REMOVAL OF PHENOL FROM WATER USING HYDROPHOBIC EUTECTIC SOLVENTS

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Chemical
Engineering with Honours**

**Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman**

May 2023

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"REMOVAL OF PHENOL FROM WATER USING HYDROPHOBIC EUTECTIC SOLVENTS"** was prepared by **KEK MING XUAN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Chemical Engineering with Honours at Universiti Tunku Abdul Rahman.

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ABSTRACT

Phenolic compounds are one of the major pollutants in industrial wastewater. Conventionally, organic solvents, which are normally toxic, highly flammable, and have high vapour pressure, are used in the liquid-liquid extraction process to remove phenolic compounds in industry. A green solvent must be developed to replace such organic solvents due to their unsustainability. The present study focuses on the synthesis of menthol-based hydrophobic eutectic solvents and determines their efficiency in phenol removal. Different types of hydrophobic eutectic solvents were synthesized using lauric acid, myristic acid, and palmitic acid as hydrogen bond donors and selected to perform liquid-liquid extraction to remove phenol from water based on their stability. Operating parameters such as initial phenol solution concentration, stirring speed, and solvent-to-solution ratio were examined to analyse their effect on the performance of the solvents. The phenol uptake capacity of the solvents was also determined by performing five cycles of liquid-liquid extraction using the same batch of solvents. From the study, it was found that the hydrophobic eutectic solvents formed with a menthol-to-lauric acid molar ratio of 2:1 (MLA) and a menthol-to-myristic acid molar ratio of 4:1 (MMA) were stable when added to water. MMA generally performed better than MLA, where removal efficiency of 63.68 % and 59.86 % was recorded respectively when 1 g of solvent was used under an initial phenol solution concentration of 2500 ppm with a 700 rpm stirring speed provided. Besides, the removal efficiency dropped slightly when the initial phenol concentration increased from 500 ppm to 2500 ppm. There was also no significant effect recorded when the stirring speed increased from 300 rpm to 1200 rpm. The removal increased drastically when the amount of solvent used increased from 0.1 g to 2 g, from around 10 % to 75 %. It was found that the MMA has a higher capacity of 42.40 mg/g compared to the MLA, which has a capacity of 33.43 mg/g. Several suggestions were made for future studies to help develop hydrophobic eutectic solvents to replace conventional organic solvents.

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LIST OF SYMBOLS / ABBREVIATIONS

Cat^+	cation
X^-	anion
Y	Lewis or Brønsted acid
z	Number of molecules Y
EE	phenol removal efficiency, %
C_0	initial phenol concentration in phenol solution, ppm
C	final phenol concentration in phenol solution, ppm
U	phenol uptake, mg/g
m	mass of solvent used, g
M	molar mass, mol/g
n	number of mol, mol
x	molar ratio of HBD
y	molar ratio of HBA
A_η	Adjustable Parameter, mPas
B_η	Adjustable Parameter, K
C_η	Adjustable Parameter, K
T	Temperature, K
η	viscosity, mPas

LLX	liquid-liquid extraction
DES	deep eutectic solvent
HDES	hydrophobic deep eutectic solvent
HES	hydrophobic eutectic solvent
POPs	persistent organic pollutants
MLA	Menthol-Lauric Acid HES at 2:1 molar ratio
MMA	Menthol-Myristic Acid HES
MPA	Menthol-Palmitic Acid HES at 12:1 moar ratio
S:S	solvent-to-solution ratio
HBD	hydrogen bond donor
HBA	hydrogen bond acceptor

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Towards the Fourth Industrial Revolution, the world is facing a rapid industrialization process. Although the COVID-19 pandemic started in 2019 somehow slowed down the process, the growth is still considerably high. A huge bounce back in industrial growth is reported at the latter stage of the pandemic in 2021 (United Nations Industrial Development Organization, 2022). Such growth had brought along the issue of pollution. Koncagül, et al. (2021) reported that 80 % of industrial wastewater is released into the environment without treatment. This caused the crisis of water scarcity globally.

In Malaysia, water pollution is also a huge problem faced. Water supply is affected due to the pollution of rivers (The Straits Times, 2020). It is also reported that 229 rivers in Malaysia are polluted (Seong Wei and Tze Yong, 2021). Organic contamination is one of the pollutants faced. Although several organic pollutants might be biodegradable, they should not be ignored. This is because most of the pollutants are highly toxic and could cause death even in a trace amount. Phenolic compounds are one of the examples. Several phenolic compounds are even classified as persistent organic pollutants (POPs) which are not biodegradable and may cause bioaccumulation in living organisms. Thus, it is important to have a proper treatment process in the industry before releasing the industrial effluent.

Several methods can be used in the treatment process of organic contaminants, especially phenolic compounds. These methods are membrane separation, adsorption and ozonation. However, these methods are either having a high operation and utility cost or having lower efficiency. In contrast, liquid-liquid extraction is a better option and an effective way to treat industrial effluent with concentrated organic pollutants. Conventionally, the solvent used in liquid-liquid extraction is various types of organic solvents such as benzene which is highly volatile and flammable (Seader, Henley and Roper, 2016). This might cause secondary pollution. Recently, a novel solvent, namely, hydrophobic deep eutectic solvent had been successfully synthesized (van Osch, et al., 2015) and had proven to be effective in organic pollutants extraction (Sas, et al., 2019). Such solvent draws interest from researchers due to its low volatility and flammability properties and thus is considered a greener option for liquid-liquid extraction solvent.

1.2 Importance of the Study

In this study, the effectiveness of hydrophobic eutectic solvents in phenol removal from wastewater was investigated. Different types of solvents are synthesized using menthol as the hydrogen bond acceptor and various types of fatty acids as the hydrogen bond donor. The synthesized hydrophobic eutectic solvents will be used in liquid-liquid extraction. The removal efficiency is determined at different phenol solution concentrations, stirring speeds, and solvent-to-solution ratios. This can help in determining the optimum operational condition that gives the best removal efficiency. The result may serve as the starting point for future wastewater treatment plant design research if liquid-liquid extraction is implemented. With a successful result, it is believed this technology can replace the current organic solvent used in industry, leading to a more sustainable future. This could be a huge step towards achieving the United Nations Sustainable Development Goals.

1.3 Problem Statement

Phenol and its family are found in the effluent of most industries. Although natural phenol itself is biodegradable, serious consequences can be caused at low concentrations due to its toxicity. Several types of phenol compounds are listed as persistent organic pollutants which are not biodegradable.

For the industry effluent, referring to Standard A, the maximum allowable discharge for phenol is 0.001 mg/L while the maximum allowable discharge of phenol for Standard B is 1.0 mg/L (Department of Environment Malaysia, 2009). Thus, to comply with the regulation, the treatment of wastewater is always required. Liquid-liquid extraction is one of the most promising methods of removing organic compounds. However, the conventional organic solvent used is classified to be not green and sustainable due to the properties of high volatility and flammability. This will be an obstacle in achieving the United Nations Sustainable Development Goals in 2030. Therefore, there is a need to develop a greener and more environmentally friendly solvent for the liquid-liquid extraction process.

1.4 Aim and Objectives

The objective of this study is to synthesize stable hydrophobic eutectic solvents and determine the effectiveness of the solvents in phenol removal. The study targeted to achieve the following objectives:

(i) To synthesize hydrophobic eutectic solvents which are stable and not solidified when added to water.
(ii) To investigate the effect of the initial phenol solution concentration, the effect of stirring speed and the effect of solvent-to-solution ratio toward solvents' phenol removal efficiency.
(iii) To investigate the phenol uptake capacity for each of the solvents synthesized.

1.5 Scope of the Study

The present study includes the method to synthesize hydrophobic eutectic solvents using menthol as the hydrogen bond acceptor and fatty acid as the hydrogen bond donor. The synthesized hydrophobic eutectic solvents were used in the liquid-liquid extraction process to investigate their effectiveness in phenol removal. Phenol was chosen as the organic contaminant in this study as it is one of the most common organic contaminants in industrial wastewater. The effectiveness of the hydrophobic eutectic solvents was to be determined. Several parameters effects on phenol removal such as initial phenol solution concentration, stirring speed, and solvent-to-solution ratios were to be investigated. The phenol uptake capacity was also to be investigated.

1.6 Outline of the Report

This study covers three main chapters:

(i) Chapter 1 covers the introduction of background, the importance of the study, the problem statement, aim and scope of the report.

(ii) Chapter 2 covers the literature review from various sources such as journal articles and books related to the research topic. A review of the phenolic wastewater and its hazardous, removal technology of phenol from wastewater had been done. The review also had been done on the novel hydrophobic deep eutectic solvents which can be used in the liquid-liquid extraction process.

(iii) Chapter 3 lists the materials and equipment required to carry out the research. The method of the research is also discussed as well as the calculation method for the removal efficiency.

(iv) Chapter 4 covers the result of hydrophobic eutectic solvents synthesis, results of parametric studies, solvents' phenol uptake capacity studies as well as the literature comparison of various types of solvents.

(v) Chapter 5 highlights the key findings in the study, provides the conclusion of the study and provides several recommendations on improvement for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, a literature review on organic containments had been carried out. The targeted containment which is the phenol has also been reviewed. It was found that phenol is widely used in the industry and is a valuable product. As phenol is listed as one type of scheduled waste, it is highly hazardous and wastewater containing phenol should be treated before releasing it into the environment. The separation methods of phenol from the water had been reviewed and it was found that liquid-liquid extraction is the most suitable method. To solve the limitation of the liquid-liquid extraction where the volatile toxic solvent was used, a new green solvent, the hydrophobic eutectic solvent was proposed to be used and the literature review had been done.

2.2 The Organic Pollution

Organic substances are a huge group of chemicals that are built up by carbon, hydrogen, oxygen, and several elements such as chlorine (van der Perk, 2014). Normally, the organic pollution in water will be expressed as the biochemical oxygen demand since the organic matter will cause the depletion of oxygen in water (Wen, Schoups and van de Giesen, 2017). In addition, certain organic substances such as phenol and benzene are highly toxic. When such chemicals enter the water, they can cause deadly effects on aquatic life and the ecosystem (van der Perk, 2014). On top of that, such chemicals may also cause certain water-borne diseases (Singh, et al., 2021) via the consumption and bioaccumulation of organic substances throughout the food chain. Organic pollutants will normally be classified through their functioning chemicals and their nature (Singh, et al., 2021). Therefore, the toxicity, persistency and bioaccumulative of organic compounds will be normally used to distinguish their hazards. The groups of different organic pollutants are shown in Figure 2.1.

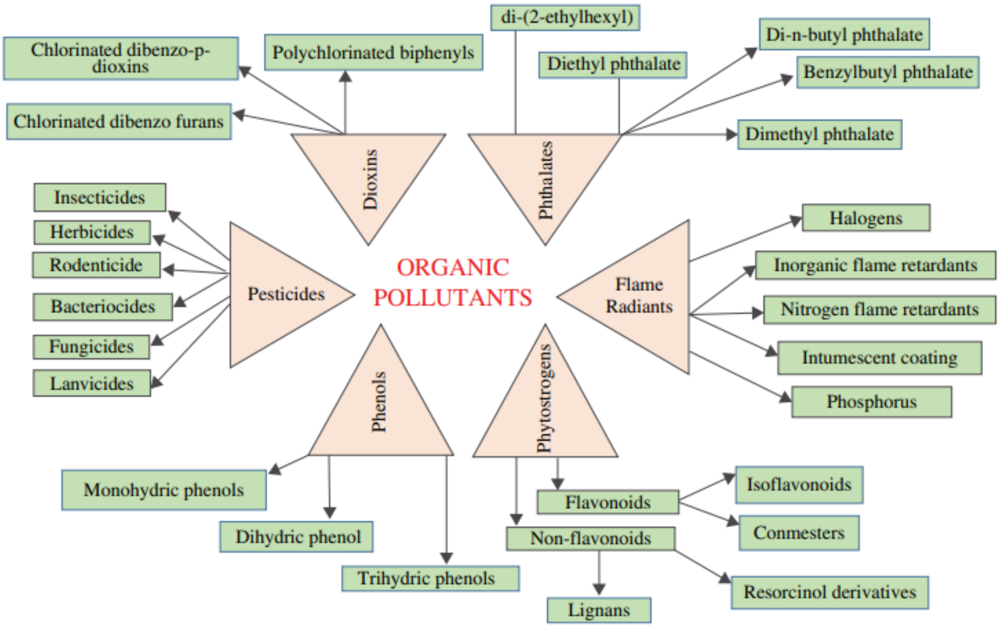

Figure 2.1: Groups of Organic Pollutants (Singh, et al., 2021).

From the report that was released by the European Environment Agency in 2018, it is found that there are 18% of water bodies (19980 water bodies) in 25 European Union countries suffer from organic pollution (Zal, et al., 2018). Also, in the report released by UNESCO in 2021, it was estimated that there are 80 % of municipal and industrial wastewater left untreated before being discharged into the environment (Koncagül, Tran and Connor, 2021). This will be the main reason that organic pollutants enter the water system. According to Wen, Schoups and van de Giesen (2017), this mechanism is called pollution loading.

It is also possible for organic pollutants to enter the water through natural processes such as the degradation process (Wen, Schoups and van de Giesen, 2017). Figure 2.2 shows the mechanisms of organic pollutants entering the environment.

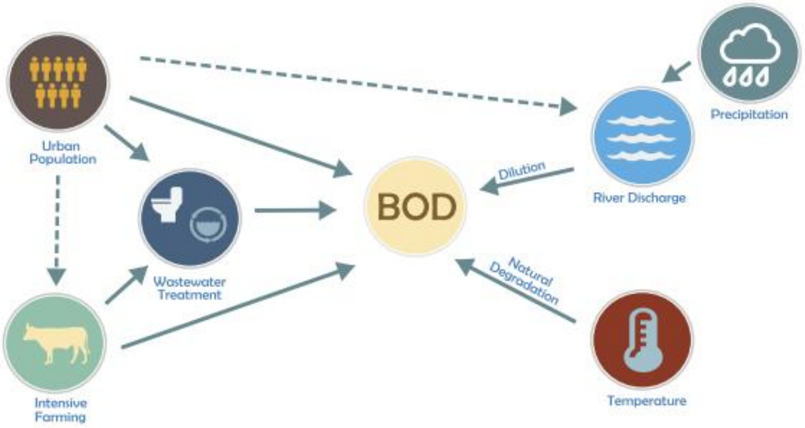

Figure 2.2: Mechanism of Organic Pollution (Wen, Schoups and van de Giesen, 2017)

2.3 Phenol

2.3.1 Background and Properties of Phenol

Phenol is a type of organic substance that has a hydroxyl group attached to aromatic rings such as benzene, as shown in Figure 2.3. At room temperature, pure phenol exists as a white crystalline solid with a sweet and tarry odour (Sabbineni, 2016), as shown in Figure 2.4. Phenol is a soluble organic compound with a water solubility of 80 g/L at room temperature. This is caused by the presence of the hydroxyl group in phenol, allowing phenol to form hydrogen bonds with water, thereby causing phenol to have higher solubility compared to benzene (Carey and Giuliano, 2017). Phenol shows acidic properties when dissolved whereby it is more acidic than alcohol but certainly less acidic than carboxylic acid, having a acid dissociation constant of approximately 10 (Carey and Giuliano, 2017). Table 2.1 summarises the appearance, physical properties and chemical properties of phenol.

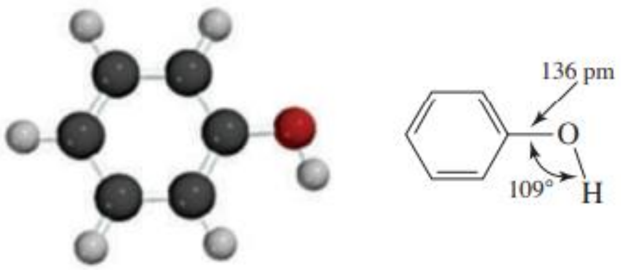

Figure 2.3: Simplest Structure of Phenol (Carey and Giuliano, 2017).

Figure 2.4: The Phenol Crystalline Solid (Sabbineni, 2016).

Table 2.1: Physical and Chemical Properties of Phenol (Mohammadi, et al., 2015)

Physical and Chemical Property	Value	Unit
Molecular Weight	94.11	g/mol
Melting Point	40.91	ºC
Boiling Point	181.75	ºC
Density	1.07	g/cm^3
Vapour Pressure at 25 ºC	0.35	mmHg
Acidity in Water	9.89	-
Solubility in Water at 20 ºC	8.3	g phenol/100 mlH2O
Solubility in Water at 25 ºC	8	g phenol/100 mlH2O
Flash Point	79	ºC

2.3.2 Production and Application of Phenol

Phenol is one of the most valuable chemicals in the world. It is the raw material for most thermoplastic polymers (Mancuso, et al., 2020). It was reported that a global phenol production of 7.82 million tons/year in 2019 and is estimated to grow to 9.72 million tons/year in 2024 (ECHEMI, 2020). This had been supported by Xie, et al. (2020) where an annual phenol production of more than 6 million tons was estimated.

Phenol can be produced through the cumene (Hock) process. This process uses benzene and propylene as raw materials, producing phenol and acetone (Mancuso, et al., 2020). Figure 2.5 shows the production scheme of phenol through the cumene process. Almost 95% of phenol production is through this process since the by-product of this process which is acetone is also a valuable chemical (Mancuso, et al., 2020).

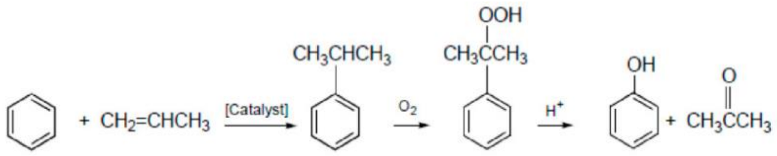

Figure 2.5: The Production Scheme of Phenol (Mancuso, et al., 2020).

Despite being produced as the main product through the cumene process, phenol can also be found as a by-product in several processes such as the coal coking process and combustion of fossil fuels (Mohd, 2022). Therefore, high phenol concentration is always detected in the wastewater produced by the coal conversion industry (Zhang and Wang, 2020). This raises an opportunity to recover the phenol from the wastewater due to the economic value of phenol and to comply with the environmental regulation.

Phenol and its derivatives are always one of the main building blocks of the industry. It is the raw material to produce bisphenol A (BPA) (Altuwair, 2018). The BPA is then used to produce plastic and epoxy resin (Mohamad Said, et al., 2021). The production of phenoxy herbicide is also one of the major applications of phenol (Mohd, 2022). This led to the contribution of phenol pollution by the agriculture sector. Besides, the phenol can also used to produce phenolic resin together with formaldehyde (Mohamad Said, et al., 2021).

2.3.3 Phenol as the Organic Pollutant

Phenol is classified as one of the major pollutants in the environment (Mohamad Said, et al., 2021) due to its highly toxic properties which will cause serious consequences to the environment. Besides the standard phenol itself, the whole group of phenolic compounds are hazardous organic substances due to their toxicity and persistency. Studies had found that several types of phenolic compounds such as pentachlorophenol had a very long half-life and had been listed as POPs in the Stockholm Convention (United Nations, 2019). Table 2.2 shows the phenol concentration reported in different industries.

Table 2.2: List of Typical Phenol Concentration in Industry Effluent

Industry	Wastewater Phenol concentration mg/L	Location	Reference
Steel	50 – 200	Iran	(Malakootian and Heidari, 2018)
Coking	370	Brazil	(Gracioso, et al., 2019)
Pulp and Paper	423 - 759	India	(Sharma, Iqbal and Chandra, 2022)
Phenolic Resin	47.6 – 279.5	-	(Gutiérrez, Urtiaga and Ortiz, 2010)
Fabric and Textile	7.85	South Sumatra	(Rusdianasari, Hajar and Ariyanti, 2019)
Pharmaceutical	21.2 – 69	Egypt	(Badawy, Wahaab and El-Kalliny, 2009)
Petroleum Refinery	94	Iraq	(Farhod Chasib, 2013)
Palm Oil Mill Effluent	1500	Thailand	(Chantho, Musikavong and Suttinun, 2016)
Coal Conversion	4300	China	(Zhang and Wang, 2020)

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Phenol-containing wastewater will cause huge problems for human health and the environment if it is directly discharged. Phenol and its derivatives can undergo fast absorption by human skin and mucous membranes in the respiratory system, leading to potential health risks (Gami, et al., 2014). At a high concentration of phenol exposure or intake, death will be the most serious consequence. For example, it was reported that a 27-year-old female died within 10 minutes after the ingestion of 4.8 g of phenol (Chand Meena, Band and Sharma, 2015).

It was stated in the report that the lowest dose that will cause death in humans is 140 mg phenol/kg body weight. According to Mohamad Said, et al. (2021), animal toxicity of phenol is recorded at 9 – 25 mg/L while the toxic level of phenol for humans is around 10 – 24 mg/L. If the phenol concentration in the blood exceeds 150 mg/100ml, it will cause death (Kulkarni and Kaware, 2013). However, this exposure limit is only applicable to standard phenol. Phenol is highly reactive and will tempt it to react with other compounds in the water. For example, phenol will tempt to react with inorganic matter such as chlorine to form a more dangerous and toxic organic compound (Mohamad Said, et al., 2021). Despite being highly toxic, phenol is also a potentially carcinogenic compound (Saputera, et al., 2021). This is mainly due to the ability of the phenols to destruct the red blood cell and liver (Singh, et al., 2021). The carcinogenic effect of phenols in the human body can be triggered at a very low concentration.

Besides, the phenol wastewater discharged into the environment might also affect the aquatic ecosystem. Firstly, an unpleasant taste and odour will be caused by high phenol concentration in water. This amount is typically at 100 μg/L to 1000 μg/L (Gami, et al., 2014). Besides, it was found that phenol can disrupt the growth of fish (Mohamad Said, et al., 2021).

On the other hand, phenol is biodegradable. It has a very low octanol-water partition coefficient of 1.47 and a shorter half-life of 1 to 9 days depending on the water type (ATSDR, 2008). This indicated that the standard phenol might not persist for a long time in the environment and have a lower risk of bioaccumulation. However, the study also found that if the phenol concentration is more than 50 mg/L in water, it has the potential to inhibit the rate of biodegradation (Saputera, et al., 2021). Although it was stated that bioaccumulation of phenol is not significant, several studies found phenols in aquatic species. Sannadurgappa, Ravindranath and Aladakatti (2007) reported that a significant concentration of phenol remained in fish 30 days after the exposure to a sublethal concentration of phenol. Furthermore, Grzelak, Michałowicz and Dukowskab (2012) also reported that there was bioaccumulated phenol (around 27.1 mg/kg) in leeches that grew in the Piasecznica River which is highly polluted by sewage water. This proves that phenol can potentially bioaccumulate in the food chain and might be exposed to humans through ingestion. The toxicology profile resealed by ATSDR (2008) also stated that phenol has the potential to be bioaccumulated through the food chain despite its low octanol-water partition coefficient. Table 2.3 summarizes the toxicity of the phenol.

Due to the toxicity and potential bioaccumulation of phenol, the phenol must be precisely treated before being discharged into the environment. The Department of Environment Malaysia had regulated a standard to control the concentration of phenol in industrial effluent. The phenol discharge is limited to 0.001 mg/L in Standard A which refers to the discharge to the drinking water catchment area (Department of Environment Malaysia, 2009). The phenol discharge to other inland waters is somehow limited to 1.0 mg/L as listed in Standard B (Department of Environment Malaysia, 2009). Besides, phenol and its derivatives have also been listed in the scheduled waste with the code SW 319 (Department of Environment Malaysia, 2005). This means that any liquid or sludge of phenolic compound must be taken care of before it can be discharged.

Table 2.3: Summary of Phenol Toxicity

Toxicity	***Value***	***Unit***	***Reference***
Toxic Level for Human	10 – 24	mg/L	(Mohamad Said, et al., 2021)
Toxic Level for Animal or Fish	9 – 25	mg/L	(Kulkarni and Kaware, 2013)
Lethal Blood Concentration	150	mg/ 100 ml blood	(Kulkarni and Kaware, 2013)
Lethal Dose	140	mg/ kg body weight	(Chand Meena, Band and Sharma, 2015)
Octanol-water partition coefficient	1.47	-	(ATSDR, 2008)
Half-life	1 - 9	days	(ATSDR, 2008)
Inhibition of Biodegradation	50	mg/L	(Saputera, et al., 2021)

2.4 The Removal Method of Phenol from Water

Because of the toxicity and potential bioaccumulation of phenol in the food chain and the serious environmental effect, it must be removed from the industrial effluent. However, phenol removal from wastewater is not an easy task. This is because phenol will form an azeotrope with water. According to Li, et al. (2014), phenol will form an azeotrope at 99.5 ºC. This azeotrope is formed with around 9.2 % of phenol and the rest is water. As the azeotropic temperature is too close to the boiling point of water, which is at 100 ºC, this makes the phenol nearly impossible to be fully separated from water through simple distillation (Li, et al., 2014). Thus, alternatives such as azeotropic distillation must be done. However, the distillation process required high energy consumption due to the condenser and reboiler, leading to high operating costs. Therefore, a separation method other than the distillation process must be utilised to remove phenol from industrial wastewater. To date, several methods had been applied in the industry.

2.4.1 Membrane Separation Process

The membrane separation process will separate a mixture through a semipermeable barrier (Seader, Henley and Roper, 2016). Figure 2.6 shows the schematic diagram of typical membrane separation. Generally, the membrane will be classified according to the separated particle size. A microfiltration membrane can separate particles in sizes ranging from 0.1 µm to 10 µm while ultrafiltration can separate particles with sizes from 2 nm to 100 nm (Haan, Eral and Schuur, 2020). At a particle size of 1nm to 2 nm, the nanofiltration membrane functioned well but when the particle size is less than 1 nm, reverse osmosis must be utilized (Haan, Eral and Schuur, 2020). According to Lorenc-Grabowska (2016), phenol is having a molecular size ranging from 0.46 nm to 0.54 nm and an effective molecular diameter of 0.75 nm. Therefore, reverse osmosis will be a normal practice if the membrane separation method is chosen. The reverse osmosis membrane is usually only permeable to water and an external force will be required to push the water from retentate to permeate,

Several works had reported that membrane filtration can be utilized to remove phenol in wastewater. Sun, et al. (2015) reported that with a combination of ultrafiltration and reverse osmosis process, a 95 % rejection of phenol can be achieved. Khazaali and Kargari (2015) also reported that a 71.7 % rejection can be reached with the low-pressure but highly alkaline reverse osmosis method. On the other hand, the membrane separation process also faces several disadvantages. One of the disadvantages of membrane separation is the fouling problem. In typical industrial wastewater, there are several other pollutants such as ions. These ions may form salts and deposited on the membrane and hence causing the depletion of membrane efficiency (Mnif, et al., 2015) which certainly increases the operational cost. Besides, the requirement of the high operating pressure of 5 bar to 50 bar is another disadvantage of membrane separation (Subha, et al., 2015).

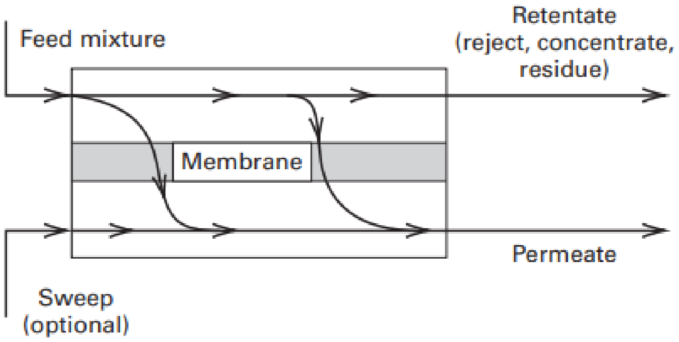

Figure 2.6: The Schematic Diagram of Membrane Separation Process (Seader, Henley and Roper, 2016).

2.4.2 Adsorption Process

The adsorption process is a type of sorption operation where impurities will be selectively transferred to the surface of an insoluble solid (Seader, Henley and Roper, 2016). Figure 2.7 shows the schematic diagram of the adsorption process on a solid adsorbent. During the adsorption process, the targeted impurities are diffused onto the surface and form a bonding with the solid surface (Seader, Henley and Roper, 2016). The adsorbent can be regenerated through the desorption process which is normally an endothermic process (Haan, Eral and Schuur, 2020). Several types of adsorbents are applied in the industry. For example, activated carbon is one of the commercialized hydrophobic adsorbents which is normally used to attract nonpolar molecules (Haan, Eral and Schuur, 2020). Silica gel is an example of a hydrophilic adsorbent where normally used to attract polar molecules (Haan, Eral and Schuur, 2020).

Several literatures reported the utilization of activated carbon as an adsorbent in phenol removal. Xie, et al. (2020) reported that the formation of the donor-acceptor complex between the activated carbon surface and phenol's aromatic ring is the main reason adsorption can occur. Besides, hydrogen bonding is also slightly contributed to the adsorption process of phenol on activated carbon (Xie, et al., 2020). In a study done by Zhang, Huo and Liu (2016), they found that activated carbon can have a maximum adsorption capacity of 144.93 mg/g under optimum conditions and the capacity might be different due to the size of activated carbon. Elbidi, et al. (2021) also found that activated carbon can have phenol removal efficiency of up to 95%. Other than activated carbon, Hamad (2021) reported an 85 % of phenol removal is observed when activated ceramic was used as the adsorbent. However, this separation method may cause several issues. The most serious problem is the possibility of secondary pollution when handling the used adsorbent (Elbidi, et al., 2021). Therefore, if the adsorption is applied in removing phenol, extra cost will be required in handling the contaminated adsorbents.

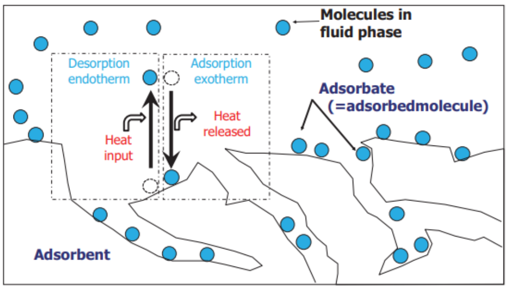

Figure 2.7: The Schematic Diagram of an Adsorption Process on Solid Adsorbent (Haan, Eral and Schuur, 2020).

2.4.3 Ozonation Process

The ozonation process is a removal technology that utilizes strong chemical oxidants such as ozone and hydroxyl radicals (Gottschalk, Libra and Saupe, 2000). In fact, ozone is a chemical that can selectively react with several chemicals including phenols (Saputera, et al., 2021). Two mechanisms are involved in the ozonation process which are the direct and indirect reactions

(Gottschalk, Libra and Saupe, 2000). The direct reaction occurs when the ozone itself reacts with the chemicals while the indirect reaction occurs when the free hydroxyl radicals produced by the ozone react with the contaminants (Gottschalk, Libra and Saupe, 2000). At room temperature, the indirect reaction is more dominant because the ozone decomposition rate will increase with temperature (Wahyudi, Ghaisani and Bismo, 2019). According to the study by Honarmandrad, Javid and Malakootian (2021), phenol will decompose into water and carbon dioxide in the end. Figure 2.8 shows the decomposition of phenol by ozonation through the indirect reaction.

Several works had reported that the ozonation process can be used to remove phenol in water. Honarmandrad, Javid and Malakootian (2021) reported that the ozonation process has 43.5 % removal efficiency at pH 3, but it can be improved to 97.8 % with the involvement of calcium peroxide. According to Wahyudi, Ghaisani and Bismo (2019), ozonation can have a 98.79% phenol removal efficiency. The possible cause of differences in the efficiency is the pH condition whereby Wahyudi, Ghaisani and Bismo (2019) confirmed that ozone solubility and hydroxyl radicals' concentration are lower at lower pH. However, the ozonation process will not allow the recovery of phenol since the phenol will be degraded into water and carbon dioxide. Besides, due to the stability of ozone, an additional ozone production process will be required which will increase the cost (Busca, et al., 2008). The process also has the risk to cause secondary pollution where disinfection by-products might be generated (Saputera, et al., 2021).

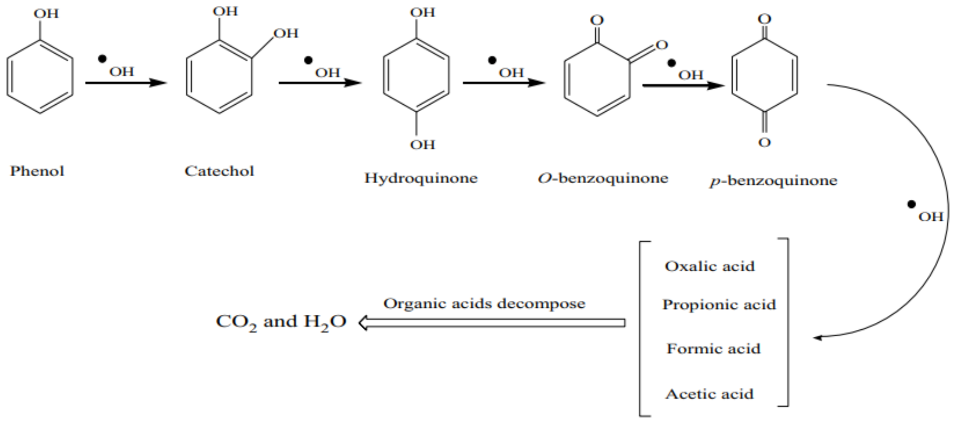

Figure 2.8: The Indirect Ozonation Process (Honarmandrad, Javid and Malakootian, 2021).

2.5 Liquid-Liquid Extraction

Liquid-liquid extraction (LLX) is one of the methods that can be applied to remove phenols from wastewater. Unlike the methods previously discussed, LLX can operate at atmospheric pressure (1 atm) (Busca, et al., 2008) while methods such as reverse osmosis required high pressure to achieve high removal efficiency. Also, since the solvent can be recovered after the process, it has a lower risk to cause secondary pollution. Besides, the phenol can also be recovered in LLX, unlike the ozonation process which will degrade phenol into uncommercialized products.

2.5.1 Mechnism of Liquid-Liquid Extraction and Its Application in Phenol Removal

Liquid-liquid extraction in the simplest case involves only three components, the carrier, the solute, and the solvent. The carrier is the liquid medium carrying the targeted solute. In the case of phenol-contained wastewater, the water is the carrier while the phenol is the solute. A liquid solvent will be used to extract the solute from the carrier. The selected liquid solvent must not be miscible with the liquid carrier and should have a higher affinity to the solute (Haan, Eral and Schuur, 2020).

The liquid-liquid extraction is a mass transfer process (Watarai, 2008). The typical liquid-liquid extraction is based on the solubility differences of the solute in the aqueous and organic phases (Watarai, 2008). Such difference is due to the difference in solvation energy of the solute in different phases, leading to a chemical potential difference (Akkermans, 2017). The potential difference will cause the solute to move from a high potential phase to a lower potential phase until equilibrium is reached. Figure 2.9 shows how the solute will flow in a typical liquid-liquid extraction and Figure 2.10 shows the schematic diagram of the liquid-liquid extraction process.

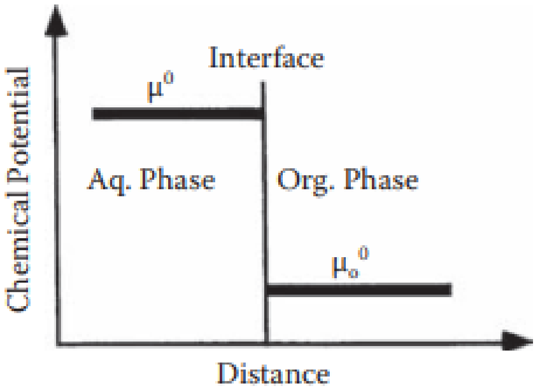

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Figure 2.9: The Conceptual Drawing of the Liquid-liquid Extraction (Watarai, 2008).

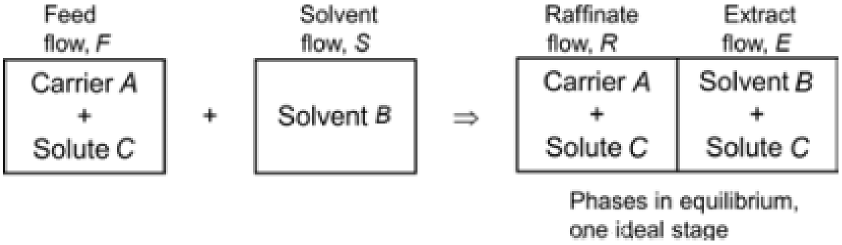


Figure 2.10: The Schematic Diagram of LLX (Haan, Eral and Schuur, 2020).

There is another mechanism that has been applied in liquid-liquid extraction. It is the reactive extraction which is usually applied in the removal of organic acid and heavy metal (Ronco, Gagliardi and Castells, 2020). In this separation process, the solute will form a solute-extractant complex with the organic phase solvent (Ronco, Gagliardi and Castells, 2020). This will produce a raffinate with nearly free from the solute. The formation of the complex is usually through the ion-pair formation but sometimes also can be caused by the hydrogen bond (Ronco, Gagliardi and Castells, 2020).

2.5.2 Recovery of Solvent and Phenol

A stripping process is commonly used to separate phenol from the solvent used. Sodium hydroxide (NaOH) had been examined in most literature that it is an effective stripping agent. This is mainly due to the sodium hydroxide reaction with phenol to form sodium phenolate (Rosly, Othman and Abdul Rahman, 2018). Studies also showed that the stripping efficiency can eventually reach up to 94 % by increasing the concentration of sodium hydroxide in the solution (Rosly, Othman and Abdul Rahman, 2018). According to Wang, et al. (2015), they had reported that using 0.75 mol/L of NaOH solution can reach 99.13 % stripping efficiency. Literature Studies had showed that sodium hydroxide is one of the most suitable stripping agents to be used due to its high stripping efficiency.

2.5.3 Conventional Solvent

Several works had been done on removing phenol through the liquid-liquid extraction process. Guo, et al. (2018) reported that 78.50 % of phenol removal can be reached when using di-isopropyl ether (DIPE) as the organic solvent. Besides, in the study done by Xu, et al. (2006), it was reported a new organic solvent which is a mixture of amine named QH-1 can achieve more than 95% of phenol removal in a single-stage extraction. Also, a study done on-site with the coal-gasification wastewater showed that 97.90 % phenol removal can be obtained using methyl isobutyl ketone (MIBK) as the solvent (Guo, et al., 2018). On top of that, Abbassian, et al. (2015) reported that a maximum of 30.0 % phenol removal can be achieved when kerosene was used as the organic solvent. In 2020, Yang, et al. reported that 99.79 % of phenol can be extracted with an organic solvent mixture that is comprised of 60 % cyclohexane, 20 % tributyl phosphate (TBP) and 20 % diethyl carbonate (DEC). Besides Seader, et al. (2016) also stated that benzene is one of the common organic solvents used in industry. This point is also supported by Haan, et al. (2020) and Jabrou (2012) reported a 70 % removal efficiency of phenol from wastewater using benzene. These studies showed that liquid-liquid extraction can achieve high phenol removal depending on the type of solvent used.

However, to date, most of the solvents selected for the liquid-liquid extraction process are still based on the organic solvent. The very first attention given to solvent selection is the selectivity of the solute (Seader, Henley and Roper, 2016; Haan, Eral and Schuur, 2020). The heuristic had told that organic solvents will always have high selectivity towards the targeted solute, in this case, phenol. This is also proven since most of the literature reported a high phenol removal using an organic solvent. Table 2.4 shows the summary of conventional solvents used and their efficiency.

Table 2.4: Summary of Conventional Solvent Used

Solvent	Efficiency (%)	Reference
Di-isopropyl Ether (DIPE)	78.50	(Guo, et al., 2018)
QH-1 Amine Mixture	95.0	(Xu, et al., 2006)
Methyl Isobutyl Ketone	97.90	(Guo, et al., 2018)
Hexanol	21.10	(Rao, et al., 2009)
Aliquat-336	65.50	(Rao, et al., 2009)
Benzene	70.0	(Jabrou, 2012)
Kerosene	30.0	(Abbassian, Kargari and Kaghazchi, 2015)
60 % Cyclohexane, 20 % Tributyl Phosphate (TBP) and 20 % Diethyl Carbonate (DEC) Mixture	99.79	(Yang, et al., 2020)

2.5.4 Drawbacks of Conventional Solvent

Despite being efficient in the phenol removal process from an aqueous solution, the usage of organic solvent also shows several drawbacks. The main drawback is the possibility of secondary pollution if leakage happened during the separation process. In Section 2.2, the effect of organic pollution had been discussed and most of the organic solvents are highly toxic even at low concentrations. The leakage of such insoluble organic solvent to surface water may lead to bioaccumulation of hazardous organic to the food chain. Besides, several organic solvents such as benzene and amine might be carcinogenic (Joshi and Adhikari, 2019). Other than that, diethyl ether and hexane have very low flash points which might easily cause an explosion (Joshi and Adhikari, 2019). Most organic solvents can also cause death in a very low concentration (Joshi and Adhikari, 2019). Most importantly, the high volatility properties of organic solvent will cause the loss of solvent easily. This is somehow not economically friendly.

In short, organic solvents can be classified as solvents which are not environmentally and economically friendly. Despite their high selectivity to phenol, they are harmful to the environment. Therefore, greener solvents should be developed and utilized in the industry field to replace harmful organic solvents to achieve the United Nations Sustainable Devolvement Goals such as “Clean Water and Sanitation” and “Industry, Innovation and Infrastructure”. One of the alternatives that draw most of the most attention is the deep eutectic solvent.

2.6 The Green Solvent

The introduction of the United Nation Sustainable Development Goals has become one of the driving forces in the development of green solvents since organic solvents are produced by non-renewable fossil fuels. To date, it was recorded that a minimum of 10 tons of conventional organic solvents had been produced annually (Marcus, 2019). This caused a huge potential for pollution by these conventional solvents. Principles had been established to classify green chemistry and the green solvent is under the green chemistry classification. The principles related to green solvents are listed in Table 2.5.

Several green solvents had become the centre of research in the past few years, such as subcritical water, deep eutectic solvent and ionic liquid (Ling and Hadinoto, 2022). However, solvents such as ionic liquids also face several criticisms which are caused by their poor biodegradability and sustainability (Paiva, et al., 2014). In contrast, the deep eutectic solvent has been reported as the more promising green solvent and it has drawn most of the interest.

Table 2.5: The Green Chemistry Principles Related to Green Solvent (Marcus, 2019)

Principles	**Explanation**
Prevention of the waste	Minimize waste from the industrial process
Safety Issue	No toxic material use
Renewable sources as feedstock	Avoiding the use of non-renewable sources such as fossil fuel
Utilization safe solvent	Recyclable solvents are preferred
Maximization of energy efficiency	Ambient temperature and pressure are preferred in industrial process
Utilization of degradable products	The used materials should be biodegradable
Minimization of potential accidents	The possibility of accidents such as fires should keep minimum

2.6.1 The Classical Deep Eutectic Solvent (DES)

Deep eutectic solvents (DES) are binary mixtures which yield liquid phase products under room conditions (Marcus, 2019). Martins, et al. (2019) have clearly defined that only when a eutectic mixture's eutectic point temperature is lower than an ideal mixture, it can be termed as the DES. Figure 2.11 shows the schematic representation of a binary eutectic mixture. The DES is generally nonreactive to water and is biodegradable (Abbott, et al., 2004). These properties made it a better choice of industrial solvent than other green solvents such as ionic liquids.

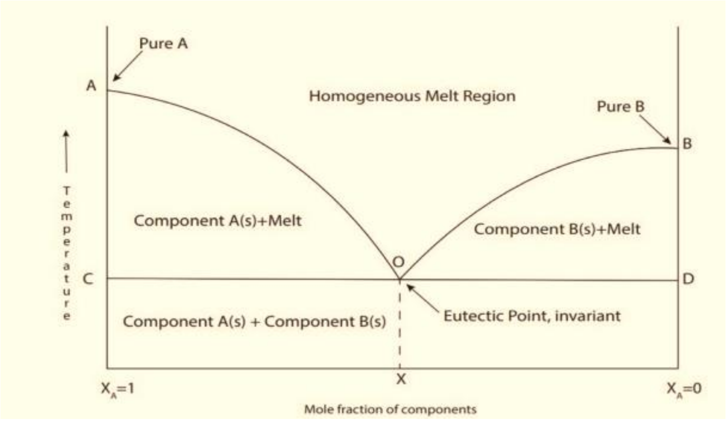


Figure 2.11: The Binary Mixture Ectectic point (Ling and Hadinoto, 2022).

The DES consist of large and nonsymmetric ions which are having low lattice energy (Smith, Abbott and Ryder, 2014). This property caused DES to have a low melting point if compared to their counterparts of raw materials. For example, the typical chlorine chloride and urea DES have a melting point of 12 ^{o}C. However, the melting point of chlorine chloride and urea is 303 ^{o}C and 134 ^{o}C respectively (Smith, Abbott and Ryder, 2014). This melting point decrement is due to the increase of the strong hydrogen bond interaction which decreases the weak interaction between the anionic and cationic groups (Zainal-Abidin, et al., 2017). For example, the hydrogen bond interaction between the halide and the hydrogen bond donor (HBD) will decrease the reaction between the anionic and cationic groups, lowering the lattice energy (Ling and Hadinoto, 2022). Thus, the melting point will become lower.

Besides forming a complex with a HBD, the cation can also form a complex with metal salts (Smith, et al., 2014). Smith, et al. (2014) classified DES into four types and a general equation can be written for all types of DES, as shown in Equation 2.1. Table 2.6 summarises all the types of DES.

$$Cat^{+}X^{-}zY \tag{2.1}$$

where

Cat^{+} = Cation, normally made up of phosphonium, sulfonium or ammonium

X^{-} = Anion, normally halide ion

Y = Lewis or Brønsted acid

z = Number of molecules Y

Table 2.6: The Classification of DES (Smith, Abbott and Ryder, 2014; Achkar, Greige-Gerges and Fourmentin, 2021).

Type	**Description**		
	Cat^+	X^-	Y
Type I	Phosphonium, sulfonium or ammonium	Halide ion	Metal salt (MCl_x) *M* = Al, Ga, In, Zn, Fe, Sn
Type II	Phosphonium, sulfonium or ammonium	Halide ion	Hydrated metal salt ($MCl_x.y\ H_2O$) *M* = Cu, Ni, Fe, Co, Cr
Type III	Phosphonium, sulfonium or ammonium	Halide ion	HBD (R-Z) *Z* = $CONH_2$, COOH, OH
Type IV	Metal salt (MCl_x) *M* = Al, Zn	-	HBD (RZ) Z = $CONH_2$, OH

The Type III DES is the most studied DES. The synthesis of this DES is based on the HBD which is relatively cheap and harmless compared to metal salts which involved heavy metals (Achkar, Greige-Gerges and Fourmentin, 2021). The first Type III DES was synthesised by Abbott, et al. in 2003 using choline chloride and urea. At the urea to choline chloride ratio of 2, mixture with a freezing point of 12 ºC can be produced (Abbott, et al., 2003). This freezing point temperature is way lower than the original melting point which is 303 ºC and 134 ºC for choline chloride and urea respectively (Abbott, et al., 2003). In the case of choline chloride and urea, the choline chloride is the HBA, and the anion urea is the HBD. The chloride ion of choline chloride will accept and form hydrogen bonding with the urea, forming a complex (Abbott, et al., 2003). Figure 2.12 shows the formation of the hydrogen bond complex where choline chloride is the hydrogen bond acceptor (HBA).

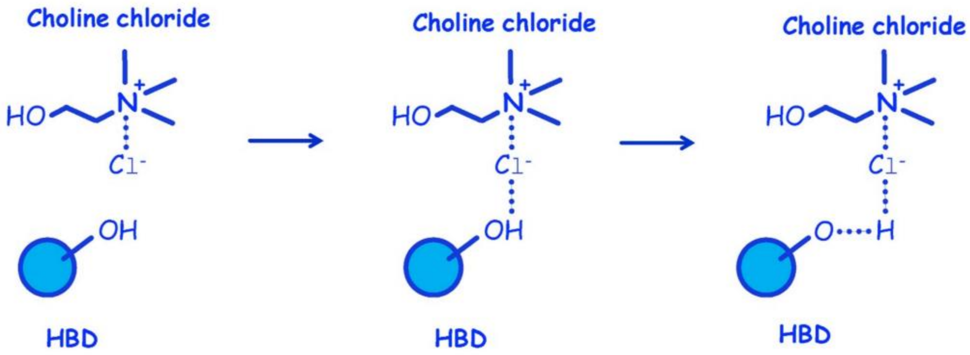


Figure 2.12: The Formation of Choline Chloride Hydrogen Bond Complex (Ling and Hadinoto, 2022).

However, one of the huge problems that affect the application of the DES in liquid-liquid extraction in water treatment is its hydrophilic properties. In general, most of the DES are hydrophilic and this is due to their ability in hydrogen bond formation (van Osch, et al., 2015). The ability of hydrogen bond formation is ascribed to the number of hydroxyl groups in the HBD (Ramón and Guillena Gabriela, 2020). This property caused most of the classical DES to be highly soluble in water. Thus, the aqueous phase and organic phase cannot be formed during the liquid-liquid extraction process. This hydrophilic property had caused the classical DES unsuitable to be chosen as a solvent to be used in the liquid-liquid extraction process.

2.6.2 The New Type: Hydrophobic Deep Eutectic Solvent (HDES)

Recently, a new type of DES had been introduced and it can be utilized in the liquid-liquid extraction process. This DES is the hydrophobic deep eutectic solvent (HDES). In 2015, van Osch, et al. synthesised the first ever HDES with combination of quaternary ammonium salt with fatty acid. Decanoic acid (DecA) which is highly hydrophobic is chosen as the HBD while the typical ammonium such as tetrabutylammonium chloride is chosen as the HBA (van Osch, et al., 2015). van Osch, et al. (2015) confirmed the hydrophobicity of the new DES since only around 1.8 wt% of water is found in the solvent after mixing with water. The hydrophobicity of the DES will be highly affected by the chemical structure of both the HBD and HBA (Makoś, et al., 2020). An organic with a longer hydrocarbon chain will show stronger hydrophobicity

(Makoś, et al., 2020). Although the ion on the HBA (typically Cl^- ion) might affect the hydrophobicity, it only showed a minor effect as per reported by Makoś, et al. (2020).

Besides, the HDES can also be produced using only molecular substance. Abranches, et al. (2019) propoesed to classify a new type of the DES which is the non-ionic deep eutectic solvent which only made up of molecular substances as Type V DES. In fact, the Type V DES is the combination of the non-ionic HBD and HBA (Abranches and Coutinho, 2022). Makoś, et al. (2020) reported that the common HBA for a non-ionic deep eutectic solvent is terpenoid-based compounds such as menthol and thymol. Fatty acid are normally acted as the HBD. Figure 2.13 shows the classification of all type DES. Figure 2.14 shows the typical HBD and HBA used to synthesise HDES. Several organic chemicals such as menthol can be used as both donors and acceptors. A clearer view of the eutectic point formation based on the HDES is shown in Figure 2.15.

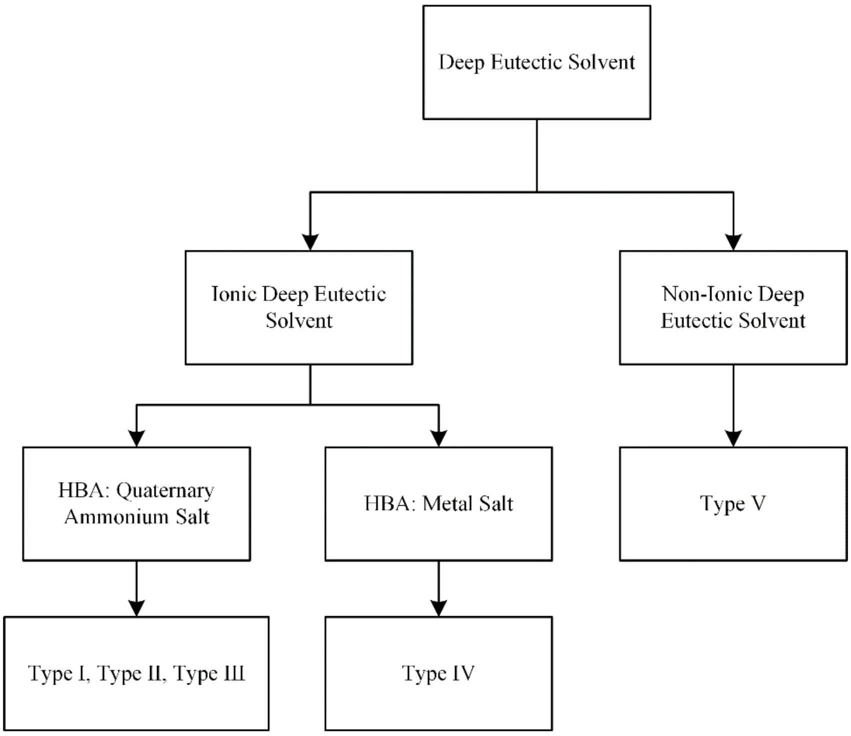


Figure 2.13: Classification of the DES (Smith, Abbott and Ryder, 2014; Abranches and Coutinho, 2022).

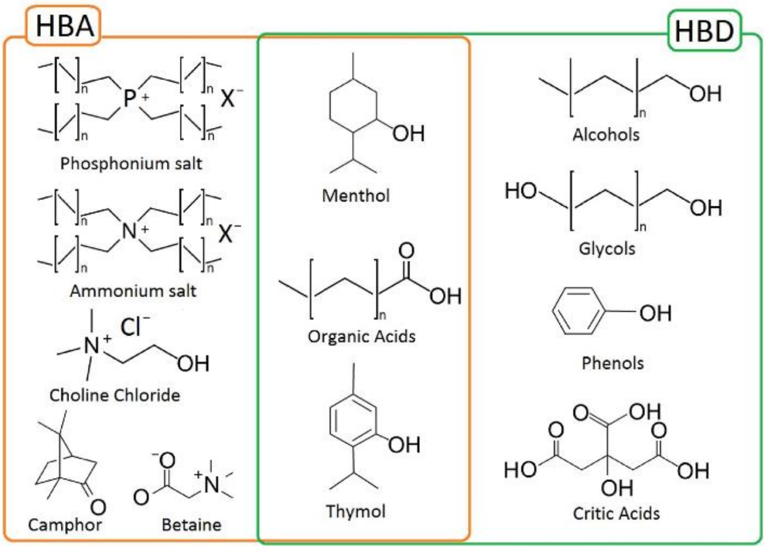


Figure 2.14: The Typical HBD and HBA (Makoś, et al., 2020).

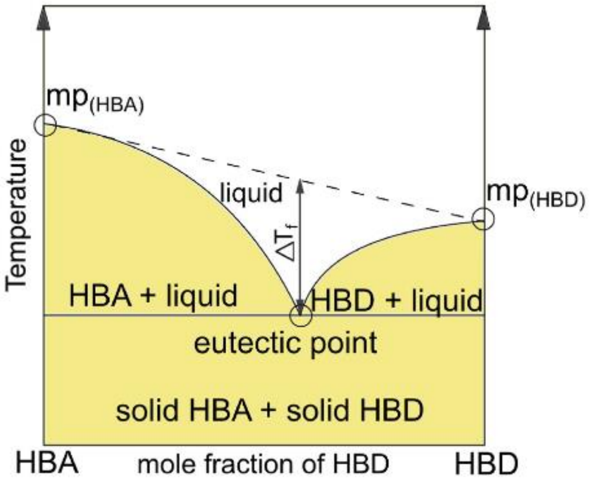


Figure 2.15: The Eutectic Point Formation of HDES (Makoś, et al., 2020).

2.6.3 Advantages of HDES in Liquid-Liquid Extraction Application

The largest advantage to use the HDES in LLX is due to its low volatility properties. van Osch, et al. (2020) determined the volatility of six typical HDES. They reported that the decanoic acid and menthol eutectic mixture has the highest volatility at a temperature range of 47 ^{o}C to 107 ^{o}C. However, when the volatility data was compared to the typical organic solvent, namely, toluene, the volatility is 150 to 1000 times smaller (van Osch, et al., 2020). This statement is supported by the study done by Dietz, et al. (2019) where they reported that the total vapour pressure of decanoic acid and menthol eutectic mixture is 430.9 Pa (0.0043 atm) at 100 ^{o}C. This value is compared to the typical organic solvents such as toluene and benzene and is found that organic solvents’ vapour pressure is much higher. The toluene is reported to have a vapour pressure of 0.7312 atm while benzene is reported to have a vapour pressure of 1.8358 atm at 100 ºC (Yaws, 2015).

Besides, the HDES are also less toxic if compared to conventional organic solvents. Some of the components used to synthesize DES are even utilized in the pharmaceutical and food industries (Cao and Su, 2021). For example, chlorine chloride is reported to be used as an additive nutrient in animal feed (European Food Safety Authority (EFSA), 2011). However, Cao and Su (2021) also reported that HDES are relatively more toxic compared to hydrophilic DES.

2.6.4 Parameters Affecting HDES Liquid-Liquid Extraction Performance

Due to the strong hydrophobicity of the HDES, it become extremely suitable to be chosen as the green solvent used in the LLX process for water treatment. However, it is known that there will be several factors affecting the performance of the extraction process using the HDES. The solvent's viscosity and polarity are the two major factors (Cao and Su, 2021).

The viscosity of the solvent will greatly affect the extraction efficiency. The viscosity of the HDES will be determined by the strength of the hydrogen bond formed (Dwamena, 2019). Chemicals with stronger hydrogen bonds formed or with more hydrogen bonds formed will have a higher viscosity (Ma, et al., 2018). When a solvent has a very high viscosity, the mass transfer process will be limited (Cao and Su, 2021). This limitation on the mass transfer process during the extraction process is mainly caused by extensive hydrogen bonding networks formed between donors and acceptors (Ling and Hadinoto, 2022). Most HDES are having lower viscosity compared to the classical DES (Cao and Su, 2021). Thus, most HDES will be preferable to be used in the liquid-liquid extraction process. Two main factors affect the viscosity of the solvent: temperature and the molar ratio of the HBD. At a higher temperature or a solvent with a higher HBD, the viscosity will be significantly lower (Ghaedi, et al., 2017). This is because, at high temperatures, the internal resistance between the molecules will decrease, leading to easier fluid flow (Ghaedi, et al., 2017). Besides, when the ratio of HBD increased, the hydrogen bonding formation will decrease which leads to a decrease in viscosity (Manurung, et al., 2019). This is because the increase in the HBD will lead to a decrease in the concentration of the HBA. Thus, more spare networks can be observed between the two groups, leading to weaker hydrogen bonding and lower viscosity (Yusof, et al., 2014).

On top of that, the polarity of the solvent will also affect the efficiency of the extraction process. Ling and Hadinoto (2022) reported that when the solvent has a polarity close to the polarity of the targeted solute, it will have a better solubilization capacity. Hence, the solvent is said to be a better choice to use in the liquid-liquid extraction process.

On the other hand, Makoś, et al. (2020) reported that the acidity of the HDES itself will not significantly affect the extraction efficiency. However, the aqueous phase pH will somehow affect the extraction efficiency using HDES during the liquid-liquid extraction process. This is mainly due to the possible donor dissociation or acceptor leaching under acidic or basic conditions (Makoś, et al., 2020). On top of that, the pH of the medium will also affect the condition of the solutes. Iqbal, Khan and Ihsanullah (20had reported that the phenol will be converted to positively charged phenonium ions at low pH. At high pH, the phenol will be dissociated into phenolate anions (Iqbal, Khan and Ihsanullah, 2005). This dissociation of phenol under different pH conditions affects the phenol removal efficiency of the HDES. This is due to the formation of hydrogen bonds will be limited.

In short, the efficiency of the extraction will be affected by the viscosity and polarity of the solvent as well as the aqueous phase acidity. Lower viscosity, more similar polarity with solutes and a neutral condition will be preferable during the extraction process. Besides, a higher temperature and higher donor-to-acceptor molar ratio will also help to increase the efficiency through decrease the solvent’s viscosity.

2.6.5 HDES in Phenolic Compound Removal

The HDES had been utilized in the removal of phenol from water. Several works had reported that HDES are efficient in the removal of phenol from water through liquid-liquid extraction. Table 2.7 shows the summary of the removal of the phenolic compound using HDES. Generally, the HDES can reach a high removal efficiency of phenol, especially at a high initial concentration. This is due to the free volume provided by the HDES (Sas, et al., 2019). When compared with the efficiency of conventional solvents as listed in Table 2.7, the efficiency of HDES is generally similar to the conventional solvents which is ranged from 70 % to 99.79 %. This indicated the applicability of HDES in the industry as the solvent in the LLX process.

Table 2.7: Summary on HDES Used in Phenolic Compound Removal

HDES	Molar Ratio	Removal (%)	Reference
Menthol: Octanoic acid	1:1	85.0	(Sas, et al., 2019)
Menthol: Decanoic acid	1:1	90.0	(Sas, et al., 2019)
Dodecanoic acid: Decanoic acid	1:2	70.0	(Sas, et al., 2019)
Dodecanoic acid: Octanoic acid	1:3	80.0	(Sas, et al., 2019)
Thymol: Menthol	1:1	95.0	(Sas, et al., 2022)
Decanoic acid: Proline	1:4.2	62	(Li, et al., 2021)

2.7 Summary

Phenol pollution is one of the major concerns that lead to water scarcity. Thus, the removal of phenol and its family compounds is always important in the industry. The conventional organic solvents, which are toxic, highly flammable, and have high vapour pressure which may lead to serious consequences if secondary pollution happens, must be replaced. However, the existing green solvent candidates, such as ionic liquid are facing the issue of high production costs. Moreover, the ionic types of DES are normally hydrophilic, making them unsuitable to be used in the LLX process to remove phenol. Therefore, the non-ionic HDES has become one of the important potential candidates for replacing organic solvents in the wastewater treatment industry to remove phenol. However, research on the non-ionic HDES, especially the HDES using long-chain fatty acids as HBD in the phenol or phenolic compound removal remains low. Thus, in this study, several menthol-based HES will be synthesised using long-chain fatty acids, and their performance in pohenol removal will be examined.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Work Plan

The overall working plan is shown in Figure 3.1. The hydrophobic eutectic solvent (HES) would be synthesized and selected through two stability tests. The tests are the water stability test and stability at room conditions. The selected HES would then be used to perform the parametric studies. Three different parameters would be studied, namely, initial concentration, stirring speed and solvent-to-solution ratio. The capacity study on the selected solvent's capacity would also be performed in this study.

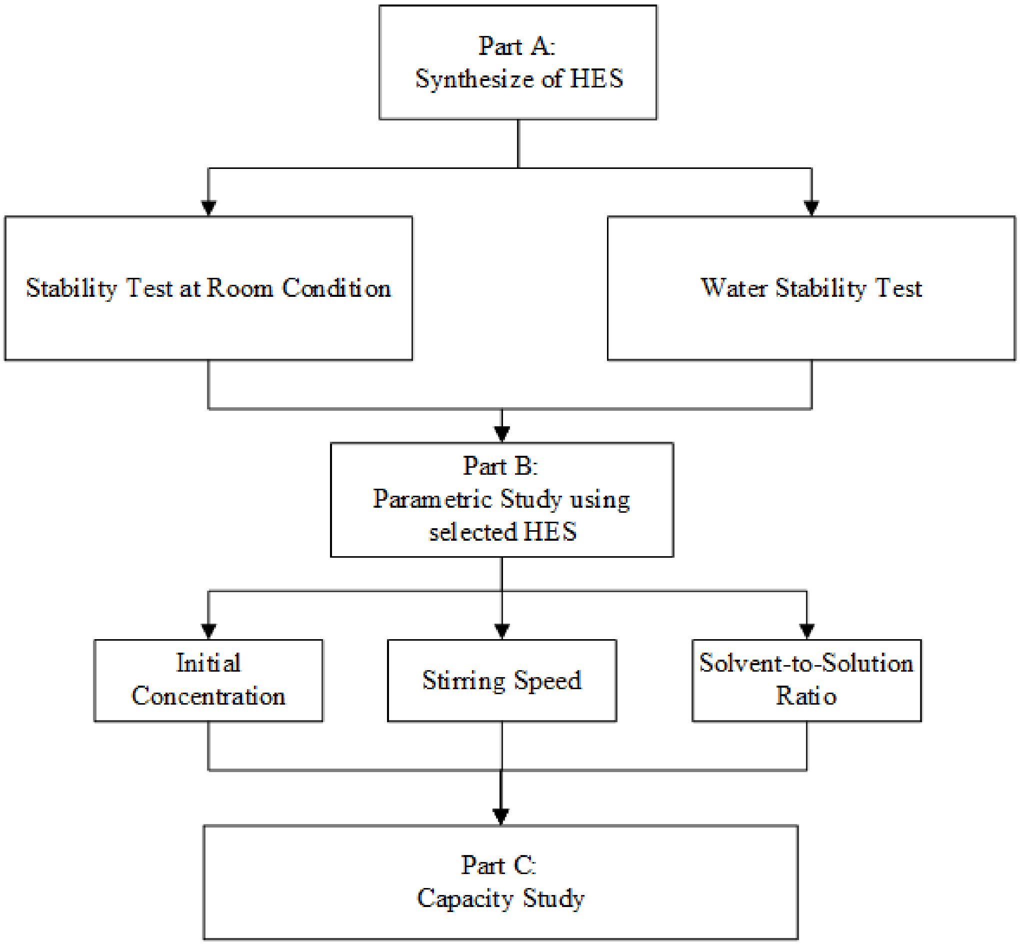


Figure 3.1: The Flowchart of the Research

3.2 Material

3.2.1 Chemicals

The chemicals involved in the research are shown in Table 3.1.

Table 3.1: Chemicals Involved in the Research

Chemical	Purpose
Phenol Crystal	To prepare synthetic phenol wastewater.
Hydrochloric Acid	To rinse the quartz cuvette.
Menthol	To prepare hydrophobic eutectic solvent.
Lauric Acid	To prepare hydrophobic eutectic solvent.
Myristic Acid	To prepare hydrophobic eutectic solvent.
Palmitic Acid	To prepare hydrophobic eutectic solvent.

3.2.2 Equipment

The equipment involved in the research is shown in Table 3.2.

Table 3.2: Equipment Involved in the Research

Equipment	Purpose
UV-Visible Spectrometer	To analyze the phenol content.
Quartz Cuvette	To analyze the phenol content.
Scintillation Vial	To store the mixture of solvent and phenolic wastewater and conduct the liquid-liquid extraction experiment.
Hot Plate Magnetic Stirrer	To provide constant stirring and heating to the mixture during solvent synthesis and liquid-liquid extraction.
Magnetic Stir Bar	To provide stirring to the mixture during solvent synthesis and liquid-liquid extraction.
Electronic Balance	To measure the weight of chemicals required.
Needle and Syringe	To extract the aqueous sample.
Centrifuge Tube	To store the aqueous sample for the UV-Visible analysis

3.3 Experimental Planning

The experiment was separated into three parts. The first part of the experiment was the synthesis and selection of the HES. The second part of the experiment was to check on the effect of initial concentration, solvent mass-to-solution volume ratio and stirring speed toward the extraction of phenol. The last part of the experiment was to check the maximum capacity of the solvent.

3.4 Procedure

3.4.1 Phenol Solution Synthesis

The 2500 ppm phenol solution was synthesized by adding 0.625 g phenol crystal to 250 ml of distilled water in the volumetric flask. The phenol solution of 2000 ppm, 1500 ppm, 1000 ppm and 500 ppm were prepared through the dilution of 2500 ppm phenol solution. 80 ml, 60 ml, 40 ml and 20 ml of 2500 ppm phenol solution was mixed with water in 100 ml volumetric flasks respectively to prepare the required concentration of the phenol solution.

3.4.2 Part A: HES Synthesis and Selection

3.4.2.1 HES Synthesis

Three different types of menthol-based HES were synthesized using different hydrogen bond donor and acceptor ratios. Table 3.3 shows the molar ratio of the HBA and HBD to synthesize different types of HES in this study. The exact mass of the menthol and fatty acid required were calculated based on the molar ratio and were added to the scintillation vial. The calculation of the mass required is shown in Appendix A. The mixed menthol and fatty acid were heated in a water bath of 50 ^{o}C and stirred at 1300 rpm for 30 minutes. To avoid any possible accumulation of pressure, the vial was not closed tightly. For the MMA which was the HES synthesized using menthol and myristic acid, several molar ratios were tested to find the optimal ratio for the application in the LLX process. The HBA to HBD molar ratio for MMA were 2:1, 4:1, 8:1 and 10:1.

Table 3.3: The Molar Ratio of HBA to HBD for different types of HES.

Abbreviation	Hydrogen Bond Acceptor	Hydrogen Bond Donor	HBA: HBD	Reference
MLA	Menthol	Lauric Acid	2:1	(Ribeiro, et al., 2015)
MPA	Menthol	Palmitic Acid	12:1	(Verma and Banerjee, 2019)
MMA[a]	Menthol	Myristic Acid	2:1, 4:1, 8:1, 10:1	(Present Study)

[a] The best HBA: HBD ratio will be determined in this study.

3.4.2.2 Selection of HES

Two selection criteria were applied in the selection of the HES. The first criteria is that the HES must be able to form a stable liquid layer when added to water. The second criteria is that the HES should not be solidified under room conditions. A HES must at least pass the first criteria for it to be able to be used in the next stage of the study.

For the test for the first criteria, 1 g of the HES was added to 10 ml of distilled water. The sample was left overnight to check its stability in water. If the HES solidified in water, it was considered not stable in water and failed the first criteria. For the test for the second criteria, the HES was left at room conditions for 1 hour. If the HES solidified, it was considered not stable and failed the second criteria.

3.4.3 Part B: Parameteric Study

The HES were used as the solvent in the LLX. The HES and synthetic wastewater (phenol solution) were added to a scintillation vial at a fixed mass-to-volume ratio of HES to wastewater (e.g., 1 g:10 ml). The LLX was done in a scintillation vial for a time of around 30 minutes under room conditions with a 700 rpm stirring speed. The sample was left for 24 hours for the phase separation process between the solvent and phenol solution. After the experiment, the aqueous samples were collected using a needle and syringe for further analysis.

3.4.3.1 Effect of Initial Phenol Concentration

The LLX was done with different initial phenol concentrations. The phenol concentration used ranged from 500 ppm to 2500 ppm with a 500 ppm interval.

3.4.3.2 Effect of Stirring Speed

The LLX was done at different stirring speeds. The stirring speed that was tested in this experiment ranged from 300 rpm to 1100 rpm with 200 rpm intervals.

3.4.3.3 Effect of Solvent Mass-to-Solution Volume Ratio

The liquid-liquid extraction was done with different solvent mass-to-solution volume ratios. The ratios tested in the experiment were 1:5, 1:10, 1:20, 1:50 and 1:100 with the respective solvent mass of 2 g, 1 g, 0.5 g, 0.2 g, and 0.1 g.

3.4.4 Part C: Solvent Capacity Study

The capacity of the HES was checked by repeating the LLX with the same HES using 2500 ppm phenol solution for 5 cycles. The aqueous solution after each cycle of the LLX was collected and analysed for phenol concentration.

3.5 Uv-Visible Spectrophotometry

The UV-Visible spectrophotometry was used to analyse the phenol concentration in the phenol solution. The aqueous phase solution was diluted with distilled water before it was analyzed by UV-Visible spectrometry. 1 ml of the aqueous phase sample was diluted to 10 ml. This gave a dilution factor of 10. The peak of phenol detected by UV-Visible Spectrometry is around 270 nm (Souza and Peralta-Zamora, 2001).

3.6 Effectiveness Determination

3.6.1 Extraction Efficiency

The extraction efficiency of the process can be calculated as shown in Equation **3.1**.

$$EE = \frac{|C_0 - C|}{C_0} \times 100\ \% \qquad \textbf{(3.1)}$$

Where

EE = Phenol Removal Efficiency, %

C_0 = Initial Phenol Concentration in Phenol Solution, ppm

C = Final Phenol Concentration in Phenol Solution, ppm

3.6.2 Phenol Uptake

The uptake of the phenol by the solvent can be calculated by Equation 3.2.

$$\mathrm{U} = \frac{(C_0 - C\ )(0.01)}{m_{HES}} \qquad \textbf{(3.2)}$$

Where

U = Phenol Uptake, mg/g

m_{HES} = Mass of Solvent Used, g

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Part A: HES Synthesis and Selection

Three different types of hydrophobic eutectic solvents were synthesized using menthol as the hydrogen bond donor and lauric acid, myristic acid, and palmitic acid as the hydrogen bond acceptor. Using the similar synthesizing method mentioned in Chapter 3, the HES with the different type of HBD and molar ratio are synthesized. Figure 4.1 shows the freshly produced HES. It was observed that all molar ratios chosen formed eutectic solvents successfully. The solvents formed are all in the form of transparent liquid.

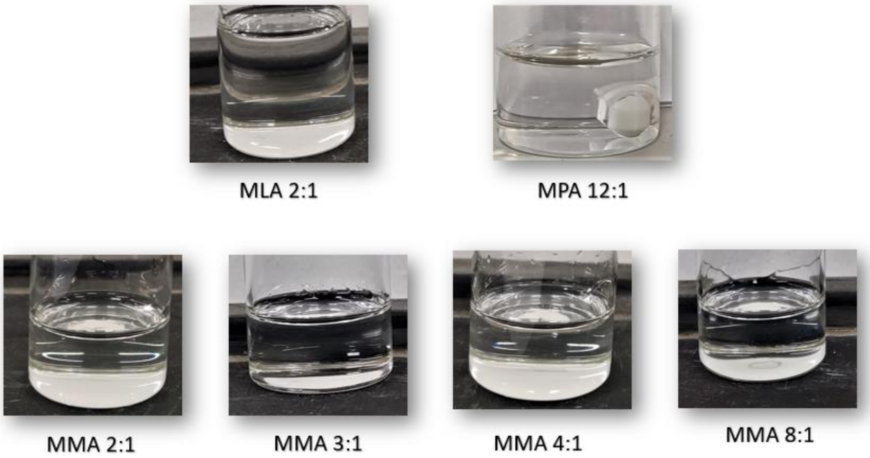


Figure 4.1: Freshly Produced MLA (Top Left), MPA (Top Right) and Different Ratios of MMA (Bottom).

The synthesized eutectic solvents are left at room condition (23 ºC, 1 atm) for 1 hour. It had found that all the solvents started to crystalline and become solid except MLA. Figure 4.2 shows all the states of the solvents after 1 hour. MPA was found to completely form a hard solid layer. A similar observation was found for MMA solvent formed with an HBA: HBD molar ratio of 8:1. Both the solid layers formed could hardly be broken using a glass rod. For MMA with the molar ratio of 2:1, 3:1, and 4:1, the texture of the solid layer formed is softer than the solid formed by the molar ratio of 8:1 where it was more likely toward gel and could be scratched using a glass rod. Among these three MMA, the MMA with a 4:1 molar ratio was more watery as some of the solvents remained in the liquid state after 1 hour. This showed that only MLA passed the second HES selction criteria.

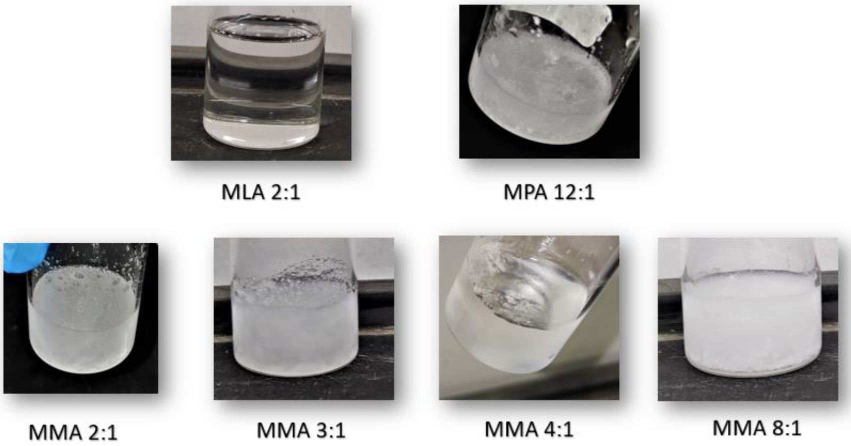


Figure 4.2: The HES Left at Room Condition (23 °C, 1 atm) after 1 hr. MLA (Top Left), MPA (Top Right) and Different Ratios of MMA (Bottom).

The phenomenon of the solidification of the solvent can be explained through the different melting points of the solvents formed. At different components or different molar ratios, the solvents formed will have different melting points. Solvents which have melting points lower than the room temperature, in this case, 23 °C, will remain in liquid form. Such a type of eutectic solvent is considered a stable solvent. It is important to form a stable liquid solvent under room temperature. This is because it can help to mitigate extra energy required to overcome the latent heat to melt the solid state HES during LLX (Koretsky, 2013).

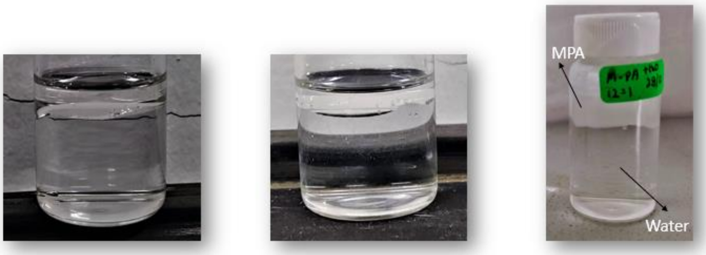
MLA solvent is always in the liquid state. This is tallied with the reported melting point of the solvent. Ribeiro, et al. (2015) reported that the MLA with a 2:1 molar ratio is having a melting point of around 14 °C which is in agreement with Verma and Banerjee (2018) and Martins, et al. (2018), whom reported that the melting point is around 18 – 19 °C. Darwish, et al. (2021) also further confirmed that the MLA HES with a 2:1 molar ratio will not be solidified even if kept at 25 °C for 1 week. This showed that its melting point is lower than the standard room condition.

In contrast, the solidification of MPA HES within 1 hour after it had been synthesized indicated its melting point is at least higher than 23 °C. Verma and

Banerjee (2019) reported that at a molar ratio of 12:1, the MPA HES should be having a melting point of around 23 ^{o}C. However, this is conflicted with the data reported by Martins, et al. (2018) where they had reported a melting point of around 35 ^{o}C. One of the reasons might be due to the type of menthol used where DL-menthol is used by Verma and Banerjee (2019) while Martins, et al. (2018) used L(-)-menthol. It had been reported that L(-)-menthol is having a higher melting point (43 ^{o}C) compared to DL-menthol (38 ^{o}C) (National Center for Biotechnology Information, 2023) leading to a higher melting point reported by Martins, et al. (2018).

In the case of MMA HES, all the MMA HES formed using four different molar ratios solidified after 1 hour. This indicated that the melting point of the MMA is at least 23 ^{o}C. This is supported by Martins, et al. (2018) where the lowest melting point reported is around 26 ^{o}C for a 4:1 molar ratio MMA.

The MLA, MMA, and MPA HES were also evaluated from the view of their stability when added to water. In the case of MMA, the eutectic solvent with a 4:1 molar ratio had been chosen to perform the water stability test due to it solidified at the slowest rate. Figure 4.3 shows the water stability test for the eutectic solvents. It was found that for MLA and MMA, a stable liquid layer is formed while a solid layer is formed on the water for MPA. This shows that MLA and MMA are suitable to be used in LLX at room temperature. The phenomenon of MMA does not form a solid layer despite having a higher melting point than room temperature is most probably due to the formation of hydrogen bonds between the solvent and water. This concluded that MLA and MMA with 2:1 and 4:1 molar ratio respectively passed the first HES selection criteria.



MLA 2:1 MMA 4:1 MPA 12:1

Figure 4.3: Water Stability Test for MLA (Left), MMA (Centre), and MPA (Right).

4.2 Part B: Parametric Study

4.2.1 Phenol Calibration Curve

The concentration of phenol in the aqueous phase is determined using ultra-violet visible spectrometry as mentioned in Chapter 3. A phenol calibration curve is plotted with five sets of known concentration phenol solutions. The concentration is from 0 ppm to 250 ppm with 50 ppm intervals. Figure 4.4 shows the calibration curve plotted with an R^2 of 0.9982. The high R^2 value of the curve indicated that the calibration curve is reliable to indicate the concentration of phenol within 250 ppm. Thus, the sample collected required to be diluted before it can be tested. The phenol calculation for concentration based on the absorbance is shown in Equation 4.1.

$$C = 0.012\ (Absorbance) \qquad (4.1)$$

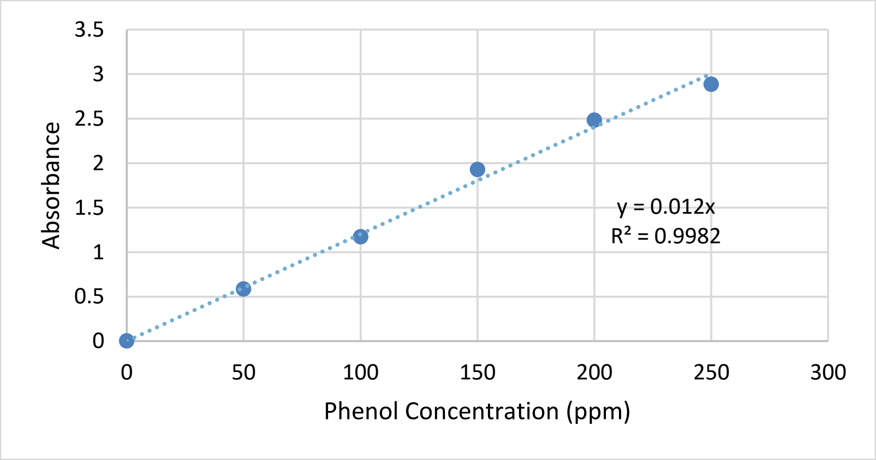


Figure 4.4: Phenol Calibration Curve

4.2.2 Effect of Initial Phenol Concentration

The effect of the initial concentration towards the removal efficiency was studied. Five different initial concentrations of phenol solution were used to perform liquid-liquid extraction with MLA and MMA. Figure 4.5 shows the results of the LLX using different initial concentrations at 700 rpm stirring speed and 1:10 solvent-to-solution ratio.

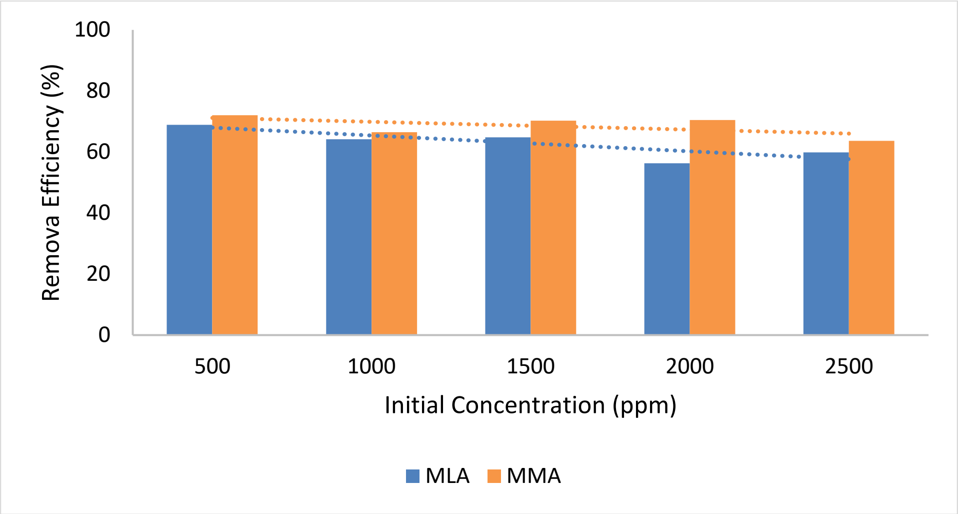


Figure 4.5: Effect of Initial Concentration on Phenol Removal Efficiency

From Figure 4.5, it was found that the removal efficiency slightly reduced when the initial concentration of phenol solution increased. Nevertheless, the phenol uptake of the solvent does increase when the initial concentration increases. For example, the phenol uptake for MMA at 500 ppm was 3.44 mg but the uptake of phenol increased to 15.18 mg when the initial concentration increased to 2500 ppm. It was encouraging to observe that the removal efficiency remained high at high phenol concentrations as most of the industrial wastewater will have high concentrations.

On the other hand, it was interesting to find that the removal efficiency of MMA is slightly better than MLA. This phenomenon is most probably due to the difference in the menthol composition. MMA with a molar ratio of 4:1 is having more menthol in the solvent than MLA with a 2:1 molar ratio. A similar model was used by Cheng, et al. (2022) to explain the increased extraction efficiency of phenol when the solvent’s menthol-to-nonanoic acid ratio increased from 2:3 to 5:2. Cheng, et al. (2022) confirmed that menthol is having a greater affinity toward phenol compared to fatty acid. This is mainly due to the phenol can act as the hydrogen bond donor and form hydrogen bonding with menthol. Thus, phenol will form DES with menthol. This is supported by Alhadid, et al. (2022) who synthesized the DES using a menthol-to-phenol molar ratio of 2:1.

4.2.3 Effect of Stirring Speed

The effect of the stirring speed was also studied. Figure 4.6 shows the results of the LLX using a concentration of 2500 ppm phenol and a 1:10 solvent-to-solution ratio.

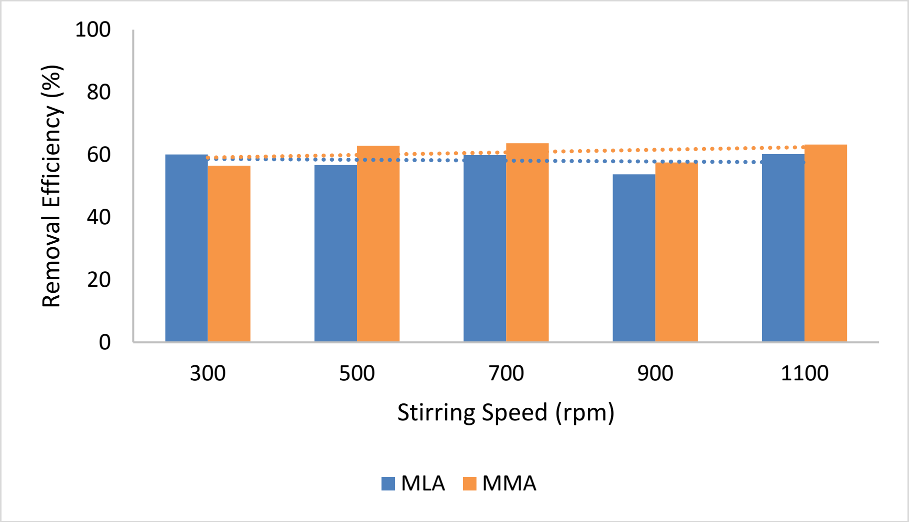


Figure 4.6: Effect of Stirring Speed on Phenol Removal Efficiency

From Figure 4.6, it was found that the stirring speed did not provide a significant effect in the removal efficiency of phenol. This is mainly due to the low viscosity of the solvent. For example, using the model proposed by Ribeiro, et al. (2015), the viscosity of MLA was estimated to be 24.50 mPas at 25 ^{o}C. It is believed that both solvents can be well applied practically as their viscosity is lower than the suggested limit for practical application. Such criteria suggested that the solvent having a viscosity lower than 100 mPas are having a higher potential to be applied practically (Cheng, et al., 2022). With a low viscosity, equilibrium can be reached faster. Hence even at a low stirring speed of 300 rpm, the removal efficiency also reached its maximum. The main reason to increase the stirring speed is to enhance the mass transfer between solvent and phenol solution. With low viscosity, the resistance of the solvent towards flow is smaller. Hence, equilibrium is easier to be achieved even if a low stirring speed is provided. It is encouraging to find that stirring speed had no significant effect on removal efficiency as this showed that less energy is required to mitigate the solvent's mass transfer resistance if it is applied in the industrial process.

4.2.4 Effect of Solvent-to-Solution Ratio (S:S)

The effect of the solvent-to-solution ratio (S:S) was studied and Figure 4.7 shows the results of the liquid-liquid extraction using a concentration of 2500 ppm phenol and a 700 rpm stirring speed.

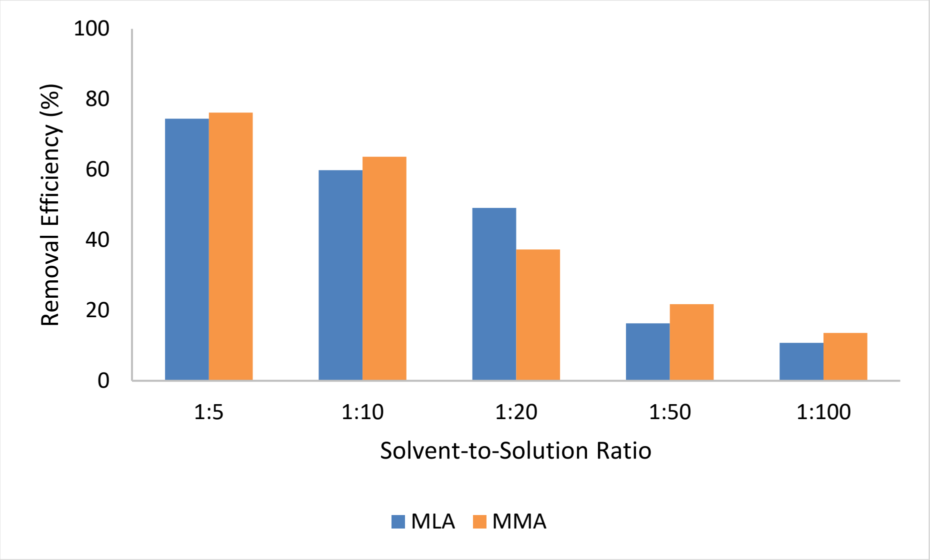


Figure 4.7: Effect of Solvent-to-Solution Ratio on Phenol Removal Efficiency

From Figure 4.7, it was found that when the amount of the solvent used decreased from 2.0 g to 0.1 g, the removal efficiency decreased from around 75 % to around 10 %. However, the phenol uptake per gram solvent was increased. For example, the phenol uptake when 2 g of MMA used was 9.52 mg/g while the uptake of phenol increased to 34.0 mg/g when 0.1 g MMA used. As the removal of phenol is highly dependent on the menthol content as explained in Section 4.2.2, if less amount of the solvent is used, less menthol content is in the solvent, thus, less space for phenol to form hydrogen bonds and the removal efficiency will decrease.

Darwish, et al. (2021) explained that the high sensitivity of the removal efficiency toward the solvent-to-solution ratio is mainly due to the solute having higher solubility in water than in the solvent. This indicates that the solvent might be having low partition coefficient. However, the performance of both MLA and MMA is encouraging when compared with several literature data. For example, diisopropyl ether required a 1:5.5 S:S ratio at 50 ºC to reach 78.5 % removal (Guo, et al., 2018). However, MMA can easily reach 76 % removal at a 1:5 S:S ratio under room conditions.

4.2.5 Literature Comparison

Table 4.1 summarizes several previous studies using organic solvents, ionic liquids, and deep eutectic solvents to remove phenol through liquid-liquid extraction. All the experimental conditions to conduct the LLX are also listed in Table 4.1. From Table 4.1, there are three types of organic solvents, namely, diisopropyl ether, methyl isobutyl ketone, and methyl propyl ketone performed better than MLA and MMA in terms of removal efficiency. However, they required extra energy input as the process required a temperature of 50 ^{0}C. Also, despite the high removal efficiency, these solvents are not sustainable as they are petroleum-based solvents.

Regarding ionic liquids, there are also some candidates that performed better than MLA and MMA. These ionic liquids are [C_2mim]FSI and [choline][NTf_2]. However, the cost of the ionic liquid is one of the major concerns when comes to practical application in industry (Binnemans and Jones, 2023).

When comparing MLA and MMA with other deep eutectic solvents, the solvent prepared using menthol and nonanoic acid gives a removal efficiency of 93.60 %. However, the high efficiency achieved is mainly due to more quantity of the solvent used. Since MLA and MMA are having a removal efficiency of around 60 % at S:S ratio of 1:10, they are still acted as a promising candidate to be used in phenol removal and it is believed that high removal can also be reached by MLA and MMA if the S:S ratio increased.

Table 4.1: Literature Comparison of Phenolic Compound Removal Efficiency

	Solvent	**Initial Concentration (ppm)**	**S:S/Temp (°C)**	**Removal Efficiency**	**Reference**
Organic Solvent	Cumene	1000	1:1 [c]/25 °C	54.50 %	(Liu, et al., 2013)
	Hexanol	2500	5:250 [c]/30 °C	21.10 %	(Rao, et al., 2009)
	Diisopropyl Ether [a]	6273	1:5.5 [c]/50 °C	78.50 %	(Guo, et al., 2018)
	Methyl Isobutyl Ketone [a]	6273	1:5.5 [c]/50 °C	97.90 %	(Guo, et al., 2018)
	Methyl Propyl Ketone [a]	6273	1:5.5 [c]/50 °C	98.80 %	(Guo, et al., 2018)
	Kerosene [a]	200	1:1 [c]/20 °C	30.00 %	(Abbassian, Kargari and Kaghazchi, 2015)
Ionic Liquid	Aliquat 336	2500	5:250 [c]/30 °C	65.50 %	(Rao, et al., 2009)
	[C$_2$mim]FSI	1000	1:2 [c]/25 °C	93.50 %	(Sas, et al., 2018)
	[choline][NTf$_2$]	5050	1:1 [b]/25 °C	80.00 %	(Cesari, Canabady-Rochelle and Mutelet, 2017)
Deep Eutectic Solvent	Menthol-Pelargonic Acid (1:1)	1000	1:1 [b]/25 °C	93.60 %	(Cheng, et al., 2022)
	Menthol-Decanoic Acid (1:1)	1000	1:1 [b]/25 °C	93.20 %	(Cheng, et al., 2022)
	Decanoic Acid-L-proline (3.5:1)	300	1:2 [c]/50 °C	53.00 %	(Li, et al., 2021)
	MLA	2500	1:10 [b]/23 °C	59.86 %	(This Work)
	MMA	2500	1:10 [b]/23 °C	63.68 %	(This Work)

[a] The efficiency was approximated from graphical illustration.

[b] Solvent Mass-to-Solution Ratio

[c] Solvent Volume-to-Solution Ratio

4.3 Solvent Capaity Study

The capacity of the solvent was investigated by repeating 5 cycles of the liquid-liquid extraction process using 2500 ppm phenol solution, 700 rpm stirring speed and 1:10 solvent-to-solution ratio. Table 4.2 shows the accumulated phenol uptake of each solvent in the 5 cycles.

Table 4.2: Solvent Accumulated Phenol Uptake

Cycle	**MLA Phenol Uptake (mg/g)**	**MMA Phenol Uptake (mg/g)**
1	15.36	16.63
2	22.63	27.33
3	26.74	31.68
4	29.77	36.34
5	32.13	39.29

The maximum capacity of the solvent for the uptake of phenol was predicted using the exponential decay model. It was predicted that the maximum capacity of the MLA and MMA is around 33.42 mg/g and 42.40 mg/g respectively. The estimated capacity of the solvent clearly showed that the reason of MMA having better performance than MLA. This was tallied with the previous observation and explanation in Section 4.2.2.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In short, stable HES in water were successfully synthesized using menthol as HBA with lauric acid and myristic acid as HBD at a molar ratio of 2:1 and 4:1 respectively. Both the HES performed well in phenol removal from water and their phenol uptake capacity are also tallied with the results obtained during the parametric study.

During the synthesize of HES, it was found that only the eutectic solvent formed using menthol and lauric acid (MLA) with a molar ratio of 2:1 is stable under room conditions. On the other hand, MLA and MMA (molar ratio 4:1) can form a stable liquid layer on water, indicating both solvent are stable in water, meeting the first HES selection criteria. Thus, MLA and MMA are chosen to perform the parametric study.

From the parametric study, it was found that MMA which has more menthol content was performing better in phenol removal. Generally, MMA has a removal efficiency of 63.68 % while MLA was only having a removal efficiency of 59.86 %. It was also found that when the initial concentration of the phenol solution increased, the removal efficiency slightly decreased. However, the phenol uptake still increased from 3.44 mg to 15.18 mg when the phenol solution concentration increased from 500 ppm to 2500 ppm for the case of MMA. This showed that HES can remain at high removal efficiency even at high concentration scenarios and this is beneficial for future application in industries.

Besides, it was found that stirring speed had no significant effect toward the phenol removal. The removal is quite constant (59.86 % for MLA, 63.68 % for MMA) when the stirring speed increased from 300 rpm to 1200 rpm indicating the system can reach equilibrium even at low stirring speed. This is mainly due to the low viscosity of the solvent. On top of that, the drastic increase in the removal efficiency when the mass of solvent used increased from 0.1 g to 2 g showed that the solvent is sensitive to the variation in the solvent-to-solution ratio. An efficiency of around 75 % can be reached by both MLA and MMA when 2 g of solvents were used but would decrease to around 10 % when only 0.1 g of solvent was used.

On top of that, it was also found that MMA phenol uptake capacity was higher than MLA. MLA only recorded a phenol uptake capacity of 33.42 mg/g while MMA recorded a phenol uptake capacity of 42.40 mg/g. This result is tallied with the previous observation during the parametric study where MMA was having slightly higher removal efficiency compared to MLA. Overall, the research showed that the MLA and MMA are having high potential to replace organic solvents in phenol removal in the industries. However, there are still several improvements required before the menthol-based HES can be adopted in industrial-scale liquid-liquid extraction.

5.2 Recommendations for future work

Several suggestions are proposed to improve the understanding of the menthol-based HES in phenol removal. Besides, recommendations are made to help enhance the competitiveness of menthol-based HES among the other solvent as well as increase its potential as a possible replacement for organic solvents in industrial applications. The recommendations are as follows:

(I) Study on the physical and thermal properties such as density, viscosity, partition coefficient, and melting point for the synthesized HES.

(II) Perform the removal test using industrial wastewater which having high phenol content.

(III) Investigate the suitable stripping agent to be used for the phenol stripping to regenerate the solvent.

(IV) Investigate the effect of temperature and pressure on the phenol removal.

(V) Investigate the performance of the HES in continuous operation to simulate the practical industrial application.

(VI) Investigate the competition effects from other pollutants if the actual industrial wastewater is used.

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APPENDICES

Appendix A: Mass of Hydrogen Bond Donor and Hydrogen Bond Acceptor

The derivation of the general equation to calculate the mass of HBD and HBA required to produce DES at a certain molar ratio is shown below.

Step 1: Total molar mass of DES	
a.	The molar mass of the DES can be calculated below. $M_{HES} = x(M_{HBA}) + y(M_{HBD})$ Where: M_{HES} = Molar Mass of DES (g/mol) M_{HBD} = Molar Mass of Menthol (g/mol) M_{HBA} = Molar Mass of Lauric Acid (g/mol) x = Molar Ratio of HBD y = Molar Ratio of HBA

Step 2: Number of mol of DES	
a.	With the calculated molar mass of the DES, the equation to calculate the mass of menthol and lauric acid required can be then derived as shown below. $n_{HES} = \frac{m_{HES}}{M_{HES}}$ Where: n_{HES} = Number of mol of DES m_{HES} = Mass of DES to be Produced
b.	Substituting the molar mass calculated by giving the equation: $n_{HES} = \frac{m_{HES}}{x(M_{HBA}) + y(M_{HBD})}$

<table>
<tr><th colspan="2">Step 3: General equation for HBA and HBD mass calculation</th></tr>
<tr><td>a.</td><td>For HBA, m_{HBA}:
$m_{HDA} = (n_{HBA})(M_{HBA})$
Where:
n_{HBA} = Number of mol of HBA
m_{HBA} = Mass of HBA required
At a molar ratio of x:y, the required HDB will have x number of mol of DES, thus, the equation can be rewritten as below.
$m_{HDA} = x\left(\frac{m_{DES}}{x(M_{HBA}) + y(M_{HBD})}\right)(M_{HBA})$
$m_{HDA} = (m_{DES})\left[\frac{x(M_{HBA})}{x(M_{HBA}) + y(M_{HBD})}\right]$</td></tr>
<tr><td>b.</td><td>For HBD, m_{HBD}:
$m_{HBD} = (n_{HBD})(M_{HBD})$
Where:
n_{HBD} = Number of mol of HBD
m_{HBD} = Mass of HBD required
At a molar ratio of x:y, the required HDB will have y number of mol of DES, thus, the equation can be rewritten as below.
$m_{HBD} = y\left(\frac{m_{DES}}{x(M_{HBA}) + y(M_{HBD})}\right)(M_{HBD})$
$m_{HBD} = (m_{DES})\left[\frac{y(M_{HBD})}{x(M_{HBA}) + y(M_{HBD})}\right]$</td></tr>
</table>

Appendix B: Viscosity of MLA

The viscosity of MLA can be estimated using the model proposed by Ribeiro, et al. (2015). The calculation is shown below.

$$\ln \eta = A_{\eta} + \frac{B_{\eta}}{\left(T - C_{\eta}\right)}$$

Where:

η = viscosity (mPas)

A_{η} = Adjustable Parameter (mPas)

B_{η} = Adjustable Parameter (K)

C_{η} = Adjustable Parameter (K)

T = Temperature (K)

The adjustable parameters are provided by Ribeiro, et al. (2015) where A_{η} = -3.599 mPas, B_{η} = 815.874 K, and C_{η} = 178.123 K for MLA. With the provided adjustable parameter, the viscosity at 25 °C can be calculated as shown.

$$\ln \eta = (-3.599\ mPas) + \frac{815.874\ K}{(298.15\ K - 178.123\ K)}$$

$$\ln \eta = 3.1984\ mPas$$

$$\eta = e^{3.1984} = 24.4933\ mPas$$