by undergoing pressure impregnation method instead of vacuum method, especially for high viscosity ionic liquids.

2.4 Selection of Liquid Membrane and Ionic Liquids

As mentioned in Section 1.2, the main objective for the present research is to determine the feasibility of ionic liquids as new types of membrane solvents for phenol removal from aqueous solution. Hence, the selection of liquid membranes and ionic liquids are based on this statement with the substantiation of Section 2.2 and Section 2.3.

2.4.1 Selection of Liquid Membrane

A comparison on the advantages and disadvantages of three types of liquid membrane systems is conducted based on the literature review discussed in Sections 2.2, as summarized in Table 2.15. The table shows that emulsion liquid membrane and supported liquid membrane have higher membrane interfacial area per unit volume. However, small membrane volume requirement and stability issues such as emulsion swelling (emulsion liquid membrane) and membrane solvent loss (supported liquid membrane) raise doubts on the suitability of using these types of liquid membranes in investigating ionic liquids' characteristics as new materials for liquid membrane.

Table 2.15: Comparison on the advantages and disadvantages between different types of liquid membranes

Type of liquid membranes	**Interfacial area/volume**	**Mass transfer rate**	**Stability issue**
Bulk liquid membrane	Low	Slow	No
Emulsion liquid membrane	Very high	Fast	Yes
Supported liquid membrane	High	Slow	Yes

In contrast, bulk liquid membrane shows simple design without membrane instability issue. Its high membrane thickness and nearly constant surface area to volume ratio make it suitable to be applied in this study. In addition, phenol transport

mechanism in the ionic liquid membranes can be well observed in all three phases and the transport kinetics can be readily obtained using this system. Therefore, bulk liquid membrane is chosen as the type of liquid membrane for preliminary study on the pertraction of phenol by ionic liquid membranes.

2.4.2 Selection of Ionic Liquids

Ionic liquids are selected as the membrane solvents due to their lower volatility and flammability in comparison to conventional organic membrane solvents. Section 2.3.4.1 shows that imidazolium ionic liquids have the potency as good extraction solvents for phenol removal. However, it is worth noting that not all types of imidazolium ionic liquids are suitable as liquid membranes. Inappropriate ionic liquid properties such as miscibility and high mutual solubility with aqueous phase tend to cause ionic liquid loss and water microenvironment formation within the ionic liquid membrane, and this ultimately leads to membrane failure, as discussed in Sections 2.3.4.2 and 2.3.4.4.

Hence, a guideline on the screening of imidazolium-based ionic liquids as membrane solvents is drafted based on Section 2.3 and is illustrated in Figure 2.7. The screening process focuses on the aqueous feed and stripping phases. Figure 2.7 shows that, in general, there are five main parameters to be considered in the selection of ionic liquid as liquid membrane, namely water miscibility, mutual solubility, moisture stability, viscosity and environmental consideration.

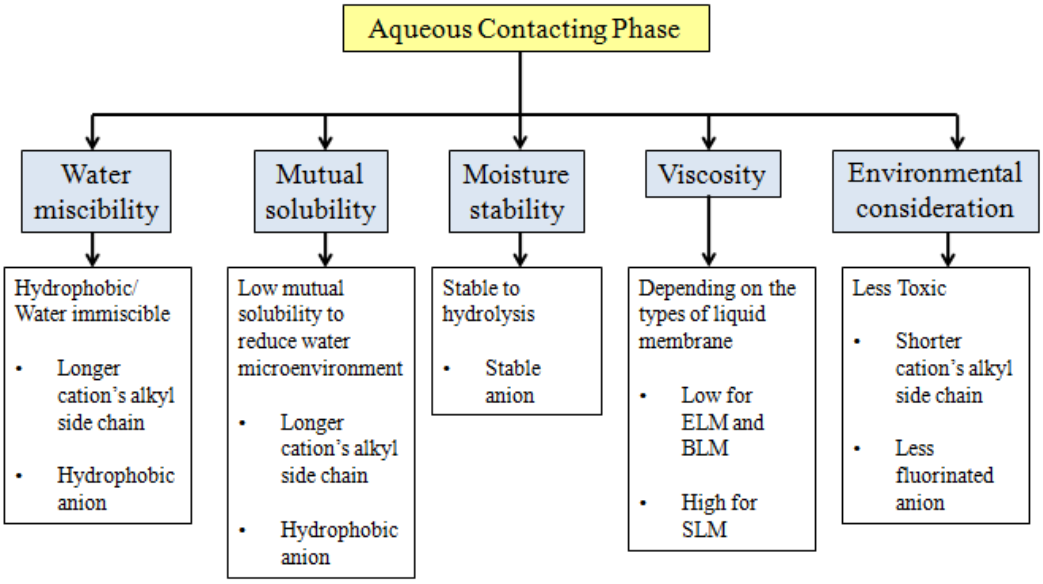


Figure 2.7: Parameters to be considered in selection of ionic liquid membranes

Firstly, for aqueous contact phase, hydrophobic/water immiscible ionic liquid has to be chosen in order to prevent membrane failure due to ionic liquid dissolution or water microenvironment when it contacts with the aqueous feed and stripping phases. The increment of the hydrophobicity of the ionic liquid reduces the mutual solubility between the ionic liquid and water proportionally, as discussed in Section 2.3.3.2. Both these parameters can be achieved by utilizing the cation with longer alkyl side chain and hydrophobic anions such as [PF_6^-], [NTf_2^-] and [FAP^-] (Section 2.3.3.1 and 2.3.3.2).

Despite the above, from the environmental viewpoint, longer alkyl side chain in the cation is less favoured due to its higher toxicity, as discussed in Section 2.3.3.5. Hence, the use of high hydrophobic anion with cation that has shorter alkyl side chain such as [Bmim][NTf_2], [Bmim][FAP] and [Bmim][PF_6] is preferred. Detailed physical properties data of these ionic liquids are available in Section 2.3.3.

Among these ionic liquids, the anions are further screened, based on their degree of moisture stability. From Section 2.3.3.3, it is known that [PF_6^-] anion is less stable in water due to its tendency to hydrolyze when it comes into contact with the aqueous phase under certain conditions. This reduces the degree of environmental friendliness for [PF_6^-] anion and thus removed from the selection. Imidazolium-based ionic liquids [Bmim][NTf_2] and [Bmim][FAP] are proposed as the appropriate membrane solvents in this study. However, [Bmim][PF_6] is also utilized as reference for performance comparison.

CHAPTER 3: METHODOLOGY

This chapter covers a description of the chemicals and apparatus used, the experimental procedures, sampling and analytical methods employed.

3.1 Chemicals and Reagents

Phenol crystal (A.R grade) was supplied by Merck Sdn Bhd. NaOH pellets, HCl (37%, A.R grade) and dichloromethane (A.R. grade) were purchased from R&M Chemicals. Kerosene (Pure) as the organic membrane solvent was supplied by Acros Organic while Cyanex923 (A.R Grade) as the organic carrier was supplied by Cytec Ltd. Ionic liquids [Bmim][PF_6], [Bmim][NTf_2], [Bmim][FAP] (Synthesis grade) were purchased from Merck Sdn Bhd. Distilled water was used for preparing the chemical solutions.

3.2 Apparatus

3.2.1 Ionic Liquid Membrane Reactor

Bulk ionic liquid membrane reactor was a specially designed glassware with inner dimensions of 12.1cm x 5.6cm x 11.9cm (Length x Width x Height) with effective contact area of 33.18cm^2 for each compartment. The reactor was separated into two compartments by a partition in the middle of the reactor with a 0.8cm opening at the bottom which enabled the fluid to flow from one compartment to another, as shown in Figure 3.1.

The reactor was designed based on the fact that ionic liquid membrane has higher density than the feed and stripping phases. Ionic liquid membrane remained as a bottom layer to separate the compartments while the feed phase and the stripping phase were at top layers. Several considerations were taken into account for the design of the reactor:

i. Stirring on both feed and stripping phases were required. Therefore, the size of the reactor must be sufficiently large enough.
ii. The contact area between both phases and ionic liquid membrane phase was maximum. Square shape was applied in this study.
iii. A narrow reactor was preferred instead of wide reactor in order to minimize the amount of ionic liquid that was required in the experiments.

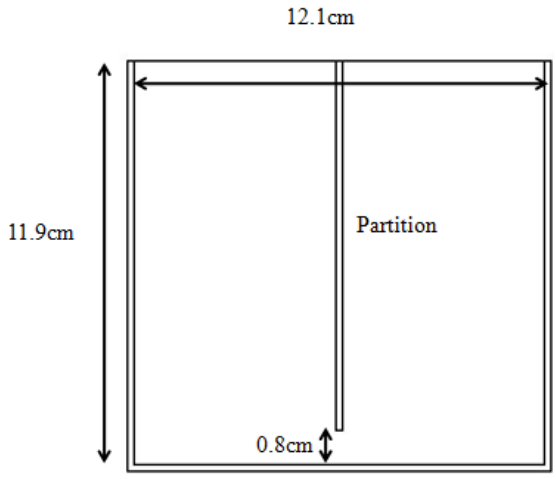


Figure 3.1: Diagram of ionic liquid membrane reactor

3.2.2 Organic Liquid Membrane Reactor

Another type of membrane reactor was used for the organic liquid membrane set-up as the density of the membrane solvent was lower in comparison to the feed phase and the stripping phase. The organic liquid membrane reactor had inner dimensions of 12.1cm x 5.8cm x 11.8cm, with an effective area of 34.51 cm^2 for each compartment. It was separated into two compartments by a 6.2cm height baffle in the middle of the reactor, without opening at the bottom of the reactor. The schematic diagram of the organic liquid membrane reactor is as shown in Figure 3.2.

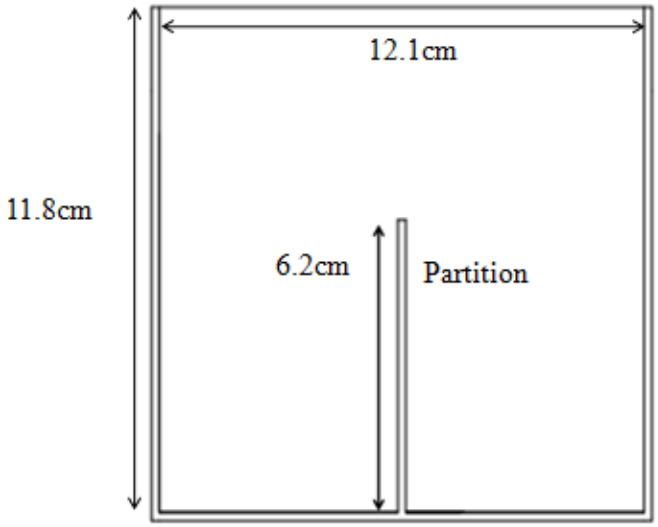


Figure 3.2: Diagram of organic liquid membrane reactor

3.2.3 Other Equipment

IKA Lab Egg RW11 mechanical stirrers for the membrane reactor were supplied by IKA and the magnetic stirrer MSH-20D was purchased from DAIHAN. The peristaltic pumps SASTEC ST-BT100-2J supplied by SASTEC were used to transfer the feed solution and the stripping solution into the membrane reactor.

3.3 Analytical Instruments

3.3.1 UV-Vis Spectrophotometer

UV-Vis spectrophotometer SECOMAM UviLine 9400 was used to analyze the concentration of phenol via absorbance measurement. The spectrophotometer has a wavelength range of 190-1100nm for absorbance measurement with wavelength accuracy of ±1nm and absorbance accuracy of ±0.003. Phenol is an organic compound which can be detected easily in the wavelength of 270nm for molecular form and 288nm for phenolate ion form. The spectrophotometer was operated by referring to its operating manual.

3.3.2 Other Analytical Instruments

pH meter Cyber Scan pH300 with accuracy of ±0.01 was used for pH measurements. Rheintacho Rotaro Tachometer which has an accuracy of ±1rpm was used for measuring the rotational speed of the mechanical stirrers.

3.4 Precautionary Steps for Chemicals Handling

The precautionary steps on the handling of chemicals and solutions are as follow:

i. Mask and gloves were worn during the preparation of phenol, HCl and NaOH solutions.
ii. Phenol and HCl solutions were prepared in fume cupboard.
iii. All the use glasswares were cleaned by soaking with detergent and rinsing with distilled water. They were dried in a dryer before used.

iv. Chemicals were stored in a dark place to prevent any possible degradation process caused by light.

3.5 Experimental Procedures

3.5.1 Preparation of Aqueous Solutions

The feed phase and the stripping phase consisted of phenol solution and NaOH solution, respectively. Phenol solution was prepared by diluting the theoretical amount of phenol crystals with distilled water in a volumetric flask. The solution was mixed by a stirrer for approximately 10 min until a homogeneous solution was obtained. Similar method was applied for the preparation of NaOH solution, a well known stripping agent for phenol treatment. HCl solution was prepared by diluting the concentrated HCl with distilled water in a volumetric flask to obtain the desired concentration. The solution was stirred to ensure homogeneity.

3.5.2 Liquid-liquid Extraction

The nature of ionic liquids either as carriers or diluents was evaluated via liquid-liquid extraction tests. The tests were conducted for phenol extraction by two types of ionic liquids, namely [Bmim][NTf_2] and [Bmim][FAP]. Fresh ionic liquids were washed with distilled water and were dried in a vacuum dryer at 348K for 2 days (Fan *et al*., 2008) before the experiments to remove any trace contaminants and excess moisture. For the applications of ionic liquids as carriers, ionic liquid/Cyanex923 was dissolved in dichloromethane at different concentrations. 1mL of this mixture was taken out by a calibrated pipette and was transferred into a 10mL glass vial. After that, 5mL of 3000ppm phenol solution was transferred into the vial and the mixture was stirred

vigorously using magnetic stirring for 30 min. It was then left for 120 min for phase separation and if necessary, centrifugation was applied. Following that, 1mL of aqueous sample was taken out from the mixture and was diluted with 0.5M HCl solution. Sample analysis was accomplished through absorbance utilizing UV-Vis spectrophotometer SECOMAM UviLine 9400 at a wavelength of 270nm.

On the other hand, the applications of ionic liquids as diluents were evaluated by dissolving a small amount of Cyanex923 into different types of ionic liquids/organic solvents at different concentrations. 1mL of the mixture was then taken and was mixed with 5mL of 3000ppm phenol solution in a glass vial. Vigorous magnetic stirring was applied to the mixture for 30 min and phase separation was allowed after the stirring process. The sampling method and analytical method followed procedure described above.

3.5.3 Bulk Ionic Liquid Membrane (BILM) Experimental Procedure

Hydrophobic ionic liquids [Bmim][PF_6], [Bmim][NTf_2] and Bmim[FAP] were used in the experiments. The ionic liquids were washed with distilled water and were dried in a vacuum dryer at 348K for 2 days (Fan *et al*., 2008) before the experiments, and this was done to remove any trace contaminants and excess moisture. However, the drying process was not applied for wet [Bmim][PF_6] as heating stimulated the hydrolysis process. For experimental purpose, wet [Bmim][PF_6] was used.

A measured volume of 80mL of ionic liquid was used as the membrane phase. The ionic liquid was weighed and transferred into the membrane reactor whereby it separated the feed and stripping compartments. A volume of 200mL phenol solution with a concentration of 300ppm at a pH of ≈6.5 and 0.5M NaOH solution were

transferred into the compartments, respectively. The configuration of the system is as shown in Figure 3.3.

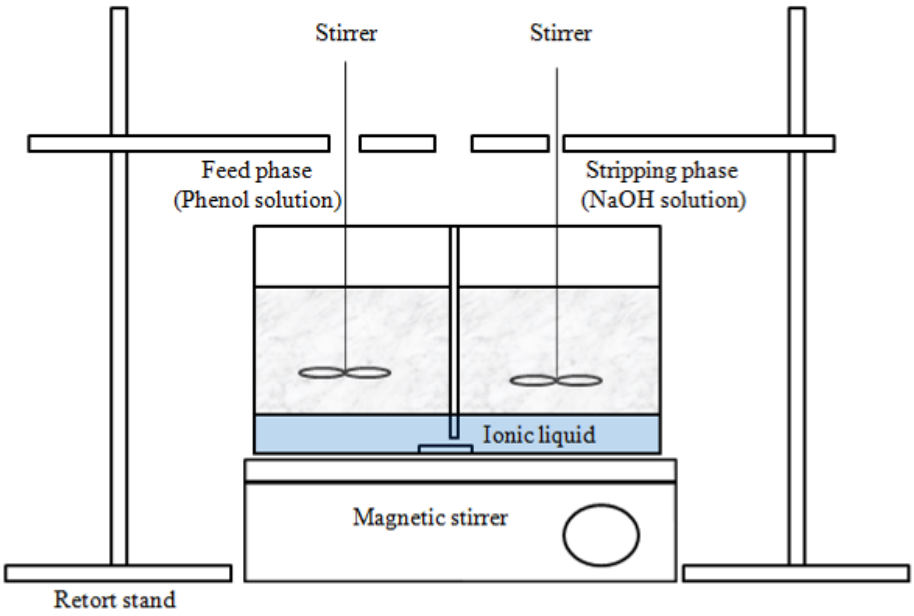


Figure 3.3: Experimental setup for bulk ionic liquid membrane system

To ensure well mixed solution, stirring in the feed and stripping compartments by IKA Lab Egg Stirrers RW11 were undertaken. The aqueous stirring speed for both of the feed and stripping phases were maintained at 200rpm while the membrane phase was stirred using magnetic stirrer MSH-20D at 100rpm so as to increase the transport rate of phenol from the membrane phase to the stripping phase. Basically, the experiment was conducted based on the above specification unless otherwise stated.

The experiment was conducted for 300 min under atmospheric temperature of 298K. Samples of volume 1mL from the feed phase and the stripping phase were taken using a calibrated pipette of 1mL capacity at 30 min time interval for the first 120 min and 60 min after the first 120 min. Prior to analysis, the feed samples were diluted with 0.5M HCl solution while the stripping samples were diluted with 0.5M NaOH solution. The absorbances of these samples were analyzed at wavelength of 270nm for feed samples and 288nm for stripping samples using UV-Vis Spectrophotometer

SECOMAM UviLine 9400. At the minimum, all experiments were duplicated and the results obtained were within an experimental error range of 4%.

The experiment for dichloromethane (organic membrane solvent) was conducted with similar configuration as it has higher density than both the feed phase and the stripping phase.

3.5.4 Bulk Organic Liquid Membrane (BOLM) Experimental Procedure

A volume of 80mL of kerosene was used as the membrane phase. As kerosene has lower density than the feed and stripping phases, a different system configuration from Section 3.5.3 was applied whereby the membrane phase became the top layer. A schematic diagram for bulk organic liquid membrane is as illustrated in Figure 3.4.

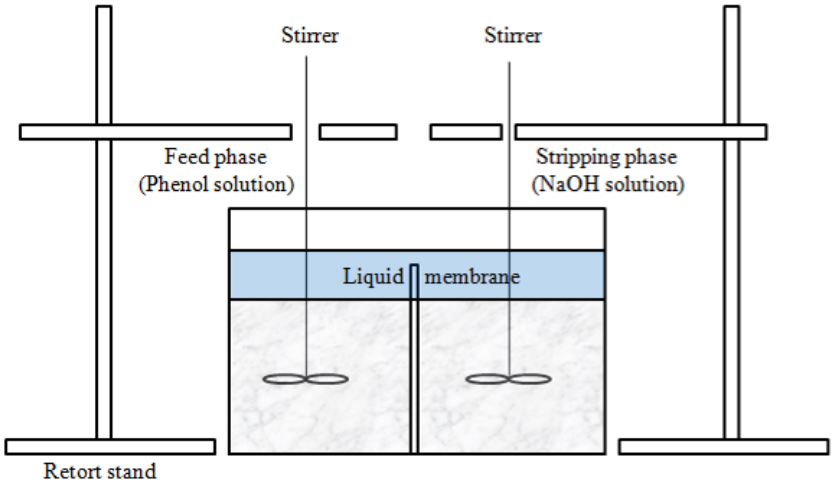


Figure 3.4: Experimental setup for bulk organic liquid membrane system

Phenol solution of 200mL with concentration of 300ppm at pH of ≈6.5 and 0.5M NaOH solution were used in the experiments. The solutions were transferred into the feed and stripping compartments, respectively, and this was followed by carefully adding kerosene to form a top layer which connected both phases. Stirring in the feed and stripping phases were applied for 300 min under environment temperature of 298K. The membrane phase remained intact as the layer was too thin to be mechanically

stirred without creating emulsion. The sampling and analytical procedures were similar to what were discussed in Section 3.5.3.

3.5.5 Regeneration and Reuse of Ionic Liquids

The method for ionic liquid regeneration was published by Wei *et al*. (2003), Vidal *et al*. (2005) and Fan *et al.* (2008). Used ionic liquid was mixed with 150mL of 0.5M NaOH solution and was stirred vigorously for 30 min to extract phenol remaining in the ionic liquid after the experiment. Phase separation was conducted after the stirring process. The aqueous sample was taken and its sodium phenolate concentration was analyzed by UV-Vis spectrophotometer at 288nm. These procedures were repeated until negligible amount of sodium phenolate was detected in the aqueous sample.

Subsequently, the ionic liquid was washed with distilled water to dissolve and remove any NaOH in the ionic liquid. This process was repeated until the pH of the ionic liquid fell in a range of 6.5-7.5. Then, the ionic liquid was dried in a dryer at 348K for 2 days (Fan *et al.*, 2008) to remove excess moisture and was later stored in a desiccator. Again, it was worth noting that high temperature drying process was not applied for [Bmim][PF_6] as the hydrolysis process was observed when wet [Bmim][PF_6] was heated.

3.6 Analytical Methods

Phenol concentrations in the different phases were determined by measuring the absorbances of the samples using UV-Vis Spectrophotometer Secomam UviLine 9400. Procedures applied are as follows:

3.6.1 Preparation of Standards and Calibration Curves

A series of standard solutions of phenol were prepared at different concentrations. The volumetric flasks and other glasswares were checked for their cleanliness and dryness before used. Dilution of phenol solution was conducted using calibrated pipettes and burettes.

The prepared solutions in an acidic medium were then scanned using UV-Vis Spectrophotometer Secomam UviLine 9400 and the absorbance at 270nm was recorded. A linear plot of absorbance versus phenol concentration was obtained. The calibration curve for the concentration of sodium phenolate (phenol in basic NaOH solution) was prepared under basic medium using similar method, except at wavelength of 288nm. These procedures were triplicate to determine the reliability of the calibration curves.

3.6.2 Dilution of Samples

Samples from the feed phase and the stripping phase were diluted before analysis due to the limitation of maximum detectable absorbance of the spectrophotometer. HCl solution of 0.5M was used to dilute the feed samples so as to ensure that only molecular phenol was present in the feed sample. On the other hand,

0.5M NaOH solution was used to dilute the stripping samples so that phenol could be changed to sodium phenolate completely under high pH condition.

3.6.3 Phenol Concentration Analysis

The wavelength used for phenol detection in the feed sample was 270nm whereas for the detection of sodium phenolate in the stripping sample was 288nm. Phenol concentration in the feed phase and sodium phenolate concentration in the stripping phase at different time interval were obtained based on the absorbance-phenol and absorbance-phenolate calibration curves. Subsequently, the concentrations and the amount of phenol in both phases were determined.

Extraction and stripping efficiencies for bulk liquid membrane system were calculated using Equations (3.1) and (3.2) based on the concentrations of phenol/phenolate obtained through the experiments:

$$\text{Extraction Efficiency, \%} = \frac{C_{f,0} - C_{f,t}}{C_{f,0}} \times 100 \tag{3.1}$$

$$\text{Stripping Efficiency, \%} = \frac{C_{s,t}}{C_{f,0} - C_{f,t}} \times 100 \tag{3.2}$$

Where:

$C_{f,0}$ = initial phenol concentration in the feed phase (mg/L)

$C_{f,t}$ = concentration of phenol in the feed phase at time t (mg/L)

$C_{s,t}$ = concentration of phenol in the stripping phase at time t (mg/L)

Phenol exists in the form of sodium phenolate only under high pH condition. The concentration of phenol in the stripping phase can be determined by converting the amount of sodium phenolate detected to the theoretical amount of molecular phenol present in the stripping phase by mole balancing of the chemical equation, illustrated in Equation (3.3). A detailed calculation method for the determination of phenol/phenolate concentration, extraction and stripping efficiencies are discussed in Appendix A.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \tag{3.3}$$

From the phenol/phenolate concentration obtained, the mass of phenol in the feed phase and stripping phase were determined. Phenol concentration in the membrane phase was estimated by performing a mass balance on the system (Equation 3.4) based on the assumption that ionic liquid does not react with phenol:

$$C_{m,t} = \frac{N_{f,0} - N_{f,t} - N_{s,t} - e}{V_m} \tag{3.4}$$

Where:

$C_{m,t}$ = concentration of phenol in the membrane phase at time t (mg/L)

$N_{f,0}$ = initial mass of phenol in the feed phase (mg)

$N_{f,t}$ = mass of phenol in the feed phase at time t (mg)

$N_{s,t}$ = mass of phenol in the stripping phase at time t (mg)

V_m = volume of ionic liquid membrane (L)

e = the cumulative amount of phenol loss due to sampling (mg)

3.6.4 Ionic Liquid Recovery

The percentage of ionic liquid recovered after the experiment was calculated based on Equation (3.5)

$$\text{Ionic Liquid Recovery},\% = \frac{N_{IL,r}}{N_{IL,0}} \times 100 \tag{3.5}$$

Where:

$N_{IL,0}$ = mass of ionic liquid before the experiment (g)

$N_{IL,r}$ = mass of ionic liquid after the regeneration process (g)

3.6.5 pH Measurement

pH of the feed phase and the stripping phase were measured by pH meter Cyber Scan pH300 (Eutech Instrument) during each sampling time. The pH meter was calibrated using buffer solutions before each experiment. Undesirable transportation of NaOH from the stripping phase to the feed phase can be detected by a drastic change of pH in the feed phase.

3.6.6 Rotating Speed Measurement

The rotational speed of the IKA Lab Egg Stirrers RW11 was checked using Rheintacho Rotaro Tachometer during each sampling time via triplicate red point detection method.

3.7 Minimization of Error

Apparatus such as stirrers and pH meter were calibrated before each experiment so as to reduce systematic error. The experiments were duplicated to verify the validity of the results. Additional experiments were conducted to reduce random error when deemed necessary. To reduce errors that could occur during measurements, readings for stirring speed, pH and absorbance were triplicated. Furthermore, the sequence of the experiments was assigned randomly using Microsoft Excel in order to average out the unknown nuisance factor.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter covers two sections, i.e. liquid-liquid extraction and bulk liquid membrane experiments. The liquid-liquid extraction experiments were carried out to determine whether the characteristics of ionic liquid in liquid membrane system were more suitable as either diluent or carrier. For bulk liquid membrane experiments, the best ionic liquid was selected among [Bmim][PF_6], [Bmim][NTf_2] and [Bmim][FAP]. Further analysis was carried out on the effect of the feed phase pH, feed concentration, NaOH concentration and stirring speeds on phenol extraction and stripping efficiencies. Following that, optimization study and efficiency comparison between the organic liquid membranes and ionic liquid membrane were conducted.

4.2 Liquid-liquid Extraction

Liquid-liquid extraction tests were conducted to study the behavior of ionic liquids as diluents and carriers before they were applied as liquid membranes.

4.2.1 Characteristic of Ionic Liquids as Carriers in Organic Solvents

4.2.1.1 Miscibility Test

Miscibility tests were conducted by mixing 1mL of ionic liquids with 5mL of kerosene, n-hexane and dichloromethane, respectively. The miscibility of different types of ionic liquids with kerosene, n-hexane and dichloromethane were observed.

Table 4.1: Miscibility of ionic liquids with organic solvents

Organic solvent	**Ionic liquid**	**Miscibility**
Kerosene	[Bmim][PF_6]	Immiscible with each other.
	[Bmim][NTf_2]	Immiscible with each other.
	[Bmim][FAP]	Immiscible with each other.
n-Hexane	[Bmim][PF_6]	Immiscible with each other.
	[Bmim][NTf_2]	Immiscible with each other.
	[Bmim][FAP]	Immiscible with each other.
Dichloromethane	[Bmim][PF_6]	Miscible
	[Bmim][NTf_2]	Miscible
	[Bmim][FAP]	Miscible

Table 4.1 shows that ionic liquids studied are immiscible with aliphatic organic solvents (kerosene and n-hexane) which are normally utilized as diluents/membrane phases. Two layers of liquid phases were observed for these tests. On the other hand, ionic liquids were miscible with dichloromethane (polar aprotic solvent), forming a homogeneous liquid phase. Hence, tests to determine phenol extraction efficiency by the mixture of organic solvent-ionic liquid were conducted only for dichloromethane.

4.2.1.2 Extraction Efficiency

Phenol extraction efficiency was studied for [Bmim][NTf_2] and [Bmim][FAP] only. Figure 4.1 shows that the presence of ionic liquids/Cyanex923 increases phenol extraction efficiency in the order of [Bmim][FAP] < [Bmim][NTf_2] < Cyanex923. In this study, organic carrier Cyanex923 showed better enhancement on extraction efficiency than ionic liquids as the best extraction efficiency of 99% was observed. In contrast, ionic liquids [Bmim][NTf_2] and [Bmim][FAP] only showed the best extraction efficiency of about 80% and 50%, respectively. Besides that, it was also found that the increment of ionic liquids/Cyanex923 concentration increased the extraction efficiency.

However, it was found that Cyanex923 only required 0.3g/mL solvent to achieve the best extraction efficiency while both of the ionic liquids needed at least 0.8g/mL solvent. Hence, ionic liquids showed no significant advantage as carriers in liquid-liquid extraction process.

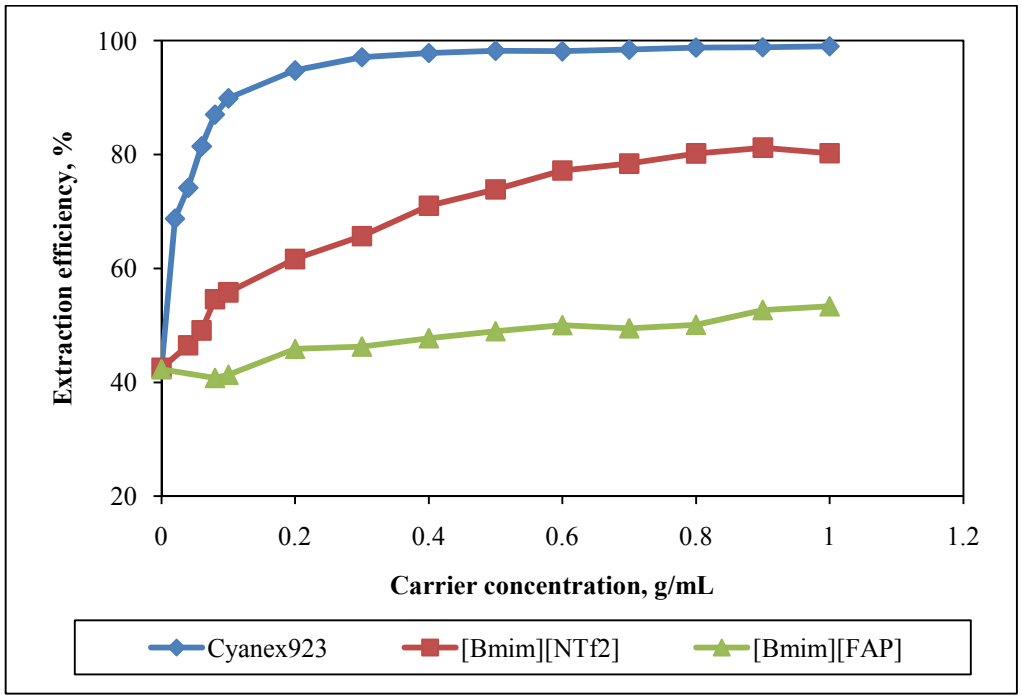


Figure 4.1: Extraction efficiency of phenol by dichloromethane at different carrier concentrations

4.2.2 Characteristic of Ionic Liquids as Diluents/Solvents

4.2.2.1 Miscibility Test

The suitability of ionic liquids as diluents/solvents were studied by mixing 1mL of ionic liquid ([Bmim][PF_6], [Bmim][NTf_2] and [Bmim][FAP]) with 1mL of Cyanex923 as an organic carrier. Table 4.2 shows that all of the ionic liquids tested dissolve Cyanex923 to form a homogeneous liquid phase with different turbidity. However, when 10mL of distilled water was added to the mixture, three layers of liquid phases were observed for [Bmim][PF_6] test.

Table 4.2: Miscibility of ionic liquids with Cyanex923

Organic carrier	**Ionic liquid**	**Miscibility**
Cyanex923	[Bmim][PF_6]	Miscible, a very viscous and turbid phase was formed.
	[Bmim][NTf_2]	Miscible. A clear phase was formed.
	[Bmim][FAP]	Miscible. A clear yellowish phase was formed.

Figure 4.2 shows that separation of ionic liquid and Cyanex923 in the presence of water only occurs for [Bmim][PF_6]. The layers are: Cyanex923 (upper layer), distilled water (middle layer) and [Bmim][PF_6] (bottom layer). This suggests that Cyanex923 tends to form weaker bond with [Bmim][PF_6] in comparison to the other types of ionic liquids in this study. As distilled water was added, density difference forced the mixture to separate according to their respective specific gravity. (Specific gravity: [Bmim][PF_6]: 1.37, Water: 1, Cyanex923: 0.88). On the other hand, tests for [Bmim][NTf_2] and [Bmim][FAP] showed that when the mixture were added with 10mL of distilled water, two layers of liquid phases were formed whereby the water phase was the upper layer and the ionic liquid-Cyanex923 mixture was the bottom layer, as shown in Figure 4.2. Hence, the study of phenol extraction efficiency by the mixture of ionic liquid-Cyanex923 was conducted for [Bmim][NTf_2] and [Bmim][FAP] only.

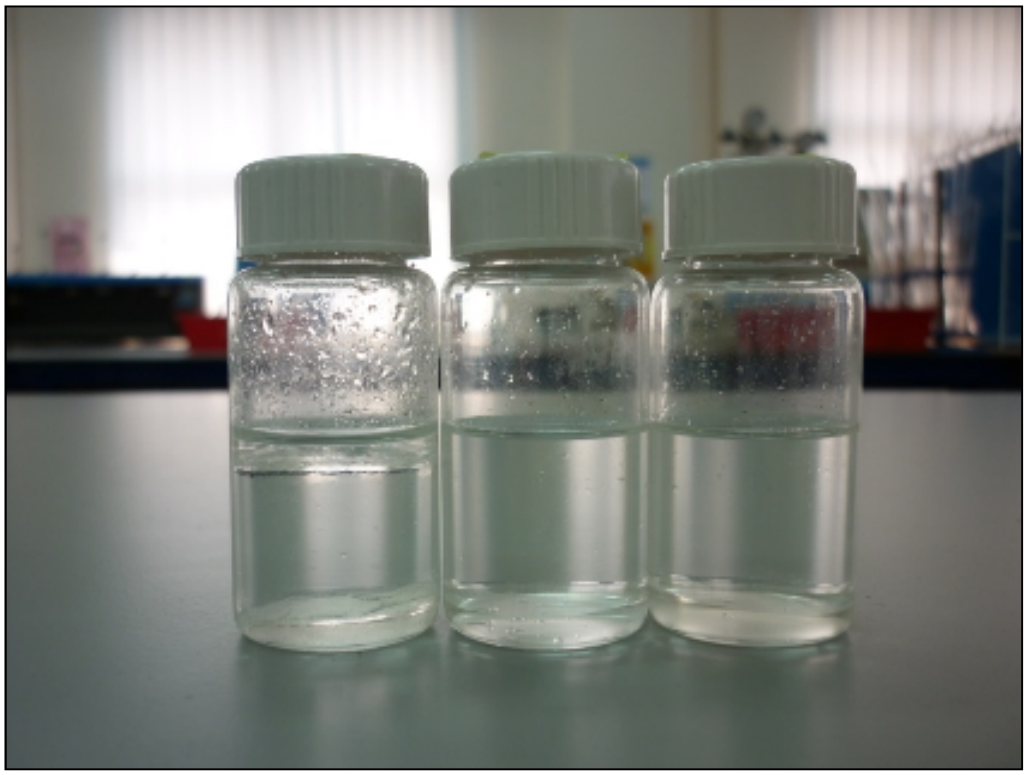


Figure 4.2: Physical observation of ionic liquids as membrane solvents (from left to right: [Bmim][PF_6], [Bmim][NTf_2], [Bmim]FAP])

4.2.2.2 Extraction Efficiency

Mixture of [Bmim][NTf_2]-Cyanex923 and [Bmim][FAP]-Cyanex923 were utilized for the extraction of phenol from aqueous solution. Figure 4.3 shows that the extraction efficiency is in the increasing order of kerosene < [Bmim][FAP] < dichloromethane < [Bmim][NTf_2] in the absence of Cyanex923. As pure diluents/solvents, [Bmim][NTf_2] gave the highest extraction efficiency in comparison to all organic solvents in this test. Besides that, it also showed higher extraction efficiency of 75.46% compared to [Bmim][FAP] which showed 37.71% due to its higher hydrogen bond basicity strength, as mentioned in Section 4.3.1.

However, when Cyanex923 was added as a carrier, the advantage of [Bmim][NTf_2] was diminished. The extraction process was believed to be mainly governed by the complex formation between phenol and Cyanex923 in this case. As the concentration of Cyanex923 was increased beyond 0.2mL/mL solvent, the extraction

efficiencies remained constant at above 90% for all types of diluents/solvents. This indicates that the performance of ionic liquid based diluents/solvents is only advantageous to the organic solvents in the absence of Cyanex923.

Other than phenol extraction efficiency, the addition of Cyanex923 as a carrier into ionic liquid diluents caused turbidity. In comparison to kerosene and dichloromethane, turbidity that was created by ionic liquid-Cyanex923 mixture after the extraction process was more significant especially in high Cyanex923 concentration, as shown in Figures 4.4, 4.5, 4.6 and 4.7. This necessitates another post treatment after the extraction process which is obviously not favoured in industrial applications.

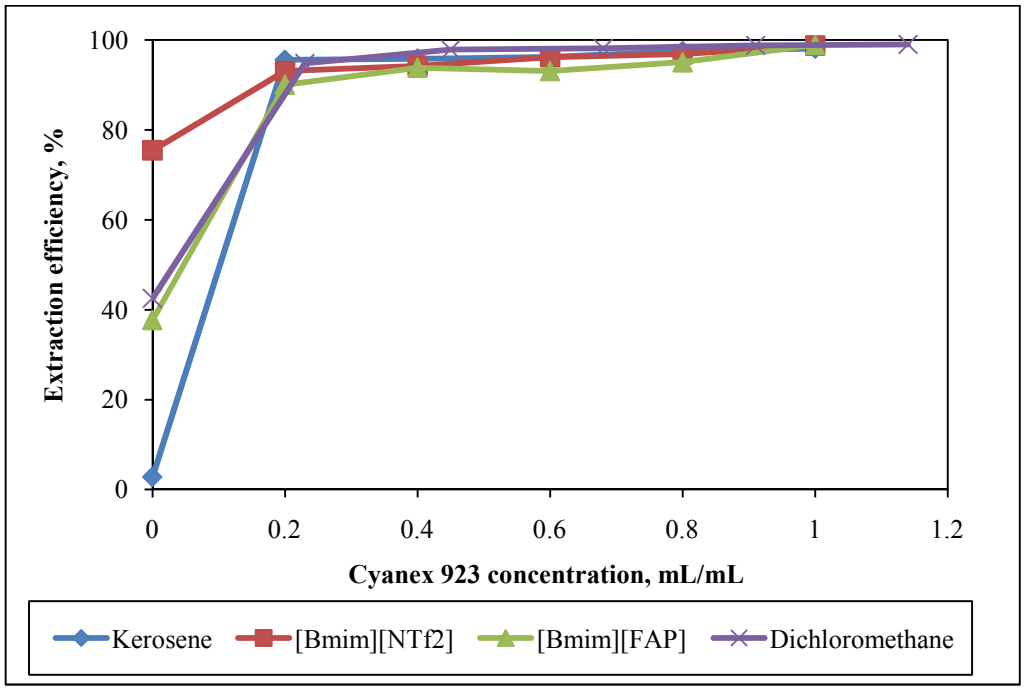


Figure 4.3: Extraction efficiency of phenol by different types of diluents at different Cyanex923 concentrations

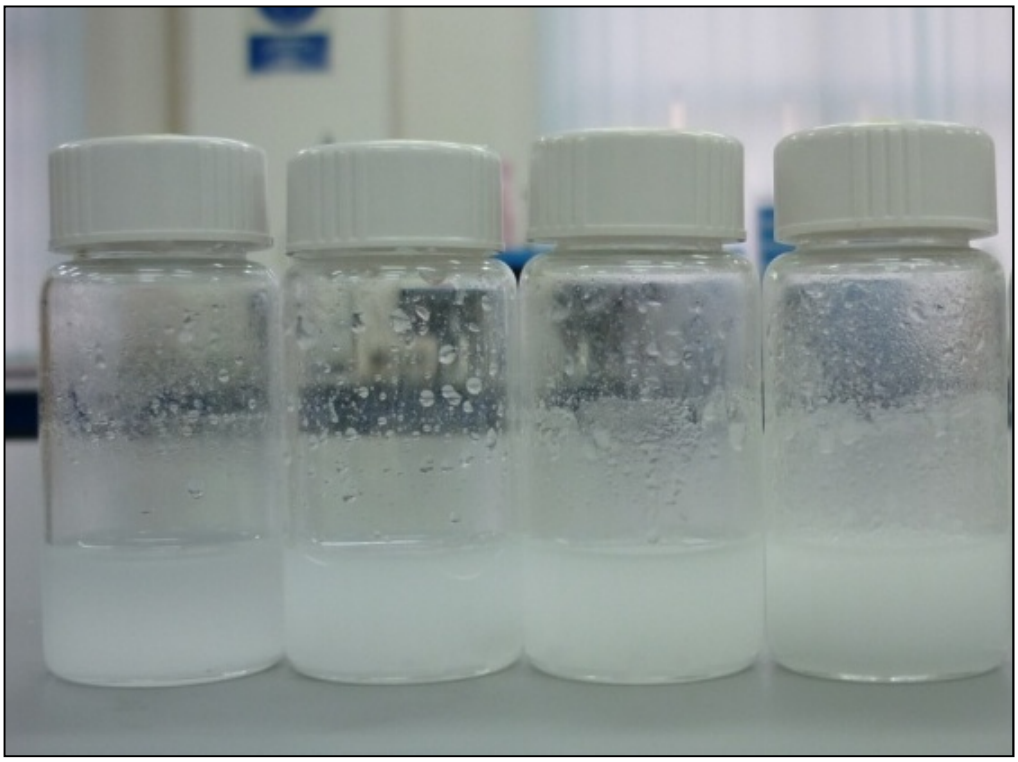


Figure 4.4: Mixture of [Bmim][NTf_2], Cyanex923 and phenol solution (from left to right: increase in Cyanex923 concentration)

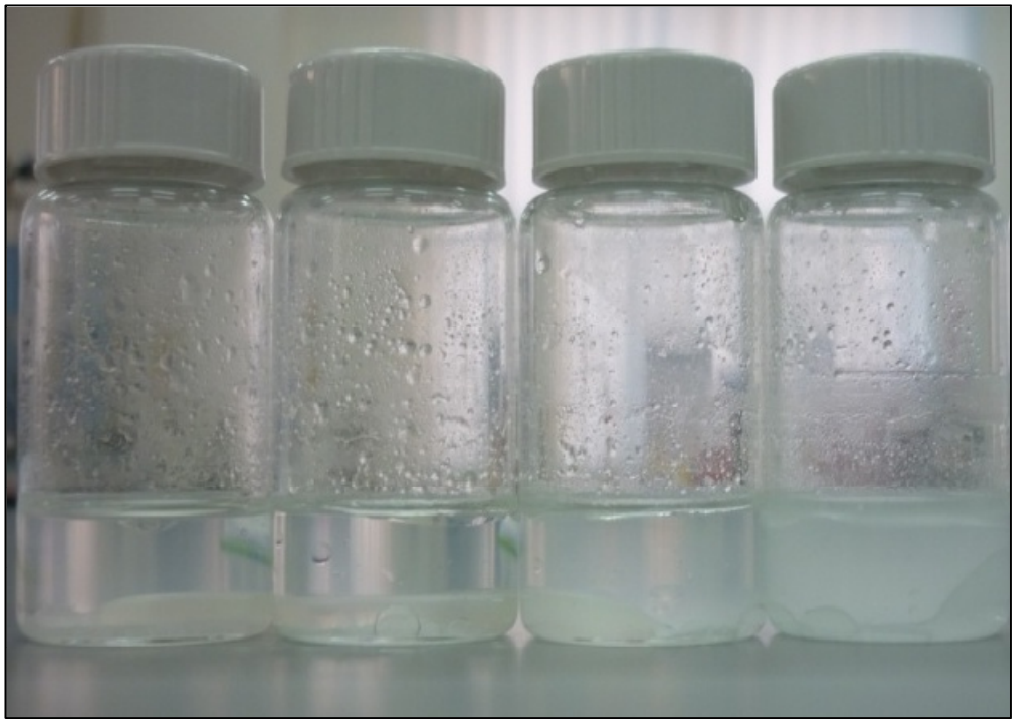


Figure 4.5: Mixture of [Bmim][FAP], Cyanex923 and phenol solution (from left to right: increase in Cyanex923 concentration)

Figure 4.6: Mixture of kerosene, Cyanex923 and phenol solution (from left to right: increase in Cyanex923 concentration)

Figure 4.7: Mixture of dichloromethane, Cyanex923 and phenol solution (from left to right: increase in Cyanex923 concentration)

4.2.3 Implication of Liquid-liquid Extraction Test on Bulk Liquid Membrane

The tests showed that ionic liquids gave lower phenol extraction efficiency than Cyanex923 when applied as carriers. The amount of ionic liquid required to achieve the best extraction efficiency was much higher in comparison to Cyanex923 and this hindered the application of ionic liquids as alternative to organic carriers.

In the application as diluents/solvents, ionic liquid [Bmim][NTf_2] showed better extraction efficiency than [Bmim][FAP], dichloromethane and kerosene. However, this advantage diminished when Cyanex923 was utilized as a carrier in the system. Further, the presence of Cyanex923 in the ionic liquids also contributed to turbidity which further restricted the application of ionic liquid-Cyanex923 mixture as extraction/membrane solvents.

Based on the above results, ionic liquids were more suitable to be applied as pure diluents/solvents than carriers due to their reasonably high extraction efficiency and the absence of turbidity. Hence, further investigations concerning bulk ionic liquid membrane utilizing plain ionic liquid were conducted. The results are discussed in the following sections.

4.3 Selection of Ionic Liquids

Performance of ionic liquids [Bmim][PF_6], [Bmim][NTf_2] and [Bmim][FAP] as bulk ionic liquid membranes (BILM) was evaluated in terms of extraction efficiency, stripping efficiency, membrane stability and ionic liquid recovery.

4.3.1 Extraction Efficiency

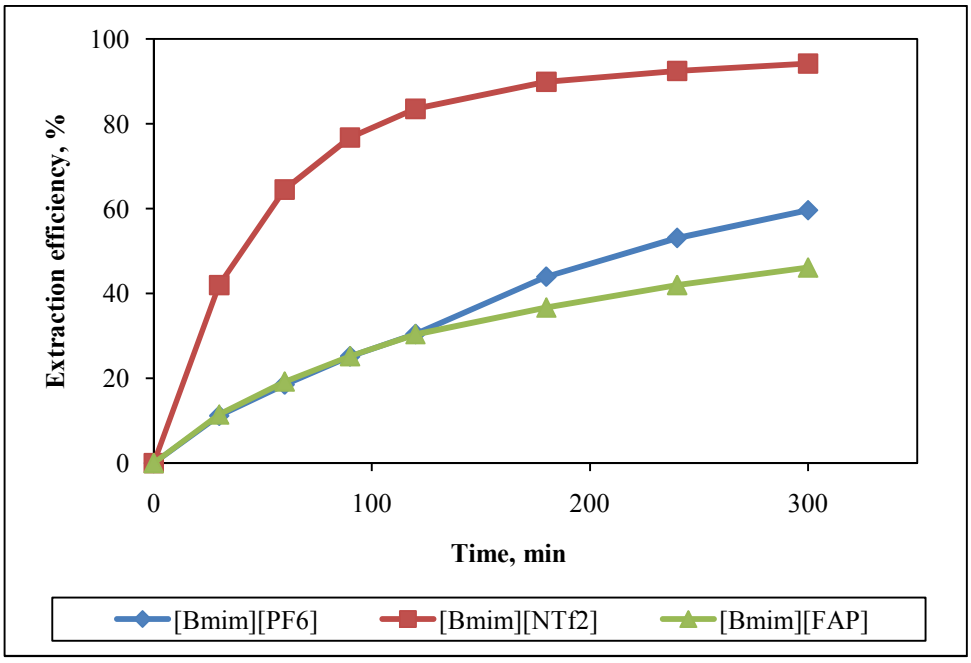


Figure 4.8: Extraction efficiency of phenol by BILM

Figure 4.8 shows that [Bmim][NTf_2] has the highest extraction rate and efficiency followed by [Bmim][PF_6] and [Bmim][FAP]. Even though the work of Fan *et al*. (2008) in liquid-liquid extraction claimed that the extraction efficiency increased with the increment of ionic liquids' hydrophobicity and hydrogen bond basicity strength, the present study showed that hydrophobicity of ionic liquids contributed by anions had little effect on dictating the extraction efficiency. The results do not follow the sequence of the hydrophobicity of the ionic liquids, which is [Bmim][PF_6] < [Bmim][NTf_2] < [Bmim][FAP]. On the other hand, it was found that the extraction efficiency was proportional to hydrogen bond basicity strength of the ionic liquid. The results are in

line with the order of ionic liquids' hydrogen bond basicity strength, whereby the sequence is [Bmim][FAP] < [Bmim][PF_6] < [Bmim][NTf_2] (Park and Kazlauskas, 2003; Habulin *et al.*, 2009; Zhao *et al.*, 2009; Poole and Poole, 2010). According to Fan *et al.* (2008), the extraction process of phenol by ionic liquid is dependent on the strength of hydrogen bonding between the anion of the ionic liquid with hydroxyl group of phenol. Hence, [Bmim][NTf_2] which has the highest hydrogen bond basicity strength among the three has the strongest bond between the anion and phenol and thus shows the highest phenol extraction efficiency.

4.3.2 Stripping Efficiency

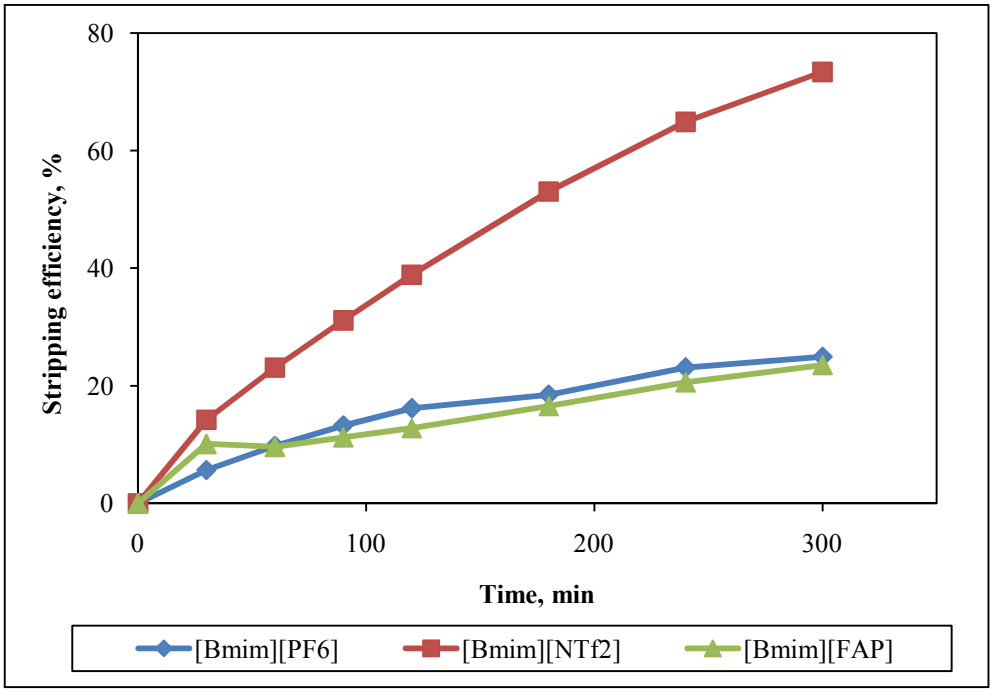


Figure 4.9: Stripping efficiency of phenol by BILM

Figure 4.9 shows that [Bmim][NTf_2] has higher stripping rate and efficiency than [Bmim][PF_6] which is similar to [Bmim][FAP]. This phenomenon was mainly contributed by the viscosity of the ionic liquids as it contributed significant mass transfer resistance in BILM. From Table 2.12, the viscosities of the ionic liquids studied are in the sequence of [Bmim][NTf_2] < [Bmim][FAP] < [Bmim][PF_6]. This was

well justified for [Bmim][NTf_2] which showed the highest stripping rate and efficiency as its viscosity is the lowest. Low viscosity membrane has lower mass transfer resistance and thus higher phenol transport rate from the membrane phase to the membrane/stripping interface can be obtained. However, this inference was not true for [Bmim][FAP] and [Bmim][PF_6] even though [Bmim][FAP] has much lower viscosity than [Bmim][PF_6]. Their stripping efficiencies were apparently close at 23.53% and 24.91%, respectively, as shown in Figure 4.9. This could possibly be caused by higher hydrophobic property of [Bmim][FAP] in comparison to [Bmim][PF_6]. [Bmim][FAP] formed higher boundary layer thickness between the membrane phase and the aqueous stripping phase when they were in contacted. Further, it created additional mass transfer resistance and thus reduced the stripping rate and efficiency even though its viscosity is lower.

4.3.3 Membrane Stability

Stability of ionic liquid membranes was evaluated based on two criteria, i.e. the reusability of the regenerated ionic liquid membrane and the transport of NaOH (water soluble compound) from the stripping compartment to the feed compartment through the ionic liquid membrane.

Ionic liquids [Bmim][PF_6], [Bmim][NTf_2] and [Bmim][FAP] were regenerated using the method that was stated in Section 3.5.5 and then were reused. The extraction and stripping efficiencies of phenol by fresh ionic liquids (Run number 1) and reused ionic liquids (Run number 2, 3, 4) after 300 min duration are as shown in Figures 4.10 and 4.11, respectively. From the figures, it is found that reused ionic liquids give equal performance which is within the range of experimental error. This indicates that the possible change in the structure of the reused ionic liquids has less effect on the

extraction and stripping efficiencies. Therefore, it can be concluded that the ionic liquid membrane is stable for repeated operations.

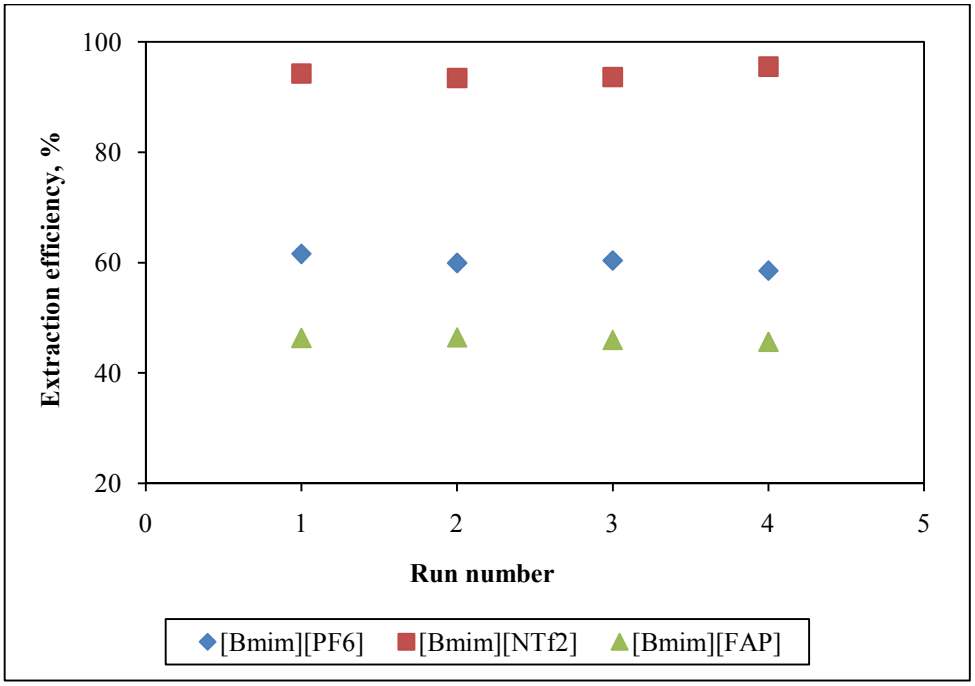


Figure 4.10: Extraction efficiency of phenol by BILM using reused ionic liquids

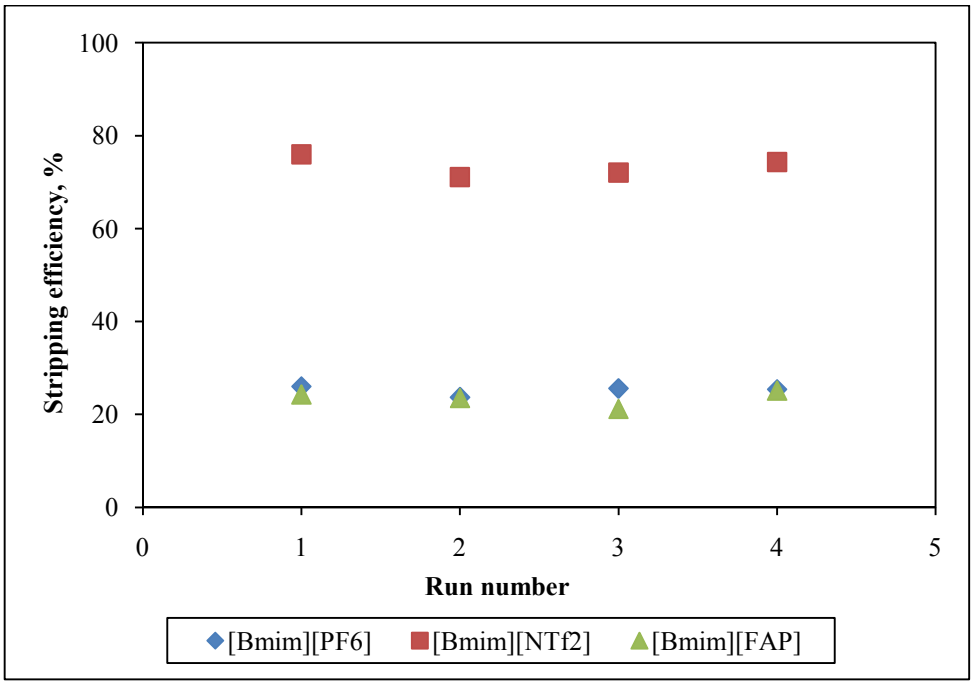


Figure 4.11: Stripping efficiency of phenol by BILM using reused ionic liquids

Besides that, the observed insignificant change of pH in the feed phase for all ionic liquid membranes indicated a stable transport process. Unlike the work of Fortunato *et al.* (2004; 2005a) and Matsumoto *et al.* (2007), the transport of water soluble compound (NaOH) to the feed phase through water microenvironment was not observed for all ionic liquid membranes tested. This may be attributed to the fast experimental duration and phenol transport rate whereby the water microenvironment path was not fully developed within the 300 min duration. In addition, utilization of membrane stirring process may be another factor that contributed to the stable transport process as water microenvironment path was normally disrupted by the turbulence in the membrane and this prevented the formation of effective microenvironment path in the membrane within the experimental duration.

4.3.4 Ionic Liquid Recovery

Ionic liquid membranes were recovered and reused. However, due to its high viscosity and its solubility in the aqueous phase, it was almost impossible to achieve a 100% recovery of the ionic liquids. The loss was mainly through pertraction of phenol, regeneration and transfer of ionic liquids between the glassware.

Table 4.3: Percentages of ionic liquids recoveries

Ionic liquid	**Solubility in water, g/g**	**Percentage of recovery, %**
[Bmim][PF_6]	0.020[c]	87.29%
[Bmim][NTf_2]	0.0072[c]	92.59%
[Bmim][FAP]	<0.0072[a,b]	95.26%

(Source: [a]Ignat'ev *et al.*, 2005; [b]Merck, 2009; [c]Poole and Poole, 2010)

Table 4.3 shows that the percentage of recovery for ionic liquid membranes are in the order of [Bmim][PF_6] < [Bmim][NTf_2] < [Bmim][FAP]. The recovery was strongly dependent on the hydrophobicity and solubility of the ionic liquids in water whereby the lower the solubility of ionic liquids in water, the higher the recovery.

Higher recovery could be achieved by utilizing ionic liquid with higher hydrophobicity. However, in such circumstance, an improved phenol transport performance could not not guaranteed.

4.3.5 Selection of Ionic Liquids

The study showed that [Bmim][NTf_2] was the best ionic liquid as it provided the highest phenol extraction and stripping efficiencies, and this can be attributed to its properties of high hydrogen bond basicity strength and low relative viscosity. Further, it behaved as a stable membrane phase for phenol transport and it possessed high ionic liquid recovery. Hence, [Bmim][NTf_2] is selected for the determination of the effect of different operating conditions such as feed phase pH, feed concentration, NaOH concentration and stirring speeds on the performance of BILM in terms of phenol extraction and stripping efficiencies.

4.4 Effect of Feed Phase pH on BILM Performance

Phenol is a weak acid which is partially soluble in water. It can exist in the aqueous phase either as neutral molecules or in ionic form, depending on the pH of the solution, as shown in Equations (4.1) and (4.2). The effect of the feed phase pH on the performance of BILM was evaluated from pH 1.13-11.19.

At pH < pK_a: $$C_6H_5OH \rightarrow C_6H_5OH \quad (4.1)$$

At pH > pK_a: $$C_6H_5OH \rightarrow C_6H_5O^- + H^+ \quad (4.2)$$

4.4.1 Efficiency Comparison

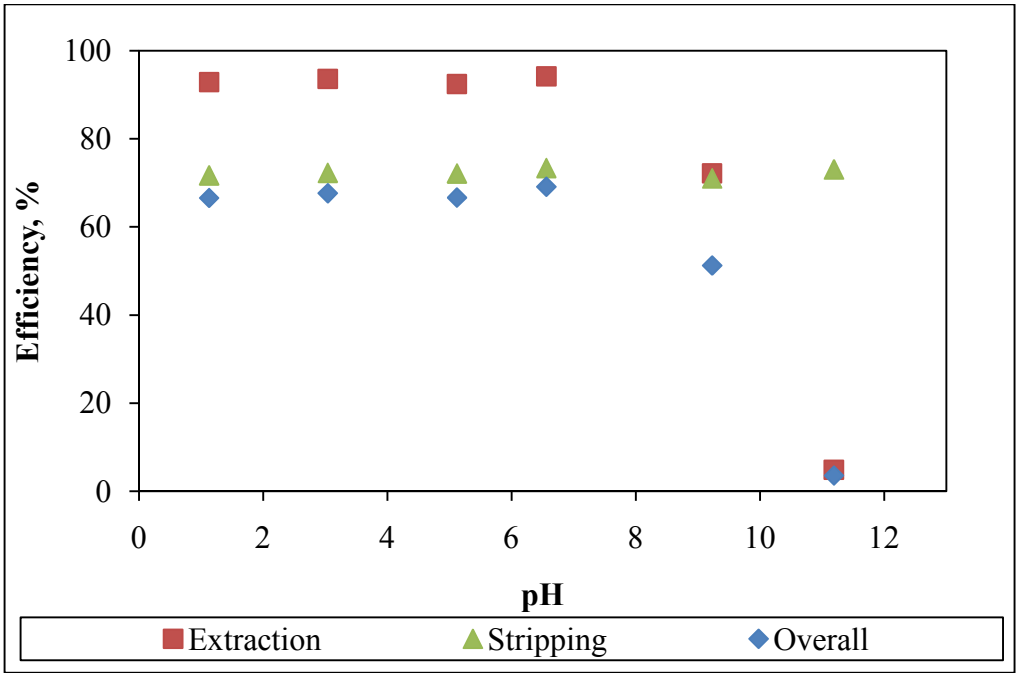


Figure 4.12: Efficiencies of BILM after 300 min experimentation under different pHs

The feed phase pH was adjusted using HCl or NaOH before the experiment. Figure 4.12 shows that the feed phase pH has higher impact on the extraction efficiency than stripping efficiency. As pH was maintained below 6.56, the extraction efficiency of BILM remained constant at 94%. It started to drop from 94.18% to 72.16% and 4.87%

as the pH was increased from 6.56 to 9.23 and 11.19, respectively. On the other hand, it was found that the stripping efficiency was less affected by this parameter, and an efficiency range of 71-73% was observed for pH range of 1.13-11.19.

4.4.2 Extraction and Stripping Rate

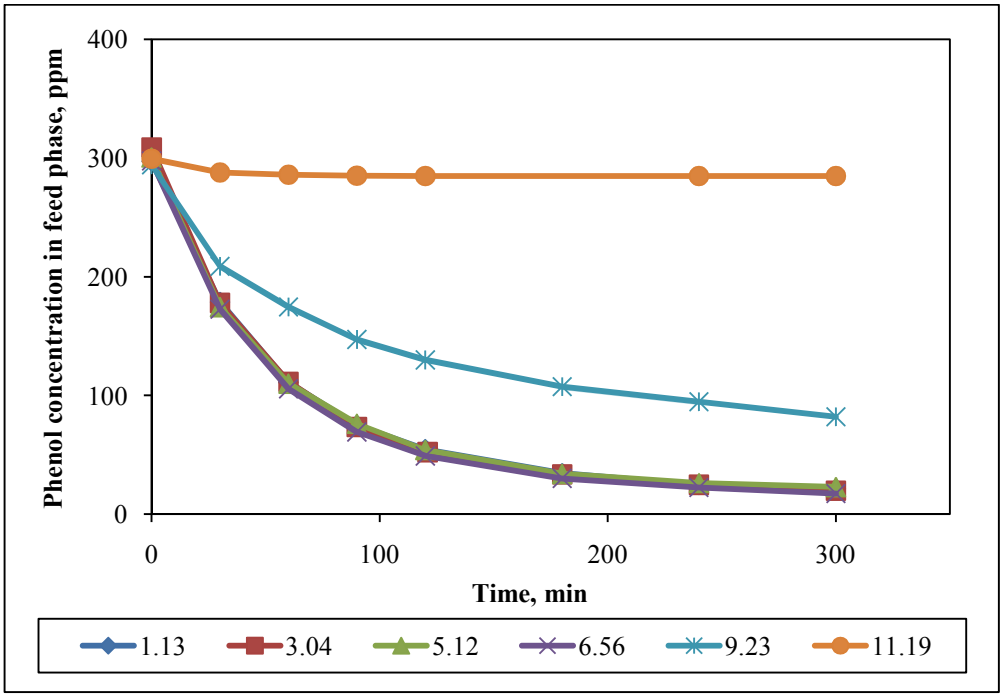


Figure 4.13: Phenol concentration in the feed phase versus time at different pHs

Figure 4.13 illustrates the time course of phenol concentration in the feed phase at different pH values. At feed phase pH of less than 6.56, extraction rate was similar. The extraction rate reduced as the pH was increased from 6.56 to 11.19. It was found that the final phenol concentration that remained in the feed phase at pH 9.23 and 11.19 were 81.93ppm and 284.80ppm, respectively, and these values were much higher than the experimental results of pH 1.13-6.56 (about 20ppm).

In comparison to organic solvents and liquid membranes (Le *et al.*, 2002; Cichy *et al.*, 2005; Park *et al.*, 2006; Shen *et al.*, 2006; Venkateswaran and Palanivelu, 2006; Reis *et al.*, 2007; Shen *et al.*, 2009; Zidi *et al.*, 2010), [Bmim][NTf_2] showed similar behavior in dissolving molecular phenol by formation of hydrogen bond instead of anion exchange mechanism. This was also observed in the works of Khachatryan *et al*. (2005), Vidal *et al*. (2005) and Fan *et al*. (2008), who utilized imidazolium-based ionic liquids with anions of [BF_4^-] and [PF_6^-]. Their works showed that phenol in molecular form (pH is lower than pK_a of 10) had higher distribution coefficient in ionic liquids in comparison to phenol in ionic form (pH is greater than pK_a). Fan *et al*. (2008) also reported that the hydrogen bonding between phenol and ionic liquid was reduced under high pH condition as a result of the ionization of molecular phenol into phenolate ion, as shown in Equation (4.2). The latter is neither soluble in [Bmim][NTf_2] nor extractable by [Bmim][NTf_2] via anion exchange mechanism and this reduced the extraction efficiency. Variation of solubility of phenol in ionic liquids at different pH had developed a stable extraction and stripping processes whereby phenol could be extracted into the ionic liquids at lower pH while stripped down by a high pH stripping agent.

On the other hand, the stripping process was less affected by the feed phase pH as similar stripping rate was observed for pH range of 1.13-6.56, as shown in Figure 4.14. However, experimental results for pH of 9.23 and 11.19 showed that stripping rate decreased and this could be due to low extraction rate whereby only a small amount of phenol was extracted into the membrane phase. Thus, the development of low concentration gradient between the membrane phase and the stripping phase resulted in a low stripping rate.

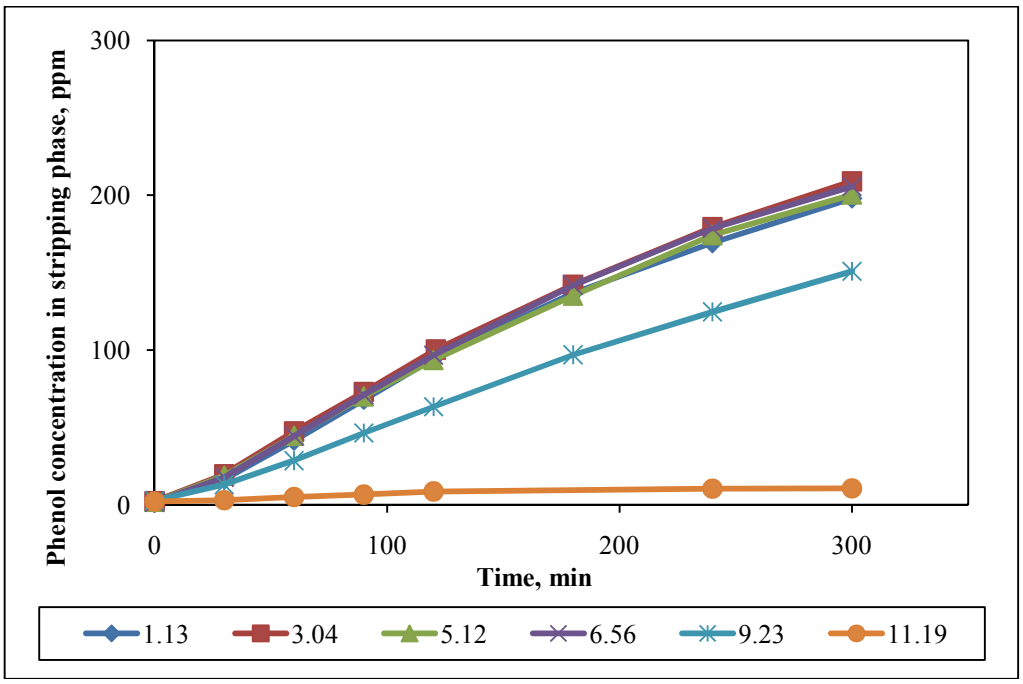


Figure 4.14: Phenol concentration in the stripping phase versus time at different pHs

4.4.3 Transport Kinetics

Transport kinetics for the extraction and stripping processes were determined by the model that was derived in Chapter 5. Figure 4.15 shows that the transport kinetics for extraction (K_1), back extraction (K_{-1}), stripping (K_2), and back stripping (K_{-2}) are less dependent on the feed phase pH as long as the pH is maintained below 6.56. However, when the feed phase pH was 9.23, K_1 decreased from 0.0182min^{-1} to 0.0124min^{-1} while K_{-1} increased from 0.0012min^{-1} to 0.0048min^{-1}, indicating a reduction in phenol extraction rate and an increment in phenolate diffusion rate into the feed aqueous phase under this condition. On the other hand, transport kinetics for both K_2 and K_{-2} remained constant. This further justified that decrement in the stripping rate at high pH was mainly caused by low phenol concentration gradient between the membrane phase and the stripping phase.

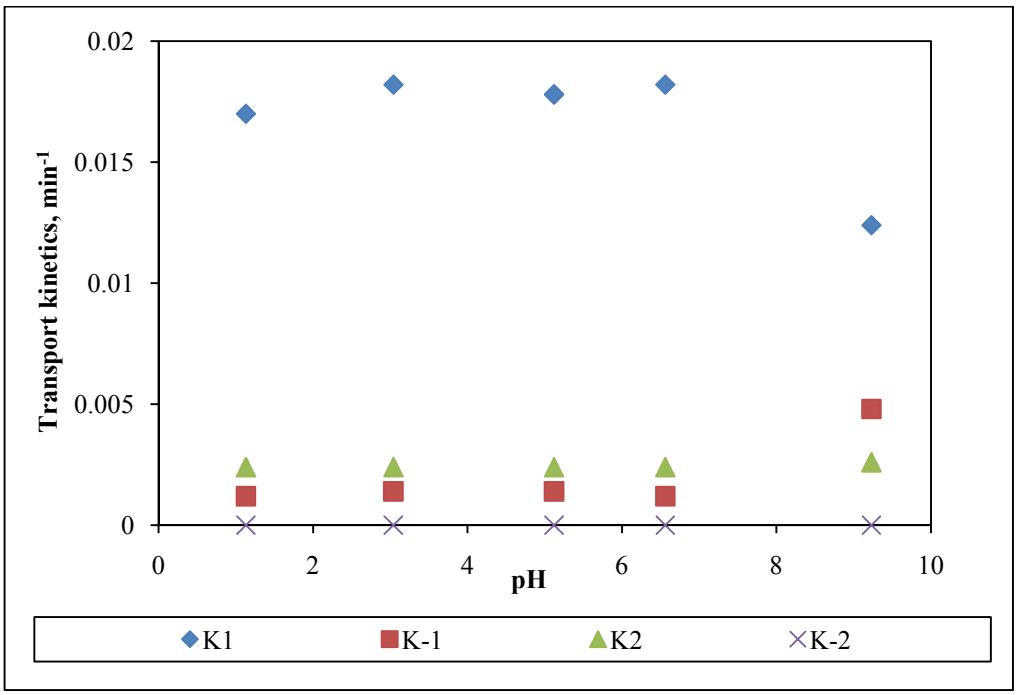


Figure 4.15: Transport kinetics of phenol in BILM under different pHs

4.5 Effect of Feed Concentration on BILM Performance

[Bmim][NTf_2] based BILM was tested with different feed concentrations ranging from 150-6000ppm. This is the typical phenol concentration range in industrial effluents, as discussed in Section 2.1.4.

4.5.1 Efficiency Comparison

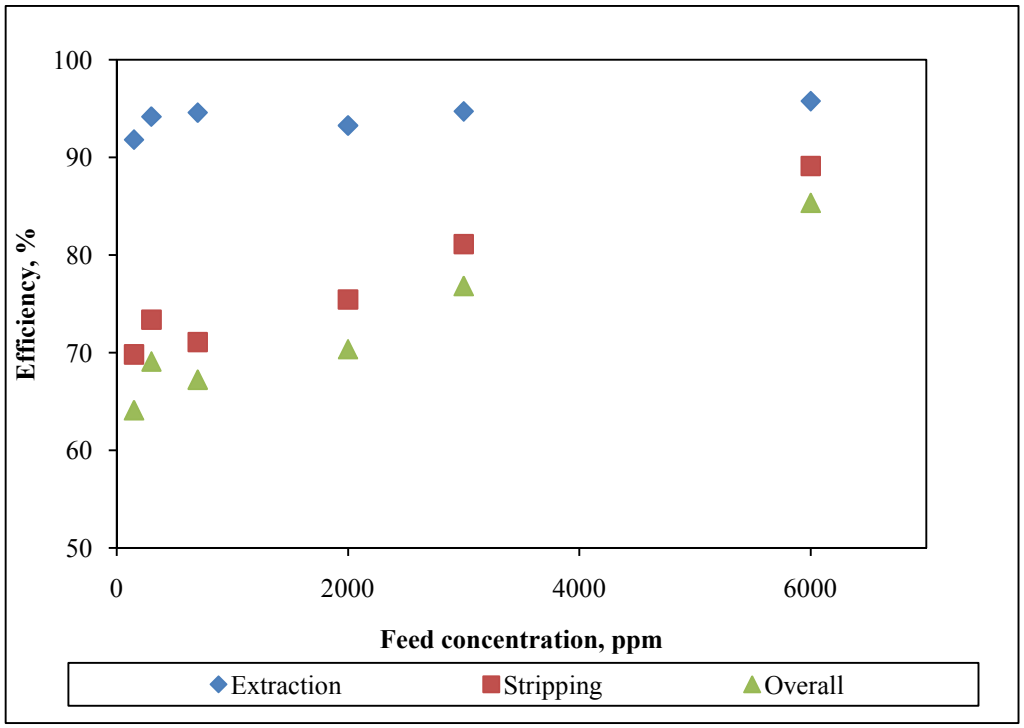


Figure 4.16: Efficiency of BILM after 300 min experimentation under different feed concentrations

Figure 4.16 shows that the extraction efficiency is less affected by the initial feed concentration whereby extraction efficiency in the range of 91-96% was obtained for every feed concentration tested. The upper limit/membrane saturation for the extraction process was not observed. This could be due to the usage of a large amount of ionic liquid as liquid membrane which provided large dissolving capacity for phenol. Furthermore, simultaneous stripping process also prevented membrane saturation. Therefore, the extraction efficiency was not disturbed.

In addition, it was found that the stripping efficiency for 150-700ppm had less variation, i.e. in the range of 69-73% after 300 min experiment. However, as the feed concentration was increased from 2000-6000ppm, the stripping efficiency increased from 75.45% to 89.13%, as shown in Figure 4.16.

4.5.2 Extraction and Stripping Rate

Figures 4.17 and 4.18 illustrate the change of phenol concentration in the feed phase and the stripping phase with time at different feed concentrations. From Figure 4.17, initial extraction rate is found to increase as the feed concentration is increased. This was mainly caused by the increase in the concentration gradient between the feed phase and the membrane phase and this can be explained by Equation (4.3):

$$J = kA\left(C_1 - C_1'\right) \tag{4.3}$$

Where:

J = mass transfer rate (mg/min)

k = mass transfer coefficient (m/min)

A = mass transfer interfacial area (m^2)

C_1 and C_1' = solute concentration in the donor phase and solute concentration in the donor phase in equilibrium with the acceptor phase, respectively (mg/L)

As the feed concentration was increased, C_1 increased and hence the extraction rate increased. It was also noted that the final concentration of phenol in the feed phase after 300 min experimentation was higher when higher feed concentration was tested. This further justified that the extraction of phenol by [Bmim][NTf_2] is dependent on the extraction equilibrium of phenol between the phases.

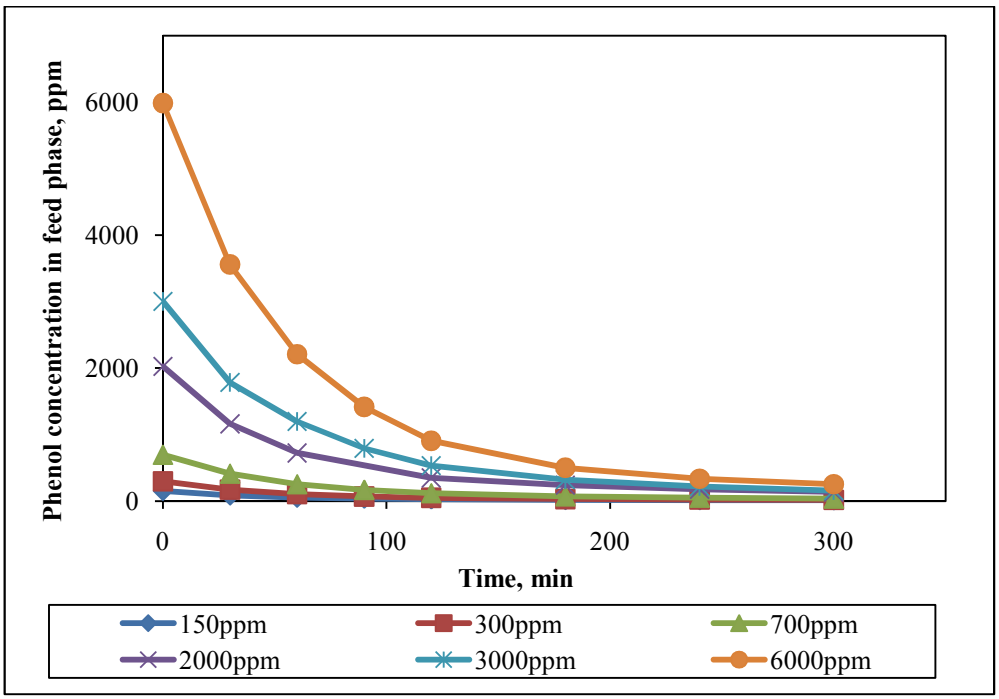


Figure 4.17: Phenol concentration in the feed phase versus time at different feed concentrations

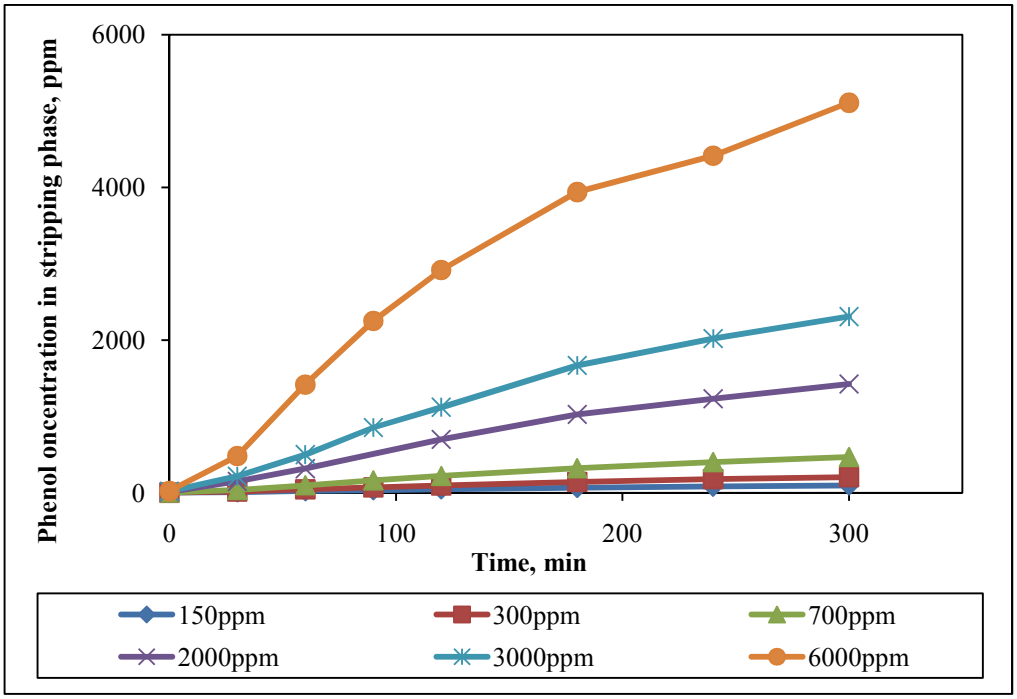


Figure 4.18: Phenol concentration in the stripping phase versus time at different feed concentrations

Figure 4.18 shows that the stripping rate of phenol increases as the feed concentration is increased. Again, this can be explained by Equation (4.3) as high phenol extraction rate from the feed phase to the membrane phase increased the concentration gradient between the membrane phase and the stripping phase. However, it was found that stripping efficiency also increased as the feed concentration was increased, as shown in Figure 4.19. For 150-700ppm of feed concentrations, the rate of stripping efficiency was in the experimental error range, but it increased as the feed concentration was increased from 2000-6000ppm. This trend was also observed in the work of Nabieyan *et al*. (2007) for passive transport of iodine in bench-scale bulk liquid membrane.

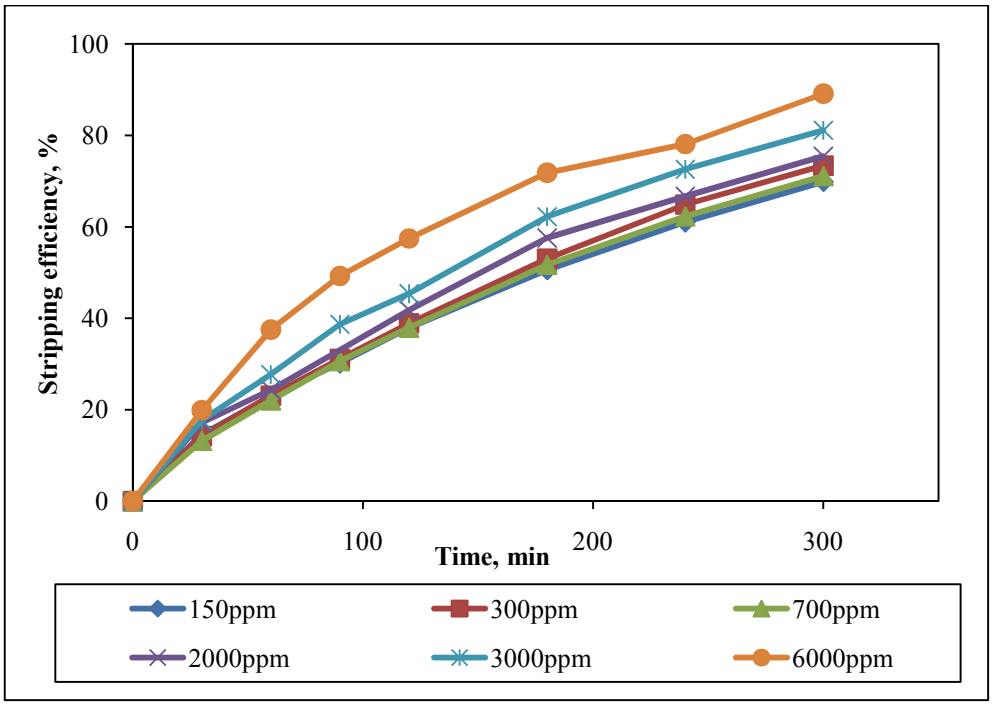


Figure 4.19: Stripping efficiency of phenol versus time at different feed concentrations

This unusual phenomenon can be explained through physical observation during the experiment whereby phenol diffusion can be observed physically through the change of turbidity of [Bmim][NTf_2]. A "smoke like" tone was observed in the membrane phase as phenol diffused into it. Thus, a transport mechanism of phenol in

BILM at different feed concentrations can be proposed based on the physical observation.

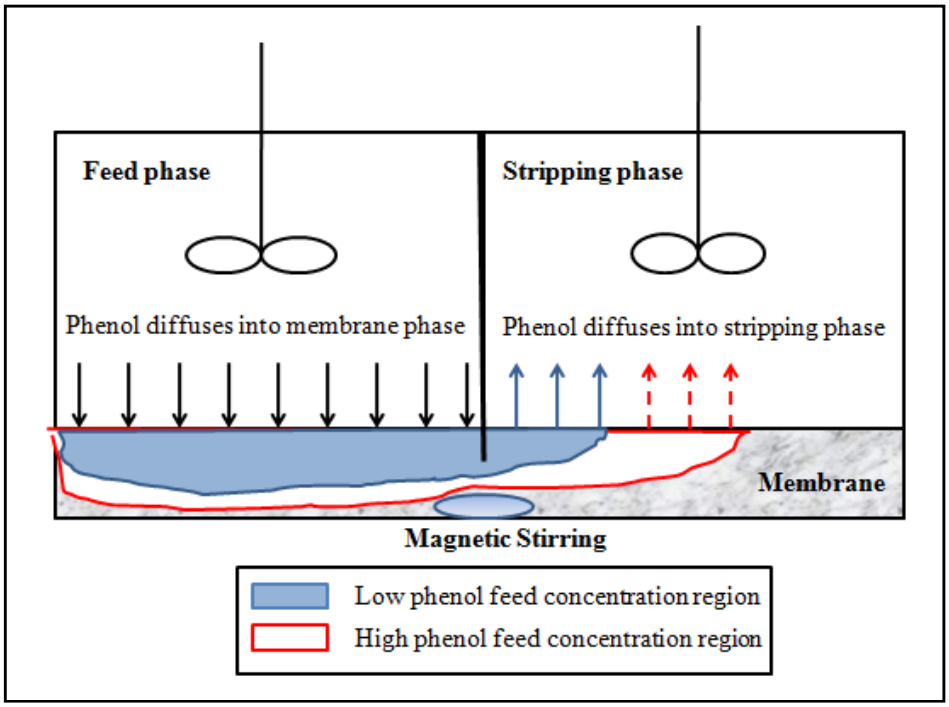


Figure 4.20: Schematic diagram for the diffusion of phenol in BILM at different feed concentrations

The design of the BILM reactor and the behavior of [Bmim][NTf_2] were the major factors that caused this unusual stripping trend. Figure 4.20 illustrates different behaviors of liquid membrane system at different feed concentration levels. At low feed concentration (150-700ppm), only a little amount of phenol diffused into the membrane phase and was transported to the stripping compartment. In this case, the stripping rate was fast enough to prevent the build-up of phenol concentration on the membrane/stripping interface and hence the stripping process utilized only a small contact area. On the other hand, higher feed concentration resulted in higher amount of phenol diffused into the membrane phase and this uneven high extraction and low stripping rates caused the build-up of phenol concentration in the membrane phase. With the aid of magnetic stirring, a significant amount of phenol was further distributed in the stripping compartment, as shown in Figure 4.20. This process eventually

increased the effective contact area between phenol and the membrane/stripping interface. Thus, the stripping rate was increased in a higher magnitude and this further increased the stripping efficiency.

From the above observation, it can be concluded that lower rate of stripping efficiency at low feed concentration is caused by ineffective utilization of contact area between the membrane phase and the stripping phase in BILM. This was mainly attributed to ineffective membrane stirring condition which failed to transport phenol to further distance in the stripping compartment. Thus, the stripping efficiency was lower in comparison to high feed concentration.

4.5.3 Transport Kinetics

The kinetics model derived is based on Fick's Law of diffusion with a general form as shown in Equation (4.4):

$$\frac{dC_1}{dt} = K\left(C_1 - C_1'\right) \tag{4.4}$$

Where:

$\frac{dC_1}{dt}$ = rate of change in concentration (mg/L.min)

K = transport kinetics (min^{-1})

C_1 and C_1' = solute concentration in the donor phase and solute concentration in the donor phase in equilibrium with the acceptor phase, respectively (mg/L)

From Equations (4.3) and (4.4), a relationship between transport kinetics, K and mass transfer coefficient, k can be expressed as Equation (4.5):

$$K = \frac{kA}{V} \tag{4.5}$$

According to Stoke-Einstein Equation and Sherwood number, mass transfer coefficient, k in the liquid phase is strongly dependent on the temperature of the system and the viscosity of the transport path (membrane phase). In this study, the same type of ionic liquid membrane was used at a constant temperature of 298K. Thus, the mass transfer coefficient, k can be considered as a constant throughout the experiment. Therefore, it can be concluded that the transport kinetics, K is proportional to the effective contact area, A while the volume of the phase, V is regarded as a constant.

Figure 4.21 shows that increment of feed concentration does not affect the extraction kinetics, K_1 and back extraction kinetics, K_{-1}. However, stripping kinetics, K_2 increased as the feed concentration was increased from 2000-6000ppm. By referring to Equation (4.5), it can be suggested that this trend is caused by the increment of effective contact area between phenol and the membrane/stripping interface under high feed concentration and this is in line with the physical observation discussed in Section 4.5.2.

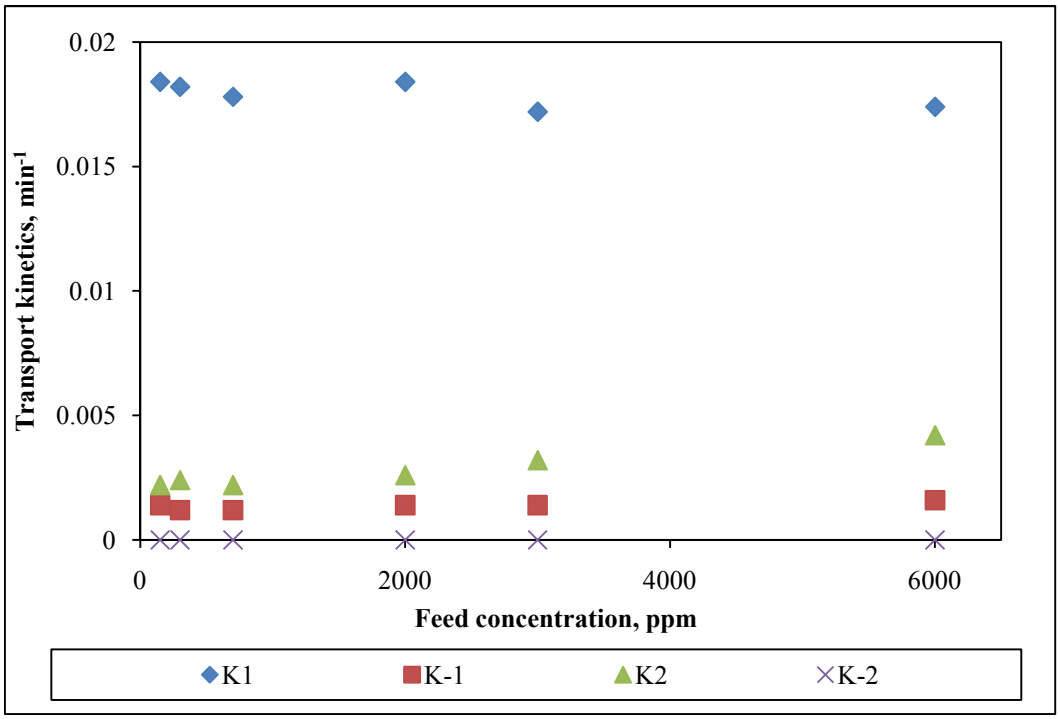


Figure 4.21: Transport kinetics of phenol in BILM under different feed concentrations

4.6 Effect of NaOH Concentration on BILM Performance

NaOH was used as a stripping agent for phenol extraction from ionic liquid membrane. NaOH concentration in the range of 0-0.5M was applied to determine the effect of NaOH concentration on the performance of BILM.

4.6.1 Efficiency Comparison

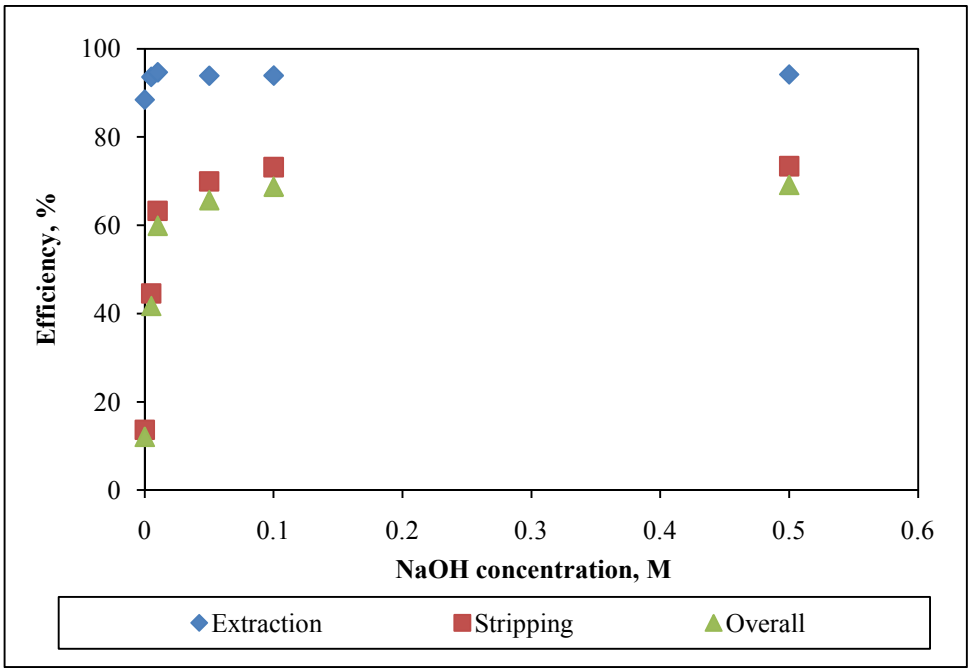


Figure 4.22: Efficiency of BILM after 300 min experimentation under different NaOH concentrations

Figure 4.22 shows that the extraction efficiency is less affected by NaOH concentration as long as NaOH is present. In terms of stripping efficiency, Figure 4.22 shows that optimum stripping efficiency in the range of 69-73% is achieved for NaOH concentration of 0.05-0.5M. However, at lower NaOH concentration of 0M, 0.005M and 0.01M, it was found that the stripping efficiencies were lower as 13.65%, 44.54% and 63.26%, respectively in comparison to higher NaOH concentration.

4.6.2 Extraction and Stripping Rate

Figure 4.23 shows that phenol concentration in the feed phase reduces at the same rate, independent from NaOH concentration. However, when distilled water was utilized as stripping agent (0M NaOH), the extraction equilibrium was achieved earlier with a higher final phenol concentration of 33.78ppm in comparison to other experiments at about 20ppm.

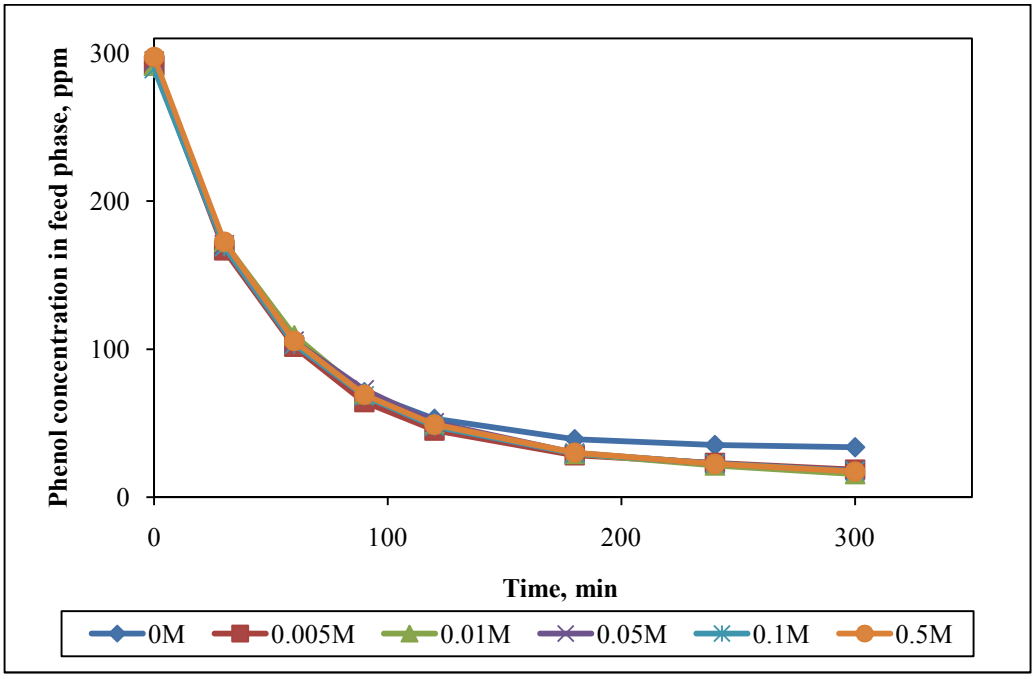


Figure 4.23: Phenol concentration in the feed phase versus time at different NaOH concentrations

On the other hand, phenol stripping rate by BILM was similar for the experiments involving 0.05M, 0.1M and 0.5M NaOH concentrations with the final phenol concentration ranging between 193-205ppm, as illustrated in Figure 4.24. The effect of NaOH became less significant as the NaOH concentration was increased beyond 0.05M. However, different stripping trends were observed for experiments involving 0.005M and 0.01M NaOH concentrations whereby, as time progressed, reductions of the stripping rate were observed for both experiments. Final phenol concentrations of 121.65ppm and 174.67ppm were achieved in the stripping phase for

0.005M and 0.01M NaOH concentrations, respectively and these were much lower than that for the experiments involving 0.05M, 0.1M and 0.5M NaOH concentrations.

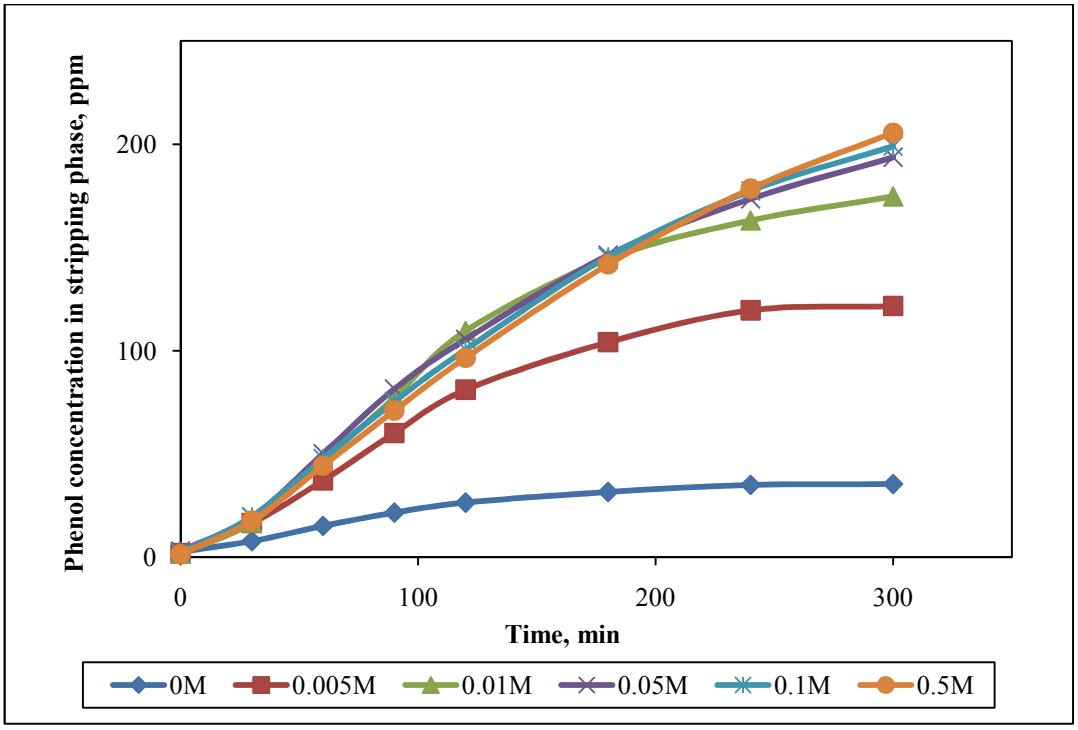


Figure 4.24: Phenol concentration in the stripping phase versus time at different NaOH concentrations

It was worth noting that for 0M NaOH concentration, the stripping rate remained significant as final phenol concentration of 35.43ppm was obtained in the stripping phase even in the absence of NaOH. Detailed explanation on the stripping processes for 0M, 0.005M, and 0.01M NaOH concentration are discussed in Sections 4.6.3 and 4.6.4.

4.6.3 NaOH Concentration at 0M

In this experiment, there was no chemical reaction in the stripping process as NaOH was not present. The stripping process was likely to be governed by the distribution coefficient of phenol between [Bmim][NTf_2] and water. Figure 4.25 illustrates the amount of phenol in all the three phases, and it is found that the amount of

phenol in the feed phase and stripping phase eventually reached the same value after 300 min.

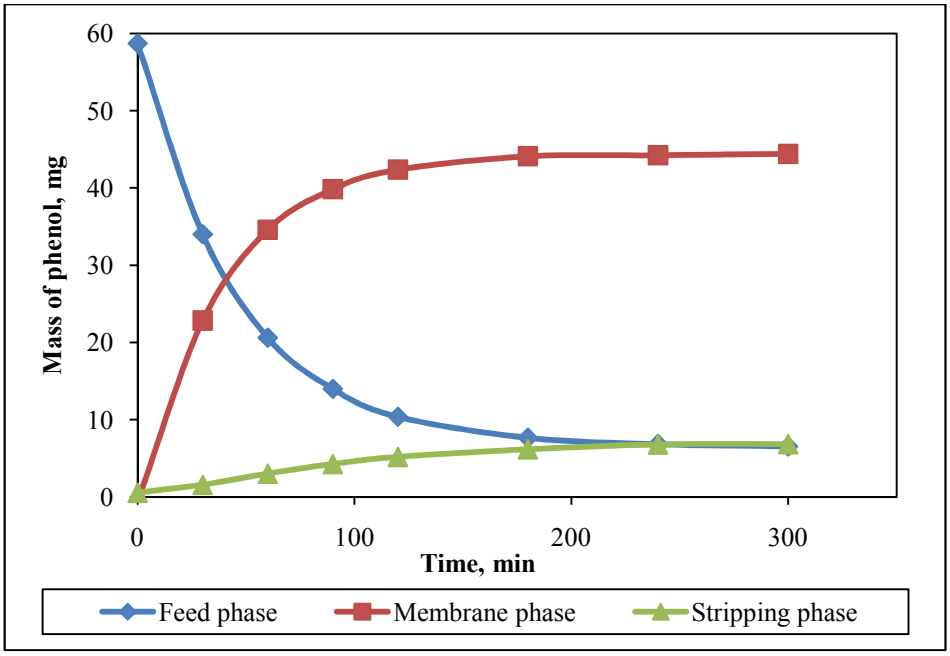


Figure 4.25: Mass of phenol in each phase versus time for 0M NaOH concentration

Table 4.4: Percentages of phenol in different phases after 300 min experiment at 0M NaOH concentration

Phase	Mass of phenol, mg	Volume of phases, L	Phenol concentration, ppm	Percentage of phenol in phases, %
Feed	6.52	0.193	33.78	11.28
Membrane	44.42	0.080	555.25	76.88
Stripping	6.84	0.193	35.43	11.84

Table 4.4 shows that 76.88% of phenol is present in the membrane phase and this is in line with the results obtained from the liquid-liquid extraction experiments (Figure 4.3). It is suggested that the stripping process is totally dependent on the distribution coefficient of phenol between [Bmim][NTf_2] and water, similar to the liquid-liquid extraction process. As phenol reached the membrane/stripping interface, it diffused into the stripping phase (distilled water) according to the distribution coefficient. The diffusion process continued until phenol in the stripping phase reached equilibrium with the membrane phase, as shown in Figure 4.25. This test also justified

that phenol pertraction process in BILM is not based on chemical reaction between [Bmim][NTf_2] and phenol.

4.6.4 NaOH Concentration at 0.005M and 0.01M

NaOH functioned as a stripping agent which reacted with molecular phenol that diffused into the stripping phase to form sodium phenolate. This reaction tends to suppress the activity of phenol in the stripping phase (Park *et al.*, 2006; Busca *et al.*, 2008) and assists phenol diffusion process from the membrane phase to the stripping phase. In other words, insufficiency of NaOH to act as reactant and to maintain high pH in the stripping phase causes a reduction in the stripping rate due to some unreacted molecular phenol in the stripping phase. This unreacted molecular phenol serves as a resistance which reduces concentration gradient between the membrane phase and the stripping phase.

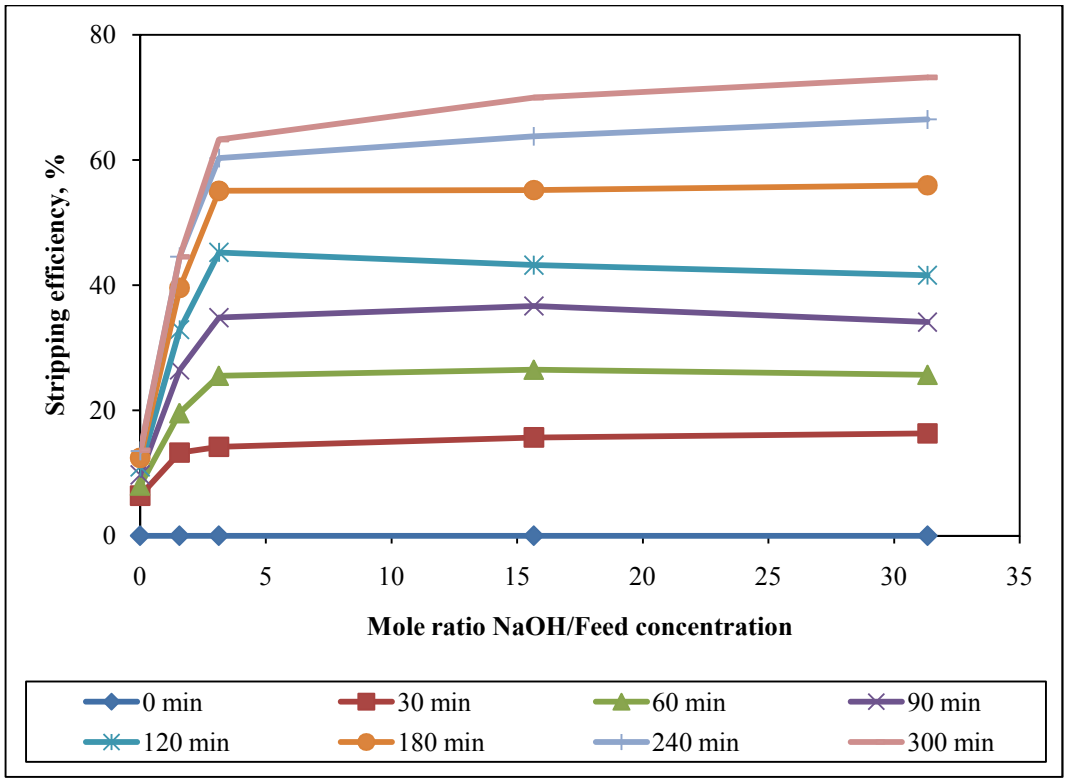


Figure 4.26: Stripping efficiency versus mole ratio of NaOH/Feed concentration at different times

Figure 4.26 shows that at mole ratio between NaOH and feed concentration less than 3, a decrease in the rate of stripping efficiency is observed at the time interval of 240-300 min. The figure also suggests that a mole ratio of at least 3 should be applied in this system in order to reduce the drop in rate of stripping efficiency. Optimum rate of stripping efficiency can only be achieved at mole ratio of more than 15. This is in agreement with the works of González-Muñoz *et al*. (2003) and Reis *et al*. (2007) who claimed that a mole ratio of 4 and 10-20, respectively were adequate to optimize the stripping efficiency. The difference in optimum mole ratio could probably be due to the use of different treatment systems, whereby BILM was utilized in the present study while hollow fiber contactor was used by González-Muñoz *et al*. (2003) and Reis *et al*. (2007).

The difficulty in providing high pH in the stripping phase reduced the stripping efficiency. The stripping phase pH of less than 12.2 was observed in the experiments for 0.005M and 0.01M NaOH concentration and lower stripping rates and efficiencies were obtained, as illustrated in Figure 4.24. These results suggested the possibility of incomplete phenol stripping process by NaOH and this was supported by Le *et al*. (2002) and Xiao *et al*. (2006), who claimed that incomplete ionization of phenol can only be prevented by maintaining the pH of the stripping phase in at least 2 units greater than its pK_a value of 10. Incomplete ionization suppressed phenol transport process by creating a lower concentration gradient between the membrane phase and the stripping phase and thus reducing the stripping rate. NaOH concentration of 0.05M was found to be optimum for treating 300ppm of phenol solution. However, 0.1-0.5M was preferable as it provided abundant NaOH as reactant while maintaining high pH in the stripping phase.

4.6.5 Transport Kinetics

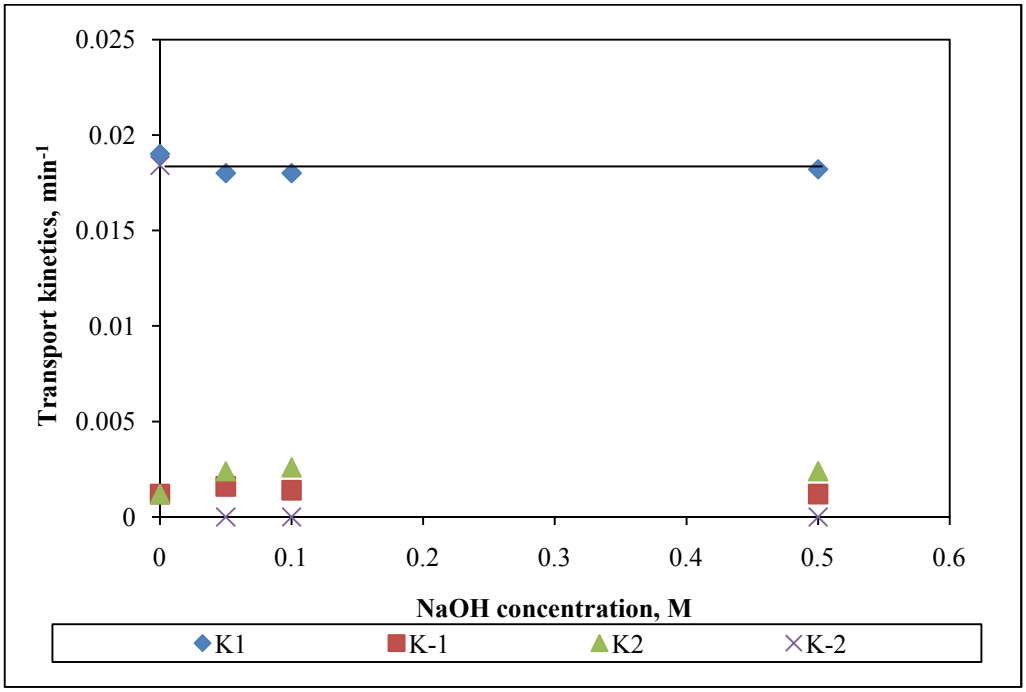


Figure 4.27: Transport kinetics of phenol in BILM under different NaOH concentrations

The transport kinetics of phenol in BILM system at different NaOH concentrations are as shown in Figure 4.27. Transport kinetics K_1, K_{-1}, K_2, and K_{-2} for 0.05M, 0.1M, 0.5M experiments were the same, indicating that the extraction and stripping processes were optimum at NaOH concentration beyond 0.05M. For stripping process, it was found that the stripping kinetics, K_2 was increased by 100% as the NaOH concentration was maintained beyond 0.05M NaOH in comparison to 0M NaOH ($0.0024min^{-1}$ versus $0.0012min^{-1}$). This indicated that the presence of NaOH in the stripping phase not only increased the concentration gradient but also increased the stripping kinetics. On the other hand, back stripping kinetics, K_{-2} for 0M NaOH test was found to be 15 times higher than its stripping kinetics, K_2 ($0.0184min^{-1}$ versus $0.0012min^{-1}$). Molecular phenol tends to dissolve easily in ionic liquid membrane than in the distilled water (stripping phase) and thus resulted in a low stripping efficiency.

It is worth noting that the transport kinetics for 0.005M and 0.01M NaOH concentration are not discussed in this section. Kinetics values that were predicted by the model showed poor R^2 values which suggested that the stripping mechanism for 0.005M and 0.01M NaOH concentrations did not match with the mechanism proposed for the model. It is believed that the stripping process is more complicated for these cases and is further discussed in Chapter 5.

4.7 Effect of Stirring on BILM Performance

Hydrodynamic condition of BILM was evaluated by applying different aqueous stirring speed in the feed and stripping phases. A set of experiments were conducted to investigate the influence of aqueous stirring speed and membrane stirring on the extraction and stripping efficiencies for BILM.

4.7.1 Efficiency Comparison

Figure 4.28 shows the extraction and stripping efficiencies of phenol by BILM after 300 min experimentation at different stirring conditions. For extraction process, the extraction efficiency was found to increase as the aqueous stirring speed was increased from 0-100rpm, regardless of the presence of membrane stirring. However, it was also found that there was no obvious increment of the final extraction efficiency beyond 150rpm, as shown in Figure 4.28. Table 4.5 shows that the presence of membrane stirring in the system also enhances the extraction efficiency. However, there was a reduction in the enhancement as the aqueous stirring speed was increased.

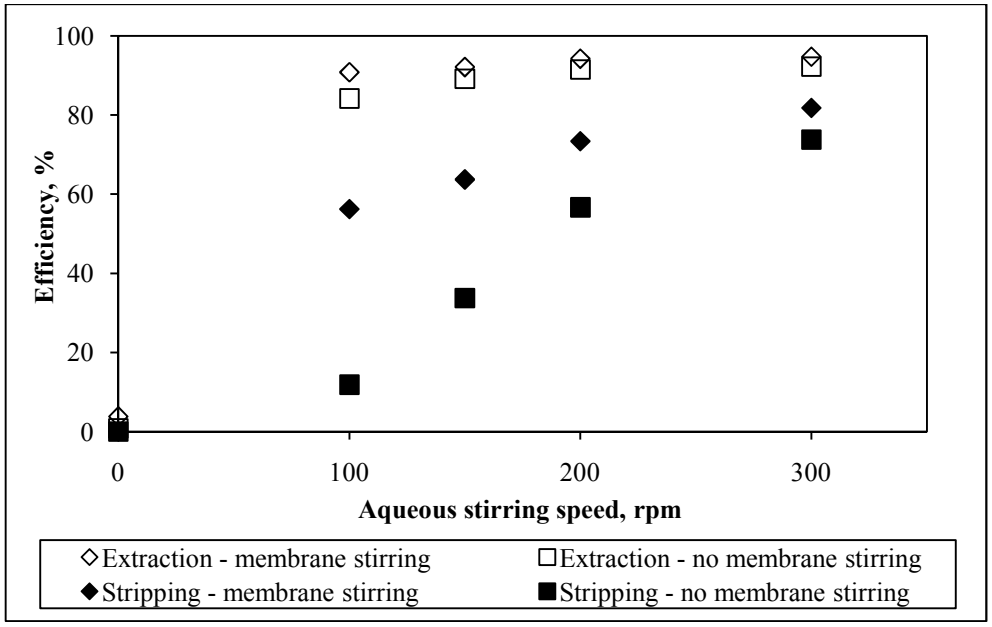


Figure 4.28: Efficiency of BILM after 300 min experimentation under different aqueous stirring speeds

Table 4.5: Extraction efficiency at different stirring conditions after 300 min experimentation

Aqueous stirring speed, rpm	**Extraction efficiency (Without membrane stirring), %**	**Extraction efficiency (With membrane stirring), %**	**Efficiency enhancement by membrane stirring, %**
100	84.19	90.77	6.58
150	89.17	92.08	2.91
200	91.51	94.18	2.67
300	92.21	94.68	2.47

Figure 4.28 also shows that the stripping efficiency increases at a high magnitude when the aqueous stirring speed is increased from 100-300rpm in both conditions, with membrane stirring and without membrane stirring. In comparison to extraction efficiency, the presence of membrane stirring boosted the stripping efficiency by a higher degree, as shown in Table 4.6. However, it was again noted that the enhancement of stripping efficiency by membrane stirring dropped as the aqueous stirring speed was increased.

Table 4.6: Stripping efficiency at different stirring conditions after 300 min experimentation

Aqueous stirring speed, rpm	**Stripping efficiency (Without membrane stirring), %**	**Stripping efficiency (With membrane stirring), %**	**Efficiency enhancement by membrane stirring, %**
100	11.86	56.21	44.35
150	33.75	63.71	29.96
200	56.66	73.39	16.73
300	73.80	81.77	7.97

4.7.2 Extraction and Stripping Rate

Figure 4.29 shows that the presence of aqueous stirring increases the extraction rate as the reduction of phenol concentration in the feed phase is faster in comparison to without aqueous stirring. As the stirring speed was increased from 100-300rpm, phenol concentration in the feed phase was reduced at a higher rate. The presence of aqueous stirring decreased the boundary layer thickness between the membrane/aqueous interface (Venkateswaran and Palanivelu, 2005; Muthuraman *et al.*, 2009; Vladimir, 2010) and also reduced the concentration polarization of phenol in the feed phase. This minimized the reduction of concentration gradient between the phases and increased the extraction rate. However, final phenol concentration was found to be less affected by the increment of aqueous stirring speed beyond 150rpm. This may be due to the equilibrium extraction between the feed phase and the membrane phase which was achieved at 300 min for these cases. Further increment on the aqueous stirring speed only increased the extraction rate and equilibrium extraction was achieved in a shorter time, but the final extraction efficiency and phenol concentration were not much affected, as can be observed in Figures 4.28 and 4.29.

In addition, Figure 4.29 shows that the presence of membrane stirring elevates the extraction rate under similar aqueous stirring speed. Membrane stirring brought the same effect in reducing the concentration polarization of phenol at membrane/aqueous interface. However, this effect diminished under high aqueous stirring speed for the extraction process. The degree of enhancement was lowered as the aqueous stirring speed was increased beyond 100rpm.

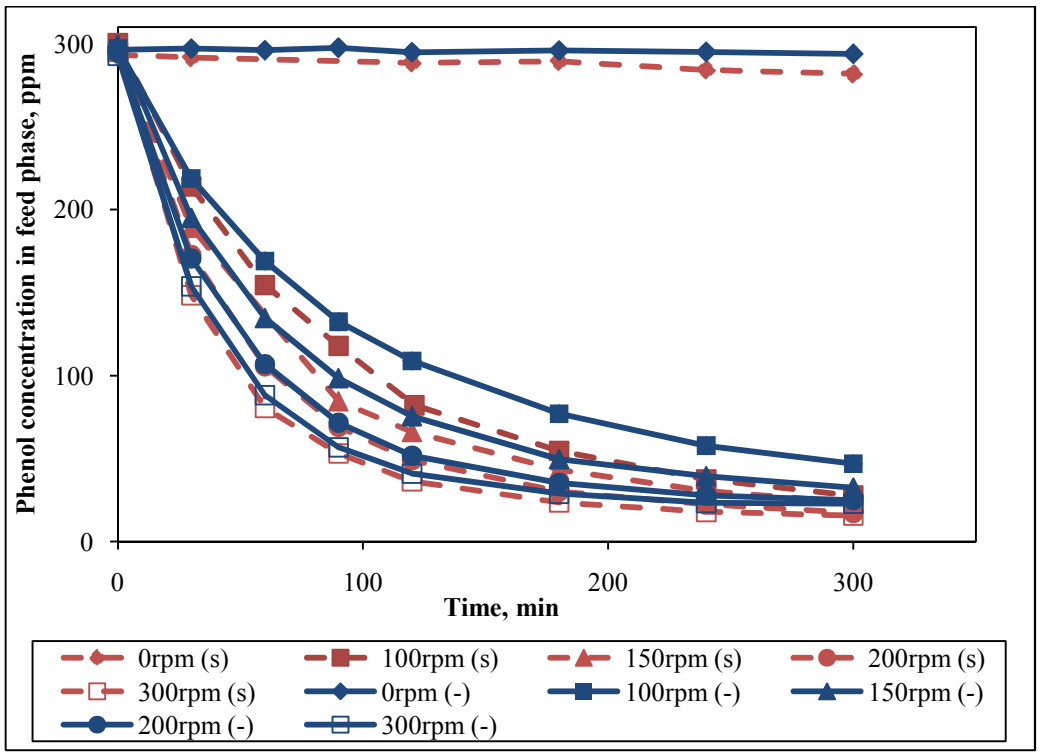


Figure 4.29: Phenol concentration in the feed phase versus time under different aqueous stirring speeds (s): membrane stirring, (-): without membrane stirring

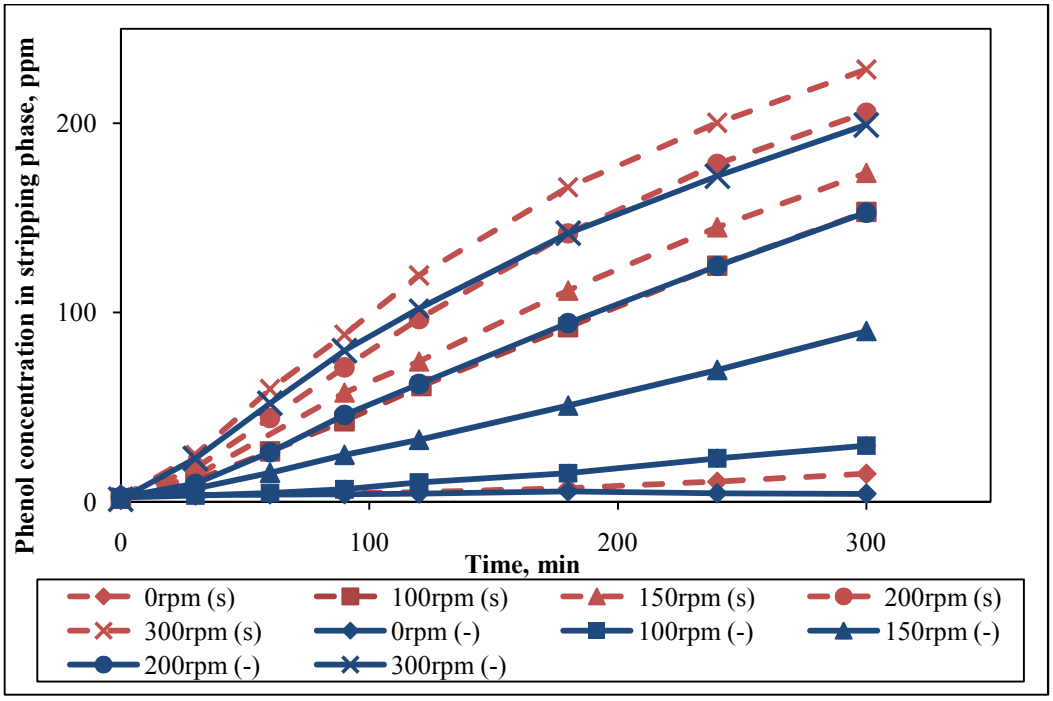


Figure 4.30: Phenol concentration in the stripping phase versus time under different aqueous stirring speeds (s): membrane stirring, (-): without membrane stirring

Figure 4.30 shows that the concentration of phenol in the stripping phase increases at a higher rate as the aqueous stirring speed is increased from 0-300rpm in both conditions, with membrane stirring and without membrane stirring. The increment of aqueous stirring speed in the stripping phase provided better mixing and reduced the boundary layer thickness between the membrane/aqueous interface, as mentioned above. This further increased phenol diffusion rate and also the reaction rate between phenol and NaOH in the stripping phase.

In addition, Figure 4.30 also shows that at the same aqueous stirring speed, the presence of membrane stirring increases the stripping rate. This could possibly be due to membrane stirring serving as an additional driving force that transported phenol through the membrane phase. However, it was worth noting that as the aqueous stirring speed increased, the enhancement by membrane stirring was reduced.

4.7.3 Transport Kinetics

Figure 4.31 shows that transport kinetics K_1, K_{-1}, K_2 increase as the aqueous stirring speed is increased from 0-300rpm. In terms of magnitude, aqueous stirring speed had the most significant effect on the extraction kinetic, K_1 in comparison to the other transport kinetics whereby the increment of aqueous stirring speed from 100-300rpm increased K_1 by 106% from 0.0106min^{-1} to 0.0218min^{-1} in the absence of membrane stirring. In addition, the stripping kinetic, K_2 also increased by 900% from 0.00024min^{-1} to 0.0024min^{-1} when the aqueous stirring speed was increased from 100-300rpm. This trend indicated that higher aqueous stirring speed reduced boundary layer thickness between aqueous and membrane phases and this increased the extraction and stripping kinetics, K_1 and K_2, according to Equation (2.2).

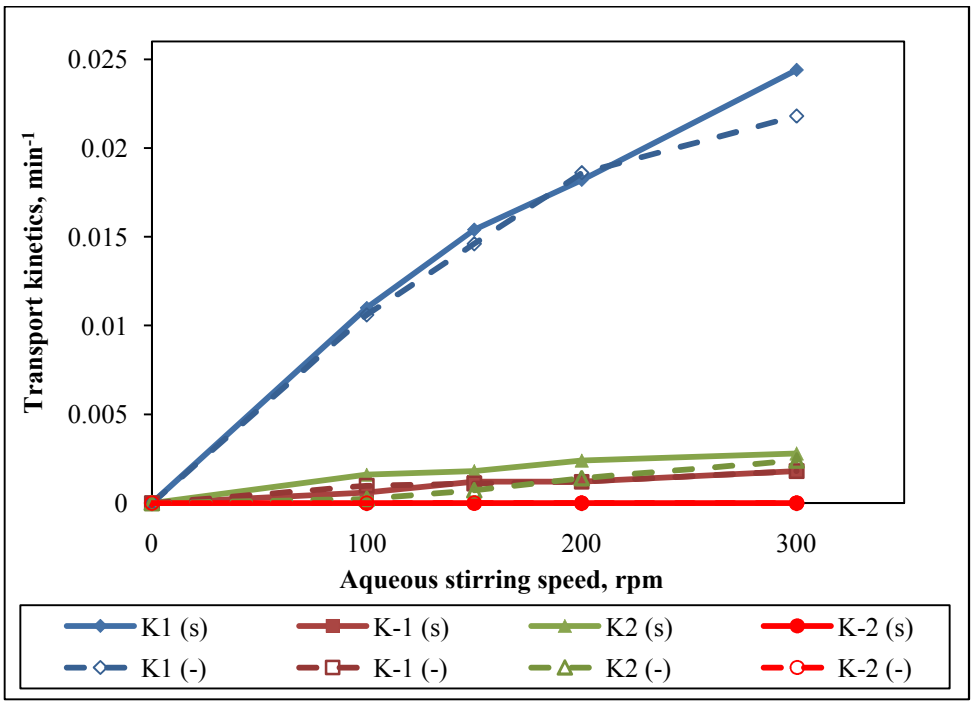


Figure 4.31: Transport kinetics of phenol in BILM under different aqueous stirring speeds (s): membrane stirring, (-): without membrane stirring

On the other hand, it was found that membrane stirring had less effect on extraction kinetics, K_1 in comparison to aqueous stirring speed, as shown in Figure 4.31. This suggested that membrane stirring does not have an effect on the extraction process in terms of kinetics. The increment in the extraction rate under membrane stirring as shown in Figure 4.29 is more likely to be caused by the increment of concentration gradient between the feed and membrane phases as a result of higher stripping rate. The presence of membrane stirring increased the stripping kinetics, K_2 to a high degree under similar aqueous stirring speed as membrane stirring provided additional forces on phenol transport through the membrane phase. This behaviour reduced the effective viscosity in the membrane phase and increased the stripping kinetics, K_2 according to Equation (2.1). However, it was found that the increment on the stripping kinetics, K_2 due to membrane stirring was reduced from 567% to 17% as the aqueous stirring speed was increased from 100-300rpm. This trend was analogous to the trend for extraction rate, as shown in Figure 4.29. Under high aqueous stirring speed, the lowering of stripping kinetics enhancement caused lower enhancement on the stripping rate. This

suggests that the rate of change of phenol concentration in the membrane phase was less affected and thus the concentration gradient between the feed and membrane phases remained close as that without membrane stirring. Hence, under high aqueous stirring speed, the extraction rate was less enhanced by membrane stirring.

4.7.4 Interrelationship between Aqueous Stirring and Membrane Stirring

Despite the increment of both extraction and stripping efficiencies, high aqueous stirring speed of 300rpm caused membrane entrainment. High turbulence caused by high aqueous stirring speed led to the entrainment of the ionic liquid membrane and this created more problems for the system. The same was observed in the study of bulk liquid membranes by other researchers (Chakraborty and Bart, 2007; Chakrabarty *et al.*, 2009).

To solve this problem, a comparison of the overall phenol recovery by BILM was made to determine the interrelationship between the aqueous stirring speed and the membrane stirring, as illustrated in Figure 4.32. It was found that similar BILM overall phenol recovery could be achieved under different stirring conditions. For example, final overall phenol recovery of 51% could be achieved by using either 100rpm aqueous stirring speed with membrane stirring or 200rpm aqueous stirring speed without membrane stirring. Another outcome was the similarity between the overall phenol recovery of 68% through employing 200rpm aqueous stirring speed with membrane stirring and 300rpm aqueous stirring speed without membrane stirring.

By applying membrane stirring, it was found that equal BILM efficiency could be achieved at lower aqueous stirring speed. This provides a means to prevent membrane entrainment. Further study on the interrelationship between aqueous stirring

speed and membrane stirring was carried out to obtain high extraction and stripping efficiencies without membrane entrainment.

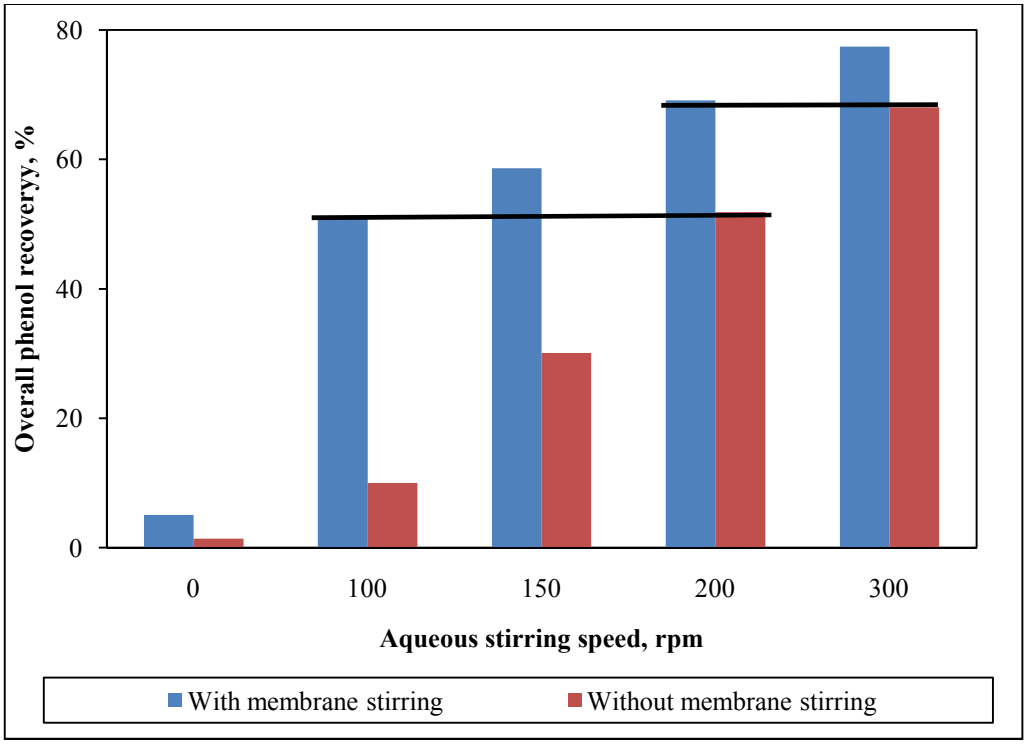


Figure 4.32: Overall phenol recovery of BILM after 300 min experimentation under different stirring conditions

4.8 Effect of Different Parameters on the Behavior of BILM

From the foregoing, [Bmim][NTf_2] based ionic liquid membrane shows similar behaviour as organic liquid membranes in phenol transport and they can both be explained by Fick's Law of diffusion and extraction equilibrium. The transport process is mainly governed by the hydrogen bonding between phenol and [Bmim][NTf_2] rather than ion-exchange mechanism as phenolate ion is not extracted by [Bmim][NTf_2].

The study described in the previous sections also shows that the effect of feed phase pH and NaOH concentration can be minimized by maintaining them below 6.56 and at 0.5M, respectively. However, higher relative viscosity of [Bmim][NTf_2] often increases the mass transfer resistance, thus resulting in low stripping efficiency. This becomes the main disadvantage for the ionic liquid membrane. Even though the study on stirring speeds shows that stripping efficiency can be enhanced by utilizing higher speed, it poses a problem associated with membrane entrainment. Hence, an optimization study on the stirring speeds was carried out with the objective of enhancing the extraction and stripping efficiencies while maintaining membrane operability.

4.9 Design of Experiment

The purpose of this study is to evaluate the interaction effect of aqueous stirring speed and membrane stirring speed on the extraction efficiency and the overall phenol recovery for BILM. Overall phenol recovery, i.e. the products of extraction efficiency and stripping efficiency was used rather than stripping efficiency as it provided a clearer trend by minimizing the error in stripping efficiency that was caused by low extraction efficiency in some of the experiments.

This is a statistical study using Central Composite Design (CCD) based Response Surface Methodology through the aid of Design Expert 6.0.5 software. Response Surface Methodology is an experimental strategy of statistical and mathematical techniques for modelling and analysis of problems in which the responses of interest are influenced by several variables and it is mainly for optimizing the responses (Montgomery, 2001). CCD is a popular statistical method for analyzing the significance and interactions between the parameters by conducting fewer experiments than the factorial methods.

The design consisted of 13 experiments which included 4 factorial experiments, 4 axial experiments and 5 centre point experiments. Five identical centre point experiments were applied to improve the precision of the experiments. In this case, the central point values were 150rpm (Level 0) for both stirring speeds. Constant parameters were feed phase pH $\approx$ 6.5, 300ppm feed concentration and 0.5M NaOH concentration. The sequence of the experiment was made at random in order to average out unknown nuisance factor. The percentage of phenol extraction efficiency and the overall phenol recovery after 300 min experimentation were recorded as the responses. Raw data obtained are as shown in Table 4.7 and the Analysis of Variance (ANOVA) is discussed in Sections 4.9.1 and 4.9.2.

Table 4.7: Raw data on central composite design

Experiments	Factor A: Membrane stirring, rpm	Factor B: Aqueous stirring, rpm	Response 1: Extraction efficiency, %	Response 2: Overall phenol recovery, %
1	300	0	48.17	41.66
2	150	200	95.86	90.59
3	150	150	93.09	80.26
4	100	150	91.41	55.74
5	0	0	1.14	1.30
6	150	150	94.50	79.63
7	150	150	94.91	78.57
8	150	100	93.53	69.26
9	200	150	95.01	92.80
10	300	300	48.28	50.23
11	0	300	92.15	68.74
12	150	150	95.05	78.90
13	150	150	91.03	79.59

4.9.1 ANOVA for Extraction Efficiency

According to the experimental results, reduced cubic model was suggested by Design Expert 6.0.5 for further analysis. The ANOVA table for the extraction process is as shown in Table 4.8.

Table 4.8: ANOVA analysis for extraction efficiency

Response: Extraction

ANOVA for Response Surface Reduced Cubic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	10091.73	6	1681.95	300.27	< 0.0001	significant
A	*4.48*	*1*	*4.48*	*0.80*	*0.4055*	
B	*0.24*	*1*	*0.24*	*0.043*	*0.8429*	
A^2	*43.99*	*1*	*43.99*	*7.85*	*0.0311*	
B^2	*13.46*	*1*	*13.46*	*2.40*	*0.1720*	
AB	*2065.70*	*1*	*2065.70*	*368.77*	*< 0.0001*	
B^3	*76.54*	*1*	*76.54*	*13.66*	*0.0101*	
Residual	33.61	6	5.60			
Lack of Fit	*22.18*	*2*	*11.09*	*3.88*	*0.1156*	*not significant*
Pure Error	*11.43*	*4*	*2.86*			
Cor Total	10125.34	12				

Table 4.8 shows that F-value of 300.27 with Prob > F of <0.0001 is found for the model which implies that the model has significant confidence of higher than 95%. There is only 0.01% chance that this model F-value this large could occur due to noise. Lack of fit F-value of 3.88 also shows that it is insignificant in relative to pure error because the probability value exceeds the threshold value of 0.05 (Anderson and Whitcomb, 2000). There is 11.56% chance that the lack of fit F-value this large could occur due to noise. Non-significant lack of fit is desired for the model.

The Predicted R^2 of 0.8255 is in reasonable agreement with the Adjusted R^2 of 0.9934 as their difference is less than 0.2 and this shows that the model is adequate to fit the data (Iqbal and Khan, 2010). Moreover, an Adequate Precision (ratio of signal to noise) of 54.092 which is greater than 4 further confirms the adequacy of the model.

Diagnosis of residuals shows that there is no abnormality for the model. Figure 4.33 shows that the predicted value fits the actual result in a deviation of less than 5% and thus the model is statistically valid. The coded statistical model is as shown in Equation (4.6) where Y_1 is the extraction efficiency, α is the membrane stirring speed and β is the aqueous stirring speed. The value of α and β are valid in the range of -1 to 1 (0rpm to 300rpm).

$$Y_1 = 94.93 + 1.03\alpha + 1.18\beta - 30.52\alpha^2 - 16.89\beta^2 - 22.72\alpha\beta + 21.60\beta^3 \quad (4.6)$$

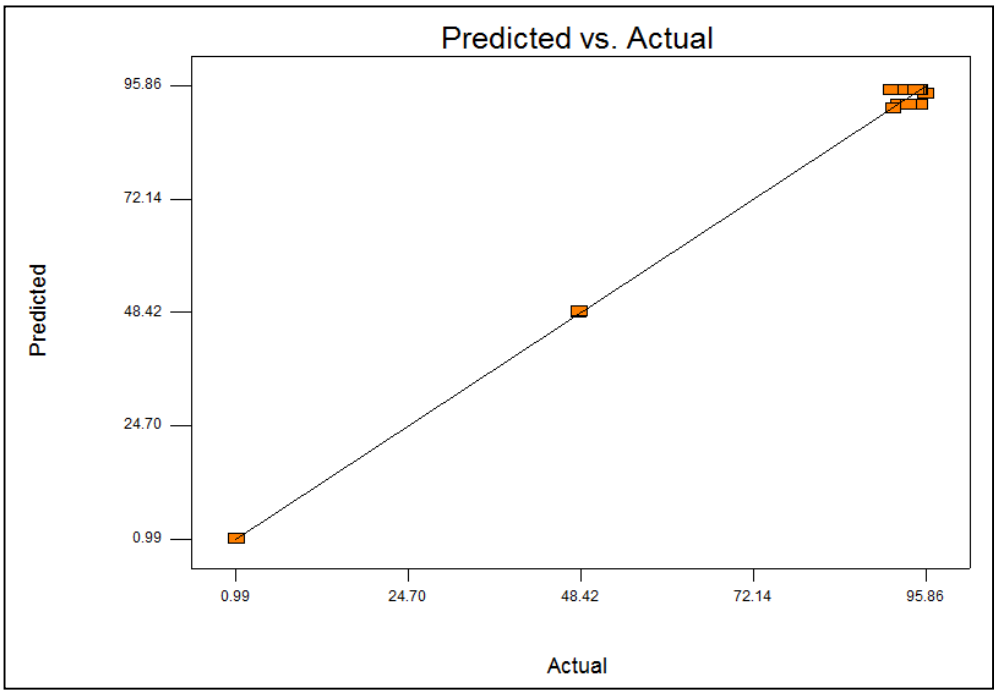


Figure 4.33: Predicted result versus actual experimental result for extraction efficiency

4.9.2 ANOVA for Overall Phenol Recovery

The fit summary analysis shows that reduced cubic model is suitable for analyzing the overall phenol recovery. The ANOVA table for the overall phenol recovery is as shown in Table 4.9.

Table 4.9: ANOVA analysis for overall phenol recovery

Response: Overall

ANOVA for Response Surface Reduced Cubic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	7363.31	7	1051.90	2862.36	< 0.0001	significant
A	*671.81*	*1*	*671.81*	*1828.10*	*< 0.0001*	
B	*199.16*	*1*	*199.16*	*541.93*	*< 0.0001*	
A^2	*97.26*	*1*	*97.26*	*264.66*	*< 0.0001*	
B^2	*2.02*	*1*	*2.02*	*5.51*	*0.0658*	
AB	*866.42*	*1*	*866.42*	*2357.64*	*< 0.0001*	
A^3	*530.71*	*1*	*530.71*	*1444.14*	*< 0.0001*	
B^3	*36.62*	*1*	*36.62*	*99.66*	*0.0002*	
Residual	1.84	5	0.37			
Lack of Fit	*0.070*	*1*	*0.070*	*0.16*	*0.7100*	*not significant*
Pure Error	*1.77*	*4*	*0.44*			
Cor Total	7365.15	12				

Table 4.9 shows that the model is significant with F-value of 2862.36 and prob > F of <0.0001. The lack of fit F-value of 0.16 is insignificant in relative to the pure error as there is 71.00% chance that the value this large could occur due to noise. In addition, the regression analysis shows that Predicted R^2 of 0.9107 is in reasonable agreement with the Adjusted R^2 of 0.9994 as the difference is less than 0.2. Adequate Precision of 192.632 further shows that the model is adequate to fit the experimental data. In term of abnormality, Figure 4.34 further justifies that there is no abnormality on the model as the model fits the experimental result with a deviation of less than 2%. The coded statistical model is as shown in Equation (4.7) where Y_2, α and β are the overall phenol recovery, the membrane stirring speed and the aqueous stirring speed, respectively. Similar to the model for extraction efficiency, the range for α and β are -1 to 1 which represent 0rpm to 300rpm, respectively.

$$Y_2 = 79.31 + 62.35\alpha + 33.95\beta - 45.38\alpha^2 + 6.55\beta^2 - 14.72\alpha\beta - 56.88\alpha^3 - 14.94\beta^3 \quad (4.7)$$

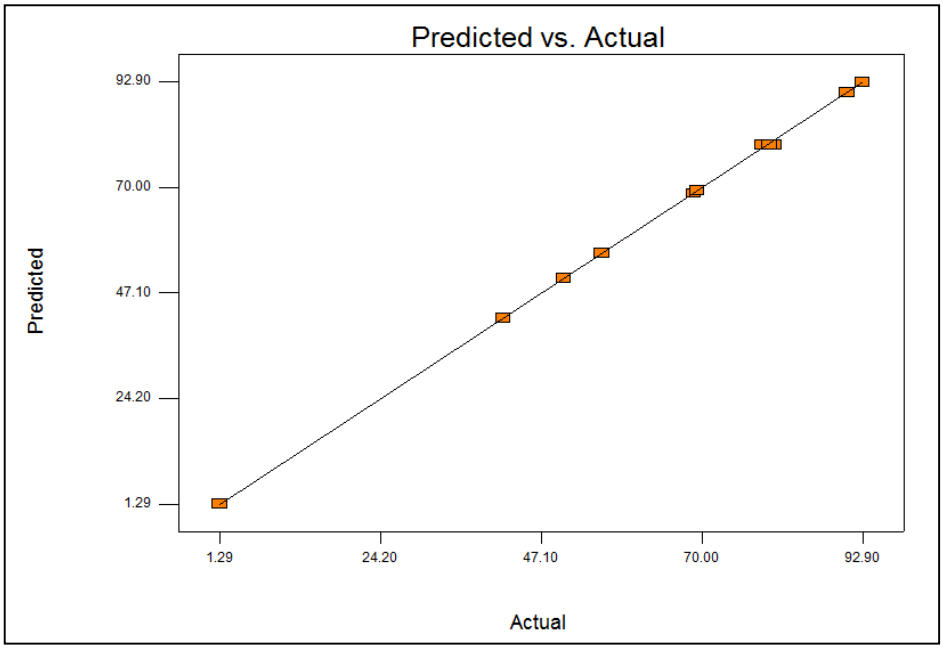


Figure 4.34: Predicted result versus actual experimental result for overall phenol recovery

4.9.3 Response Surface (Contour) Plots

Figure 4.35 illustrates a 3D contour plot for extraction efficiency versus membrane stirring speed and aqueous stirring speed. In general, the extraction efficiency increased through the increment of aqueous stirring speed and membrane stirring speed, with the same effect as discussed in Section 4.7.2. However, a drastic decrease in the extraction efficiency was observed when both aqueous stirring speed and membrane stirring speed were held at high level (level 1).

In addition, the overall phenol recovery was enhanced by the increment of aqueous stirring speed and membrane stirring speed, as illustrated in Figure 4.36. The figure also shows that membrane stirring speed has more significant effect in dictating the overall phenol recovery as compared to that of aqueous stirring speed as the former increases the recovery in a higher magnitude. However, it was worth noting that the membrane stirring had an optimum speed on the level of -0.2 - 0.5. The increment of membrane stirring speed beyond level 0.5 showed a reduction in the overall phenol recovery due to the failure of BILM.

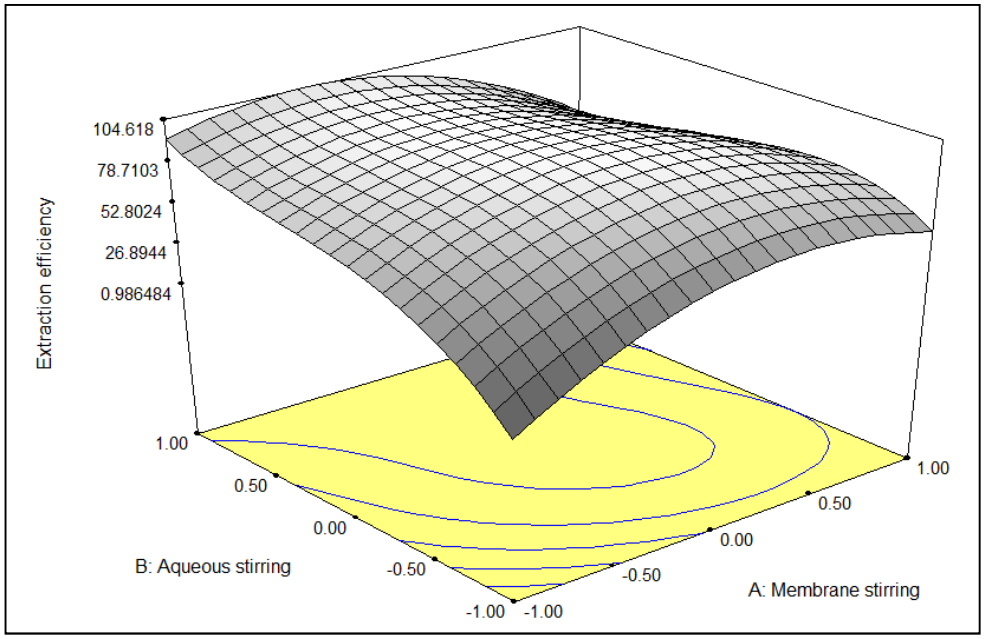


Figure 4.35: 3D contour plot for extraction efficiency

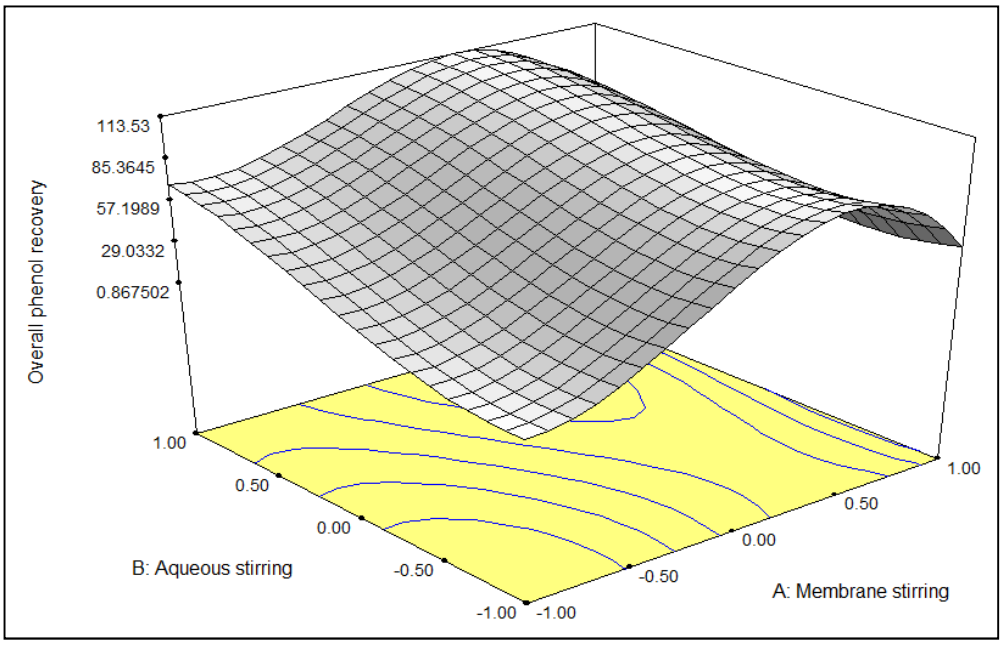


Figure 4.36: 3D contour plot for overall phenol recovery

Failure of BILM was observed in both the extraction and overall phenol recovery processes at high membrane stirring speed (Level 1), as shown in Figures 4.35 and 4.36, and at this point, high turbulence and vortex were observed experimentally in the membrane phase. The unstable membrane caused the unfavourable mixing between the feed phase and the stripping phase, thus causing a failure in the transport process. In addition, at very high aqueous stirring speed (Level 1), membrane entrainment was observed, as stated in Section 4.7 but it did not cause any significant reduction in efficiencies.

4.9.4 Optimization Study

Design Expert 6.0.5 provides optimization feature by utilizing mathematical models to estimate the extraction efficiency and the overall phenol recovery, as shown in Equations (4.6) and (4.7). Based on Figures 4.35 and 4.36, the range of both stirring speeds required to achieve optimum extraction efficiency and overall phenol recovery are as tabulated (Table 4.10).

Table 4.10: Range of stirring speeds for optimization purpose

Coded parameters	**Low level**	**High level**
Membrane stirring speed	-0.2	0.5
Aqueous stirring speed	0	1

A series of combinations between both stirring speeds were obtained using the software based on the range as summarized in Table 4.10. As membrane entrainment can be detected by physical observation, all of the combinations obtained through the software were justified experimentally. The combination that provided the best extraction efficiency and overall phenol recovery without any membrane entrainment was determined.

Table 4.11 shows that membrane stirring speed of 135 rpm (Level -0.10) and aqueous stirring speed of 255rpm (Level 0.70) result in optimum extraction efficiency of 96.03% and overall phenol recovery of 95.80%. The predicted results were found to be reasonably close to the experimental results with deviations of 0.18% and 1.41% for extraction efficiency and overall phenol recovery, respectively.

Table 4.11: Optimum stirring speeds for the best extraction efficiency and overall phenol recovery

Parameters	**Membrane stirring speed, rpm**	**Aqueous stirring speed, rpm**
Optimum value (Coded)	-0.10	0.70
Optimum value (Uncoded)	135	255
	Predicted result	**Experimental result**
Extraction efficiency, %	96.03	96.21
Stripping efficiency, %	Not tested	98.10
Overall phenol recovery, %	95.80	94.39

4.10 Comparison between BILM and Bulk Organic Liquid Membranes

4.10.1 Efficiency Comparison

Technical feasibility of ionic liquid [Bmim][NTf_2] as liquid membrane was further justified by conducting an efficiency comparison between BILM and BOLM. Organic membrane solvents utilized in this study were dichloromethane and kerosene. The optimum extraction and stripping efficiencies of phenol by BILM and BOLMs after 300 min experimentation are as shown in Figure 4.37.

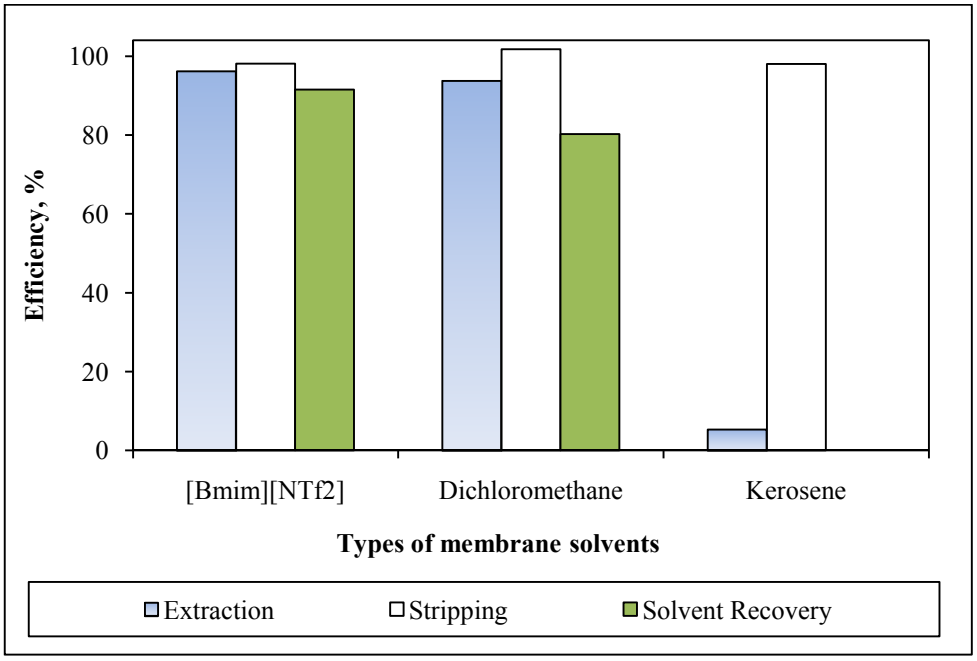


Figure 4.37: Optimum efficiencies comparison between different types of membrane solvents after 300 min experimentation

Figure 4.37 shows that BILM based on [Bmim][NTf_2] provides better performance than kerosene (5.35% for extraction efficiency and 98.03% for stripping efficiency) while it shows a comparable performance with dichloromethane (93.79% for extraction efficiency with nearly 100% of stripping efficiency). It is worth noting that although the viscosity of [Bmim][NTf_2] is several magnitude higher than kerosene and dichloromethane, phenol stripping process in BILM can be enhanced by fine-tuning the stirring speeds. This is mainly due to the fact that BILM can withstand higher stirring speeds in comparison to BOLMs, thus causing a reduction in the viscosity effect, hence a high liquid membrane performance was achieved.

4.10.2 Solvent Recovery

Figure 4.37 also shows that [Bmim][NTf_2] has higher solvent recovery of 91.52% in comparison to 80.24% for dichloromethane. It is to be noted that all ionic liquids tested in this study had higher solvent recovery than dichloromethane, as shown in Table 4.3 and Figure 4.37. This is due to the fact that ionic liquids are characteristically more hydrophobic and have negligible vapour pressure, thus the loss is limited.

Furthermore, it was found that the effect of feed phase pH, feed concentration, NaOH concentration and stirring speeds had less effect on the loss of [Bmim][NTf_2]. Figure 4.38 shows that [Bmim][NTf_2] has an average loss of 8.80 ± 1.10g which is equivalent to the ionic liquid recovery of 92.09±0.99% and this is in line with the data presented in Table 4.3 and Figure 4.37. Thus, [Bmim][NTf_2] is a better alternative to organic membrane solvent as it gives high and stable performance with better solvent recovery.

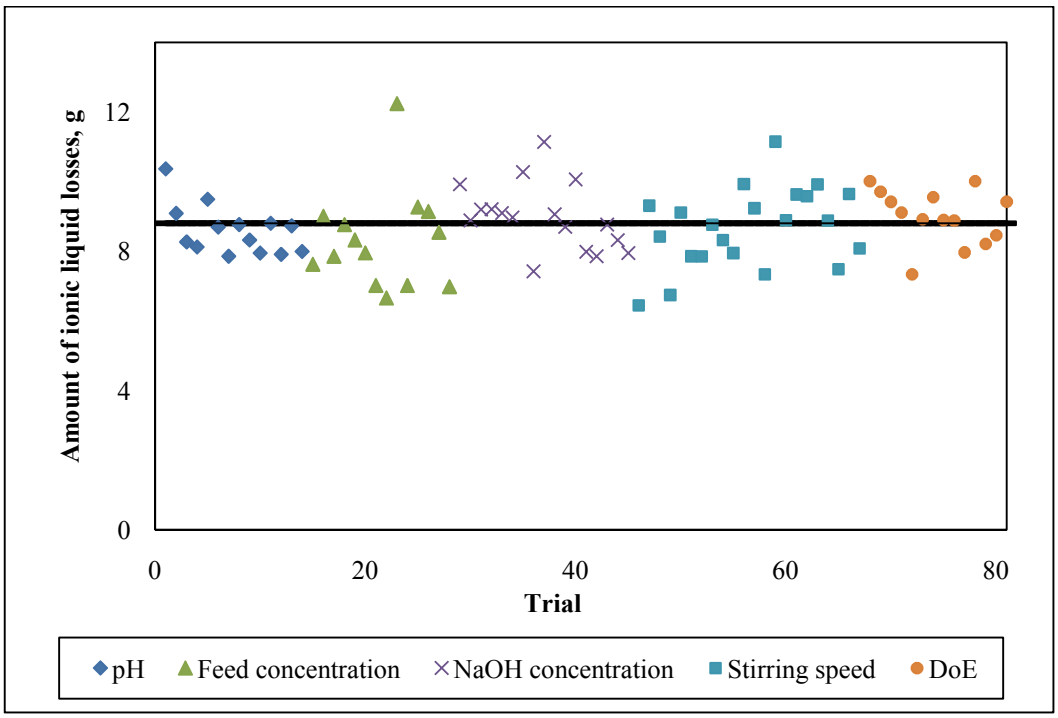


Figure 4.38: Loss of ionic liquids in [Bmim][NTf_2] based BILM

CHAPTER 5: TRANSPORT KINETICS MODELING

Based on the experimental data presented in Chapter 4, a transport mechanism of phenol through BILM is proposed and transport kinetics of phenol in the system are estimated. The transport mechanism is as suggested in Equation (5.1) based on several assumptions which will be discussed in section 5.1 and 5.2.

$$C_6H_5OH_{aq} \Leftrightarrow C_6H_5OH_{IL} \xrightarrow{NaOH} C_6H_5ONa + H_2O \quad (5.1)$$

5.1 Extraction Mechanism

Phenol is transported from feed phase to membrane phase in the extraction process, as illustrated in Figure 5.1. In the absence of a carrier, it is assumed that the extraction process is mainly governed by the distribution coefficient of phenol between the ionic liquid (membrane phase) and water. The extraction mechanism can be presented by Equation (5.2). As in liquid-liquid extraction, this process is governed by the extraction equilibrium of phenol between the phases (Khachatryan *et al*., 2005).

$$C_6H_5OH_{aq} \Leftrightarrow C_6H_5OH_{IL} \quad (5.2)$$

The extraction model is derived based on the diffusion of phenol between feed/membrane interface, as illustrated in Figure 5.1, and the assumptions are:

- the system operates at constant temperature of 298K,
- the aqueous phases are well mixed,
- the diffusion process occurs only for molecular phenol,
- the extraction system obeys Fick's Law,
- loss of ionic liquid membrane during the experiment is negligible,

- volume change due to sampling is negligible, and
- the extraction process is completely dependent on the concentration gradient between the feed phase and the membrane phase.

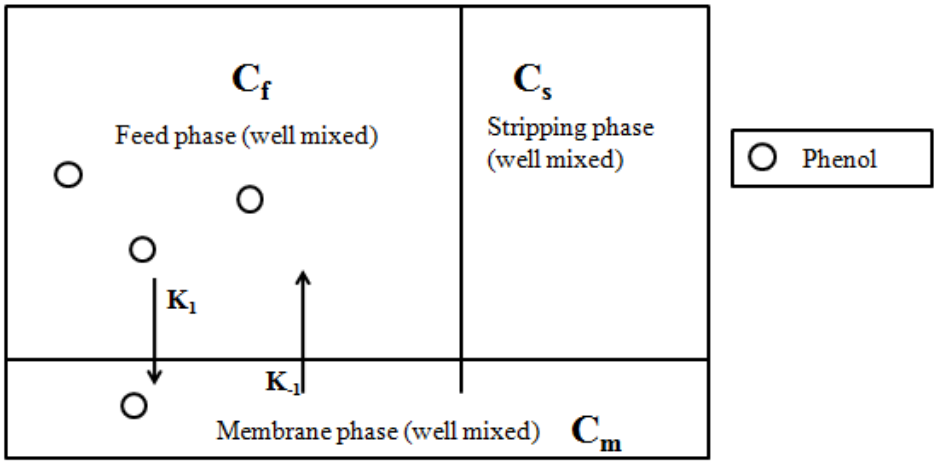


Figure 5.1: Phenol extraction mechanism in BILM

Based on the above, the extraction of phenol by ionic liquid membrane can be explained by Fick's Law. The rate of change of phenol concentration in the feed phase, $\frac{dC_f}{dt}$ is as shown in Equation (5.3):

$$\frac{dC_f}{dt} = -K_1\left(C_f - C_f^{'}\right) \tag{5.3}$$

Where:

K_1 = extraction kinetics (min^{-1})

C_f = phenol concentration in the feed phase (mg/L)

$C_f^{'}$ = phenol concentration in the feed phase (interface) in equilibrium with the membrane phase (mg/L)

Equation (5.3) can be expressed as in Equation (5.4), as claimed by Kubišová *et al*. (2004).

$$\frac{dC_f}{dt} = -K_1\left(C_f - \frac{C_m}{D_1}\right) \tag{5.4}$$

Where:

C_m = phenol concentration in the membrane phase (mg/L)

D_1 = distribution coefficient of phenol between the membrane phase and the feed phase.

Generally, $D_1 = \frac{C_m^*}{C_f^*}$, where C_m^* is the equilibrium phenol concentration in the membrane phase while C_f^* is the equilibrium phenol concentration in the feed phase. At equilibrium state, the net mass transfer rate between the feed phase and the membrane phase is zero, where:

$$J_f^* = J_m^* \tag{5.5}$$

$$k_1 A C_f^* = k_{-1} A C_m^* \tag{5.6}$$

Hence,

$$\frac{C_m^*}{C_f^*} = D_1 = \frac{k_1}{k_{-1}} = \frac{k_1\left(\frac{A}{V_f}\right)}{k_{-1}\left(\frac{A}{V_f}\right)} = \frac{K_1}{K_{-1}} \tag{5.7}$$

Based on Equation (5.7), Equation (5.4) can be simplified into rate law term, as in Equation (5.8) which has the same form as that expressed by Ma *et al.* (2004) for the transport kinetics of amino acids in bulk liquid membrane system.

$$\frac{dC_f}{dt} = -K_1 C_f + K_{-1} C_m \tag{5.8}$$

Where:

K_{-1} = back extraction kinetics (min^{-1})

5.2 Stripping Mechanism

NaOH was used as a stripping agent for phenol removal, and it has two functions: (i) as a reactant for chemical reaction with phenol to suppress phenol's activity (Park *et al.*, 2006; Busca *et al.*, 2008) and (ii) to maintain high pH in the stripping phase. Phenol tends to dissolve as phenolate ion in high pH aqueous solution rather than in ionic liquids due to its characteristic as a weak acid (Busca *et al*., 2008; Zidi *et al*., 2010). Thus, it is stripped from the ionic liquid membrane.

Figure 5.2 shows that phenol is diffused into the stripping phase due to the concentration gradient between the membrane phase and the stripping phase. Under high pH and abundance of NaOH, phenol that is diffused through the boundary layer is reacted with NaOH in the stripping phase by 1:1 mole ratio via acid-base reaction and yields sodium phenolate (C_6H_5ONa) (Xiao *et al.*, 2006). Phenolate ion is insoluble in ionic liquid membrane, as discussed in Section 4.4. Thus, back stripping of phenol from the stripping phase to the ionic liquid membrane is prevented. According to Garea *et al.* (1993), Correia and de Carvalho (2003) and Xiao *et al.* (2006), the reaction between phenol and NaOH is instantaneous in comparison to the diffusion of phenol into the stripping phase. Thus, the stripping process in this model only takes into consideration the diffusion of phenol in the stripping system. Moreover, as the NaOH concentration in the stripping phase is of significantly higher concentration than phenol in the feed phase, phenol is considered as the limiting reactant such that the stripping mechanism is highly dependent on phenol diffusion rate.

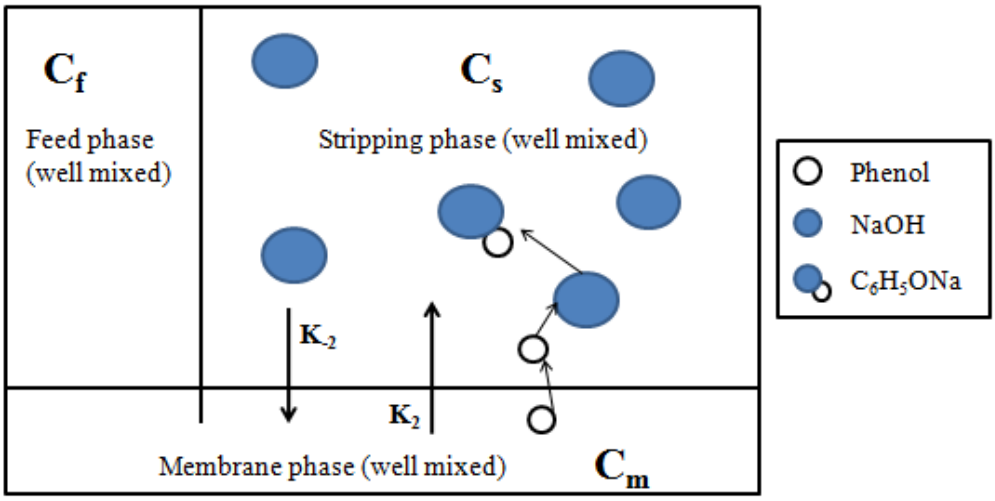


Figure 5.2: Phenol stripping mechanism in BILM

The concentration of phenol in the stripping phase, C_s was calculated by converting the concentration of sodium phenolate, C_s^{Ph} in the stripping phase using mole balance, as stated in Section 3.6.3. Even though the actual activity for molecular phenol is negligible, the amount of theoretical phenol present in the stripping phase remains important in order to determine the stripping kinetics, K_2 for the system. The assumptions made are:

- the system operates at constant temperature of 298K,
- the aqueous phases are well mixed,
- chemical reaction between phenol and NaOH is instantaneous. Phenol diffusion is the limiting step,
- the stripping process obeys Fick's Law,
- volume change due to sampling is negligible, and
- the loss of ionic liquid membrane during the experiment is negligible.

Based on the above assumptions, the rate of change of phenol concentration in the stripping phase is derived based on Fick's Law and mass balance as the stripping process is mainly governed by the diffusion process.

$$\frac{dC_s}{dt} = K_2\left(C_m - C_m^{'}\right) \tag{5.9}$$

Where:

K_2 = stripping kinetics (min^{-1})

C_s = phenol concentration in the stripping phase (mg/L)

$C_m^{'}$ = phenol concentration in the membrane phase (interface) in equilibrium with the stripping phase (mg/L)

Equation (5.9) can be expressed as Equation (5.10), as discussed in Section 5.1 (Kubisová *et al*., 2004):

$$\frac{dC_s}{dt} = K_2\left(C_m - \frac{C_s}{D_2}\right) \tag{5.10}$$

Where:

D_2 = distribution coefficient of phenol between the stripping phase and the membrane phase.

Generally, $D_2 = \frac{C_S^*}{C_m^*}$. From the concept discussed in Section 5.1, the distribution coefficient, D_2 at equilibrium can be derived as Equation (5.11), where K_{-2} is the back stripping kinetics of phenol into the membrane phase.

$$D_2 = \frac{K_2}{K_{-2}} \tag{5.11}$$

By substituting Equation (5.11) into Equation (5.10), the equation for the stripping process is simplified into rate law term, as shown in Equation (5.12) where:

$$\frac{dC_s}{dt} = K_2 C_m - K_{-2} C_s \tag{5.12}$$

5.3 Rate of Change of Phenol Concentration in BILM and Transport Kinetics

Based on Equations (5.8) and (5.12), the rate of change of phenol in the membrane phase is determined by mass balance, as shown in Equation (5.13) with the assumptions that no phenol is lost from the system and no irreversible reaction occurs between the ionic liquid and phenol. Equation (5.13) can be elaborated in concentration term, as shown in Equations (5.14) and (5.15).

$$\frac{dN_f}{dt} + \frac{dN_s}{dt} + \frac{dN_m}{dt} = 0 \tag{5.13}$$

$$\left(\frac{V_f}{V_f}\right)\frac{dN_f}{dt} + \left(\frac{V_s}{V_s}\right)\frac{dN_s}{dt} + \left(\frac{V_m}{V_m}\right)\frac{dN_m}{dt} = 0 \tag{5.14}$$

$$V_f \frac{dC_f}{dt} + V_s \frac{dC_s}{dt} + V_m \frac{dC_m}{dt} = 0 \tag{5.15}$$

Where:

N_f = mass of molecular phenol in the feed phase (mg)

N_m = mass of molecular phenol in the membrane phase (mg)

N_s = mass of molecular phenol in the stripping phase (mg)

V_f = volume of the feed phase (L)

V_m = volume of the membrane phase (L)

V_s = volume of the stripping phase (L)

The volumes of the feed and stripping phases are the same, $V_f = V_s$ = Volume of aqueous phase, V_{aq}. By dividing V_{aq} on both sides, Equation (5.15) can be written as:

$$\frac{dC_f}{dt} + \frac{dC_s}{dt} + \left(\frac{V_m}{V_{aq}}\right)\frac{dC_m}{dt} = 0 \tag{5.16}$$

Thus, the rate of change of phenol concentration in the membrane phase is as shown in Equations (5.17) and (5.18) with an assumption that the ratio between volume of aqueous phase, V_{aq} and volume of membrane phase, V_m is constant throughout the experiment.

$$\frac{dC_m}{dt} = \left(\frac{V_{aq}}{V_m}\right)\left(-\frac{dC_f}{dt} - \frac{dC_s}{dt}\right) \tag{5.17}$$

$$\frac{dC_m}{dt} = \left(\frac{V_{aq}}{V_m}\right)\left(K_1 C_f - (K_{-1} + K_2)C_m + K_{-2}C_s\right) \tag{5.18}$$

Hence, the rate of change of phenol concentration in the system will be:

Feed phase $$\frac{dC_f}{dt} = -K_1 C_f + K_{-1} C_m \tag{5.8}$$

Membrane phase $$\frac{dC_m}{dt} = \left(\frac{V_{aq}}{V_m}\right)\left(K_1 C_f - (K_{-1} + K_2)C_m + K_{-2}C_s\right) \tag{5.18}$$

Stripping phase $$\frac{dC_s}{dt} = K_2 C_m - K_{-2} C_s \tag{5.12}$$

The ODEs were solved by using *ode45* command in MATLAB R2007b. In this study, K_1, K_{-1}, K_2 and K_{-2} were the unknowns. Hence, a set of K arrays were used to fit the model and phenol concentration in the phases that were predicted by the model and were compared with the experimental data. Combination of K values which gave the highest coefficient of determination, R^2 between the predicted results and the experimental results was determined. The MATLAB m-files and the goodness of fit for the model are as shown in Appendices B and C, respectively.

Tables 5.1-5.4 show the transport kinetics of phenol in BILM and the coefficients of determination of the curves, R^2 for the model. From the tables, it is found that R^2 for the model is at least 0.96 which is sufficient to explain the transport trend of phenol in BILM. Thus, it is concluded that the proposed transport mechanism and the

assumptions for this model are valid for these cases. Further analysis on the transport kinetics at different parameters was discussed in Chapter 4.

Table 5.1: Transport kinetics of phenol in BILM and coefficient of determination at different pHs

pH	K_1 (min^{-1})	K_{-1} (min^{-1})	K_2 (min^{-1})	K_{-2} (min^{-1})	Coefficient of determination, R^2		
					Feed	Membrane	Stripping
1.13	0.0170	0.0012	0.0024	0	0.9972	0.9922	0.9913
3.04	0.0182	0.0014	0.0024	0	0.9965	0.9903	0.9909
5.12	0.0178	0.0014	0.0024	0	0.9970	0.9911	0.9911
6.56	0.0182	0.0012	0.0024	0	0.9978	0.9968	0.9942
9.23	0.0124	0.0048	0.0026	0	0.9970	0.9935	0.9949

Table 5.2: Transport kinetics of phenol in BILM and coefficient of determination at different feed concentrations

Feed Concentration, ppm	K_1 (min^{-1})	K_{-1} (min^{-1})	K_2 (min^{-1})	K_{-2} (min^{-1})	Coefficient of determination, R^2		
					Feed	Membrane	Stripping
150	0.0184	0.0014	0.0022	0	0.9962	0.9949	0.9859
300	0.0182	0.0012	0.0024	0	0.9978	0.9968	0.9942
700	0.0178	0.0012	0.0022	0	0.9975	0.9945	0.9902
2000	0.0184	0.0014	0.0026	0	0.9978	0.9964	0.9917
3000	0.0172	0.0014	0.0032	0	0.9981	0.9917	0.9960
6000	0.0174	0.0016	0.0042	0	0.9918	0.9812	0.9833

Table 5.3: Transport kinetics of phenol in BILM and coefficient of determination at different NaOH concentrations

NaOH Concentration, M	K_1 (min^{-1})	K_{-1} (min^{-1})	K_2 (min^{-1})	K_{-2} (min^{-1})	Coefficient of determination, R^2		
					Feed	Membrane	Stripping
0	0.0190	0.0012	0.0012	0.0184	0.9994	0.9997	0.9885
0.05	0.0180	0.0016	0.0024	0	0.9921	0.9672	0.9651
0.1	0.0180	0.0014	0.0026	0	0.9955	0.9878	0.9869
0.5	0.0182	0.0012	0.0024	0	0.9978	0.9968	0.9942

Table 5.4: Transport kinetics of phenol in BILM and coefficient of determination at different aqueous stirring speeds

Aqueous Stirring Speed, rpm	K_1 (min^{-1})	K_{-1} (min^{-1})	K_2 (min^{-1})	K_{-2} (min^{-1})	Coefficient of determination, R^2		
					Feed	Membrane	Stripping
100 (s)	0.0110	0.0006	0.0016	0	0.9972	0.9951	0.9856
150 (s)	0.0154	0.0012	0.0018	0	0.9984	0.9926	0.9888
200 (s)	0.0182	0.0012	0.0024	0	0.9978	0.9968	0.9942
300 (s)	0.0244	0.0018	0.0028	0	0.9985	0.9932	0.9933
100 (-)	0.0106	0.00098	0.00024	0	0.9971	0.9952	0.9776
150 (-)	0.0146	0.0011	0.00072	0	0.9989	0.9960	0.9865
200 (-)	0.0186	0.0012	0.0014	0	0.9993	0.9984	0.9962
300 (-)	0.0218	0.0018	0.0024	0	0.9945	0.9901	0.9821

* (s): with membrane stirring; (-): without membrane stirring

The model is applied to most of the cases in this study, as shown in the tables above. However, it is found that several tests such as pH 11.19, 0.005M and 0.01M NaOH concentration do not fit the model well. The validity of the model is further clarified in Section 5.5.

5.4 Simplification of the Stripping Model under Different Conditions

The stripping model in Equation (5.12) is valid when phenol diffusion is the only limiting step in the stripping process. Based on the results in Tables 5.1 – 5.4, it is found that this situation occurs under two conditions:

- absence of NaOH as stripping agent, and
- NaOH is in excess in stripping phase (pH >12)

The stripping process for the first case was similar to the extraction process whereby the transport mechanism was completely dependent on the diffusion process and the distribution coefficient of phenol between the membrane phase and the stripping phase. The activity of phenol in the stripping phase had a significant effect on the stripping process, as discussed in Section 4.6.3. Both the stripping and back stripping kinetics should be considered in the model. Hence, the model is the same as in Equation (5.12).

The second case showed that abundance of NaOH in the stripping phase caused instantaneous reaction between NaOH and phenol which diffused into the stripping phase, thus suppressing the activity of phenol. Under this condition, it can be assumed that phenol diffused into the stripping phase and was converted into sodium phenolate, and the activity of phenol in the stripping phase was negligible, hence back stripping kinetics, K_{-2} is near to zero.

Based on this additional assumption, the term K_{-2} in Equation (5.12) is negligible, thus it can be further simplified into Equation (5.19).

$$\frac{dC_s}{dt} = K_2 C_m \tag{5.19}$$

The rate of change of phenol concentration in the membrane phase in Equation (5.20) is determined by substituting Equation (5.19) into Equation (5.17).

$$\frac{dC_m}{dt} = \left(\frac{V_{aq}}{V_m}\right)\left(K_1 C_f - (K_{-1} + K_2)C_m\right) \tag{5.20}$$

Hence, the rate of change of phenol concentration in all three phases will be:

Feed phase $$\frac{dC_f}{dt} = -K_1 C_f + K_{-1} C_m \tag{5.8}$$

Membrane phase $$\frac{dC_m}{dt} = \left(\frac{V_{aq}}{V_m}\right)\left(K_1 C_f - (K_{-1} + K_2)C_m\right) \tag{5.20}$$

Stripping phase $$\frac{dC_s}{dt} = K_2 C_m \quad (5.19)$$

It is worth noting that this model is only applicable when the amount of NaOH in the stripping phase is in excess (pH > 12) as this model gives similar results as the data shown in Tables 5.1-5.4 except for the case when 0M NaOH concentration was applied.

5.5 Validity of the Models

The suggested models generated kinetics values which can generally described the transport behavior of phenol in BILM. Good regressions were obtained for the predicted results even though phenol loss due to sampling was neglected in the models. However, it is to be noted that these values may not accurately represent the actual system as there were a number of experimental errors that were not taken into account in the models, e.g. loss of phenol and aqueous phase during sampling and actual loss of ionic liquid during experiment.

There are also some limitations of the validity of the models whereby the models are only valid when the feed phase pH is less than pK_a value of phenol of 10 in which majority of phenol solutes are present in the feed phase as neutral molecules. On the other hand, for the stripping process, these models are valid only when phenol diffusion is the limiting step in BILM system, as discussed in Section 5.4. The models are not applicable for certain NaOH concentration such as 0.005M and 0.01M. For these cases, a mixture of molecular phenol and sodium phenolate are present in the stripping phase due to the shortage of NaOH, as discussed in Section 4.6 and as claimed by Cichy *et al*. (2005). The stripping process becomes complicated as it is not only diffusion controlled,

but also controlled by the activity of molecular phenol (in the stripping phase). Thus, the experimental data for these cases are not well fitted by the models.

Furthermore, the models are unable to determine the transport kinetics for low phenol transport rate as the coefficient of determination, R^2 is not satisfied. Although a reduced concentration model had been applied, the results remained the same.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Hydrophobic ionic liquids [Bmim][NTf_2] and [Bmim][FAP] were selected as liquid membrane for phenol removal due to their favourable properties in terms of water immiscibility, lower mutual solubility with water, good moisture stability and lower viscosity in comparison to the currently popular [Bmim][PF_6]. However, [Bmim][PF_6] was used in this study as a reference for comparison purposes.

Liquid-liquid extraction experiments showed that [Bmim][NTf_2] and [Bmim][FAP] were suitable as pure diluents/solvents rather than carriers as they showed poorer performance than organic carrier Cyanex923. For the application as pure diluent, [Bmim][NTf_2] showed higher phenol extraction efficiency of 75.46% in comparison to the organic solvents of dichloromethane (42.53%) and kerosene (2.82%).

The study of bulk ionic liquid membrane was carried out based on the results obtained from the work on liquid-liquid extraction whereby pure ionic liquids in the absence of carrier were utilized. The result confirmed that all the ionic liquids tested showed good membrane stability and reusability. Unlike the work of Fortunato *et al.* (2004; 2005a) and Matsumoto *et al.* (2007), the effect of water microenvironment was not observed within the experimental duration employed in this study. In terms of BILM performance, phenol extraction efficiency was strongly dependent on the hydrogen bond basicity strength of the ionic liquids whereby [Bmim][NTf_2] showed the highest phenol extraction efficiency of 94.18% after 300 min in comparison to [Bmim][PF_6] (59.62%) and [Bmim][FAP] (46.11%). The stronger the hydrogen bond basicity, the higher the extraction efficiency. On the other hand, increasing the hydrophobicity of the ionic liquids by employing different types of anions showed

lesser effect of phenol extraction efficiency. However, this parameter affected ionic liquid recovery significantly as the experimental result proved that the most hydrophobic ionic liquid, [Bmim][FAP] was recovered in 95.26%, followed by [Bmim][NTf_2] (92.59%) and [Bmim][PF_6] (87.29%).

In contrast, the stripping efficiency for BILM was mainly governed by the viscosity of the ionic liquid. [Bmim][NTf_2] which has the lowest viscosity among the ionic liquids studied gave the highest stripping efficiency of 73.39% after 300 min duration. However, a different trend was observed for [Bmim][FAP] whereby it showed similar stripping efficiency with [Bmim][PF_6] even though its viscosity is much lower. A high boundary layer thickness caused by high hydrophobicity of [Bmim][FAP] may be the main reason.

Preliminary studies suggested that [Bmim][NTf_2] was the best ionic liquid membrane. The study on the effect of the feed phase pH revealed that phenol was only extracted by [Bmim][NTf_2] in molecular form via hydrogen bonding as the extraction efficiency was maintained at 94% as long as the pH was in range of 1.13-6.56. In contrast, the extraction efficiency decreased when the pH was further increased to 9.23 and 11.19 as [Bmim][NTf_2] did not extract phenolate ion either by hydrogen bonding or ion-exchange mechanism. The ability of [Bmim][NTf_2] to transport molecular phenol while rejecting phenolate ion provided a stable phenol extraction and stripping processes.

The study on the effect of feed concentration and NaOH concentration showed that the extraction efficiency was independent of these parameters as [Bmim][NTf_2] based BILM provided high phenol dissolution capacity which prevented membrane saturation and early equilibrium. In contrast, the increments of the feed concentration and NaOH concentration were found to increase the stripping rate and efficiency mainly due to the respective increment of the effective contact area and also the reaction rate between phenol and NaOH. This observation showed that [Bmim][NTf_2] had similar behavior as organic liquid membranes for phenol transport as the mass transfer mechanism was found to be similar. The transport of phenol in [Bmim][NTf_2] based BILM can be explained by Fick's law and the extraction equilibrium of phenol between [Bmim][NTf_2] and the aqueous phases.

Stirring speeds in the aqueous phase and the membrane phase had the most significant effect for BILM. In comparison to other parameters, the respective extraction and stripping efficiencies were found to increase significantly from 84.19-92.21% and 11.86-73.80% when the aqueous stirring speed was increased from 100-300rpm as the boundary layer thickness and the concentration polarization were reduced. The efficiencies were further increased in the presence of membrane stirring condition as it provided additional force for the transport of phenol through the thick membrane in BILM. The extraction and stripping efficiencies under this condition were found to be in range of 90.77-94.68% and 56.21-81.77%, respectively for the aqueous stirring speed of 100-300rpm. Even though high aqueous stirring speed of 300rpm was found to contribute to membrane entrainment, the utilization of membrane stirring was found to reduce the entrainment by reducing the necessity of high aqueous stirring speed while maintaining the performance.

An optimization study to fine-tune these stirring speeds was conducted at the feed phase pH of ≈6.5, 300ppm feed concentration and 0.5M NaOH concentration as their effects were minimized under this condition. The results showed that a stable ionic liquid membrane with the best extraction and stripping efficiencies of 96.21% and 98.10%, respectively was achieved at the membrane stirring speed of 135rpm and the aqueous stirring speed of 255rpm without any membrane entrainment. This shows that ionic liquid membrane based on [Bmim][NTf_2] can achieve reasonably high phenol extraction and stripping efficiencies.

The performance of [Bmim][NTf_2] based BILM was compared with the organic membrane solvents, namely dichloromethane and kerosene. In terms of extraction and stripping efficiencies, [Bmim][NTf_2] showed better performance than kerosene while it was comparable to dichloromethane. Furthermore, [Bmim][NTf_2] also showed higher solvent recovery of 91.52% in comparison to 80.24% of dichloromethane. Hence, [Bmim][NTf_2] emerged as a better choice as it provided higher phenol extraction and stripping efficiencies with higher solvent recovery in comparison to dichloromethane and kerosene.

6.2 Recommendations for Future Studies

The work described earlier emphasizes the appropriateness of BILM system in determining the role of ionic liquids in phenol transport and [Bmim][NTf_2] has proven to be a stable liquid membrane. However, the high membrane thickness and the requirement for large amount of [Bmim][NTf_2] restrict its application due to high cost of [Bmim][NTf_2]. This points to the fact that there is an urgent need for investigation on other membrane modules that require lesser amount of membrane solvent. Membrane configuration such as supported liquid membrane and hollow fiber contactor should be investigated, especially in the context of extraction duration, operability and efficiency. Further, there is a need for the incorporation of a cooling/heating jacket on the membrane reactor such that the effect of temperature on the ionic liquid membrane can be investigated. The current design for the membrane reactor which features hotplate heating device is not suitable as it cannot give a stable temperature during operation.

The present investigation revealed that the parameters such as hydrogen bond basicity strength and mutual solubility with water (hydrophobicity) are important for ionic liquid membranes in phenol removal as they govern the efficiency of BILM and ionic liquid recovery. Even though the ionic liquids tested show better solvent recovery in comparison to the organic membrane solvents, the loss of ionic liquids is significant. This not only increases the consumption of the ionic liquids in the system, but also increases the risk of pollution to the aquatic environment. Taking into consideration of factors mentioned above, it is therefore necessary to emphasize the importance of synthesizing new ionic liquids which have the favourable characteristics such as high hydrogen bond basicity, high hydrophobicity, low cost and are environmental friendly.

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Appendix A: Determination of Phenol/Sodium Phenolate Concentration

Appendix A.1 Relationship between Absorbance and Concentration

Phenol/sodium phenolate concentration can be calculated from the samples' absorbances that are obtained from the UV-analysis. From Figure A.1, the relationship between phenol concentration and absorbance of a sample can be represented by a linear equation, as shown in Equation (A.1):

$$A_1^{'} = 0.0148 C_f \tag{A.1}$$

where $A_1^{'}$ is the phenol absorbance and C_f is the corresponding phenol concentration. For sodium phenolate, a correlation can be also established from Figure A.2, as shown in Equation (A.2):

$$A_2^{'} = 0.0209 C_s^{Ph} \tag{A.2}$$

where $A_2^{'}$ is the absorbance for sodium phenolate and C_s^{Ph} is the sodium phenolate concentration.

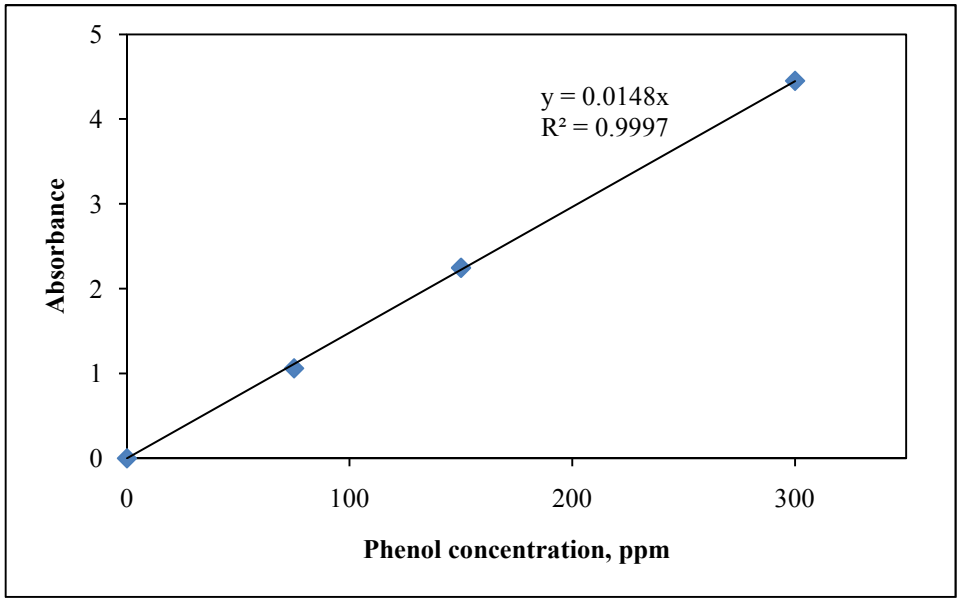

Figure A.1: Example of calibration curve for phenol concentration

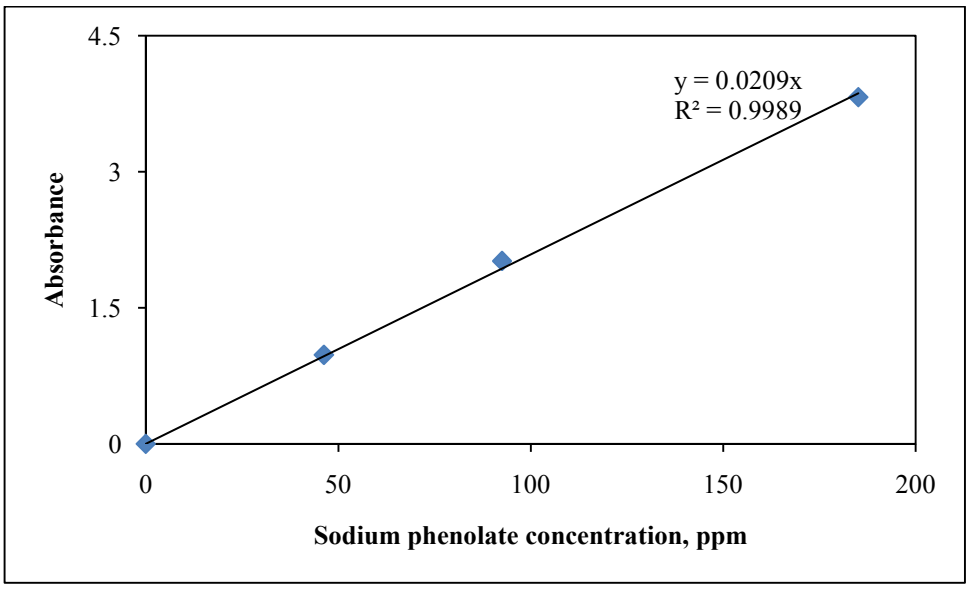

Figure A.2: Example of calibration curve for sodium phenolate concentration

Appendix A.2 Determination of the Extraction Efficiency

Extraction efficiency was determined in both liquid-liquid extraction and bulk liquid membrane experiments. The extraction efficiency was calculated based on the phenol concentration that was present in the samples using Equation (A.1).

However, due to the maximum detectable absorbance by UV-Spectrophotometer SECOMAM UviLine 9400, a dilution on the samples before the absorbance measurement is necessary. Hence, Equation (A.1) was modified into Equation (A.3) where DF is the dilution factor.

$$A_1^{'} = 0.0148\left(\frac{C_f}{DF}\right) \tag{A.3}$$

Rearranging Equation (A.3), phenol concentration can be determined as a function of sample's absorbance, as shown in Equation (A.4).

$$C_f = \frac{A_1^{'}(DF)}{0.0148} \tag{A.4}$$

From the phenol concentration obtained, extraction efficiency was determined by utilizing Equation (A.5).

$$\text{Extraction Efficiency},\% = \frac{C_{f,0} - C_{f,t}}{C_{f,0}} \times 100 \tag{A.5}$$

where $C_{f,0}$ is the initial phenol concentration and $C_{f,t}$ is the concentration at the sampling time, t.

Appendix A.3 Determination of the Stripping Efficiency

Stripping efficiency was calculated for bulk liquid membrane experiments only. By taking into consideration the dilution, Equation (A.2) was modified, as shown in Equation (A.6).

$$A_2^{'} = 0.0209\left(\frac{C_s^{Ph}}{DF}\right) \tag{A.6}$$

Rearranging Equation (A.6),

$$C_s^{Ph} = \frac{A_2^{'}\left(DF\right)}{0.0209} \tag{A.7}$$

From the sodium phenolate concentration obtained, the amount of theoretical phenol in the stripping sample was calculated by utilizing the mole balance where 1 mol of sodium phenolate is equivalent to 1 mol of phenol, as shown in Equation (A.8).

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \tag{A.8}$$

The molecular masses for phenol and sodium phenolate are 94g/mol and 116g/mol, respectively. Hence, the theoretical phenol concentration in the stripping phase, C_s can be calculated by:

$$C_s = \frac{A_2^{'}\left(DF\right)}{0.0209}\left(\frac{94}{116}\right) \tag{A.9}$$

Stripping efficiency is defined as the percentage of phenol that is extracted from the membrane phase, as shown in Equation (A.10);

$$\text{Stripping Efficiency},\% = \frac{C_{s,t}}{C_{f,0} - C_{f,t}} \times 100 \qquad \text{(A.10)}$$

where $C_{s,t}$ is the concentration of phenol in the stripping phase at time t.

Appendix B: Transport Kinetics Modeling

Appendix B.1: m-file for Phenol Transport in BILM

```
function k=model2(t,y)

clc

global k1 k2 k3 k4 n o p q;
% Key in Experimental data

t = [0 30 60 90 120 180 240 300]';    % Sampling time for the
experiments

feed_real=[292.57 153.72 88.18 56.76 40.88 28.89 23.31 22.80]';        %
phenol concentration in feed phase
membrane_real=[0 288.47 378.47 387.34 370.07 303.98 244.40 180.38]';   %
phenol concentration in membrane phase
stripping_real=[0 22.88 52.05 79.87 102.07 141.91 172.05 199.10]';     %
phenol concentration in stripping phase


k1=[0.0150: 0.0002: 0.0200];  % Estimate kinetics for extraction, K1
k2=[0.0010: 0.0002: 0.0030];  % Estimate kinetics for back extraction,
K-1
k3=[0.0010: 0.0002: 0.0050];  % Estimate kinetics for stripping, K2
k4=[0.0000: 0.0002: 0.0000];  % Estimate kinetics for back stripping,
K-2

%loop

for n=1:numel(k1);
    for o=1:numel(k2);
        for p=1:numel(k3);
            for q=1:numel(k4);

                [T,Y]=ode45(@BLM2,t,[292.57 0 0]);

% Curve Fitting R square Calculation

                SSR(:,1)=sum((feed_real(:,1)-Y(:,1)).^2);
                SSR(:,2)=sum((membrane_real(:,1)-Y(:,2)).^2);
                SSR(:,3)=sum((stripping_real(:,1)-Y(:,3)).^2);

                mean1=(sum(feed_real)/numel(feed_real));
                mean2=sum(membrane_real)/numel(membrane_real);
                mean3=sum(stripping_real)/numel(stripping_real);

                m1=mean1*ones(8,1);
                m2=mean2*ones(8,1);
                m3=mean3*ones(8,1);

                SST(:,1)=sum((feed_real(:,1)-m1).^2);
                SST(:,2)=sum((membrane_real(:,1)-m2).^2);
                SST(:,3)=sum((stripping_real(:,1)-m3).^2);

% R square Calculation

                R2(:,1)=1-(SSR(:,1)/SST(:,1));
```

```
                R2(:,2)=1-(SSR(:,2)/SST(:,2));
                R2(:,3)=1-(SSR(:,3)/SST(:,3));
                R2(:,4)=1.;


                if R2>[0.99 0.99 0.99 0];
                    k=[k1(1,n) k2(1,o) k3(1,p) k4(1,q)];
                    A=[k; R2]'
            end
             end
        end
    end
end
```

Appendix B.2: m-file for the ODEs for Phenol Transport in BILM

```
function dy=BLM2(t,y)

global k1 k2 k3 k4 n o p q;

dy=zeros(3,1);
dy(1)=-k1(1,n)*y(1)+k2(1,o)*y(2);
dy(2)=(2.5)*(k1(1,n)*y(1)-k2(1,o)*y(2)-k3(1,p)*y(2)+k4(1,q)*y(3));
dy(3)=k3(1,p)*y(2)-k4(1,q)*y(3);

% y(1) is phenol concentration in the feed phase
% y(2) is phenol concentration in the membrane phase
% y(3) is phenol concentration in the stripping phase
```

Appendix C: Goodness of Fit

Appendix C.1: pH

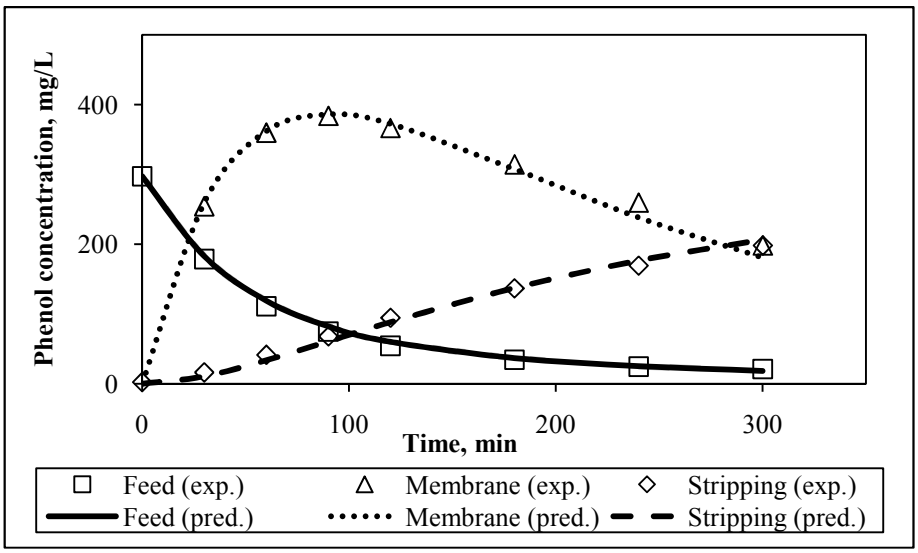

Figure C.1: Goodness of fit for pH 1.13 experiment

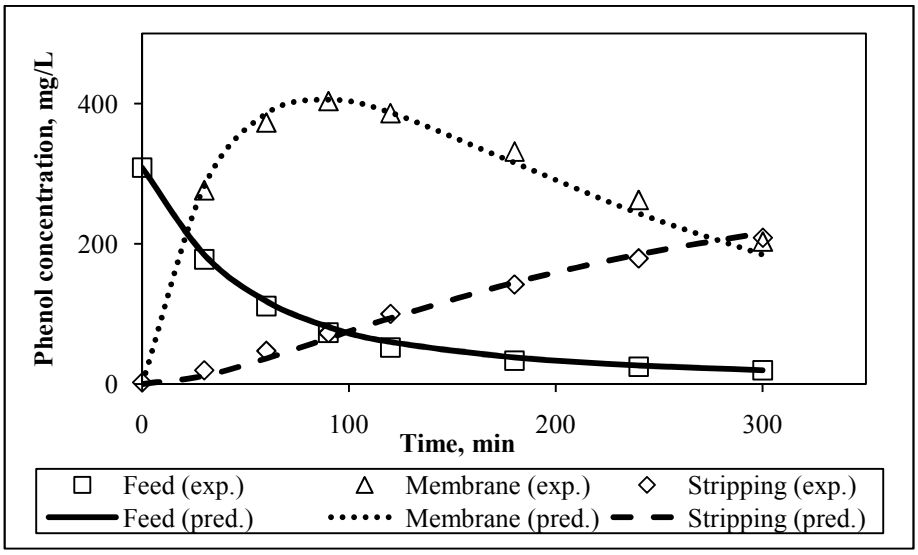

Figure C.2: Goodness of fit for pH 3.04 experiment

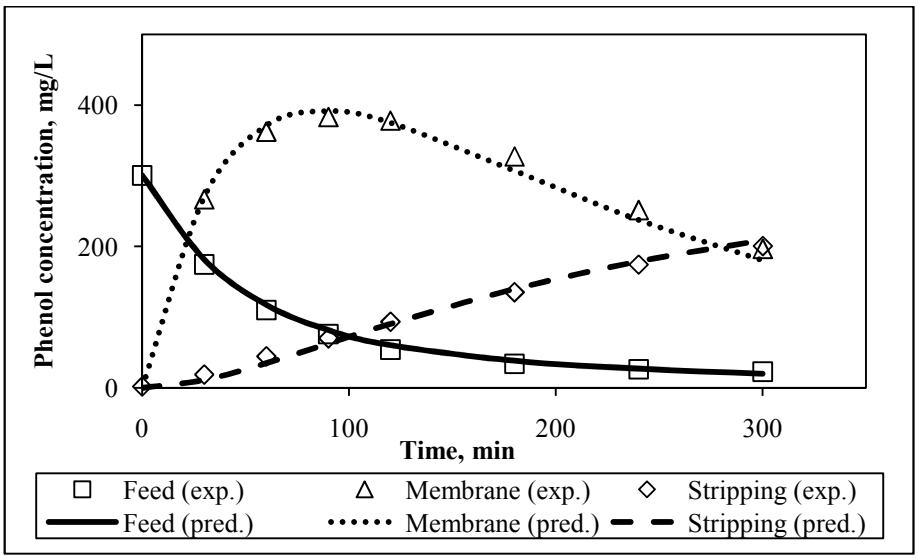

Figure C.3: Goodness of fit for pH 5.12 experiment

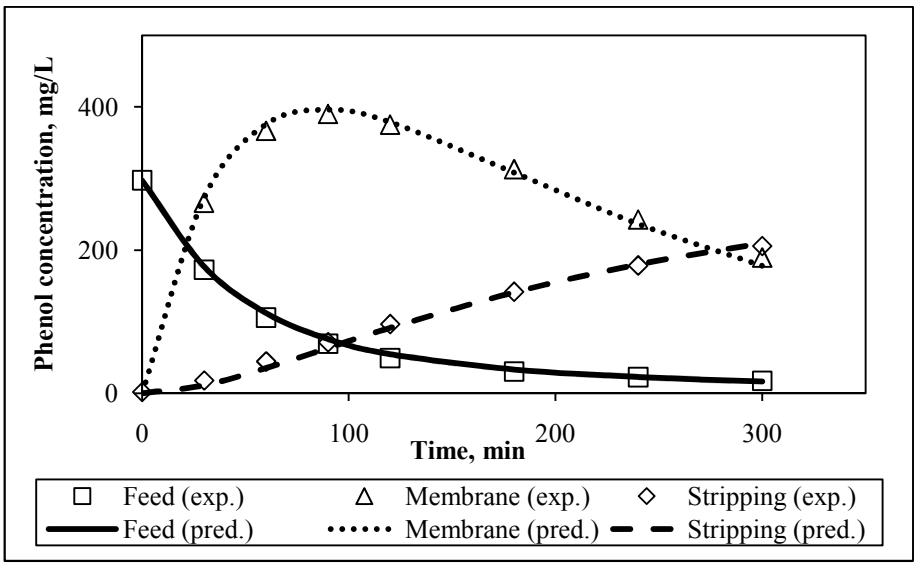

Figure C.4: Goodness of fit for pH 6.56 experiment

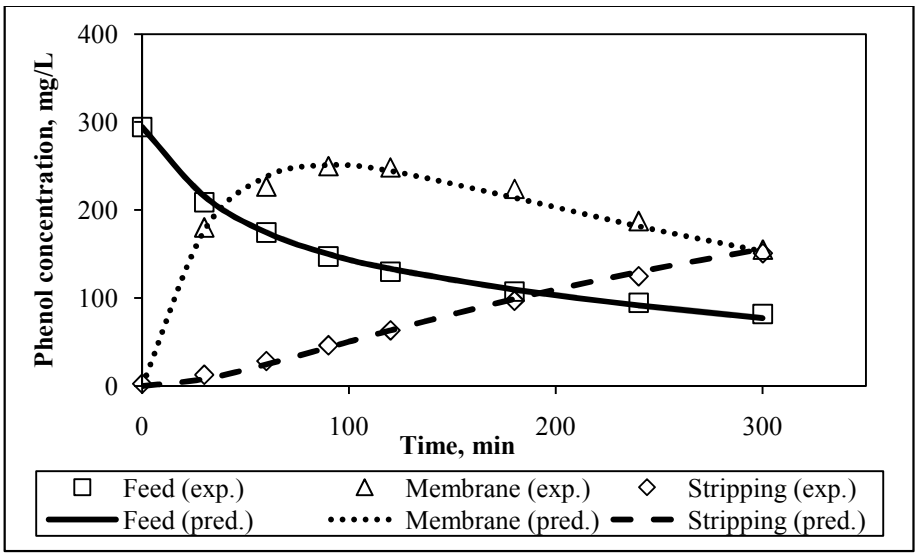

Figure C.5: Goodness of fit for pH 9.23 experiment

Appendix C.2: Feed Concentration

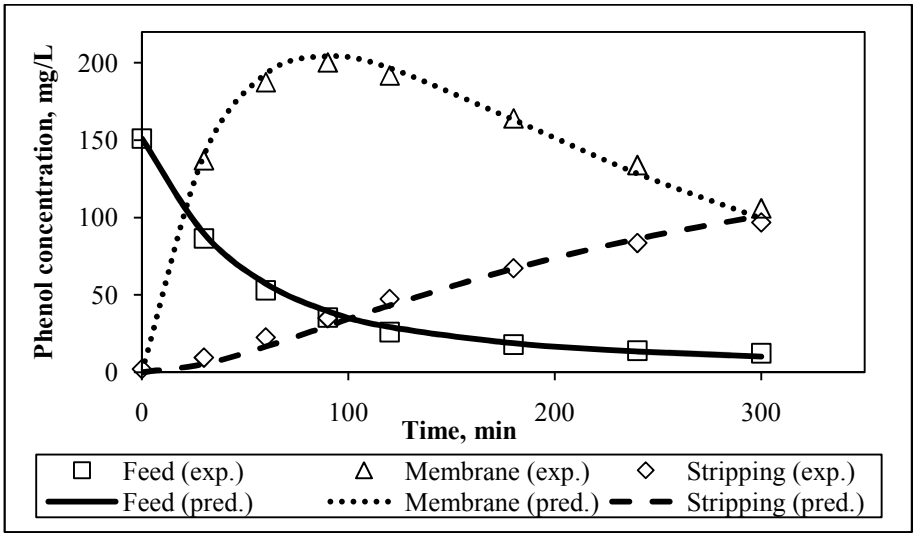

Figure C.6: Goodness of fit for 150ppm experiment

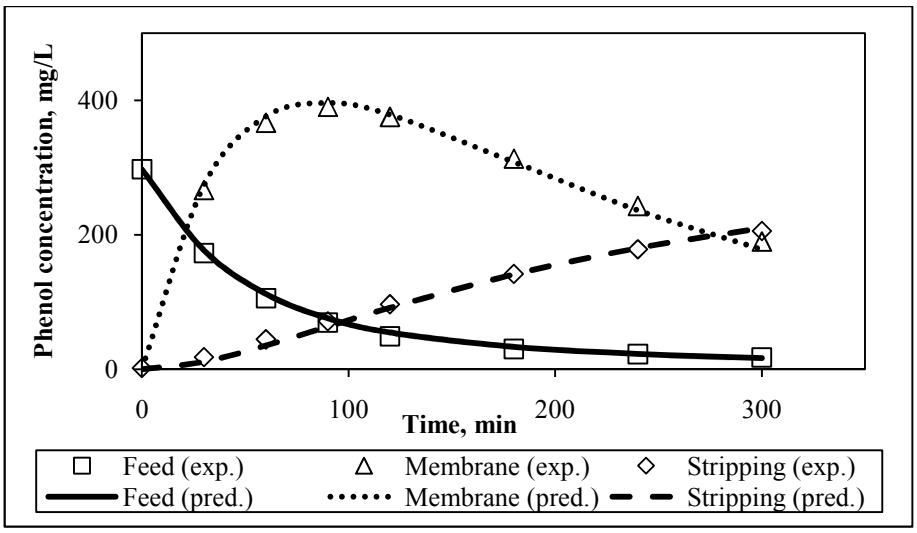

Figure C.7: Goodness of fit for 300ppm experiment

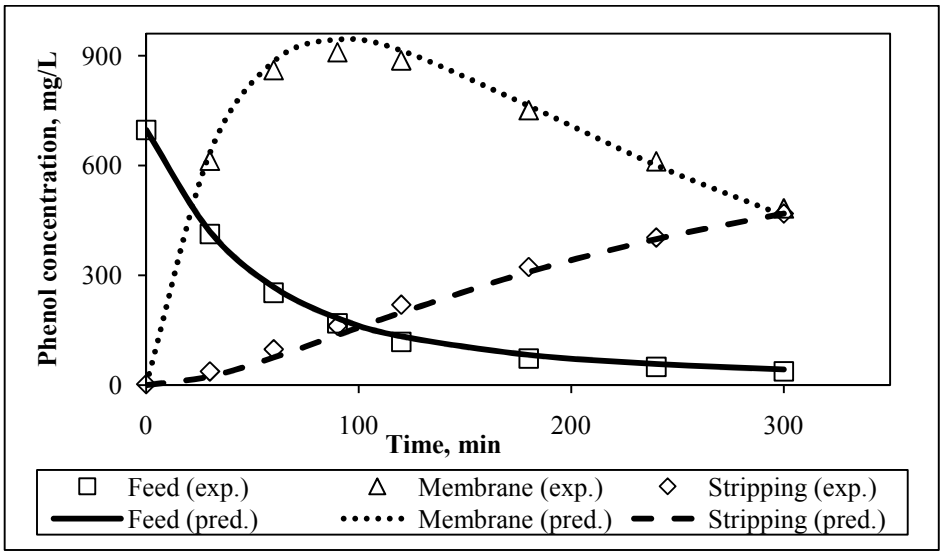

Figure C.8: Goodness of fit for 700ppm experiment

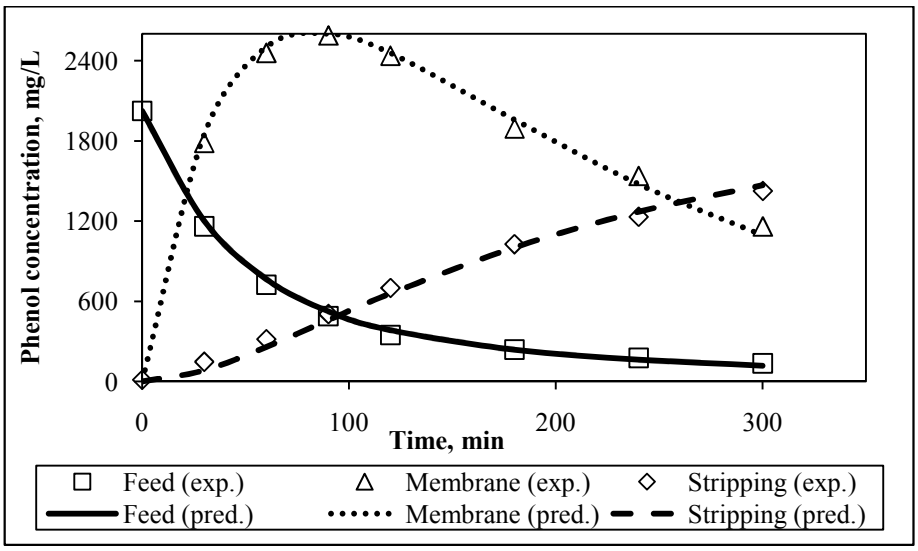

Figure C.9: Goodness of fit for 2000ppm experiment

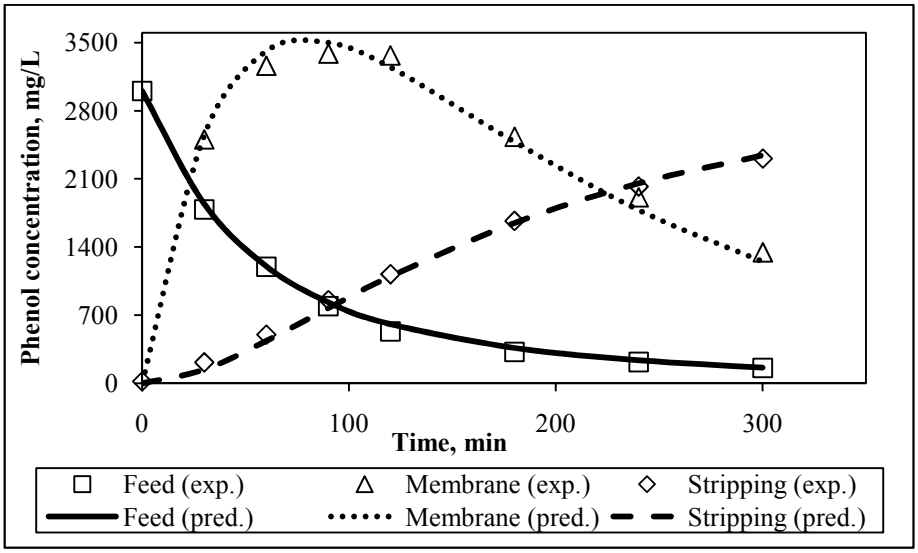

Figure C.10: Goodness of fit for 3000ppm experiment

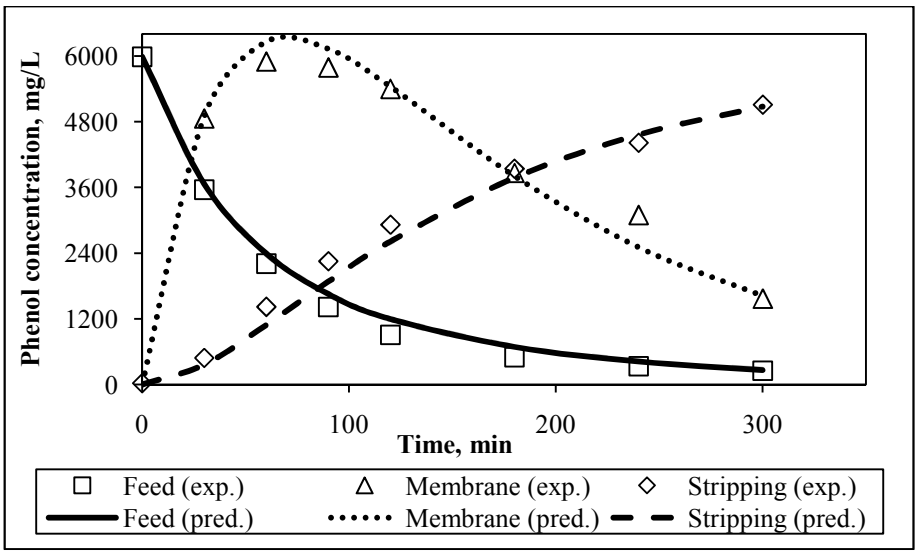

Figure C.11: Goodness of fit for 6000ppm experiment

Appendix C.3: NaOH Concentration

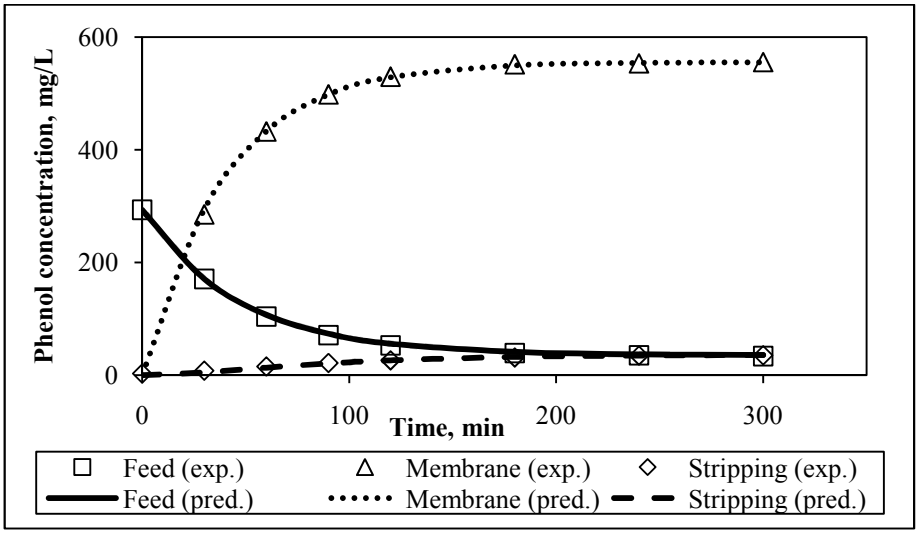

Figure C.12: Goodness of fit for 0M NaOH experiment

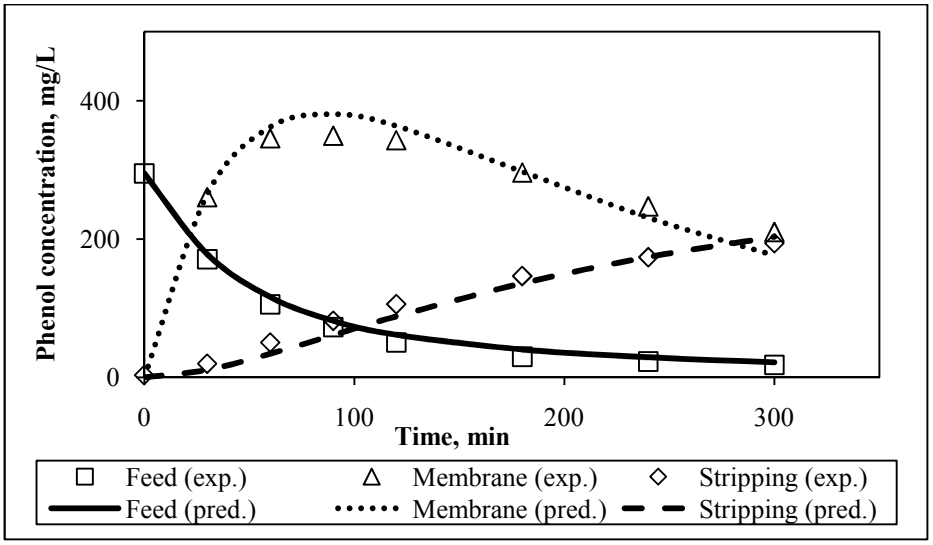

Figure C.13: Goodness of fit for 0.05M NaOH experiment

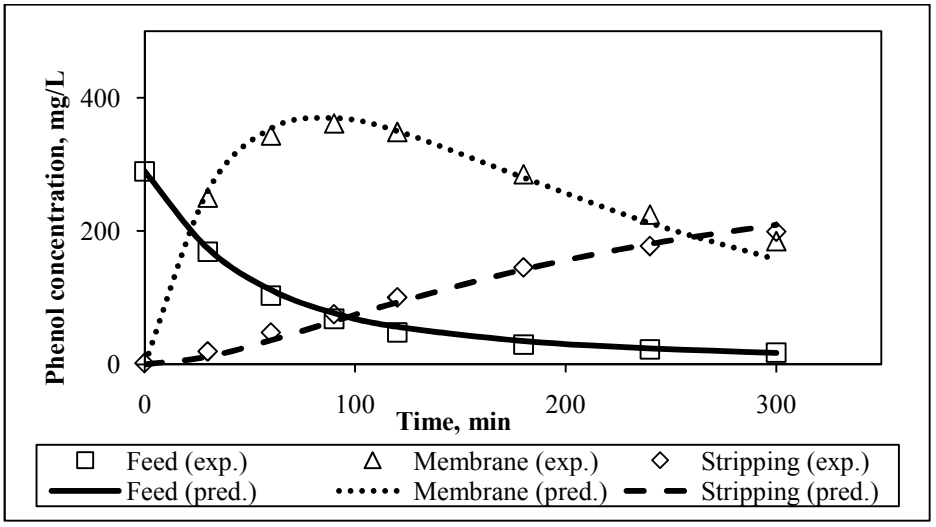

Figure C.14: Goodness of fit for 0.1M NaOH experiment

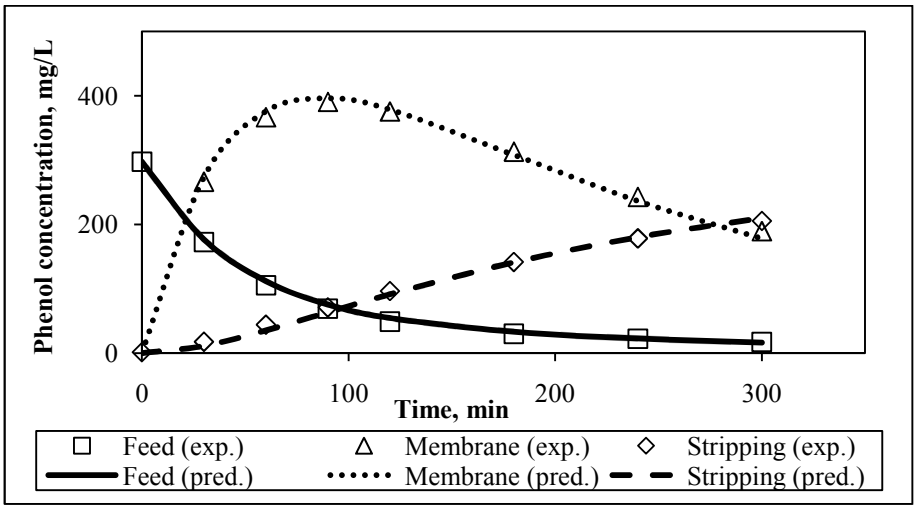

Figure C.15: Goodness of fit for 0.5M NaOH experiment

Appendix C.4: Stirring Speeds

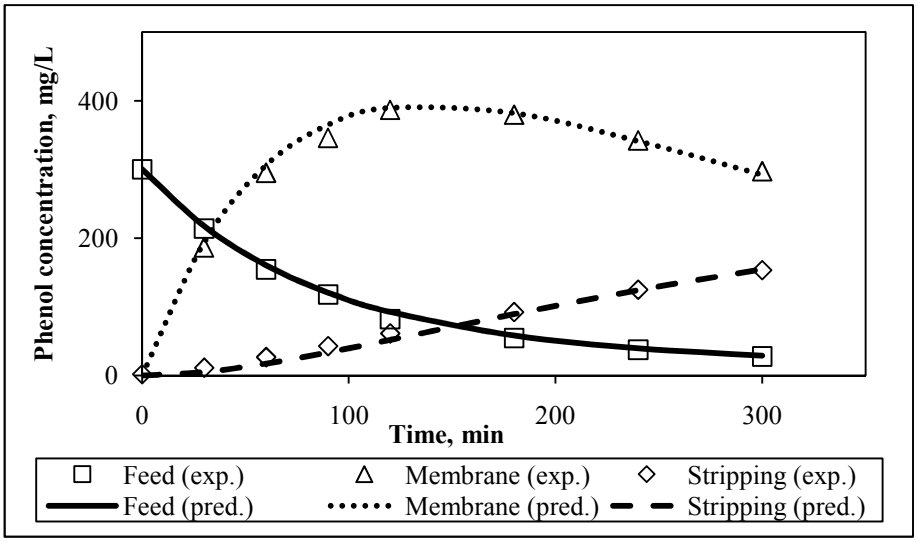

Figure C.16: Goodness of fit for 100rpm (s) experiment

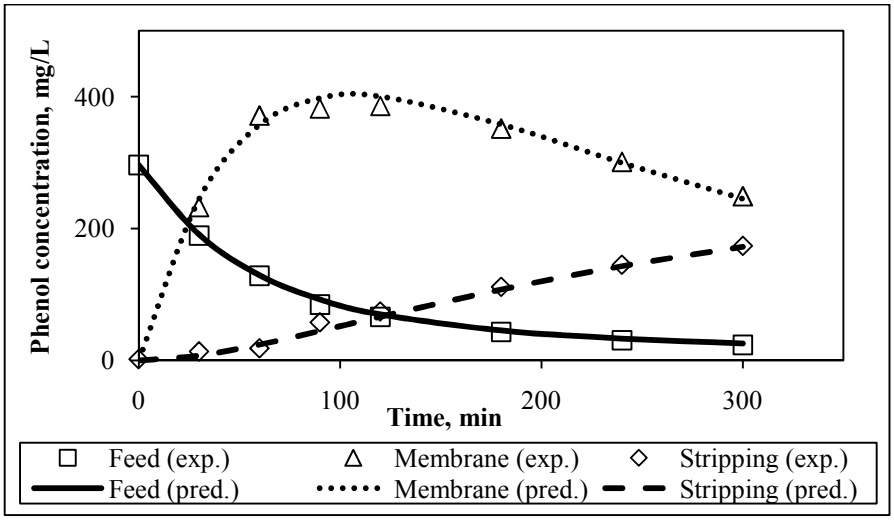

Figure C.17: Goodness of fit for 150rpm (s) experiment

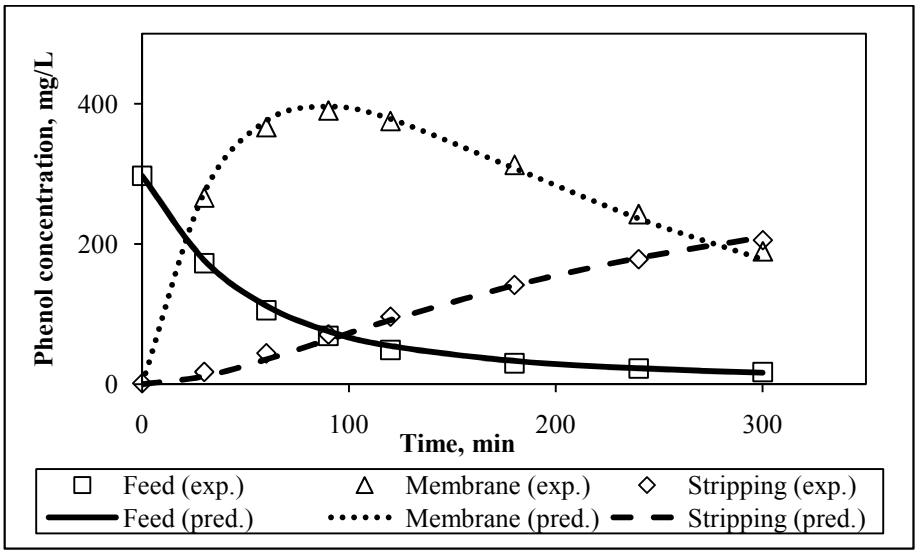

Figure C.18: Goodness of fit for 200rpm (s) experiment

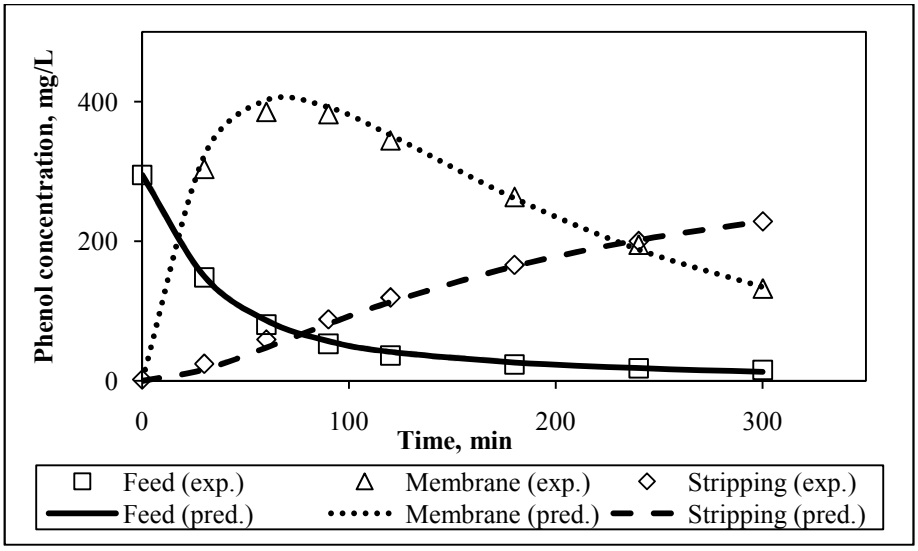

Figure C.19: Goodness of fit for 300rpm (s) experiment

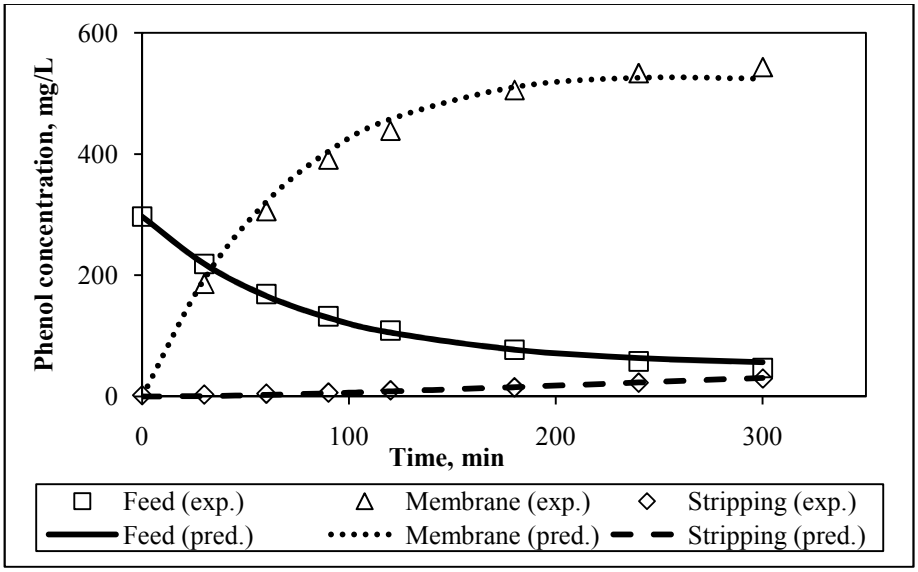

Figure C.20: Goodness of fit for 100rpm (-) experiment

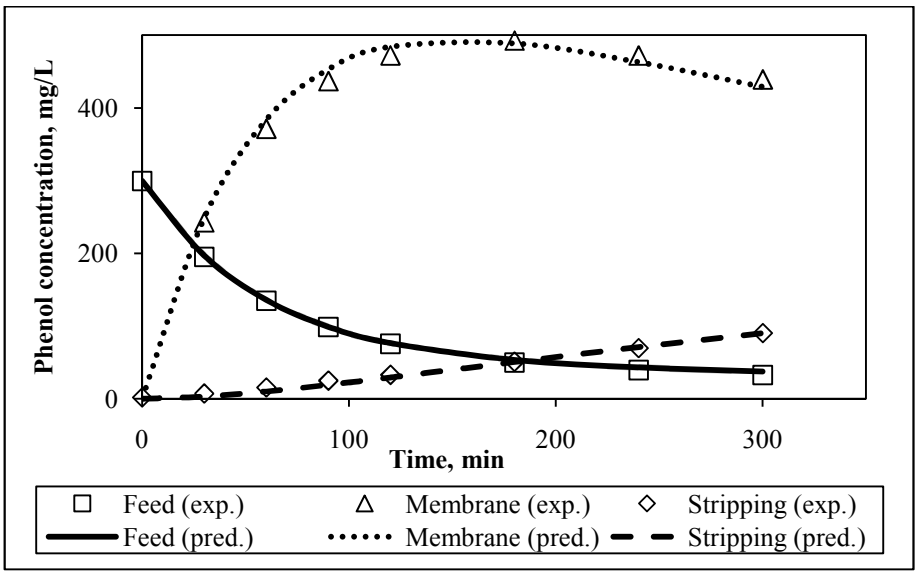

Figure C.21: Goodness of fit for 150rpm (-) experiment

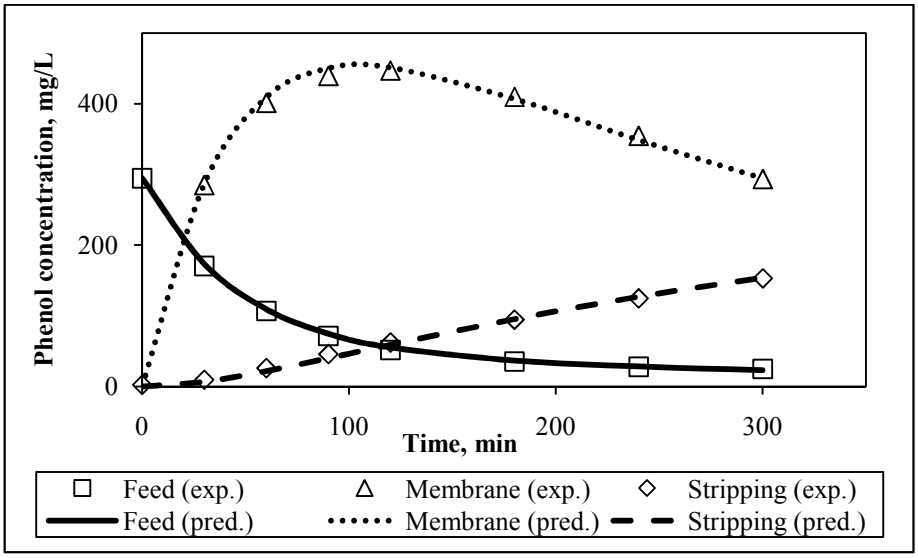

Figure C.22: Goodness of fit for 200rpm (-) experiment

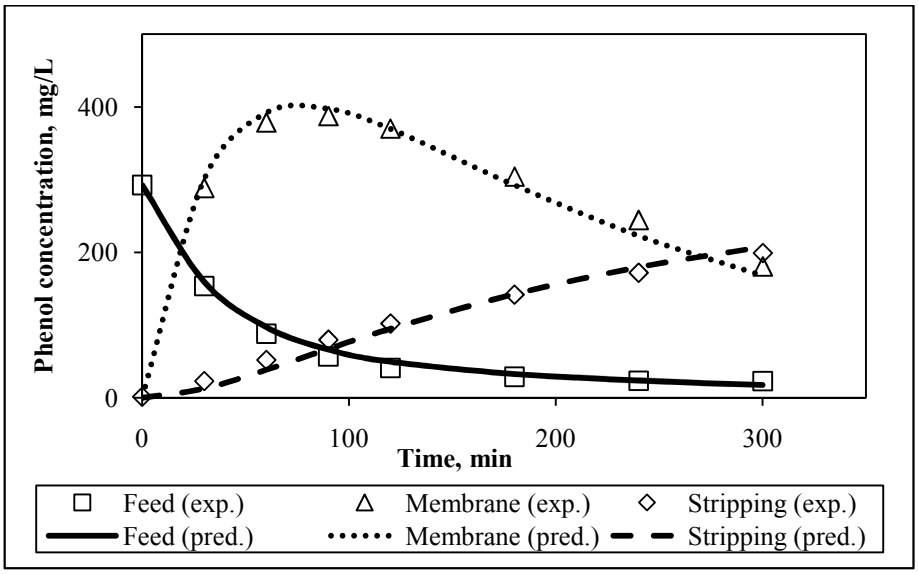

Figure C.23: Goodness of fit for 300rpm (-) experiment