EMULSION IONIC LIQUID MEMBRANE FOR IBUPROFEN REMOVAL FROM SYNTHETIC WASTEWATER USING ALIQUAT 336

LOGAISRI RAJANDRAM

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by

LOGAISRI RAJANDRAM

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TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

Symbol	Description	Unit
C_f	Final concentration of IBP	(mg/L)
C_o	Initial concentration of IBP	(mg/L)
$C^{i}_{OH^-}$	Initial concentration of OH^- in internal phase	(M)
pH	Final pH of feed phase	
pH_o	Initial pH of feed phase	
V_{ext}	Initial volume of feed phase	(mL)
V_i	Initial volume of internal phase	(mL)
V_s	Volume of internal phase leaked into feed phase	(mL)

LIST OF ABBREVIATIONS

Aliquat 336	Trioctylmethylammonium chloride
AOP	Advanced oxidation process
ASW	Artificial sweetener
BILM	Bulk ionic liquid membrane
BLM	Bulk liquid membrane
CEC	Contaminants of emerging concern
D2EHPA	Di-2-(ethylhexyl) phosphoric acid
EC	Emerging contaminant
EDC	Endocrine-disrupting compound
EILM	Emulsion ionic liquid membrane
ELM	Emulsion liquid membrane
FR	Flame retardant
FTIR	Fourier transform infrared
GAC	Granular activated carbon
HCl	Hydrochloric acid
HLB	Hydrophilic-lipophilic balance
H_2SO_4	Sulphuric acid
IBP	Ibuprofen
IL	Ionic liquid
LLE	Liquid-liquid extraction
LOQ	Limit of quantification
Na_2CO_3	Sodium carbonate
NaOH	Sodium hydroxide

NH_4OH	Ammonia solution
NSAID	Non-steroidal anti-inflammatory drug
O/I	Volume ratio of membrane phase to internal phase
O/W/O	Oil-in-water-in-oil
PAC	Powdered activated carbon
PILM	Poly ionic liquid membrane
PPCP	Pharmaceutical and personal care product
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SDG	Sustainable development goal
SILM	Supported ionic liquid membrane
SLM	Supported liquid membrane
Span 80	Sorbitan monooleate
TOA	Trioctylamine
W/O	Water-in-oil
W/O/W	Water-in-oil-in-water
WWTP	Wastewater treatment plant

MEMBRAN CECAIR IONIK EMULSI UNTUK PENYINGKIRAN IBUPROFEN DARIPADA AIR SISA SINTETIK MENGGUNAKAN ALIQUAT 336

ABSTRAK

Ibuprofen (IBP) merupakan salah satu ubat anti-radang bukan steroid (NSAIDs) yang diklasifikasikan sebagai pencemaran kebimbangan yang muncul dan telah menarik minat penyelidik dari seluruh dunia untuk mencari teknik pengasingannya yang terbaik daripada air sisa. Membran cecair emulsi (ELM) berpotensi untuk mengekstrak IBP daripada air sisa di mana sistem ini mempunyai beberapa kepentingan, termasuk penggunaan yang mudah, selektiviti yang tinggi dan proses pelucutan dan pengekstrakan dalam satu peringkat dengan keperluan tenaga yang minimum. Walau bagaimanapun, ELM mempunyai kelemahan dalam mengekalkan kestabilannya. Penggantian cecair ionik sebagai pembawa dalam ELM adalah salah satu penyelesaian untuk meningkatkan kestabilan membran. Untuk membentuk membran cecair ionik emulsi (EILM), proses saringan telah dijalankan untuk memilih pelarut, pembawa dan agen pelucutan yang sesuai untuk menyingkirkan IBP daripada air sisa sintetik. Pada masa yang sama, Span 80 telah ditetapkan sebagai surfaktan membran sepanjang tempoh kajian. Sistem EILM yang terdiri daripada heksana (pelarut), Aliquat 336 (pembawa) dan 0.1M natrium karbonat, Na_2CO_3 (agen pelucutan) telah memberi kecekapan penyingkiran IBP yang lebih baik iaitu 82.6%. Selain itu, parameter seperti kepekatan pembawa, kepekatan surfaktan, kelajuan pengadukan dan masa pengemulsian telah dikaji dengan lebih lanjut untuk mencari keadaan yang terbaik untuk aplikasi EILM yang telah dirumus. Keadaan yang terbaik untuk menghasilkan membran yang paling stabil dengan kecekapan penyingkiran IBP tertinggi didapati pada 2 wt% Aliquat 336, 4 wt% Span 80, 300 rpm kelajuan pengadukan dan 10 minit masa pengemulsian. Pada keadaan ini, kecekapan penyingkiran IBP telah mencapai 91.3% dengan 0.016% pecah membran. Pencirian membran juga telah dilakukan bagi menentukan saiz titisan emulsi dan kumpulan berfungsi yang dibentangkan dalam fasa membran EILM dengan menggunakan mikroskop optik dan spektroskopi inframerah transformasi fourier (FTIR). Kesimpulannya, EILM yang dirumus berpotensi tinggi untuk menyingkirkan IBP daripada air sisa dengan cekap dan juga dengan kerosakan membran yang minimum.

EMULSION IONIC LIQUID MEMBRANE FOR IBUPROFEN REMOVAL FROM SYNTHETIC WASTEWATER USING ALIQUAT 336

ABSTRACT

Ibuprofen (IBP) is one of the non-steroidal anti-inflammatory drugs (NSAIDs) which is classified as an emerging concern and has attracted a huge interest from the researchers around the globe in search of better wastewater separation techniques. Emulsion liquid membrane (ELM) has the potential to treat the IBP presented in the wastewater where this system offers a number of benefits, including easily operated, high selectivity and single stage extraction-stripping process with minimal energy consumption. However, maintaining the stability of the membrane is crucial. Ionic liquid carrier becomes one of the alternative carriers to increase the stability of the system. To formulate an emulsion ionic liquid membrane (EILM), a screening process was carried out to choose a suitable diluent, carrier and stripping agent for the removal of IBP from synthetic wastewater. Sorbitan monooleate, Span 80 was fixed as the surfactant of the membrane throughout the study. The EILM system consisted of hexane (diluent), Aliquat 336 (carrier) and 0.1M Na_2CO_3 (stripping agent) was the best EILM formulation from the screening process which provided the IBP removal efficiency of about 82.6%. The effects of parameters such as carrier concentration, surfactant concentration, stirring speed and emulsification time were further investigated to obtain the best experimental conditions for the removal of IBP using the formulated EILM system. The best experimental conditions to produce the most stable membrane with the highest IBP removal efficiency was found at 2 wt% of Aliquat 336, 4 wt% of Span 80, 300 rpm of stirring speed and 10 minutes of emulsification time. Hence, the removal efficiency of IBP was improved to 91.3% with 0.016% of membrane breakage. Membrane characterization also was done by capturing the emulsion droplets size of EILM at the best experimental conditions using an optical microscope. Meanwhile, Fourier transform infrared spectroscopy (FTIR) was used to determine the functional groups presented in the membrane phase of the formulated EILM. In short, the formulated EILM has high potential to remove the IBP from synthetic wastewater efficiently with minimal membrane breakage.

CHAPTER 1

INTRODUCTION

1.1 Background research

Contaminants of emerging concern (CEC) have become a worldwide problem and many scientists are working to discover a long-term solution. CEC is defined as any naturally occurring, manufactured or artificial chemicals that have recently been found or are suspected of being present in various environmental media and whose toxicity or prolonged existence are likely to dramatically change a living thing's metabolism (Sauvé and Desrosiers, 2014). Generally, it is susceptible to poor removal of CECs through conventional wastewater treatment plants (WWTPs) which results in release back the CECs into the environment in concentrations ranging from ng/L to mg/L (Salimi et al., 2017). The presence of these CECs in the aquatic environment creates a major challenge to the environment and human health.

There are several categories of CECs such as pharmaceuticals and personal care products (PPCPs), flame retardants (FRs), artificial sweeteners (ASWs), pesticides and endocrine-disrupting compounds (EDCs). Among all of these categories, PPCPs are considered to have a greater potential to impair the ecosystem and water quality compared to any other pollutants because of their bioactive nature and harmful toxic metabolites (Chopra and Kumar, 2020). For instance, in 2015, the contamination level of emerging contaminant (EC) in aquatic sources of India was reviewed and 41 studies reported that 24% of the total ECs were only resulted from PPCPs (Gani and Kazmi, 2017). Arpin-pont et al. (2019) also reported that in seawater, maximum pharmaceutical contaminant's concentration found in a large range from limit of quantification (LOQ) at 0.084 ng/L to 230,000 ng/L where maximal concentration only for non-steroidal anti-inflammatory drugs (NSAIDs) was detected ranging from 0.7 ng/L to 6100 ng/L. Figure 1.1 shows the pathway of ECs from the origin to the environment where ECs together with their metabolites are being released into the environment through various channels such as industry, residences, hospital and lands. The ECs will eventually end up in surface and also ground waters.

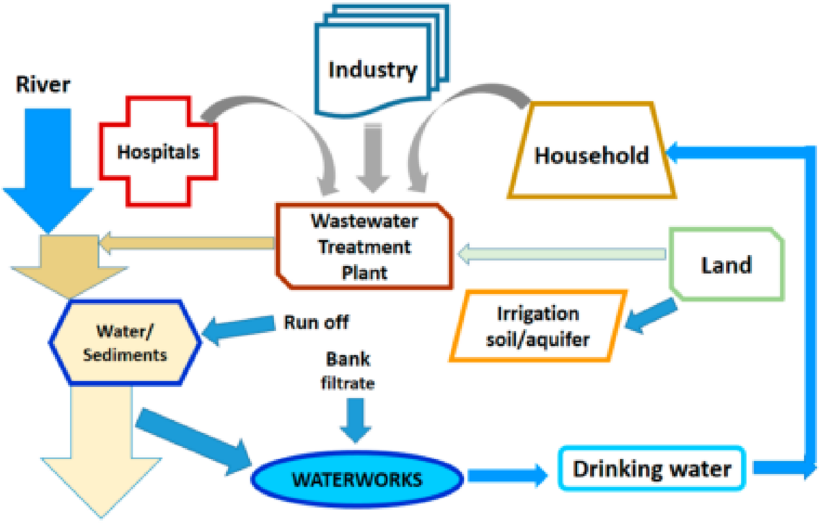

Figure 1. 1 Origin of ECs and their routes in the environment (Vasilachi et al., 2021)

In this current study, ibuprofen (IBP) which is one of the PPCPs is being focused to be removed from the environment, especially from the wastewater. IBP, also known as phenylpropanoic acid, is an organic compound with a structure that contains a benzene ring conjugated to a propanoic acid as shown in Figure 1.2. Meanwhile, Table 1.1 demonstrates the physical and chemical properties of the IBP.

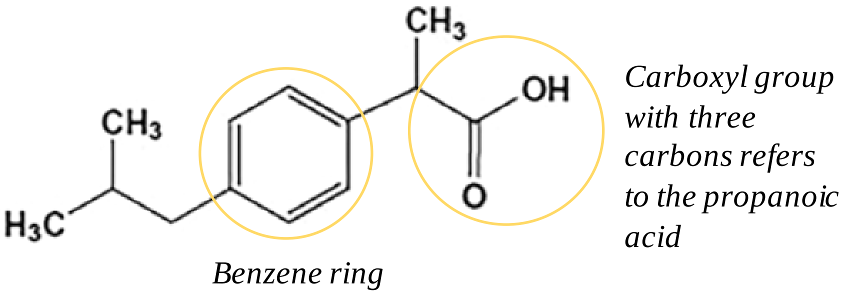

Figure 1. 2 Chemical structure of IBP (Davarnejad et al., 2018)

Table 1. 1 Physical and chemical properties of IBP (Davarnejad et al., 2018)

IUPAC name	2-(4-(2-Methylpropyl) phenyl) propanoic acid
Molecular formula	$C_{13}H_{18}O_2$
Molar mass	206.29 g/mol
Density	1.03 g/cm^3
Melting point	75 to 78 ^oC
Boiling point	157 ^oC
Solubility in water	0.021 mg/cm^3 (at 20 ^oC)
pKa	4.52 (weak acid)

IBP is the third most consumable NSAID (a subclass of PPCPs) in the world which can be detected in many water bodies (Chopra and Kumar, 2020). Since the pharmaceutical is not completely absorbed by the body, it eventually enters the aqua-environment in the form of wastewater. As more IBP are being consumed as a result of increased population pressure, more IBP can be discovered in the water matrices. Because of the high yearly consumption of around 200 tonnes of IBP and the poor metabolite conversion of IBP in the human body, IBP conjugates can be found in WWTPs, surface water and even drinking water (Ivanets et al., 2020). Several studies have shown that most drugs are considerably recalcitrant which cannot be eliminated through conventional WWTPs. As a result, the pharmaceuticals and their metabolites continued to enter the aquatic environment, disrupting the natural balance of rivers, lakes and other ecosystems while also damaging groundwater, surface water and drinking water (Frascaroli et al., 2021).

Apart from that, IBP and other pharmaceutical chemicals are usually used in aquaculture to treat fish infections and they will persist in the aquaculture wastewater at the end for an extended period since the compounds cannot be detected or removed by the wastewater or water treatment plant due to its low concentrations (usually appear in environment in ng/L and µg/L concentrations) (Oba et al., 2021). The low concentration of IBP is still unsafe for living organisms as it leads to long-term adverse effects that can be caused by the continual interaction of these chemicals with the biological system. Hence, it is really important to study about the removal strategies of IBP from the environment, in this case, wastewater.

1.2 Problem statement

Until now, removing or separating IBP from the wastewater has been a serious hurdle considering its poor degradation rate and low detection limit (Ahmad et al., 2021). As an alternative to typical absorption methods of removing IBP, advanced oxidation processes such as ozonation, photocatalytic ozonation and Fenton oxidation had previously been studied. However, these technologies were seemed ineffective to remove IBP due to their several drawbacks such as energy intensive, formation of oxidation products, high capital and operating cost as well as difficulty in operating procedures (Davarnejad et al., 2018; Ivanets et al., 2020; Oba et al., 2021). In addition, IBP is a low aqueous soluble component as stated in Table 1.1, which has a detrimental impact on the use of advanced oxidation and adsorption techniques. Hence, a superior advanced method was required for the separation process of IBP.

At this point, liquid membranes, particularly emulsion liquid membranes (ELM) had piqued the interest of researchers due to their unique characteristics such as high selectivity and fluxes, simultaneous removal and recovery of solutes in a single unit operation, low energy requirement and non-equilibrium mass transfer (Azwan and

Wahab, 2016). However, emulsion stability has become a critical factor that impacts the emulsion performance which has limited its application in the industry (Merouani and Hamdaoui, 2017). Factors that affect the emulsion instability are globule rupture and osmotic swell (Vladimir S. Kislik, 2010). Water from the feed phase diffuses through the membrane barrier and expands the internal phase, causing emulsion swelling. Due to emulsion swell, the internal phase expands and causes further breaking and dilution of the concentrated droplet phase. Besides having surfactant properties, the carrier present in the ELM plays a vital role for the emulsion stability. Carrier exhibits hydrophilic character to minimize the coalescence of water and organic (membrane) phases while maintaining the emulsion from breaking (Razo-Lazcano et al., 2014).

Ionic liquid, often addressed as a green carrier, appears to be an alternative carrier in the ELM formulation to form emulsion ionic liquid membrane (EILM) which can enhance the membrane stability. Ionic liquids' unique properties such as their negligible vapour pressure, low melting point and tuneable physicochemical properties (Petra and Katali, 2011), make them ideal candidates for replacing organic carriers in the ELMs and as a result, for developing environmentally friendly as well as cost-effective membrane separation processes. According to literature reported by Zheng et al. (2020), ionic liquids are greener and more stable to be used as carrier in the EILM when compared to traditional ELM that made up of organic extraction solvent or carrier since the ionic liquid overcomes the evaporation loss of the organic extraction solvent (carrier) used. Aliquat 336 is one of the versatile ionic liquids that is being used in liquid membranes to remove various metal ions, reactive dye and also acetaminophen (Ahmad et al., 2016; Sulaiman et al., 2020; Chaouchi and Hamdaoui, 2014). Besides having ionic liquid as the carrier, selection of diluent and stripping agent for the formulation of EILM is vital since they are also playing major roles in defining the effectiveness of the membrane. Suitable stripping agent that is compatible with the carrier used enhances the removal of the solute from the feed while a good diluent selection allows to facilitate the mass transfer of the solute across the membrane. Even though a good formulated EILM has the stability that is significantly better than the traditional ELM, the emulsion swelling and breakage still occur during the extraction process. Hence, these problems can be minimized by investigating parameters that affect the performance of EILM on the removal of IBP such as ionic liquid carrier concentration, surfactant concentration, stirring speed during IBP removal process and emulsification time. To the best of knowledge, no experiments have been done using ionic liquid-based ELM to remove IBP pollutants from the wastewater, particularly pharmaceutical wastewater. Therefore, this research aims to determine the efficacy of a new EILM formulation by using Aliquat 336 as an ionic liquid carrier and also to study the best experimental conditions for the removal of IBP from synthetic wastewater.

1.3 Research objectives

1. To formulate a suitable EILM for removal of IBP from synthetic wastewater and determine the IBP removal efficiency using the formulated EILM.
2. To investigate experimental parameters that affect the removal of IBP from synthetic wastewater.
3. To analyse the stability of the EILM for the removal of IBP by determining the percentage of membrane breakage.

1.4 Scope of thesis

Interest in the application of liquid membrane especially ELM for wastewater treatment is rising day by day due to the easy and energy intensive operations. Greener and stability enhancement characteristics of ionic liquid captivates the performance of EILM in wastewater treatment, in this case, removal of IBP from the wastewater. Hence, creating the best EILM formulation and understanding of parameters that affect the performance of the membrane are significant. The scope of this project is, first, to formulate an effective EILM system as it is composed of several components such as surfactant, carrier and diluent in membrane phase and also stripping agent as internal phase. Secondly, the parameters that affect the IBP removal efficiency as well as the membrane stability are studied in order to maximize the IBP removal efficiency with least membrane breakage.

To achieve the objectives, preliminary study is done by emulsion screening for the type of diluent, carrier and stripping agent to obtain the membrane formulation with the highest IBP removal efficiency. After the screening process, experiments on the effects of parameters such as carrier concentration, surfactant concentration, stirring speed and emulsification time are carried out. Lastly, membrane breakage is also calculated during the study on the effects of parameters to determine the best conditions that result in the membrane with the greatest stability.

1.5 Sustainability elements in research

The research project should implement the sustainability elements as it can ensure that the conducted project can reduce the environmental damages by protecting our ecosystem, improving the quality of lives as well as by preserving the natural resources for future generations (Mondal, 2013). According to Sustainable Development Goals (SDGs), there are 2 main goals related to the current project.

First and foremost, Goal 6 which is clean water and sanitation where it aims that the water quality is improved by minimizing pollution, eliminating dumping and decreasing the discharge of harmful chemicals and materials. It is also considered the protection and restoration of water related ecosystems such as rivers, lakes, mountains, forests, and wetlands (Nations, 2015; United Nations, 2016). As IBPs are discharged to the environment in the form of wastewater, thus Goal 6 is suitable for the project where the ecosystem is protected by treating and decreasing the pollutants discharged to the environment, especially to the aquatic environment and it also protects the water related ecosystems such as rivers.

Life below water which is the Goal 14 is another SDG that can be applied to the current project. Goal 14 depicts that all kinds of marine pollution must be prevented and reduced significantly (Nations, 2015; United Nations, 2016). Aforementioned, IBP which is one of the PPCPs, will eventually enter the aquatic environment and disrupt the natural balance of the oceans, seas and marine environment. This project focuses on reducing marine pollution by removing ECs such as IBP, hence it can achieve Goal 14 as listed in SDG.

CHAPTER 2

LITERATURE REVIEW

2.1 Treatment technologies of IBP

Several researches were done to remove pharmaceutical waste, particularly IBP, from water bodies due to their harmful impacts on the environment and humans as well as inadequate removal by traditional wastewater/water treatment plants. Adsorption is one of the most common and well-known methods for removing pollutants from wastewater as this method has benefits such as low-cost, low-energy requirement, chemical-free, and simple to use. Oba et al. (2021) mentioned that adsorption, which is a physical method, is effective for removing NSAIDs in wastewater. Electrostatic interaction, hydrophobic interaction such as Van der Waals, ∏-∏ and electron donor-acceptor and hydrogen bonding are the major mechanisms involved in the adsorption of IBP. Traditionally, activated carbon is widely used as adsorbent for the water treatment. Meanwhile, it is also removing the partial concentration of IBP that was found in the wastewater. Granular activated carbon (GAC) and powdered activated carbon (PAC) are the two categories of activated carbon used as the adsorbent. Chopra and Kumar (2020) stated that 5 g/L and 10 mg/L of PAC concentration removed the IBP with concentration of 100 ng/L and 40 mg/L respectively from the surface and synthetic water. Apart from the activated carbon, graphene was also used in the adsorption method to remove IBP with concentration of 10 mg/L from synthetic water which was given a higher removal efficiency of IBP at approximately 95%. Ivanets et al. (2020) also reported that adsorption methods were well suited to remove trace amounts of pharmaceutical pollutants as well as cleaning relatively small amounts of water. However, this method also has some drawbacks, mainly the regeneration of the adsorbent is costly and it also destroys the adsorbed toxic pharmaceuticals or their metabolites. Not only that, the performance is highly influenced by the type of the pollutant that needs to be removed and the adsorbent used (Oba et al., 2021; Ivanets et al., 2020).

Advanced oxidation processes (AOPs) including ozonation and Fenton oxidation are also alternative ways to remove IBP from the environment. Ozonation is an oxidation method where the IBP is removed by the presence of ozone. Strong non-selective oxidizing activity of hydroxyl radical is the main principle of the ozone and the formation of the hydroxyl radicals is the mechanism of the ozonation. Based on literature reported by Chopra and Kumar (2020), ozonation was used to form ultra-pure water by removing IBP from 160 mg/L to 1 mg/L and 12 g/L to 0.1 mg/L in 20 minutes at pH 9 and temperature of 25 ^{o}C. In contrast, the ozonation process is a high energy consumption method. Moreover, it is featured by the formation of oxidation products in large amounts which are more toxic than the parent pharmaceutical pollutants (Ivanets et al., 2020). Davarnejad et al. (2018) also mentioned that the degradation of IBP by direct ozonation was much slower when compared to photocatalytic ozonation. Photo-catalytic ozonation processes have advantages such as high energy efficiency and great mineralization but the presence of toxic oxidation metabolites was the major disadvantage of applying the ozonation method. On an industrial scale, the photocatalytic method is not commonly used due to their high sensitivity towards wastewater turbidity, the difficulty in designing catalytic reactors with appropriate condition to destruct the pollutants effectively and the requirement of UV irradiation for achieving a high degree of the pharmaceutical contaminants' mineralization (Ivanets et al., 2020).

Ivanets et al. (2020) also stated that Fenton oxidation with the application of heterogeneous catalyst based on iron oxides and metal ferrites was a promising way to remove the IBP. Due to its affinity for a variety of contaminants, strong catalytic activity across at a wide pH range and minimal metal ion leaching, magnesium ferrite was an excellent candidate to be used as a Fenton-like catalyst. As a result, magnesium ferrite had a strong affinity for both inorganic and organic contaminants which resulted in increased catalytic efficiency due to the concentration of the eliminated molecules in the surface sites. Fenton oxidation is an oxidation process that produces hydroxide and hydroxyl radical by reacting Iron (II) or Iron (III) (Fe^{2+} or Fe^{3+}, respectively) with hydrogen peroxide (H_2O_2) in order to increase the degradation of organic pollutants. The concentration of H_2O_2 was very important for an effective IBP removal through heterogeneous Fenton oxidation. This was because excessive amounts of H_2O_2 caused low efficiency of reactive oxygen-containing species, low lifetime of hydroxyl radicals and fast recombination of produced hole-electron pairs. Ahmad et al. (2021) reported that the removal efficiency of 0.1mM of IBP was only achieved approximately 50% using an ozone system Fe^{3+}. Besides that, Fenton oxidation also has challenges in disposal of iron sludge and is an energy intensive method (Davarnejad et al., 2018). In short, Table 2.1 below summaries the advantages and disadvantages of the discussed IBP treatment technologies.

Table 2. 1 Summary of advantages and disadvantages of treatment technologies of IBP

Treatment Technology	**Advantages**	**Disadvantages**	**References**
Adsorption	• Low-cost	• Regeneration of the adsorbent is costly	(Oba et al., 2021);

	• Low-energy requirement • Chemical-free • Simple to use	• Performance is highly dependent	(Ivanets et al., 2020)
Ozonation	• Strong disinfection properties • Clean	• High energy consumption • Formation of oxidation products (more toxic than the parent pharmaceutical pollutants)	(Oba et al., 2021); (Ivanets et al., 2020)
Photocatalytic ozonation	• High energy efficiency • Great mineralization	• High sensitivity towards wastewater turbidity • Difficulty in designing catalytic reactors	(Ivanets et al., 2020); (Davarnejad et al., 2018)
Fenton oxidation	• Iron is non-toxic and available abundantly	• Challenges in iron sludge disposal • Energy intensive • Produce more toxic intermediates due to oxidation process	(Ivanets et al., 2020); (Davarnejad et al., 2018)

2.2 Liquid membrane

Liquid membrane technology is a membrane technology that combines liquid-liquid extraction (LLE) and membrane separation in a single continuous operating apparatus or device. This technology has become appealing due to its own benefits and it can also overcome the limitations that the advanced oxidation technologies possessed. Liquid membranes can be classified in three types such as bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM) (Vladimir S. Kislik, 2010). Each type of the liquid membrane is briefly discussed further with its advantages and disadvantages as follows.

2.2.1 Bulk liquid membrane

BLM contains two phases which are a bulk aqueous feed and a receiving phase where both of these phases are separated by a bulk organic. This bulk organic is the water-immiscible liquid phase that acts as the organic membrane and it consists of a carrier that is dissolved in an organic solvent. Vladimir S. Kislik (2010) stated that the feed and receiving phases could be separated from the liquid membrane by using microporous supports or the module could be configured without microporous support. The BLM experimental device, also known as the Schulmann bridge, is a U-shaped tube in which the three phases such as feed, membrane and receiving phases are brought into contact. This system ensures that the hydrodynamic conditions are stable. Generally, the equipment for BLM transport experiments has the benefit of being simple and good membrane stability (Bartsch and Way, 1996; Parhi, 2013). In contrast, BLM has drawbacks of low transfer rates due to small mass transfer area per unit volume, long transportation path with a higher resistance of membrane (Chang, 2016). Hence, BLM also takes a longer time than other liquid membranes for the reaction. It was proved by a literature report by Li et al. (2016) where the optimum reaction time was 60 minutes to treat cyanide from the wastewater using BLM. Besides, BLM also has relatively large data standard deviations and difficulty in sorting out surface active effects in the system (Izatt et al., 1988). Based on the study done by Pourkhanali, Saleh and Khayati (2018), the removal efficiency of *p*-nitrophenol, one of the most hazardous organic pollutants, was achieved about 63% only in 150 minutes using BLM.

2.2.2 Supported liquid membrane

SLM is a type of liquid membrane where the liquid impregnated or immobilized in a porous material used as a support and the support can be a chemically stable inert microporous polymer such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE) (Eljaddi et al., 2017). The supports are usually impregnated with an organic solvent which is immiscible in water and contains a carrier. SLMs have a high selectivity for extraction of chemicals due to the interaction of solute and the carrier which will result in formation of carrier-substrate complexes. The carrier acts as a catalyst and it is required in only small quantities (Eljaddi et al., 2017). SLMs have high transport rates and appreciable fluxes can be achieved even at low concentrations of solute ("Chapter 9. Supported Liquid Membranes," 2005). On the other hand, SLMs also have some limitations such as loss of the immobilized liquid, carrier deactivation and membrane instability in terms of long time performance which results in low solute flux (Parhi, 2013). There are several reasons on the carrier and/or membrane solvent loss in SLM such as pressure difference over the membrane, wetting of supported pores by aqueous phases and existence of gradient of osmotic pressure across the membrane. Othman et al. (2015) studied the performance of SLM in removal of phenol from phenol solution. The results showed that only 35% of maximum removal efficiency was obtained at the optimum conditions due to the membrane instability and it took about 8 hours to yield the maximum removal efficiency.

2.2.3 Emulsion liquid membrane

ELM which is also known as double emulsion and water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) system, consists of three phases such as internal phase (or stripping phase), membrane phase and external phase (or feed phase). There are 4 components present in the ELM which include extractant, stripping agent, diluent and surfactant. Extractant or known as carrier is presented in the membrane phase and it plays a vital role to promote the solute transportation through the membrane phase. For the stripping agent, base or acid can be utilized as the internal phase in the ELM while diluent is a major component of the membrane that reduces the viscosity of the membrane phase to enhance the permeation rate of the solute through the membrane. Lastly, surfactant is a surface acting agent that stabilizes the emulsion. The key benefits of ELMs are a substantially reduced solvent consumption (by approximately 90%) than traditional extraction and a very wide interfacial area (106 m^2 /m^3), which impacts the process kinetics (Kamiński and Kwapiński, 2000). In other words, a relatively thin membrane of ELM results in a rapid solute transportation due to the large surface area (Izatt et al., 1988). However, emulsion instability of ELM is still a drawback of ELM applications in industries (Bartsch and Way, 1996; Merouani and Hamdaoui, 2017).

Following Table 2.2 summaries the benefits and limitations of the liquid membrane types. Meanwhile, Figure 2.1 shows the different configurations of the three types of the liquid membranes. Vladimir S. Kislik, (2010) stated that ELM can be a promising liquid membrane technique as it can achieve the highest mass transfer area compared to the other two types of liquid membranes.

Table 2. 2 Summary about benefits and limitations of different types of liquid membranes

Type	Benefits	Limitations	References
BLM	• Simplicity • Good membrane stability	• Low transfer rates • Higher membrane resistance • Relatively large data standard deviations • Difficulty in sorting out surface active effects	(Chang, 2016); (Parhi, 2013); (Bartsch and Way, 1996); (Izatt et al., 1988)
SLM	• High selectivity • High transport rates • Appreciable fluxes	• Loss of the immobilized liquid • Carrier deactivation • Membrane instability	(Eljaddi et al., 2017); (Parhi, 2013)
ELM	• Reduced solvent consumption • Very wide interfacial area • Rapid solute transportation	• Emulsion instability	(Merouani and Hamdaoui, 2017); (Kamiński and Kwapiński, 2000); (Bartsch and Way, 1996); (Izatt et al., 1988)

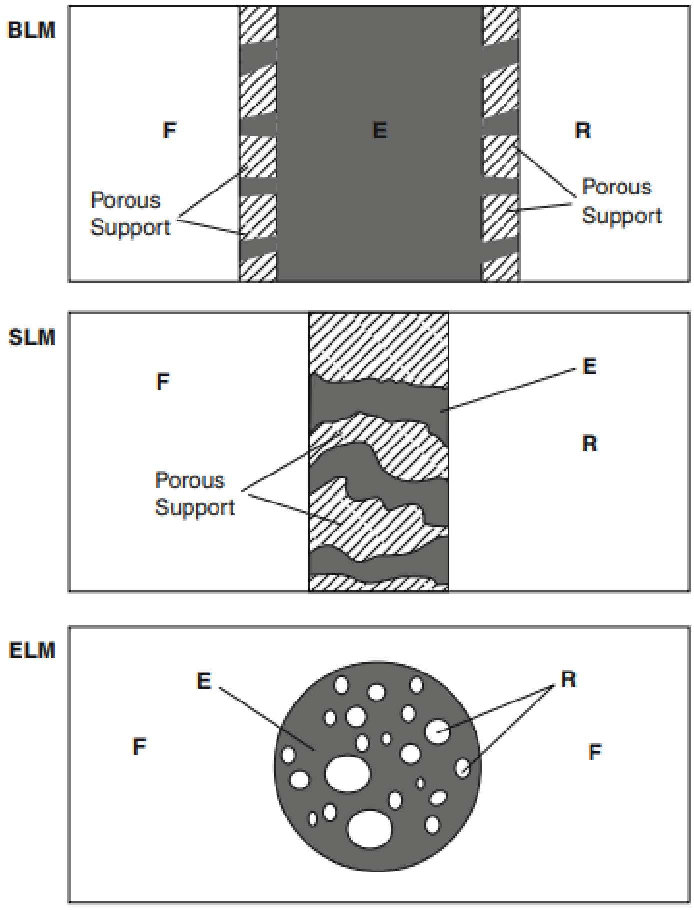

Figure 2. 1 Comparison of BLM, SLM and ELM systems (F is the feed phase, E is the liquid membrane and R is the internal phase) (Vladimir S. Kislik, 2010)

2.3 ELM for IBP removal and its transport mechanism

Recently, the potential technology of ELM has been lightened up as an alternative way to remove a persistent pharmaceutical contaminant, especially IBP from the wastewater. Ahmad et al. (2021) reported that 89% of removal efficiency was achieved by implementing the ELM separation method in a shorter time at optimum conditions. Meanwhile, Razo-Lazcano et al. (2014) showed the highest recovery of IBP at > 99% with a very fast kinetic transfer at 5 minutes of contact. ELM is a promising technique to remove IBP from the environment as it has some attractive benefits such as simple operation with high efficiency, minimal energy consumption, extraction and stripping in one step, increased interfacial area and continuous operation (Ahmad et al., 2021; Brunetti and Felice, 2016). In ELM, the carrier plays a vital role for the removal of IBP from the feed phase. Razo-Lazcano et al. (2014) also stated that carrier significantly influenced the performance of ELM where a stable and highly efficient ELM obtained using only a low concentration of trioctylamine (TOA) carrier during the recovery of IBP from aqueous solution. Table 2.3 displays the IBP removal efficiency using ELM with its respective formulation.

Table 2. 3 ELM formulations with their removal efficiency of IBP

ELM Formulation	**Removal efficiency**	**Reference**
Stripping agent: 0.1M Ammonia; Carrier: 6 wt% Trioctylamine (TOA); Surfactant: 2 wt% sorbitan monooleate (Span 80); Diluent: Kerosene	89%	(Ahmad et al., 2021)
Stripping agent: 0.05M NaOH; Carrier: 0.1% w/V TOA; Surfactant: 5 w/V% modified polyether-polysiloxane (Abil EM 90); Diluent: Parleam 4	>99%	(Razo-Lazcano et al., 2014)
Stripping agent: 0.1N Na_2CO_3; Carrier: N/A; Surfactant: 3 wt% Span 80; Diluent: Hexane		(Dâas and Hamdaoui, 2014)

Remark: In this case, the removal efficiency of IBP varied based on the feed phase type	
(a) IBP from distilled water	99.3%
(b) IBP from natural mineral water	97.3%
(c) IBP from sea water	94.0%

Generally, there are three types of transport mechanisms that can be performed for the transportation of a solute from feed phase to receiving phase in the liquid membranes such as simple permeation, Type I and Type II facilitated transport mechanisms. Simple permeation is a passive transport which does not require any energy to transport the solutes from one phase to another. Meanwhile, the transportation of the solute occurs due to its concentration gradient until it reaches the equilibrium across the membrane (Stillwell, 2016). Apart from that, both Type I and Type II facilitated transport mechanisms are active transports which require energy to transport the solutes from one phase to another. These two mechanisms are different in terms of their source that is used to facilitate the solute transportation. In Type I facilitated transport mechanism, the mass transfer rate of the solute across membrane is increased by assimilating stripping agent in the internal phase of the liquid membrane, especially ELM, where the solute reacts with the stripping agent and produce a membrane insoluble product that cannot be transported back across the membrane phase. On the other hand, Type II facilitated transport mechanisms incorporate a carrier as a reactive component in the membrane phase. The carrier will promote the solute transportation by carrying the diffusing solute across the membrane to the internal phase (S.Kislik, 2016). Figure 2.2 and Figure 2.3 show the simple permeation and Type I facilitated transport mechanisms respectively where the solute (S) is moved from feed phase (F) to receiving phase (R) through liquid membrane phase (E).

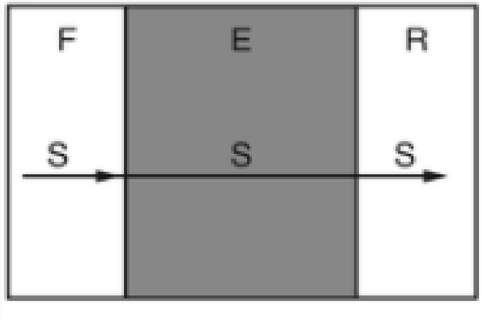

Figure 2. 2 Transport mechanism of solute via simple permeation method (S.Kislik, 2016)

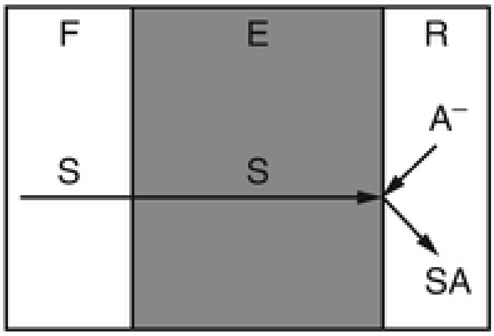

Figure 2. 3 Type I facilitated transport mechanism (S.Kislik, 2016)

For the transport mechanism in the ELM, Ahmad et al. (2021) highlighted that the mechanism used in the ELM was the Type II facilitated transport which consisted of a carrier in the membrane phase to carry out the extraction process. Based on Merouani and Hamdaoui (2017), the Type II facilitated transport mechanism improved the effectiveness of extraction by applying two mechanisms such as converting the solute into an ion state by using an internal phase agent so that it cannot be transferred back through the membrane phase to feed phase and forming a carrier-solute complex.

Generally, the target solutes or pollutants transport from the feed phase to the internal phase across the membrane phase by the concentration difference as the driving force. According to Ahmad et al., (2021), the Type II facilitated transport was started from the protonation or deprotonation of IBP in the feed phase. Addition of acid in the feed phase, for example hydrochloric acid, protonated the IBP to $IBPH^+$ which then formed an ion-complex pair with the carrier during the extraction process at feed-membrane interface. At the membrane-internal interface, the ion-complex diffused and chemically stripped by a stripping agent during the striping process. Figure 2.4 shows the ELM mechanism for the pollutant removal using Type II facilitated transport method.

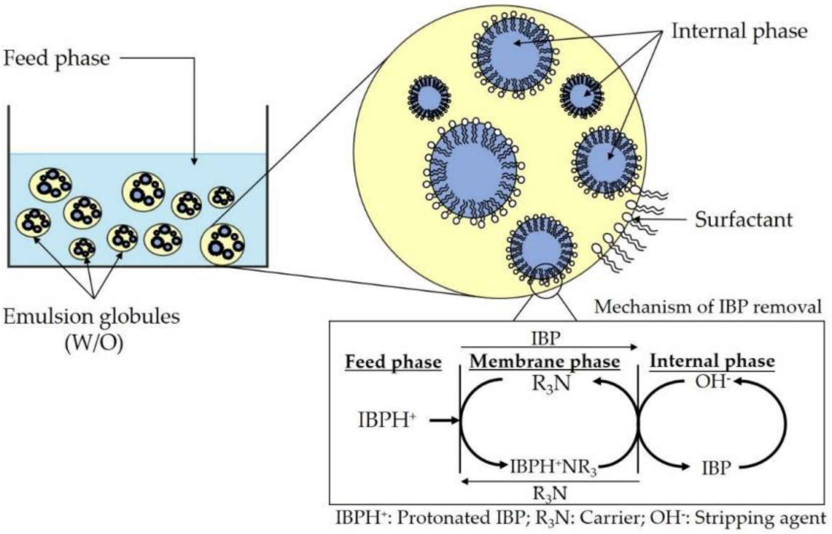

Figure 2. 4 ELM mechanism for the IBP removal (R_3N denoted by the carrier) (Ahmad et al., 2021)

2.4 Ionic liquid (IL) in liquid membranes

Ionic liquids (ILs) are a type of non-molecular compound which is entirely composed of ions with a melting point lower than 100 °C (Lei et al., 2017; Zhao and Anderson, 2012). Basically, ILs are in liquid phase at room temperature or near room temperatures. Based on literature reported by Isosaari, Srivastava and Sillanpää

(2019), IL has organic cations and inorganic anions where the thermochemical properties of the ILs can be tuned easily through combinations of these anions and cations for specific requirements. For instance, the structure of an IL, 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF4]), with the anion and cation portions is shown in Figure 2.5.

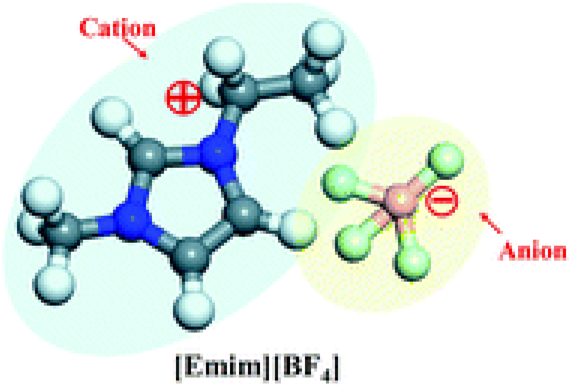

Figure 2. 5 Structure of [Emim][BF4] (Ma et al., 2018)

In addition, ILs' miscibility also highly depends on the ions that they are composed of and the anions in the ionic liquid is significant in determining the hydrophobicity of it. The hydrophobic characteristics of IL allow them to be used in such treatments to extract pollutants from aqueous solutions. ILs are having excellent properties such as low melting point, strong polarity, negligible vapor pressure, tuneable physicochemical properties and a good ability to dissolve many inorganics, organic as well as polymeric materials (Zheng et al., 2020; Petra and Katali, 2011; Isosaari, Srivastava and Sillanpää, 2019). Due to its unique attractive properties, more stable and greener ILs have been scrutinized in separation processes especially in membrane separation processes as an alternative to the traditional organic solvents.

Zheng et al. (2020) also reported that ILs have 4 major roles or functions in fabricating membranes for the liquid separations. Generally, the ILs are used as raw membrane materials, physical additives, chemical modifiers and also as solvents in membrane separations. Even ILs have a lower vapor pressure but they have the characteristics of possessing a good solubility for the organic and inorganic compounds. Hence, the ILs can be utilized directly as the raw materials in the fabrication of liquid membranes such as bulk IL membrane (BILM), supported IL membrane (SILM), emulsion IL membrane (EILM) and also poly IL membrane (PILM) (Zheng et al., 2020). Table 2.4 shows the various applications of ILs that had been studied in the separation technologies using liquid membranes.

Table 2. 4 ILs and their applications in liquid membranes

Ionic liquid	**Liquid membrane type**	**Compound to separate**	**Reference**
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfon-yl)imide [BMIM][NTf2]	BILM	Levulinic acid; acetic acid	(Baylan and Çehreli, 2018); (Baylan and Çehreli, 2019)
	BILM and EILM	Phenolic compound	(Chasib et al., 2022); (S. A. M. Mohammed et al., 2018)
	EILM	Chromium (Cr)	(Goyal et al., 2011)
1-Butyl-3-methylimidazolium	BILM	Levulinic acid; phenolic	(Baylan and Çehreli, 2018);

hexafluorophosphate [BMIM][PF6]		compound; chlorophenol	(Chasib et al., 2022); (Brinda Lakshmi et al., 2013)
	EILM	Phenolic compound	(Balasubramanian and Venkatesan, 2012)
1-Hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF6]	BILM	Levulinic acid; phenolic compound	(Baylan and Çehreli, 2018); (Chasib et al., 2022)
1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF4]	BILM	Chlorophenol	(Brinda Lakshmi et al., 2013)
	SILM	Gas separation of CO_2/N_2	(W. Zhao et al., 2012)
Tri-n-octyl methyl ammonium chloride (TOMAC)	EILM	Lactic acid; chromium	(Kumar et al., 2018); (Goyal et al., 2011)
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [HMIM][Tf2N]	BILM	Levulinic acid	(Baylan and Çehreli, 2018)