Title of thesis	IONIC LIQUID BASED EMULSION MEMBRANE FOR THE EXTRACTION OF BIOLOGICALLY ACTIVE COMPOUNDS FROM WASTEWATER

I HUMA WARSI KHAN

hereby allow my thesis to be placed at the Information Resource Center (IRC) of Universiti Teknologi PETRONAS (UTP) with the following conditions:

1. The thesis becomes the property of UTP
2. The IRC of UTP may make copies of the thesis for academic purposes only.
3. This thesis is classified as

☑ Confidential

☐ Non-confidential

If this thesis is confidential, please state the reason:

Publication and patent application

The contents of the thesis will remain confidential for 5 years.

Remarks on disclosure:

Endorsed by

Dr. MUHAMMAD MONIRUZZAMAN
Associate Professor
Chemical Engineering Department
Universiti Teknologi PETRONAS

Signature of Author

Signature of Supervisor

Permanent address: 445/545
Rohili Tola, Puliya Wali Masjid,
Old City Bareilly-243005, U.P,
India

Name of Supervisor
Assoc. Prof. Dr. Muhammad Moniruzzaman

Date : 07/09/2022

Date : 8/9/2022

UNIVERSITI TEKNOLOGI PETRONAS

By

HUMA WARSI KHAN

The undersigned certify that they have read, and recommend to the Postgraduate Studies Programme for acceptance of this thesis for the fulfillment of the requirements for the degree stated.

Signature: _____

Dr. MUHAMMAD MONIRUZZAMAN
Associate Professor
Chemical Engineering Department
Universiti Teknologi PETRONAS

Main Supervisor: Assoc. Prof. Dr. Muhammad Moniruzzaman

Signature: _____

AP Dr Mohamad Azmi Bin Bustam@Khali
Chemical Engineering Department
Universiti Teknologi PETRONAS

Co-Supervisor: Assoc. Prof. Dr. Mohamed Azmi Bustam @Khalil

Signature: _____

Assoc. Prof. Ir Dr Abdul Halim Shah Maulud
Chair
Chemical Engineering Department
Universiti Teknologi PETRONAS

Head of Department: Assoc. Prof. Ir. Dr. Abd Halim Shah bin Maulud

Date: 8/9/2022

IONIC LIQUID BASED EMULSION MEMBRANE FOR THE EXTRACTION OF BIOLOGICALLY ACTIVE COMPOUNDS FROM WASTEWATER

by

HUMA WARSI KHAN

A Thesis

Submitted to the Postgraduate Studies Programme

as a Requirement for the Degree of

DOCTOR OF PHILOSOPHY

CHEMICAL ENGINEERING

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR,

PERAK

SEPTEMBER 2022

DECLARATION OF THESIS

Title of thesis	IONIC LIQUID BASED EMULSION MEMBRANE FOR THE EXTRACTION OF BIOLOGICALLY ACTIVE COMPOUNDS FROM WASTEWATER

I HUMA WARSI KHAN

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

Huma

Witnessed by

Signature of Author

Signature of Supervisor

Dr. MUHAMMAD MONIRUZZAMAN
Associate Professor
Chemical Engineering Department
Universiti Teknologi PETRONAS

Permanent address: 445/545
Rohili Tola Puliya wali Masjid,
Old City, Bareilly. U.P India

Name of Supervisor
Assoc. Prof. Dr. Muhammad Moniruzzaman

Date : 7/08/2022_

Date : 8/9/2022

DEDICATION

Dedicated to my beloved Mummy Daddy, Phupi Sahib, and my husband Dr. Parvez Alam Khan who were a strong pillar of support in my every up and down

Also, to my niece Tarheema Khan, Brothers and Bhabi and my pet cats who were always my stress busters.

ACKNOWLEDGEMENTS

All praises for Allah, the supreme Lord of all the worlds. Peace and blessings upon Nabi Akram Muhammad S.A.W. and all Ambiyas.

First of all, I would like to acknowledge my supervisor Assoc. Prof. Dr. Mohammed Moniruzzaman, for his kind guidance, support and motivation during my Ph.D journey. His encouragement and kindness gave me the strength and confidence to achieve my objectives. I would like to extend my sincere gratitude to my co-supervisor Assoc. Prof. Dr. Mohamed Azmi Bustam@Khalil for his utmost guidance, suggestions and help during my PhD studies. I would also like to acknowledge Prof. Mohamed Mahmoud Elsayed Nasef and Dr. Ambavaram Vijay for his encouragement, valuable suggestions and help throughout my research work.

I would like to extend my thanks to all the research officers for their support and guidance in carrying out my laboratory work. I would also like to thank all the technicians at Center of research in ionic liquids who helped me to carry out my research work. I would like to thank Research and Innovation Office University Teknologi Petronas Malaysia for providing a graduate assistantship throughout my years as graduate student.

I am very much grateful to all my mentor Mr. M. S Karuna, Ms. Moina Athar and friends Mrs. Huma Siddiqui, Ms Bhavya Mishra, Ms. Kuljeet, Mrs. Kusum Lata, Ms. Masooma Nazar, Ms. Shairoon, Ms. Safiah Dagang for all their motivation and support during my studies. I would like to thank Dr. Mohammad Yusuf, Mrs. Samar Yusuf, and my lil one Baby Fatima Yusuf who were my family here in Malaysia for all their support and motivation. I would like to thank brother Dr. Al Ameen for his continuous guidance and support.

Finally, I would like to thank my beloved parents, Phupi Sahib, my husband Dr. Parvez Alam Khan, brothers (Mr. Munassir and Mr. Paikar Ilmas), Mrs. Shabnam Bhabi, niece Tarheema Khan, and my in laws for their every prayer and motivation to make my PhD journey a success.

ABSTRACT

Emulsion liquid membrane (ELM) has received significant attention for the removal of biologically active compounds (BACs) due to its high selectivity and simple operation. The limitations of conventional ELMs are the instability of emulsion, use of petroleum-based solvents and edible oils. To address such challenges, the aim of this study was to formulate a green and stable ELM for the removal of BACs. Ionic liquids (ILs) were employed as a carrier to improve the stability. Conductor-like screening model for real solvents (COSMO-RS) was used to screen ILs from thousands of ILs. Waste vegetable oil (WVO) was employed as green diluent to eliminate the environmental constraint. The screened IL was used to formulate WVO based ionic liquid emulsion membrane (WVO-ILEM). Span 80 was used as an emulsifier meanwhile sodium hydroxide and nitric acid were used as a stripping agent. The formulated WVO-ILEM was used to extract diclofenac (Dcf), ibuprofen (Ibf), and lactic acid (LA) from aqueous streams. To optimize the extraction process, the effect of various parameters including concentration of surfactant, stripping agent and carrier, phase ratio, homogenizer speed and time, treat ratio, stirring speed, stirring time on stability and extraction efficiency was investigated. Optimization was carried out using response surface methodology (RSM). The best IL screened for BACs was tetramethylammonium sulfate [TMAm][SO_4]. A highly stable WVO-ILEM was developed using screened IL with maximum stability for more than two hours. Maximum extraction efficiency was achieved using developed WVO-ILEM at the optimized conditions obtained using one factor approach. RSM optimized results were in good agreement with experimental results leading to maximum stability and efficacy of WVO-ILEM. The extraction followed first-order rate kinetics with high permeation rates. It was found that WVO-ILEM can be reused up to five to six times with good extraction efficiency. This study suggests that WVO-ILEM are a promising alternative for removing BACs.

ABSTRAK

Membran cecair emulsi (ELM) telah mendapat perhatian yang ketara untuk penyingkiran sebatian bioaktif (BAC) kerana ia mempunyai selektiviti yang tinggi dan operasi yang mudah. Limitasi ELM konvensional adalah ketidakstabilan emulsi, penggunaan pelarut berasaskan petroleum dan minyak makan. Untuk menangani cabaran tersebut, kajian ini bertujuan untuk merumuskan ELM yang mesra alam dan stabil untuk penyingkiran BAC. Cecair ionik (IL) digunakan sebagai pengangkut untuk meningkatkan kestabilan. Model saringan (COSMO-RS) telah digunakan untuk menyaring IL terbaik daripada ratusan IL. Sisa minyak sayuran (WVO) digunakan sebagai pelarut mesra alam. IL yang disaring digunakan untuk merumuskan membran emulsi cecair ionik berasaskan WVO (WVO-ILEM). Span 80 digunakan sebagai pengemulsi manakala natrium hidroksida dan asid nitrik digunakan sebagai agen pelucutan. WVO-ILEM yang dirumus digunakan untuk mengekstrak ibuprofen, diclofenac, dan asid laktik daripada saliran akueus. Untuk mengoptimumkan proses pengekstrakan, kesan pelbagai pemboleh ubah termasuk kepekatan surfaktan, agen pelucutan dan pengangkut, nisbah fasa, kelajuan dan tempoh homogenisasi, nisbah rawatan, kelajuan dan tempoh adukan telah diselidik ke atas kestabilan dan kecekapan pengekstrakan. Pengoptimuman telah dijalankan menggunakan metodologi tindak balas permukaan (RSM). Selepas saringan, IL yang terbaik untuk BAC ialah tetrametilamonium sulfat [TMAm][SO_4].

WVO-ILEM yang dihasilkan menggunakan IL yang disaring mempunyai kestabilan maksimum melebihi dua jam. Kecekapan pengekstrakan yang maksimum menggunakan WVO-ILEM telah dicapai melalui pendekatan satu-faktor (*one-factor)*. Keputusan optimum yang diperoleh menggunakan metodologi permukaan tindak balas (RSM) adalah berpadanan dengan keputusan eksperimen, yang membawa kepada penghasilan WVO-ILEM yang mempunyai kestabilan yang tinggi dan keberkesanan maksimum. Proses pengekstrakan yang berlaku mematuhi kinetik kadar urutan pertama yang mempunyai kadar resapan yang tinggi. WVO-ILEM yang dihasilkan juga didapati boleh digunakan semula sehingga lima hingga enam kali dengan kecekapan pengekstrakan yang baik. Oleh itu, kajian ini mencadangkan bahawa WVO-ILEM adalah alternatif yang berkesan untuk mengeluarkan BAC.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AC^{id}	Activity coefficient at infinite dilution
ACTP	Acetaminophen
APIs	Active pharmaceutical ingredients
AMX	Amoxicillin
BACs	Biologically active compounds
BBD	Box behken design
BLM	Bulk liquid membrane
BP	Becke Perdew
CCD	Central composite design
CECs	Contaminants of emerging concern
CH_2Cl_2	dichloromethane
CIP	Ciprofloxacin
CLM	Contained liquid membrane
COSMO-RS	Conductor like screening model for real solvents
D_2EHPA	di(2-ethylhexyl) phosphoric acid

Dcf	Diclofenac
DES	Deep eutectic solvents
DFT	Density functional theory
DLS	Dynamic light scattering
ECs	Emerging contaminants
ELM	Emulsion liquid membrane
FTIR	Fourier transform infrared spectroscopy
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
HPLC	High performance liquid chromatography
Ibf	Ibuprofen
IFT	Interfacial tension
ILEM	Ionic liquid emulsion membrane
ILs	Ionic liquids
LMT	Liquid membrane technology
MD	Molecular dynamics
Mt/yr	metric tonne per year
MWCNT	Multi-walled carbon nano tubes

NF	Nanofiltration
NMR	Nuclear magnetic resonance
O-W-O	Oil in water in oil
PBM	Polymer based membrane
PI	Performance index
RBO	Rice bran oil
RI	Resolution identity
SFO	Sunflower oil
SLM	Supported liquid membrane
TDA	Tridodecylamine
TRIC	Triclosan
TZVP	Triple zeta valence potential
UF	Ultrafiltration
W-O-W	Water in oil in water
WVO	Waste vegetable oil
WVO-ILEM	Waste vegetable oil ionic liquid emulsion membrane
[ALAMINE 336]	N,N-dioctyl-1-octanamine
[ALIQUAT 336]	Tricaprylemthylammonium chloride

[BMIm][BF_4]	1-butyl 3-methylimidazolium tetrafluoroborate
[BMIm][PF_6]	1-butyl 3-methylimidazolium hexafluorophosphate
[BMIm][Tos]	1-butyl 3-methylimidazolium tosylate
[BtM] [tf_2N]	1-butyl-trimethyl ammonium bis(trifluoromethylsulfonyl) imide
[CYPHOS 101]	trihexyl(tetradecyl)phosphonium chloride
[CYPHOS 104]	trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate
[CYPHOS 167]	trihexyl(tetradecyl)phosphonium chloride
[EMIm][BF_4]	1-ethyl 3-methyl imidazolium tetrafluroborate
[EMIm][Ntf_2]	1-ethyl 3-methylimidazolium bis(trifluoromethylsulfonyl) imide
[OMIm][PF_6]	1-octyl 3-methylimidazolium hexafluorophosphate
[TBAm][Br]	tetrabutylammonium bromide
[TBAm][Cl]	tetrabutylammonium chloride
[TBPh][Br]	tetrabutylphosphonium bromide
[TBPh][Cl]	tetrabutylphosphonium chloride
[TOMAC]	trioctylmethylammonium anthranilate
[TOMAC]	Trioctylmethylammonium chloride
[TOPO]	Tri-n-octyl phosphine oxide

CHAPTER 1

INTRODUCTION

1.1 Background

One of the emerging pollutants in aqueous streams is biologically active compounds (BACs). Amongst BACs, pharmaceuticals, personal care products, and fermentation products are emerging contaminants of concern globally. Most of these BACs are insoluble in water and, therefore, accumulate in the bodies of both terrestrial and aquatic species. These contaminants are toxic, non-regulated, and biologically active, which, when found in waste streams, undergo further reactions giving rise to other harmful contaminants [1]. These byproducts are more hazardous to the environment than the parent compound. They occur in considerable amounts in sewage treatment plants, surfaces, and drinking water [2]. The removal and recovery of these substances are a worldwide concern attributable to their hazardous effects on the environment and individuals, even at low concentrations [3]. Non-steroidal anti-inflammatory drugs (NSAIDs), analgesics, antidepressants, antibiotics, personal care products, fermentation products, etc., are the standard classes that are biologically active [4][5]. NSAIDs are a biologically active group accepted universally and available readily [6]. Amongst NSAIDs, diclofenac (Dcf) and ibuprofen (Ibf) contribute to the top ten exacerbating BACs detected globally commonly used as first aid for pain relief [7]. The concentration of Dcf and Ibf in aqueous streams varies from 1-1000 ng/L [8] [9]. Personal care products are another widely used pharmaceutical as skincare products. Lactic acid (LA) is a widely utilized BACs in skincare products found in the pharmaceutical industry, water effluents, and fermentation broths [10]. The concentration of LA in food waste and fermentation broths varies from 350 - 1500 ng/L [11]. The primary sources of these BACs in water are human excretion, manufacturing companies, industrial discharge, hospitals, and expired and unused medicine. [12].

Adsorption [3], nano-filtration [13], solvent extraction [14], membrane reactor, and advanced oxidation processes [13] are the most common methods employed for the removal of BACs from aqueous streams. Liquid membrane technology (LMT) is one of the efficient techniques used for the removal and recovery of various metals [15], gases [16], organic pollutants [17], [18] and biomolecules [19]. It also finds applications in removing BACs[20][21]. Liquid membranes (LMs) are liquids that separate two aqueous phases of the organic phase and external solute phase. LMs are divided into three types which are bulk liquid membrane (BLM), supported liquid membrane (SLM), and emulsion liquid membrane (ELM). ELM is one of the emerging LM technologies in the separation processes. It has the advantage of high extraction efficiency, high permeation flux owing to the large interfacial area [14], ability to remove solute in minute quantities [18], fast extraction, easy regeneration, and reuse of ELM without further modifications. The only problem with the ELM is the instability of emulsion use of petroleum-based solvents (PBS) and edible oils. An external agent termed "carrier" is added to improve the stability of ELM. Conventional carriers employed are toxic and hazardous to the environment. One immediate alternative is to explore alternative carriers that are less harmful, easy to recover, and environmentally friendly to address these issues. Ionic Liquid (ILs), a class of eco-friendly solvent, may be an effective alternative that possesses excellent properties to overcome the disadvantages of conventional solvents [22].

Carrier selection is crucial for the target molecule and maximizes transport with high selectivity. Ionic liquids (ILs) are also referred to as "architect solvents" because they can be tuned appropriately according to their application [23]. The type of bonding between the ions of ILs, which may is mainly due to hydrogen bonding, dissolved chemicals, and surfaces, making ILs suitable for various applications. In addition, low vapor pressure, high melting point, thermal stability, and inflammability are the excellent characteristics that make them ideal for applications in water treatment technologies [24]. They are also environmentally friendly or "green solvents" because of their lower environmental impact and low toxicity [25]. Therefore, it is believed that ILs will serve as better carriers for the extraction of target BACs from aqueous streams. The only challenge is screening specific IL from the pool of millions of ILs.

The choice of diluent is crucial in the formulation of ELM. Petroleum-based solvents (PBS) are commonly utilized as diluents in ELM applications for BACs. Despite its effectiveness, PBS-based ELM has numerous disadvantages, including toxicity and environmental hazards. It is desirable to design environmentally friendly ELM procedures that do not need the usage of PBS. As a result, recent studies have used virgin vegetable oil (VO) as a diluent in ELM formulation [26] [19]. Furthermore, using VOs over POS is advantageous for non-toxic, biodegradable, renewable, and surface-active [27]. However, with the increase in food crisis, the use of VOs is challenging. Waste vegetable oil (WVO) can play an essential role in addressing this issue. WVO is a sustainable, greener alternative to be used as diluent for ELM formulation by making beneficial reuse of this waste in large quantities. Furthermore, being a waste product, it is inexpensive and widely available in nearly every country. WVO coupled with ILs as a carrier will formulate the eco-friendly, sustainable green membrane.

1.2 Problem statement

ELM is promising and advantageous in terms of efficiency, simultaneous extraction, stripping, selective removal of the target molecule, and treating almost all waste (heavy metals, toxic pollutants, pharmaceuticals, and gases) [28]. However, the instability of emulsion has limited the use of ELM in industrial applications. Unstable emulsion results in emulsion breakage, resulting in leakage of the internal stripping agent into the external solution. As a result, the extraction efficiency decreases [20]. On the contrary, highly stable emulsion hinders the demulsification for the recovery of ELM and internal stripping agents. An external agent known as a carrier is employed to overcome this problem.

Ionic liquids (ILs) have received attention as carriers in the formulation of ELM. Polarity, bonding abilities, less toxicity, and high surface activity are excellent characteristics that make them appropriate as carriers [29]. Some studies have shown the practical significance of the use of IL as the carrier for the removal of phenol [30], lactic acid [19], heavy metals [31], and diclofenac [32]. The ILs used are

Trioctylmethylammonium chloride (TOMAC) [19], Tetrabutylammonium bromide [TBAm][Br] [32], 1-Butyl 3 Methylimidazolium bistriflurosulfonnimide [BMIm][Ntf_2] [33]. Although these ILs improved the stability and extraction efficiency, less attention has been given to comprehensive ILs screening for the target compound. Since there are million ILs, the experimental detection of ILs with excellent dissolving properties is highly cumbersome. As a result, predictive methods must be used to prevent experimental screening for ILs for target BACs. COSMO-RS is an efficient method that can be used to predict the best cation-anion combination for IL selection. The advantage of COSMO-RS is that it only requires the molecule's chemical structure for prior predictions.

Another problem with the existing ELM methods is that they employ either petroleum-based solvents (PBS) or vegetable oils (VOs). PBS is highly toxic and expensive. Although VOs are environment-friendly, apart from being costly, they are also essential food sources; as a result, it's not advisable for use due to the global food diversity crisis (more than one million people are starving for food globally) [34]. Since WVO is readily available worldwide, its disposal is hazardous to the environment, and its consumption is dangerous to one’s health. WVO as a diluent will minimize waste and, as a result, the environmental issues associated with ELM. The use of WVO will reduce the cost of ELM as it is cheap and readily available. WVO-ILEM will address the problems related to the disposal of WVO, toxic PBS, and viscosity issues resulting in more sustainable ELM development. Additionally, to check the efficacy of WVO-ILEM characterization is important. If proper characterization does not take place the WVO-ILEM developed will be unstable and hence less effective.

To obtain a stable emulsion and hence high extraction efficiency of BACs understudy, the selectivity of WVO-ILEM formulation, including surfactant, carrier, internal stripping agent concentration, phase ratio, treat ratio, etc. is essential. Investigating the process parameters during the extraction is also crucial to understanding the BACs extraction process using WVO-ILEM. Since many factors affect the stability and extraction efficiency of WVO-ILEM, optimization of parameters is essential.

Another problem with ELM systems is that the study of permeation rates and kinetics is important. For low permeation rates the ELM developed is unstable and

hence less effective. Hence it is important to study the permeation rates, and kinetics of ELM. In order to reuse the organic phase, demulsification is an important process. Also, the recycling of membrane must be considered to ensure that process is economical.

1.3 Objective

The overall objective of this study is to develop a waste vegetable oil-ionic liquid-based emulsion membrane (WVO-ILEM) using screened IL through COSMO-RS to remove BACs, Dcf, Ibf, and LA. The main objective of this research are:

1. To screen ionic liquids (ILs) via COSMO-RS for BACs removal using diclofenac, ibuprofen, and lactic acid as model compounds.
2. To develop and characterize waste vegetable oil- ionic liquid-based emulsion membrane (WVO-ILEM) using screened IL to remove model BACs.
3. To investigate the effect of various parameters on the stability and extraction efficiency of WVO-ILEM. Also, to optimize different reaction parameters affecting the stability and extraction efficiency of WVO-ILEM using response surface methodology (RSM).
4. To study permeation rates for BACs removal and demulsification to recycle and reuse WVO-ILEM at optimum conditions.

1.4 Scope

This work aims to develop green waste vegetable oil and ionic liquid-based emulsion membrane to extract Dcf, Ibf, and LA from aqueous streams.

Initially, IL was screened through COSMO-RS selecting six cations (aromatic and non-aromatic) and 20 anions. Activity coefficient, capacity, selectivity, and performance index were evaluated to screen the potential IL for BACs. The screened IL was used as a carrier to develop a waste vegetable oil-ionic liquid-based emulsion membrane (WVO-ILEM).

WVO-ILEM was developed using WVO as the diluent, Span 80 as the surfactant, NaOH and HNO_3 as stripping agents, and IL as a carrier was screened. WVO-ILEM was characterized by measuring the density, viscosity, interfacial tension, stand-alone stability, pH, FTIR, emulsion diameter, and breakage.

One factor approach was used to investigate the effect of various reaction parameters on the stability and extraction efficiency of the WVO-ILEM. The parameters include surfactant concentration (0.5-2.5 wt.%), stripping agent concentration (0.05-0.25 M for Dcf, 0.01-0.025 M for Ibf and 0.05-0.25 M for LA), IL concentration (0.1-0.5 wt.%), phase ratio (0.15-0.35), homogenization speed (3200-7200 rpm), homogenization time (1-13 min). The effect of these parameters on density, viscosity, interfacial tension, stand-alone stability, pH, emulsion diameter, breakage and extraction efficiency were investigated. The application of WVO-ILEM for BACs extraction was studied. The parameters that affect the extraction efficiency were investigated. The parameters were, treat ratio (1:1-5:1), stirring speed (160-380 rpm), stirring time (15-35 min for Dcf, 1-13 min for Ibf, and 15-30 min for LA), settling time (1-10 min), feed concentration (Dcf=100 μg/mL, Ibf=100 μg/mL, LA=5000 μg/mL). These parameters were studied to determine the optimum conditions of the WVO-ILEM process for BACs extraction. Also, this was beneficial in determining the range of significant parameters for the next objective.

Response surface methodology (RSM) was employed to optimize the parameters that significantly impact WVO-ILEM stability and extraction efficiency. A set of statistical experimental design was created to optimize the process parameters, including surfactant concentration (0.5-2.5 wt.%), internal stripping agent concentration (0.05-0.25 M for Dcf, 0.01-0.025 M for Ibf and 0.05-0.25 M for LA), carrier concentration (0.1-0.5 wt.%), phase ratio (0.15-0.3), and treat ratio (1-4). 50 experimental runs were conducted based on five variable central composite designs (CCD) using Design expert 13.0. Equations of the model obtained were validated through statistical tests known as the analysis of variance (ANOVA). Response surfaces were plotted to determine the individual and interactive effects of the variables on the removal of Dcf, Ibf, and LA.

At the optimized conditions obtained using RSM, the permeation rates, diffusivity, and kinetics was evaluated for Dcf, Ibf, and LA. Recycling and reusing

WVO-ILEM is an essential feature in the ELM process economically and environmentally. To achieve this, demulsification was carried out. WVO-ILEM was recovered and reused after emulsification for further extraction of BACs.

1.5 Thesis Outline

This chapter comprises five chapters:

Chapter 1: Introduction: This chapter presents a brief introduction of pharmaceutical waste and ELM, ILs, COSMO-RS, and WVO-ILEM, including the research background, problem statement, research objectives, scope, and thesis outline.

Chapter 2*: *Literature review: This chapter provides an overview of pharmaceutical wastes and conventional methods used to treat pharmaceutical wastes and their drawbacks. Also, it presents a study on liquid membrane technology (LMT), ELM, its type, and different constituents. Also, it discusses the screening of ILs through COSMO-RS. This chapter also includes the impact of various reaction parameters that affect the stability and extraction efficiency of ELM. This chapter presents a brief description of the optimization method, response surface methodology, permeation rates, kinetics, recovery and reuse of ELM.

Chapter 3*: *Research Methodology*:*** This chapter presents material and methods, the COSMO-RS screening procedure used for IL, and the experimental procedure used to formulate WVO-ILEM. Further, this chapter presents the characterization of WVO-ILEM. Next, the stability, breakage, extraction efficiency were determined. In addition, this chapter also discusses the RSM optimization procedure for optimizing various parameters to achieve optimum extraction efficiency. Also, at optimized conditions it presents the permeation rates, kinetics of separation and demulsification for the recovery and reuse of WVO-ILEM.

Chapter 4*: *Result and Discussion: The complete modeling and experimental results for an effective WVO-ILEM formulation are present in this chapter. It presents the COSMO-RS screening of the model compounds Dcf. Also, this chapter discusses

various factors that affect the stability and the extraction efficiency of WVO-ILEM for the extraction of selected Dcf. WVO-ILEM was further optimized using response surface methodology (RSM) to extract Dcf. Best optimized conditions were obtained using RSM. Also, it presents the demulsification study for the recovery and reuse of WVO-ILEM. Lastly, it gives the permeation rates and kinetics of the separation of Dcf using WVO-ILEM.

***Chapter 5*:** This chapter summarizes the main findings of the present study and recommendations for future work for the WVO-ILEM.

CHAPTER 2

LITERATURE REVIEW

This chapter discusses the biologically active compounds and their adverse effects on the environment. Emulsion Liquid membrane, its limitations, and its different constituents are reviewed, and the necessity for an environment-friendly emulsion liquid membrane is highlighted. The potential of ionic liquids as carriers and waste vegetable oil as diluent is discussed. In addition, the selection of IL for specific BAC from millions of ILs using COSMO-RS is explored. The effect of various reaction parameters on stability, extraction efficiency, and response surface methodology optimization is reviewed. This chapter also presents the permeation, kinetics, and demulsification for the recovery and reuse of ELM.

2.1 Biologically active compounds

An emerging environmental issue is the presence of biologically active compounds (BACs) in aqueous streams. Pharmaceuticals and fermentation industries are significant contributors of BACs [35]. The pharmaceutical industries are one of the most influential and growing sectors worldwide. The only sector working twenty-four-seven, even in a pandemic, is pharmaceuticals. With the increase in population, there's a tremendous rise in the usage of pharmaceutical products. This is the increased consumption of medications to treat various diseases. These compounds have emerged as a global pollution problem [36]. When disposed to water bodies and the environment, these life savior diseases possess adverse effects on flora and fauna, aquatic life, and humans [4]. These products are termed contaminants of concern (CECs) or emerging contaminants (ECs) [37]. These drugs are biologically active and undergo further reactions producing hazardous toxic compounds, resulting in an adverse effect on the ecosystem, aquatic life, and humans [1]. In many areas, the presence of these contaminants in drinking and irrigation water raises health concerns and poses water management issues. The prevalence of these developing pollutants is particularly of great concern in areas where drinking water is scarce and management is challenging [38]. Several factors contribute to this circumstance, including the end of therapy, expired medication, dose adjustments, unpleasant side effects, carelessness, and

forgetfulness [39][36]. The leading cause of these BACs entering water streams is excretion, unused medicines, and the manufacturing industries [40][41]. However, the concentration of these contaminants is ng/L - µg/L [42]. Because of their bioactive nature and biogeochemical cycle, this quantity is sufficient to harm aquatic life and humans [43][44]. These compounds have adverse effects, harming different organs, tissues, cells, biomolecules, etc. [45].

Pharmaceuticals, personal care products, and fermentation waste are the common BACs in aqueous streams. Fig. 2.1 depicts the statistics of selected BACs in aqueous streams. Dcf, Ibf, and LA can be easily detected in aqueous streams because of their availability and easy reach without prescription. Apart from this, Dcf and Ibf cause their adverse effects are included in the top ten exacerbating contaminants [1]. LA is the widely found BAC in aqueous streams with considerable concentration as it finds vast applications in personal care products, medical, polymer, and other sectors [10]. Considering their easy availability, reach, and harmful effects Dcf, Ibf and LA were selected as model compounds. Table 2.1 shows the physicochemical properties of Dcf, Ibf and LA.

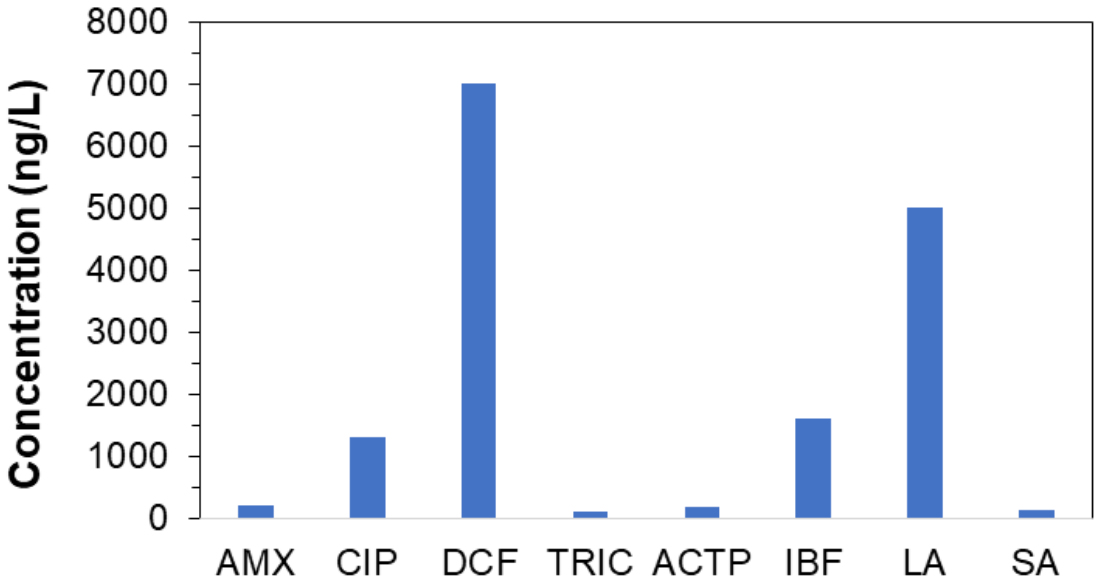


Figure 2.1: Statistics of BACs in aqueous streams [1][46]

2.1.1 Diclofenac as a model compound

Diclofenac (Dcf) is the most extensively used pain reliever in the world. It is used to treat arthritis, osteoarthritis, spondylitis, and several other diseases. Dcf is readily available over the counter with or without a prescription making it one of the waste stream contaminants [47]. It is sold under a variety of tradenames such as Volini, Voltaren, diclofenac etc., worldwide. Global consumption of Dcf is estimated to be greater than 1500 tons; however, this statistics incorporates only human consumption as veterinary data is not available [7]. Dcf, when consumed, undergoes several reactions and is transformed into harmful metabolites. The drawback treatment methods eradicate 30-70% of Dcf from wastewater treatment plants (WWTPs). The untreated Dcf reaches surface water. Due to its persisting biologically active nature, it transforms into toxic compounds in water bodies. The transformed compounds or metabolites are more harmful than the proto compound. Due to its poisonous effects, it's been encompassed in the 100 emerging contaminants and also in European (EU) decisions [8]. Dcf occurs in surface, ground, and seawater [2]. The concentration usually found in water bodies ranges from 1-1000 ng/L [8]. It's an emerging contaminant of concern because they are neither biodegradable nor can be removed easily from aqueous streams [48]. It is highly toxic to marine life and humans. Natural methods are unable to handle these contaminants, necessitating the development of new techniques. As a result, these products accumulate in the environment harming aquatic life and the ecosystems [44]. To protect the environment, the removal and recovery of these BACs are essential. Table 2.1 presents the physicochemical properties of Dcf.

2.1.2 Ibuprofen as a model compound

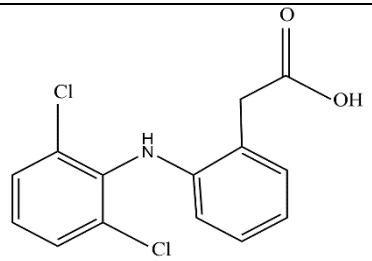
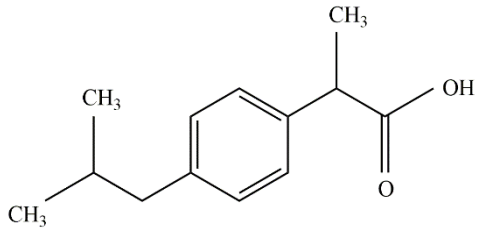
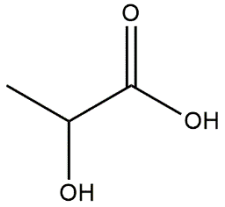
Ibuprofen (Ibf) is another emerging contaminant of concern and popular drug used to treat arthritis, rheumatic disorders, and fever by inhibiting prostaglandin [49]. Ibf is one of the fundamental medications on the World Health Organization's (WHO) "Essential Drug list" and is produced in large quantities worldwide. It is available easily without any prescription over the counter [50]. It is an acidic drug used in the treatment of arthritis, inflammation,

and fever. The accumulation rate of Ibf in waste streams is high as it is sparingly soluble in water. The production of Ibf is estimated to be in kilotons. It exists in water bodies such as drinking water, sewage water, and seawater. The concentration of Ibf in waste streams varies from 1.2-100 μg/L [9]. Ibf, when undergoes biological activity, it transforms into more harmful products. These byproducts affect algae, aquatic life [51] and sometimes result in death [52]. Ibf, metabolizes as hydroxy and carboxy in aqueous streams, causing an accumulative effect and major ecosystem changes [53]. The accumulation of Ibf in water bodies impacts marine life and aquatic life as well. Hence the removal of Ibf from aqueous streams is of concern. Table 2.1 presents the physicochemical properties of Ibf.

2.1.3 Lactic acid as a model compound

LA is one of numerous regularly utilized BACs found in water effluents from pharmaceutical, cosmetics, and fermentation broths [54]. LA is used to cure gum diseases, emulsifying agents, skincare products, and supplements in pharmaceutical industries [55]. The amount of LA in a dilute aqueous stream varies from 1-20%. Due to its widespread application in personal care products, fermentation waste, bio solvents, etc., LA was selected as a model analyte for the extraction and removal from aqueous streams. Considering its general use, high cost, and rising demand in various sectors, the recovery of LA from water streams is highly beneficial. Besides the extraction and recovery of LA, its removal from drinking water sources ensures safety for human consumption. Table. 2.1 shows the physicochemical properties of LA.

Table 2.1: Physico chemical properties of model biologically active compounds

Molecule name	**Chemical Structure**	**Chemical formula**	**Mol. Wt. (g/mol)**	**Wavelength (nm)**	**Melting point (°C)**	**Solubility (mg/mL)**
Diclofenac		$C_{14}H_{10}C_{l2}NO_2$	318.13	270 nm	279-289 °C	50.0
Ibuprofen		$C_{13}H_{18}O_2$	203.13	220 nm	75-77°C	0.021
Lactic acid		$C_3H_6O_3$	90.078	390 nm	18°C	miscible

2.1.4 Conventional methods used for the removal of BACs

Traditional methods used for the treatment of pharmaceutical wastes can be classified as

i. Physical methods

ii. Biological methods

iii. Advanced Oxidation Process

Physical methods involve phase change. Adsorption is the most commonly used physical method. Activated carbon, graphene, and carbon nanotubes are the commonly used adsorbents for pharmaceutical compounds [56]. Other methods include membranes, in which the solute to be removed gets transferred into another phase. Biological methods involve the use of a microorganism for the removal of solute. These processes are aerobic and anaerobic [57]. Advanced oxidation processes involve using an oxidizing agent and an energy source [58]. Aqueous biphasic systems (ABS) is another widely used method for separating BACs. Liquid-liquid extraction, Solid-liquid extraction using molecularly imprinted polymers (MIPs), etc., are the common extraction techniques used to extract BACs. However, these all methods possess several disadvantages. The adsorbents employed in adsorption are costly, deteriorate with time, and possess less removal efficiency. Extraction employs a wide range of toxic solvents, and solvent recovery is expensive. MIPs are ineffective in selective extraction of BACs [59]. Biological methods are less efficient, unable to quantify and identify compounds in complex mixtures. The microorganisms are affected by pH, temperature, etc. [44]. The disadvantages of the conventional methods are present in Fig. 2.2. The separation of BACs utilizing ABS [60], adsorption [61], MIPs, are effective. They do, however, have a few disadvantages. Solvent recovery is expensive. The solvents are toxic and result in adverse effects on the environment, and it might be difficult to extract biologically active molecules if they are present in low concentrations. MIPs are ineffective in selective extraction and can't extract BACs simultaneously [59].

Membrane technology is a viable alternative utilized to treat wastewater due to its numerous benefits in recent times. It takes up less space and can handle water of various compositions. Ultrafiltration (UF), microfiltration (MF), nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO) are the commonly used membrane-based systems in wastewater treatment. These membranes are c[14]ostly. Furthermore, because numerous membranes are flimsy, the pores in the supported membrane technique become blocked, making the approach less efficient. Liquid Membrane Technology (LMT) has emerged as an alternative and efficient method for removing BACs.

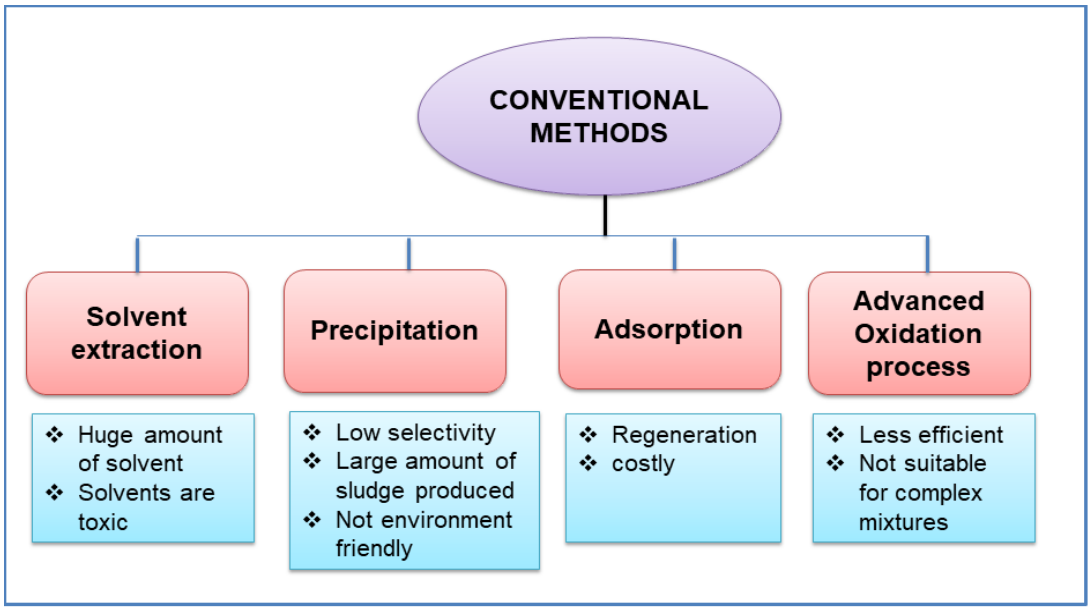


Figure 2.2: Conventional methods and their disadvantages [44][58]

2.2 Liquid Membrane Technology

Membrane technology is one of the emerging techniques for separating various components. Various processes such as filtration, ultrafiltration, nanofiltration, reverse osmosis is used to remove and recover various solutes, including metals, gases, biologically active solutes, etc. However, when the solute concentration is in minute quantities, these membranes sometimes become less efficient and possess less mass transfer and selectivity [62]. To overcome these limitations, Liquid membranes (LM) were developed. A liquid membrane (LM) can be defined as a "homogeneous, non-porous, thin film of organic liquid embedded between two aqueous phases of distinct composition" [63]. The phase on both

sides of the membrane can be either liquid or gaseous [64]. The fabrication of LM dates back to 1902 by Nernst [65][66]. LM finds diverse applications in biotechnology, organic chemistry, chemical engineering, and wastewater treatment. Generally, LM is categorized as with support and without support. The membranes that do not support are bulk liquid membrane (BLM) and emulsion liquid membrane (ELM). Those employing support are labeled as the supported liquid membrane (SLM) and contained liquid membrane (CLM).

Bulk Liquid Membrane (BLM): The simplest form of LM is BLM. This type of separation of two miscible phases, usually the external aqueous phase (feed) and stripping agent, by a third immiscible organic phase. The mass transfer occurs from the external aqueous phase to the internal phase by a third phase consisting of a carrier. BLM is not recommended for large-scale operation cause of its large width, low flux rates, low selectivity, and high cost [67][65]

Supported Liquid Membrane (SLM): The name suggests these membranes employ support, eg. liquid is trapped inside the pores. The membrane is compressed between two cells filled with a feed and receiving phase (stripping agent). Hence it is termed immobilized or supported LM. Supports are usually made of polymers. Commonly used polymers as a support are propylene, polysulfone, polyvinylidene, etc. [67]. The main drawback of SLM is instability, corrosion of polymeric materials, loss of carrier, and short lifetime of the process [68]

Poly Inclusion membrane (PIMs)

Polymer inclusion membranes are fabricated by casting cellulose triacetate from an organic solution to form a thin stable film. The solution is composed of an ion carrier and a membrane plasticizer. The resulting membrane does not contain organic solvent and can separate the source and receiving phases in the PIMs systems while preserving ionic species transport. The only constraint of PIMs is that it finds applications in the separation of metal ions and small organic molecules [69] and lesser flux.

2.3 Emulsion Liquid membrane

Emulsion liquid membrane (ELM) is the most effective method for separating and concentrating solutes in trace amounts. ELM has emerged as an effective technique as compared to other LM technologies because of its esteem advantages.The development of ELM with improved mass transfer dates back to 1968 by Norman Li. ELM proved advantageous in the treatment of wastewater as compared to other separation methods such as ion exchange, chemical precipitation, adsorption, nanofiltration, ozonation, etc. ELM is also termed as “liquid surfactant membranes” or “double emulsion membranes.” Emulsifying two phases fabricate ELMs: organic or diluent and internal stripping, usually aqueous [70]. The prepared emulsion is dispersed into another external aqueous phase containing the solute to be removed. ELM can be further subdivided as oil in water in oil (O-W-O) and water in oil in water (W-O-W). In O-W-O, the dispersion of oil droplets occurs in larger water droplets dispersed in the oil phase. In W-O-W emulsion, the aqueous phase (external feed phase) gets dispersed in the oil phase distributed in the water phase [71]. The concentration gradient across the membrane is the driving force for solute transport from the external feed phase to the internal stripping phase. Fig. 2.3 shows the schematic representation of ELM formulation.

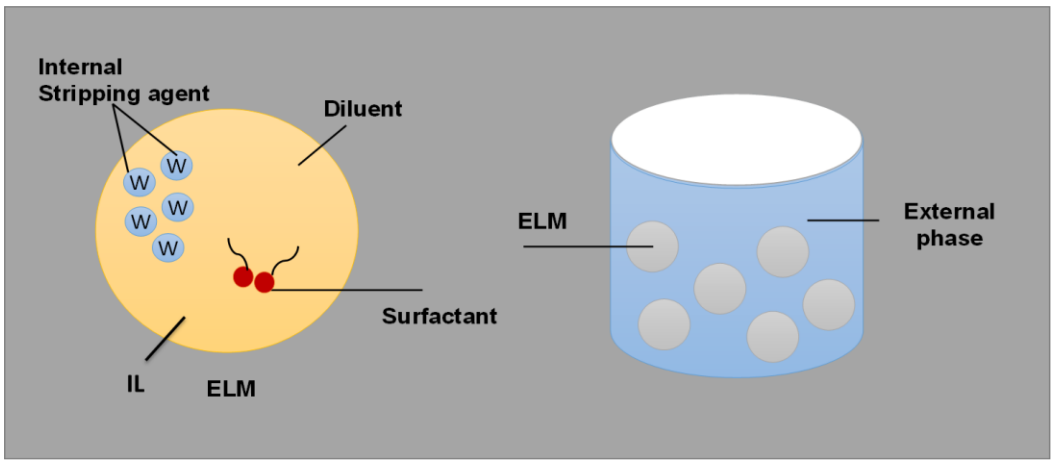


Figure 2.3:ELM components representation

2.3.1 Components of ELM

The three essential components of ELM are:

i. Membrane phase: consists of organic diluent that separates the internal droplets in the external phase. It incorporates an organic diluent, a surface-active agent or emulsifier, and an extractant or carrier.

ii. Internal phase: This is usually aqueous and is constituted by a stripping agent.

iii. External phase: it consists of solute to be removed and is aqueous

2.3.1.1 Diluent

A diluent is any substance that is either a liquid or a homogenous mixture of liquids. Diluent selection is critical in the formulation of ELM since it is a vital component of the membrane phase and is responsible for membrane stability [72]. It also substantially impacts membrane properties such as diffusion coefficient, stability, and ELM performance. The diluent selected must be capable of dissolving the extractant. The specific properties of diluent are:

i. Must be mutually soluble with the extractant

ii. Must possess high solvency for the solute to be extracted

iii. Must be insoluble in the aqueous phase

iv. Have low surface tension

v. Cheap and readily available

Several other properties must be considered while selecting the organic diluent, such as specific gravity, viscosity, flash point, and polar nature. Commonly used solvent for the ELM formation is aliphatic as compared to aromatics.

- *Petroleum-based solvents*

  Generally, petroleum-based solvents (PBS) such as n-hexane, kerosene, cyclohexane, benzene, toluene, etc. [19] are employed to separate solute. Table 2.2

summarizes some PBS-based ELM systems for various applications. Although PBS-based systems provide good extraction efficiency, several disadvantages are associated with them. Since PBS possess less viscosity, the ELM formed is highly unstable. Other disadvantages are toxicity, volatility, non-degradable, and non-renewable. According to the world health organization, the acceptable amount of PBS in water is 0.05mg/L, which is far greater than that [73]. As a result, they're tough to work with, and they pose an ecological risk to the aquatic environment owing to solvent degradation caused by aqueous phase entrainment. As a result of increasing PBS usage and the loss of solvents, costs rise. Also, due to the decline of petroleum supplies, PBS is a costly solvent. To overcome these challenges and ensure a greener process, greener diluents are gaining interest [74]. Vegetable oils are suitable alternatives to PBS.

Table 2.2: PBS based ELM systems

S.No.	PBS	Solute to be removed	Carrier	Surfactant	Stripping agent	Efficiency (%)	Reference
1.	Kerosene, Butyl Sulfate	Amoxicillin	Aliquat 336, TOA	Span 80	Na_2CO_3, NaCl	98.20	[21]
2.	DCM	Diclofenac	TBAB	Span 80	NaOH	99.65	[32]
3.	n-heptane	Diclofenac	TOA, D_2EHPA	Span 80	HNO_3	95	[75]
4.	Hexane	Ibuprofen	-	Span 80	NaOH	99.3	
5.	n-octanol	Bioactive Compounds	-	Span 80	$FeCl_3$-HCl	98.08	[76]
6.	Kerosene	4-Nitrophenol	[BMIm][Ntf_2]	Span 80	NaOH	99	[77]
7.	Chloroform	Tropane Alkaoids	[PTr][PF_6]	Span 80	NaOH	94.14	[78]
8.	Heptane	Tetracyline	TBP	Span 80	HCl		[79]
9.	kerosene	Uranium	TTFA	Span 80	HCl	99.8	[80]
10.	Kerosene	Phenol, Chlorophenol, Nitrophenol	[BMIm][Ntf_2]	Span 80	NaOH	81, 91, 95	[33]
11.	kerosene	Lead	D_2EHPA	Span 80	H_2SO_4	97.2	[81]
12.	Kerosene	Dysprosium	CYANEX 272	Span 80	HNO_3	90	[82]

13.	Kerosene	Acetaminophen	TOA	Span 80	NH_4	85	[83]
14.	Kerosene n-heptane	Acetaminophen	TOA	Span 80	NH_4	85	[84]
15.	n-heptane	Ciprofloxacin (CIP)	nano-Fe_2O_3, TBP	Span 80	HCl	98	[85]
16.	Kerosene	Benzoic acid	[BMIm][Ntf_2]	Span 80	NaOH	99.7	[86]
17.	Kerosene	Polyphenols	TBP	Span 80	NaOH	91	[87]
18.	Kerosene	Gadolinium	D_2EHPA	Span 80	HNO_3	99	[88]
19.	Kerosene	Ibuprofen	TOA	Span 80	NH_4	89	[89]
20.	Octanol	Bio-succinic acid	TOA	Span 80	NaOH	99	[90]

- *Vegetable oil*

As the name suggests, Vegetable oil is a naturally derived oil from plants and fruits. Most vegetable oils are derived from soybean, coconut, palm, sunflower, canola, etc. It is a valuable commodity produced worldwide and is used in the food sector, primarily for cooking and producing soaps, pet food, fragrances, and cosmetics. Fig. 2.4 shows the use of vegetable oils in various sectors [74]. VOs are advantageous since they have surfactant properties, high viscosity, are environmentally benign, renewable, and cheap. Also, as compared to PBS, VOs are green solvents because of their vast bioresources and ease of processing [28] and hence can be utilized as a diluent in ELM formulation. Several authors reported ELM formulation using vegetable oils (VOs) such as palm oil, rice bran oil (RBO), sunflower oil, and olive [91], [19] [92]. The use of VOs results in a stable emulsion, thereby improving the extraction efficiency. Table 2.3 summarizes research carried out using VO as a diluent for ELM formation.

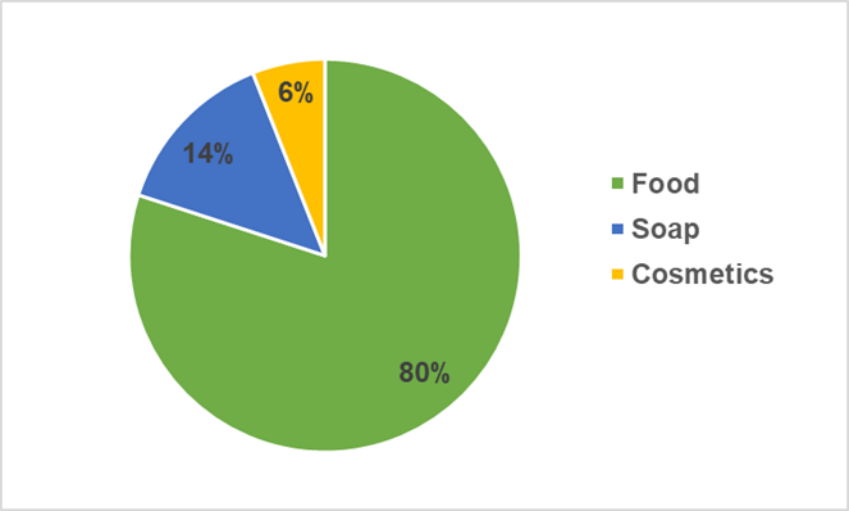


Figure 2.4: Uses of vegetable oils in different sectors [74]

Table 2.3: VOs based ELM systems for different solutes

S.No.	Solute to be removed	VOs	Carrier	Surfactant	Stripping agent	Efficiency (%)	Reference
1.	Lactic acid	Sunflower oil	Aliquat 336	Span 80	NaOH	99	[26]
2.	Succinic acid	Palm oil	Amberlite LA-2	Span 80	Na_2CO_3	70	[93]
3.	Lactic acid	Rice bran oil (70%)	TOMAC	Span 80	NaOH	90	[19]
4.	Succinic acid	Palm oil	Amberilite LA-2	Span 80	Na_2CO_3	100	[94]
5.	Chromium	Palm oil	TOMAC	Span 80	NaOH	97	[15]
6.	Phenol	Palm oil	[BMIm][Ntf2]	Span 80	NaOH	83	[95]
7.	Phenol	Palm oil	TOA	Span 80	NaOH	93	[18]
8.	Chromium	Palm oil	TOMAC	Span 80	NaOH	99	[96]
9.	Reactive red dye 3BS	Palm oil	TDA	Span 80	$NaHCO_3$	90	[97]
10.	Chromium	Sunflower oil	Aliquat 336	Span 80	NaOH	99	[98]

11.	Chromium	Sunflower oil	TOPO	Span 80, Tween 20,	Na_2CO_3	96	[72]

However, since VOs are the primary ingredient for the food industry, the food crisis is the main challenge in most developing countries with an increase in population. As a result, using virgin VOs as a diluent is not recommended. Waste vegetable oil (WVO) could be a suitable alternative as a diluent for ELM to overcome this.

- *Waste vegetable oil (WVO)*

WVO is one of the significant food wastes and is found up to 25% wt. on a dry basis apart from carbohydrates and starch. It is generated from household kitchens, restaurants, casinos, and other food facilities. The current global production is estimated from 20-32% of total vegetable oil consumption (41-52 Nt/yr) [99]. WVO consumption is harmful, and disposal is another challenge cause of irresponsible behavior and lack of environmental restrictions. Vegetable oils solidify at lower temperatures due to the differing characteristics of oil and water. WVOs are frequently disposed of in sinks, with solid kitchen trash disposed of in landfills. WVO deterioration causes metal corrosion and concrete components, among other things, and WVO disposal causes blockage of pipelines and sewage systems [34].

With the rise in environmental concerns, measures and research on WVO use are being taken. Biodiesel production [100], urea production [101], soap manufacturing [102], and fodder are amongst the few applications. WVO is still being utilized less, even though it is being produced more. Hence, it is suggested to employ WVO as a feed-in for various processes. Based on the literature, the composition of WVO mainly consists of free fatty acids, some water, mono, di, and triglycerides, sodium, boron, and phosphorous [103]. Using WVO as a diluent includes its low cost, non-toxicity, renewable nature, non-volatility, non-flammability, and biodegradability.

The use of WVO as a diluent in ELM will be economical, sustainable, and eco-friendly [74]. There have been very few studies on the preparation of ELM from WVO. In a recent study, WVO was used to make ELM, which was then utilized to remove methyl violet from wastewater. The ELM was composed of WVO as a diluent, Span 80 as a surfactant, and hydrochloric acid as an internal stripping agent. The authors concluded that the ELM formed was efficient for the removal of methylene violet [103].

2.3.1.2 Surface active agent/emulsifier

An emulsifier is a crucial factor in determining the stability of an emulsion. It is also termed a "surfactant", which is a substance that, when present in minute concentrations, possesses the property to be adsorbed on the surface. It can reduce the interfacial tension between two immiscible surfaces, decreasing the droplet diameter [72]. A surfactant is a molecule that consists of both hydrophobic and hydrophilic groups, i.e., one group attached to it has a high affinity for the solvent, and the other group has less attraction for the solvent. When surfactant dissolves in the solvent, the hydrophobic moiety alters the structure of the solvent; as a result, the free energy of the system is enhanced. While at the same time, the hydrophilic group does not allow the complete expulsion of surfactant from the solvent. As a result, the presence of surfactant causes the interfacial tension to reduce, thereby improving the emulsion stability [71].

The surfactant adsorbs on the layer between water and oil, forming a highly effective electrical and strict barrier that prevents globule coalescence [104]. The classification of the type of surfactant, i.e., hydrophilic or lipophilic, depends upon the HLB value, i.e, Hydrophilic lipophilic balance. HLB value varies from 1-to 40 depending upon the polarity of the surfactant; as the hydrophilic balance increases, the HLB value increase [71]. If the HLB < 9, the surfactant is lipophilic, soluble in oil, and hence suitable for the formation of water-oil emulsion whereas, if HLB >11, it is classified as hydrophilic, soluble in water, and forms oil in water emulsion [75][62]. HLB value of some surfactants are given in Table 2.4.

Table 2.4: HLB of surfactants

S.No	Surfactant name	HLB value
1.	Sorbitan monoleate (Span 80)	4.3
2.	Sorbitan monolaureate (Span 20)	8.6
3.	Polyethylene sorbitan monooleate (Tween 80)	15
4.	N-cetyl N-ethyl morpholinium ethosulfate (Atlas G-263)	27

To be suitable for ELM, a surfactant must have the following characteristics:

i. Lowers the breakup rate of emulsion droplets
ii. Prevent the swelling up of emulsion globules
iii. Increase the extractability of BAC
iv. Provides high selectivity for the BAC separation
v. Must be stable

For oil-water emulsion, the hydrophobic chain resides in the oil phase and the hydrophilic group in the water phase, whereas for water-oil emulsion, the reverse happens. The selection of surfactants in the formulation of ELM is essential. The surfactant selected must be such that it stabilizes the emulsion to the extent that it's not a problem in the demulsification process.

2.3.1.3 Internal stripping agent

The stripping agent is essential in removing the target molecule in membrane formation. This stripping agent is also internal and is usually aqueous. Depending on the analyte or molecule under study, the stripping agent can be acidic, neutral, or alkaline. A stripping agent enhances the rate of removal of solute [62]. Commonly used stripping agents are NaOH, HCl, HNO_3, and NH_4 [19][75][83].

2.3.1.4 Carrier

A carrier is an external agent, also termed an extractant, used in the membrane to facilitate the removal of the target molecule. It works by forming a complex with the target solute to be removed. The presence of a carrier enhances the stability and efficacy of ELM. Sometimes carriers tend to decrease the stability of ELM by adsorbing on the interface. The chemical behavior of these carriers can be classified as acidic, basic, and solvating. Fig. 2.5 shows types of carriers and their examples. There are three types of carriers, acidic, basic and solvating. These carriers are advantageous in enhancing the extraction efficiency of ELM's; some greener alternatives are to be used with the rise in environmental concerns.

Ionic liquids, a novel class of eco-friendly solvents, can be used as a carrier in ELM. ILs enhance the stability of emulsion and hence the extraction efficiency of ELM [20].

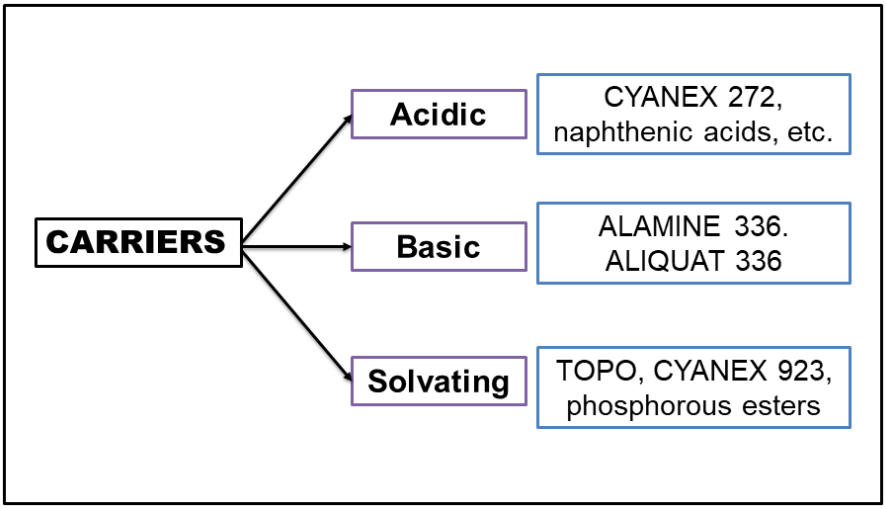


Figure 2.5: Type of carriers used in ELM

2.4 WVO-ILEM stability

The stability of WVO-ILEM is an important parameter that affects the performance and hence the separation of solute. It is related to how resistant the membrane is to leakage under high shear stress during the extraction operation of the target solute in the ELM. Stable emulsion formation with a large oil-water surface would favor low interfacial tension. The reasons that lead to emulsion destabilization include membrane leakage, coalescence, and emulsion swelling [105]. Leakage of the droplets of the internal stripping agent causes a reduction in extraction efficiency [106]. The ELM is better for extraction as it has more extended stability. Stability is the major issue that restricts ELM industrial use. As a result, it is recommended that ELM stability be high to solve this issue [107]. However, it's worth noting that an excessively stable emulsion is also not favorable. This is because it inhibits demulsification and, as a result, the recovery of the organic membrane phase and the target solute.

ELM stability is a product of two phenomena: breakage and swelling. The emulsion breaks when the internal stripping agent spills into the removed solute in the external phase. As a result, the driving force for mass transfer decreases, and the concentration of the external phase rises, lowering extraction performance [108]. Also, sometimes during

storage, destabilization takes place causing inner and outer droplet coalescence, swelling, shrinkage, etc.[109]. Emulsion swelling happens as the volume of the emulsion increases during operation when external feed solution is introduced into the emulsion globules. As a result, the solute extracted through an internal agent is diluted, the driving force for solute extraction is reduced, the emulsion breaks, and the extraction efficiency reduces. For the ELM system, swelling $\leq$ 10% is acceptable. If this percentage is more significant, the extraction ability is lost [108]. Emulsion swelling is of two types: entrainment and osmotic. Entrainment swelling occurs when the external phase gets entrained into the internal phase due to repeated coalescence and dispersion of emulsion globules. Consequently, the volume of the internal phase increases. On the other hand, osmotic swelling is caused by the osmotic pressure that exists between the internal and external phases. As a result, the internal phase volume increases because the ion strength in the internal phase is more significant than in the external phase. The water from the external phase leaks to the internal phase. However, vice versa occurs if the external phase's ion strength is greater then the internal phase. Hence emulsion swelling can be both positive and negative [108]. Swelling is harmful for three reasons

i. it lowers the driving force for solute extraction by diluting the solute in the external phase

ii. Decreases thickness of the membrane

iii. It affects the viscosity of the membrane

Designing and selecting appropriate surfactants, diluents, stripping agents, and carrier selection are essential to solving this instability issue. Increased surfactant concentration and membrane viscosity are being used in studies to improve the stability of ELM. The viscosity of ILEM is directly proportional to the stability [105]. However, it must be kept in mind that sufficiently stable ILEM is enough for separation and recovery. Because if the emulsion is highly stable, the recovery of the target molecule is affected. Surfactant concentration, internal stripping agent, carrier concentration, homogenization speed, homogenization time, and phase ratio are all variables that influence ELM stability [103]. As a result, different calculations can be used to calculate the percent breakage of ILEM.

2.4.1 Techniques to enhance stability

The common methods to enhance the stability of liquid membrane incorporated the addition of more surfactant and increased the membrane phase's viscosity.

Surfactant concentration: Surfactant is used for emulsification as it reduces the interfacial tension and hence improves emulsification. If the emulsion is unstable, the concentration of surfactant is increased. With the increase in surfactant concentration, the interfacial tension decreases, giving rise to the emulsion with a smaller diameter, enhanced static stability, and lesser breakage, thus a stable emulsion [20]. However, there's a limit to increasing the surfactant concentration. If surfactant concentration increases to the optimum value, swelling occurs, and the emulsion destabilizes. Also, a high concentration of surfactant hampers the mass transfer of the solute by increasing interfacial resistance, affecting the extraction efficiency [110] and delaying the demulsification process [104]

Enhanced membrane viscosity: The phase ratio and the concentration of the stripping agent determines the viscosity of W/O emulsion. The viscosity of the emulsion is directly proportional to the stability of the emulsion. Therefore, employing highly viscous oil as a membrane phase is desirable for stable emulsion. The only limitation of enhanced viscosity is it decreases the rate of solute transfer. Also, extremely high viscosity and stable emulsion possess severe problems during the recovery of the emulsion phase and solute. This is because the emulsion is unable to break [104].

Ionic liquids: Ionic liquids recently have been used as stabilizers and carriers in ELM. The incorporation of IL results in enhanced stability, thereby improving the performance efficiency of ELM [20]. The advantages of using ILs in membrane over conventional solvents are:

i. Easy fabrication
ii. Stripping and extraction in a single step
iii. Less energy requirements
iv. Less amount of IL required

v. More stable

vi. Easy recovery of emulsion and stripping phases [111]

2.4.2 Ionic liquids as a carrier in WVO-ELM

One of the most prospective fields of ILs is in the treatment of wastewater [24]. The application of ILs as solvents and cosolvents extends to biotechnology such as in bioactive molecule separation [112], pharmaceuticals such as in initial drug formulation [113], drug delivery [114], carrier for drug molecules, and also for the extraction of natural medicinal ingredients [115], removal and recovery of these biologically active drugs from aqueous streams [20].

Ionic liquids (ILs) are a novel class of solvents due to their outstanding properties which find application in separation processes. ILs also termed as "green" or "designer" or "eco-friendly" solvents cause of their high stability, low vapor pressure, melting point, enhanced solubility, and miscibility as compared to conventional solvents [25]. Additionally, strong polarity, molecular interactions such as ion-pairing, dipole interactions, and the bonding nature (Hydrogen bond and Vander waals) [25] apply in every separation process. Because of their versatility and excellent properties, ILs find application in membrane formation. ILs find applications as starting materials, additives, plasticizers, modifiers, carriers, and solvents in membranes [29]. Membranes employing ILs are termed ionic liquids membranes (ILMs). In these membranes, the feed and internal phases are separated by a thin film consisting of ILs [111].

In ELM, ILs find application as a carrier that acts as a stabilizer. Studies report that IL as a carrier improves removal efficiency and enhances the stability of emulsion [20]. ILs-based membranes are eco-friendly and stable as compared to membranes without ILs. It's also proved that ILs can overcome the evaporation loss of organic solvents [29]. Table 2.5 shows applications of ILs in the formulation of ELM.

Table 2.5: Application of ILs as carrier in ELM

S.No.	ILs used	Target molecule name	Findings	Ref.
1.	[TBAm][Br]	Diclofenac	IL enhanced the efficiency of extraction	[32]
2.	[BMIm][Ntf2]	4-nitrophenol	IL improved the stability of system to 81%	[77]
3.	[BMIm][NTf_2]	Phenol	the enrichment ratio of phenol was 11 times upon incorporation of IL	[95]
4.	[PTr][PF_6]	Tropane alkaloids	IL resulted in a stable emulsion resulting in fast extraction	[78]
5.	[ALIQUAT 336]	Amoxicillin	ILs improved the extraction capacity of ELM	[116]
6.	TOMAC	Chromium	97% extraction was achieved using IL as the carrier	[15]
7.	[BMIM][Ntf_2]	Phenols, chlorophenols (CP), nitrophenols (nps)	Emulsion stability increased using IL as carrier	[33]
8.	TOMAC	Lactic acid	IL increased the stability and hence extraction efficiency	[19]
9.	ALIQUAT 336	Acetaminophen	ALIQUAT as carrier enhanced the extraction efficiency by stabilizing the emulsion	[117]

10.	[OMIm][PF_6]	Lead (Pb(II)	IL improved the stability of emulsion 2-3 times	[118]
11.	[BMIm][NTf_2]	Nanosilver	IL improved stability and hence performance efficiency.	[119]
12.	[BMIm][PF_6]	Phenol	Emulsion stability was enhanced 5 times using IL as the carrier	[120]
13.	[BMIm][NTf_2]	Chromium	The addition of IL enhanced the stability of the emulsion.	[121]
14.	[TOMAC]	Benzimidazole	IL aided the transport of benzimidazole	[122]
15.	ALIQUAT 336	Cadmium	IL as carrier reduces breakage, improving the stability of the emulsion	[123]
16.	[BMIm][NTf_2]	Benzoic acid	99.7% efficiency of benzoic acid with minimal breakage was achieved using IL as a carrier	[86]

The membrane stability is due to columbic interaction of the charges on the ions of ILs and surfactant, organic solvent, and internal stripping agent. If the IL possesses positive cation and anions, repulsion occurs, whereas the attraction occurs if opposite charges are present. Attractive forces in the opposite ions of ILs cause strong hydrogen bonding interactions and avoid coalescence, thereby emulsion breakage [122]. IL forms a complex enhancing emulsion stability[119]. Also, IL forms the complex with the molecule. This complex moves from the external phase towards the membrane phase and travels to the internal phase. The internal phase reacts with the complex molecule resulting in the salt formation of the molecule, and the carrier is regenerated [19]. The advantages of incorporating carriers in liquid membranes can be summed up as:

i. It enhances the mass transfer area, hence high diffusion coefficients.
ii. Carrier in ELM enhances the stability of the emulsion; hence better removal efficiencies are obtained.
iii. The amount of carrier used is very minute; hence expensive carriers can also be used [71][118].
iv. ILs are less toxic as compared to conventional carriers.

To summarize, ELM's stability is a crucial aspect influencing ELM’s performance. ILs improve the system's stability, removal efficiency, and solute recovery, which is a key benefit of using ILs. A number of ILs have been synthesized for this purpose. The literature reveals that investigated ILs were centered around imidazolium, phosphonium, and ammonium. Nevertheless, there is substantial room to further select the ILs with better extraction efficiencies and thermodynamic properties. Since the number of cations and anions forming ILs is huge, it is challenging to identify ILs with excellent extracting properties experimentally. An alternative solution is using a simulation tool, such as a conductor-like screening model for real solvents (COSMO-RS). Such a simulation tool predicts the activity coefficient at infinite dilution (AC^{id}) values of the associated species to estimate the capacity and selectivity of ILs for solubility studies [124].

2.5 Conductor like modeling for real solvents (COSMO-RS)

COSMO-RS is a predicting tool that depends on quantum chemical calculations using a conductor-like screening model for fluids and liquid mixtures [125]. The estimates are made by placing solute understudy in a molecule-shaped cavity, and the surrounding solvent is termed a continuum. The σ-profiles, in the form of histograms, depict the solute's surface charge densities and polarity [126]. σ-profiles help predict molecules' chemical nature and are very useful for determining thermodynamic properties [127]. According to Klamt, the $p_i(\sigma)$ for a molecule is the probability of finding a segment with surface charge density using the following equations [128]. The σ-profile for a mixture is represented as the weighted average of σ using equation 2.1.

$$p_i(\sigma) = \sum_i^N x_i p_i \tag{2.1}$$

In COSMO-RS, the IL can be defined as the mixture of cation and anion, and calculations are made distinctly. The interactions between segments are due to electrostatic force misfit (E_{misfit}), Hydrogen bonding (E_{HB}), and van der waals (E_{vdW}). The interactions of the solvent are represented by $p_s(\sigma)$, the chemical potential for all compounds for any arbitrary mixture at a given temperature can be derived by using equation 2.2

$$\mu_S^X = \mu_{C,S}^X + \int p^X(\sigma)\mu_S(\sigma)d\sigma \tag{2.2}$$

These results are used for further COSMO predictions σ ($\sigma_{acceptor}$) and σ' (σ_{donor}) if the sections belong to the H-bond donor or acceptor. Thermodynamic properties can be derived using the above equation 2.2. The potency of any liquid for the separation of an individual solute can be determined by evaluating the activity coefficient at infinite dilution AC^{id}. This is because AC^{id} is related to the solute's affinity for IL due to interactions between IL and solute. It is further related to the selectivity of IL for the given process [129]. The activity coefficient of component 'i' is obtained by definition from the values of chemical potential in the mixture and pure state and is calculated using equation 2.3.

$$\gamma = exp\left(\frac{\mu - \mu^0}{RT}\right) \tag{2.3}$$

μ= chemical potential of the solvent

μ^0= chemical potential in compound

The capacity is defined as amount of IL needed for the removal of solute from solution during extraction and is represented by equation 2.4 [127]

$$C_{12}^{\infty} = \left(\frac{1}{\gamma_1^{\infty}}\right)^{\text{IL phase}} \tag{2.4}$$

The selectivity is defined as the ratio of the amount of solute IL-rich phase to the amount in the aqueous phase (IL lean phase) and is represented by equation 2.5.

$$S_{12}^{\infty} = \frac{\gamma_2^{\infty}}{\gamma_1^{\infty}} \tag{2.5}$$

Subscripts 1 and 2 refer to water and the solute (target solute).

The higher the capacity, the lesser the amount of IL required. Likewise, selectivity reflects the extraction ability of the IL understudy for the recovery of solute molecules. Values must be high for the IL selection capacity and selectivity, whereas AC^{id} must be low. Another important property that is sufficient to determine the potency of IL is the performance index (P.I). It is the product of capacity and selectivity and can be represented by the equation 2.6.

$$P.I = C_{12}^{\infty} * S_{12}^{\infty} = \frac{\gamma_2^{\infty}}{\gamma_1^{\infty 2}} \tag{2.6}$$

AC^{id}, capacity, selectivity, and P.I are enough to determine the potency of IL for its selection as a carrier [112].

COSMO-RS is advantageous compared to other thermodynamic models such as the Non-random two liquid model (NRTL), Universal Quasi-Chemical Model (UNIQUAC), and Universal Quasi-Chemical Functional Group Model (UNIFAC) method used for the estimation of various conventional solvents [130]. These methods are inadequate in computing the AC^{id} of ILs because they cannot calculate the interaction parameter between cations and anions of ILs [124]. On the contrary, COSMO-RS could calculate the molecular interactions based on surface charge densities histogram. The results are presented in sigma profiles, which require only molecular structure for quantum calculations [131]. Other variables such as Gibb's energies, equations of state incorporating various parameters, etc., are not necessary for systems under study. Table 2.6 presents COSMO-RS screening carried out for biologically active compounds.

As observed, COSMO-RS is an efficient tool for screening ILs in separation processes. In ELM, ILs are incorporated as carriers to enhance the extraction efficiency, thereby improving separation. The literature reveals that there's no study carried out for the ELM system to screen ILs to be used as a carrier. Hence, in this study, COSMO-RS was used to screen ILs. Furthermore, this IL was used as a carrier in the formation of ELM.

Table 2.6: Application of COSMO-RS for the screening of ILs for BACs

S.No	Biologically active compound	Solvent/ILs	Finding	Ref.
1.	Quercetin Curcumin Gallilic acid	DES (combination of cholinium chloride and xylitol)	The solubility increased 1000 times with the use of these DES	[132]
2.	Alverine	[Alv][Tos] [Alv][Sa] [Alv][cin] [Alv][amp]	API-ILs for alverine resulted in an increased solubility as compared to the parent compound.	[133]
3.	5-hydroxymethylfurfural	Conventional solvents	The screening results suggest that ethyl acetate and methyl propionate are suitable solvents for HMF.	[134]
4.	Gamavuton-0 (GMV)	Conventional solvents	The solubility of GMV was evaluated using COSMO-RS	[135]
5.	Cyclosporin, Loratadine, Simvasatin, Zafirlukast	Conventional solvents (acetic acid, acetone, etc.)	Evaluated the accuracy of the COSMO-and QSPR method to determine the HSP for solvents. The deviation between the results was quite less.	[136]
6.	Acyclovir	Biodegradable ILs	[Am] based ILs are potential for the dissolution of ACV	[137]

7.	Methotrexate	Ammonium based ILs [TMAm][Ac] [TMAm][Cl] [TMAm][Br]	The solubility of methotrexate was highly dependent upon the HB nature. Hence ammonium ILs with [Ac] were found to be highly favorable for its dissolution.	[138]
8.	Danazol	Conventional solvents	COSMO-RS is helpful for the selection of solvents in the drug formulation	[113]
9.	Ibuprofen Acetaminophen Benzoic acid Salicylic acid 4-Aminobenzoic Acid	Conventional solvents	COSMO and other optimizing methods were found to help predict solubilities.	[139]
10.	Aspirin Paracetamol Ibuprofen	Conventional solvents	COSMO-RS was used to screen solvent for the purification of selected molecules in the formulation process	[140]
11.	Phenol	Cyanex 923 TOA [CYPHOS 105] [CYPHOS 109]	The results show that for phenol, the IL possessing less sterically hindered anion is a better extractant.	[141]

12.	Diclofenac	DMSO	Dcf shows less solubility in acetone and ethyl acetate. The result was in good verification with experimental results	[142]
13.	Aspirin Caffeine Mannitol	Conventional solvents	The results helped predict the solubility of selected compounds and carry out the study further.	[143]
14.	Ibuprofen, Cinnarizine Naproxen	API-DES	DES was found to be a potential alternative to conventional solvents.	[144]

2.6 Eco-friendly waste vegetable oil ionic liquid emulsion membrane

The application of ILs in various extraction processes has been highlighted as green solvents across multiple separation techniques [27]. In this work, screened IL and WVO were used to formulate eco-friendly ELM. To prepare a stable emulsion, the size of internal droplets must be minimal (1-3 μm). This can be accomplished by using a high-speed homogenizer for the formation of an emulsion. The resulting ELM is assumed to be a green because of the incorporation of waste vegetable oil (WVO), a renewable product as a diluent, ILs as extractant, and the use of non-ionic surfactant. Although ILs are costly, this effect is not considered since the quantity of IL used is in micrograms. The other components of WVO-ILEM will be a non-ionic surfactant and stripping agent.

2.7 Extraction mechanism for ELM

The difference in chemical potential in ELM causes solute transport, which serves as a driving force for the extraction of the target BAC. Unlike traditional solvent extraction methods, using an additional agent known as an extractant makes the extraction process easier and has higher removal efficiencies [27]. In ELM, there are two methods for extraction. When no external extractant is used, it is classified as Type-I, and when an external agent is used, it is classified as Type-II.

2.7.1 Type-I extraction through ELM

Since no extractant or external agent is used, Type-I transportation is known as "unfacilitated" transportation. Because of its solubility, the solute percolates through the membrane. The internal stripping agent and the feed phase are miscible, but concentration differences separate them via the membrane. When the concentration reaches equilibrium, transportation ceases. The solute to be extracted travels from the organic phase to the internal stripping phase, where it interacts with the internal stripping agent, forming the product Fig. 2.6 As soon as equilibrium is achieved, the product formed cannot pass back through the membrane [145].

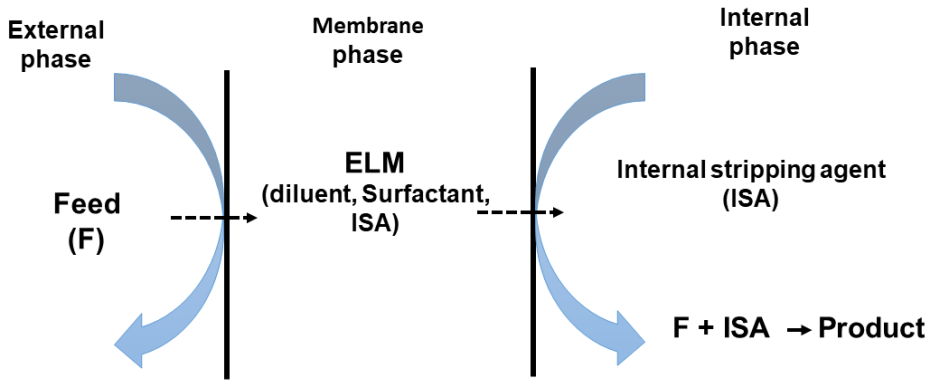


Figure 2.6: Unfacilitated transport through ELM. F=feed, ISA=internal stripping agent, P=product

2.7.2 Type-II mechanism

When extraction using ELM takes place via carrier, i.e., an external agent, facilitated transport. In systems in which the target molecule is not soluble in the organic membrane phase; hence an external agent termed the carrier is required [146]. It is also termed carrier incorporated transport, termed Type II mechanism. This addition of carrier results in the complex formation at the membrane interface and external phase. Furthermore, the complex enhances the transport of target compounds across the membrane towards the internal stripping agent. It involves two reactions, one at the interface between external feed and organic membrane phase and the other at the interphase between the membrane and internal phase. The transfer occurs due to a concentration gradient that exists at two places, one when the external agent reacts with the carrier forming a complex and moving towards the internal phase. Second concentration gradients when this complex from the membrane phase proceeds to the internal phase. Due to the high concentration gradient, the solute is stripped off, and the carrier is regenerated Fig. 2.7 shows the carrier-mediated transport for ELM.

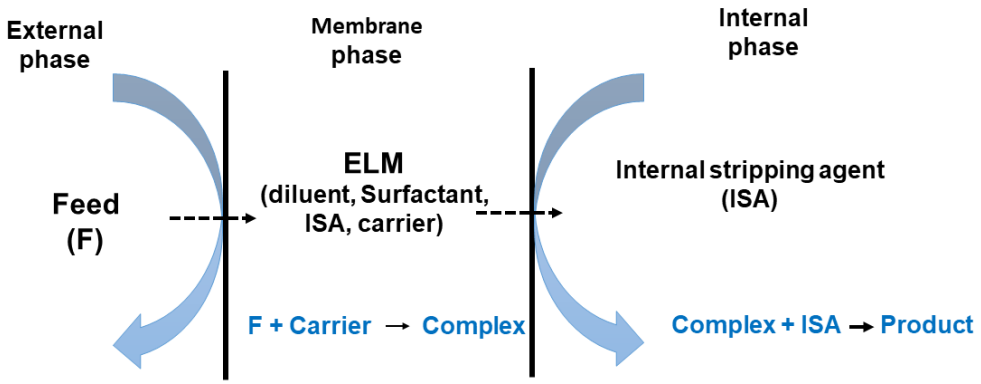


Figure 2.7: facilitated transport through ELM. F=feed, ISA=internal stripping agent

The steps involved in the carrier-mediated mechanism can be listed as:

i. Mass transfer BAC from the external aqueous phase to the exterior edge between the external and organic phases.

ii. The biologically active molecule reacts with IL, forming a complex at the membrane and external phase boundary.

$$BAC + IL \rightarrow BAC{:}IL\,(complex) + H^{+}$$

iii. Mass transfer of BAC:IL in membrane phase from external/membrane interface to the membrane/internal phase.

BAC:IL (external/membrane phase) ⟶ *BAC:IL(complex, membrane/internal phase)*

iv. Complex reacts with an internal agent where BAC is stripped of as salt and IL is regenerated

BAC:IL (membrane/internal phase) + A (Stripping agent, acid/base) BAC:A + IL

Mass carrier transfer from membrane/internal interphase to the external/membrane interphase. IL is regenerated. Fig. 2.8 presents the complete mechanism.

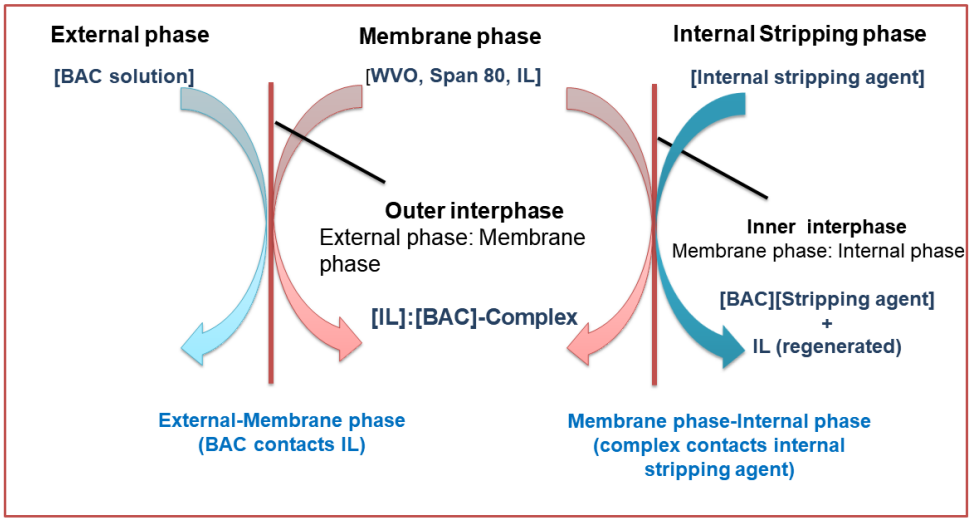


Figure 2.8: Schematic illustration of WVO-ILEM

2.8 Advantages and disadvantages of ELM

ELM is an efficient process as compared to other conventional methods. The advantages of ELM can be summed up as:

1. The mass transfer area is large; hence the extraction efficiency is high.
2. As compared to other separation techniques, initial input energy is relatively less.
3. It is a potential method to remove the solutes even if present in trace amounts. The reason behind this is that extraction and stripping take place together.
4. Incorporating an additional carrier can achieve higher selectivity and mass transfer flux in the organic phase.

2.9 ELM Applications

Because of the advantages over other techniques, ELM finds application in the removal of organic and inorganic pollutants: These applications can be classified as:

1. **Heavy metal ion removal:** ELM finds application in the removal of various heavy metals such as chromium [147], lead [81], silver [148], cadmium [149]

2. **Pharmaceutical removal:** The application of ELM further extends to the removal of pharmaceutical products from waste streams. These include the removal of acetaminophen [83], norfloxacin [150] , lactic acid [19], diclofenac [32], ibuprofen [151], methylparaben [152], phenol [18].
3. **Hydrocarbons and gases:** ELM also finds application in the removal of gases such as carbon dioxide [16] and also aromatic pollutants such as phenols [153], and nitrophenols [93].
4. **Practical applications:** Industrially, ELM removes and recovers zinc ions in Len zing, Austria. The plant capacity is 75 m^3/hr.

2.10 Factors affecting ELM stability and extraction efficiency of WVO-ILEM

To attain a highly stable WVO-ILEM, it is important to investigate the effect of various factors that affect the stability and performance of WVO-ILEM.

2.10.1 Factors affecting stability

Several studies focused on the stability of WVO-ILEM and studied the effect of various parameters on stability. Emulsion liquid membrane performance highly depends upon the viscosity of the emulsion formed. The viscosity of emulsion influences the stability of emulsion [154]. Other factors responsible for the stability of ELM are emulsion diameter and breakage. The higher the stability of the emulsion, the better the removal efficiency obtained for the target molecule. The factors that strongly influence the viscosity, hence the stability of the emulsion, are homogenizer speed, homogenizer time, the concentration of surfactant, concentration and volume of stripping agent, and the concentration of carrier [155]. Table 2.7 shows some of the research carried out to study the stability of ELM. Furthermore, it also shows the various factors investigated that affect the stability.

Table 2.7: Stability studies on ELM

S.No	Solute name	Stability parameter	Factors affecting stability	Reference
1.	Acetaminophen	Emulsion size, membrane breakage	Stripping agent concentration, agitation speed, extraction time, treat ratio	[107]
2.	Lactic acid	Statistical stability time	Surfactant concentration, stripping agent concentration, phase ratio, homogenization speed, homogenizer time,	[156]
3.	Chromium	Viscosity, swelling	Surfactant and modifier concentration, homogenizer speed, emulsification time	[15]
4.	Diclofenac	Backscattering	HLB value of surfactant mixture, homogenizer speed, internal phase concentration	[75]
5.	Succinic acid	The volume of aqueous phase as a function of time	phase ratio, homogenization speed, homogenizer time, surfactant conc, surfactant blend	[157]

6.	Cadmium	Membrane breakage	Carrier concentration, surfactant concentration, phase ratio, homogenization time, stripping agent concentration, stirring speed	[158]
7.	Acetaminophen	Membrane breakage, diameter	Surfactant concentration, carrier concentration, homogenization time, phase ratio,	[41]
8.	Cationic dye	Membrane breakage	Ultrasonic power, emulsification time, carrier concentration surfactant concentration, phase ratio, treat ratio, stirring speed, contact time	[159]
9.	Phenols	Leakage, Swelling	Surfactant concentration, osmotic pressure, membrane viscosity, phase ratio, stirring speed	[154]
10.	Ciprofloxacin	Membrane breakage	homogenizer speed, emulsification time, nanoparticles concentration, external phase pH, internal to membrane volume	[85]

			ratio, internal phase concentration and extractant concentration.	
11.	Methylene blue	Membrane breakage	Homogenization time, surfactant concentration, stripping agent concentration	[160]
12.	cadmium	Emulsion diameter, membrane breakage	Homogenization time, surfactant concentration, carrier concentration, phase ratio	[161]
13.	Phenol	Membrane breakage, emulsion diameter	HLB value, mixed surfactant concentration, homogenizer speed, emulsification time, phase ratio	[95]
14.	Ethylparaben	Stability index	Carrier concentration	[162]
15.	Rhodamine 6G dye	Breakage	Homogenizer speed, emulsifying time, stripping agent concentration, carrier concentration	[163]

Instability of ELM occurs as a result of high viscosity leading to larger emulsion globules and enhanced breakage. Surfactant concentration is an essential parameter in determining the stability of emulsion as it acts by reducing interfacial tension. However, too high surfactant concentration is undesirable as it results in emulsion swelling, resulting in an unstable emulsion. Internal stripping agent and carrier concentration are other factors that affect the emulsion globule's size and hence the emulsion's stability. The viscosity of the emulsion is too high if the concentration of the stripping agent and carrier exceeds the optimum value. Since surfactant concentration, stripping agent concentration, and carrier concentration influence emulsion viscosity significantly, decreasing emulsion stability. Hence an optimum value of these parameters is required to formulate ELM [154][85]. Other parameters such as homogenization speed and homogenization time that affect the emulsion diameter and stability are essential for the uniformity of emulsion formed. A homogenous emulsion is stable as compared to an inhomogeneous emulsion. Table 2.8 reveals that membrane breakage, statistical stability, and emulsion diameter are essential parameters to evaluate the stability of ELM.

2.10.2 Factors affecting the extraction efficiency of WVO-ILEM

Apart from factors that affect the stability of the emulsion, there are other factors that affect the extraction efficiency. Table 2.8 presents several studies carried out evaluating the factors that affect the extraction efficiency of ELM. Treat ratio, stirring speed, stirring time account for the dispersion of WVO-ILEM in the external affects the extraction efficiency. An optimum treat ratio is necessary for the extraction of solute. It controls the interfacial mass transfer, which may directly affect the extraction efficiency through the amount of BACs removed in the feed phase solution [117]. At low treat ratios, the dispersion is not proper as the highly viscous WVO-ILEM is unable to disperse appropriately in the external solution. At higher treat ratios, the volume of the stripping agent becomes less to obtain maximum efficiency. Hence an optimum value of the treat ratio is necessary. Stirring speed is important for proper dispersion of WVO-ILEM. If the emulsion is not dispersed properly the extraction will be incomplete, reducing efficiency. Stirring time is important as it governs the kinetics of WVO-ILEM. An optimum time is necessary for proper contact and

mass transfer of the ELM phase and external phase. Settling is another critical parameter that governs the performance of WVO-ILEM. Initially, at time t=0, no separation occurs. After some time, the layers are formed. As settling time increases and exceeds the optimum value, the internal stripping agent will leak into the external phase, decreasing membrane efficacy [20].

Table 2.8: Factors affecting the performance of ELM

S.No	Solute Name	Factors affecting performance	Reference
1.	Lactic acid	Surfactant concentration, stripping agent concentration, Carrier concentration, homogenization speed, homogenization time, phase ratio, treat ratio, stirring speed, stirring time, feed concentration	[20]
2.	Tetracycline	homogenization speed, homogenization time, phase ratio, stripping agent concentration, carrier concentration	[79]
3.	Polyphenols	Carrier concentration, feed pH, stripping agent concentration, treat ratio, feed concentration	[87]
4.	Ciprofloxacin	Homogenizer speed, emulsification time, carrier concentration, feed pH, internal phase concentration, phase ratio, mixing time	[85]
5.	Diclofenac	Carrier type, internal phase concentration, surfactant HLB value	[75]
6.	Acetaminophen	Stripping agent type, Stripping agent concentration, membrane to internal phase volume ratio, feed concentration	[84]

7.	Lactic acid	Surfactant concentration, stripping agent concentration, extractant concentration, stirring speed, phase ratio, treatment ratio	[26]
8.	Bio-succinic acid	Stripping agent concentration, carrier concentration, treat ratio, effect of other components	[90]
9.	Phenols, chlorophenols (CP), nitrophenols (NPs)	Carrier concentration, phase ratio, internal phase concentration	[33]
10.	Lactic acid	Feed concentration, internal agent concentration, phase ratio, treat ratio, temperature, stirring speed, stirring time	[19]
11.	Chlorpheniramine	Surfactant concentration, carrier concentration, phase ratio, treat ratio	[164]
12.	Acetaminophen	Surfactant concentration, carrier concentration, emulsification time, internal phase concentration, sulphuric acid concentration, phase ratio, treat ratio, ACTP initial concentration, diluent type	[117]
13.	Acetaminophen	Surfactant concentration, extractant concentration, ultrasonic power, emulsification time, stirring speed, extraction time	[83]

14.	Organic pollutants	Stripping agent concentration, feed concentration, extraction time	[17]
15.	Ibuprofen	Emulsification time, stirring speed, internal agent type, acid type in external phase, internal agent concentration, stirring speed, phase ratio, treat ratio, diluent type, initial feed concentration	[45]
16.	Ibuprofen	Surfactant concentration, emulsification time carrier concentration, stripping agent concentration	[151]
17.	Phenol	Surfactant concentration, carrier concentration, stripping agent concentration, emulsification time, phase ratio, treat ratio, stirring speed, external phase pH	[165]
18.	Benzoic acid	Surfactant concentration, organic to internal phase ratio, emulsion to feed ratio, stirring speed, extraction time	[86]

Since many factors affect the stability and extraction efficiency of ELM, optimization of these factors is necessary to get better efficiencies.

2.11 Optimization using Response surface methodology

Design of experiments (DOE) is a planning stage whereby activities and requirements have to be charted and important decisions made, setting the basis for all the other phases. One of the important decisions which must be performed in the most accurate and precise manner is the determination of parameters and respective range of concentration for each quality specification for the development of stable ILEM. Response surface methodology (RSM) combines mathematical and statistical techniques, widely used as a simulation tool for process parameters optimization. It was developed by Box and Wilson in 1951 [166]. RSM has been successfully applied in the modeling and optimizing various operations like chemical, petrochemical, and microbiology [167]. Without prior knowledge of the composition and physicochemical features of the test sample, RSM offers the advantage of eliminating a large number of experimental runs for all the parameters while saving time and money and minimizing experimental errors [168]. It works by optimizing the process parameters while considering their interactions and identifying essential factors influencing the response [169]. RSM finds application in the formulation of ELM. Table 2.9 shows various researches carried out to optimize different parameters for the formulation of ELM.

Central composite design (CCD) and Box-Behnken design (BBD), are the main methods for generating response surface designs. It predicts the best-operating conditions to achieve optimum removal efficiency [170]. BBD designs are efficient and do not contain combinations for all factors simultaneously at their highest and lowest levels. Hence, the number of experiments is less compared to other designs. The only limitation is that it is not suitable for more than 4. CCD is advantageous and can predict all main effects, interactions, and quartile conditions [21]. Furthermore, CCD possesses better fit quadratic models and fewer experiments [171]. In this work, initially, CCD was selected to examine the interactions between the desired parameters as the interaction chosen parameters were 5. Based upon experimental results, the parameters and their ranges were selected. Furthermore, the RSM model was qualitatively evaluated and validated using analysis of

variance (ANOVA). The model is estimated using ANOVA based on several parameters such as:

i. Analysing significant input variables

ii. R^2 values

iii. Lack of fit analysis

iv. Perturbation graphs to assess the sensitivity of the input variable to the output response

ANOVA was used for finding the error, effective factors, gives information about the relationship between different factors and provides optimum working conditions. The 3D graphs, which provide detailed information about the relationship between two input variables and their effect on the output response, are the most important characteristic of ANOVA. These graphs provide details about the point between experiments that were not calculated experimentally. Furthermore, the most important consequence of RSM is that it uses experimental data to assess the optimal values for process variables [167]. Lastly, the optimization was carried out. The results which gave maximum WVO-ILEM extraction efficiency at optimized conditions were selected. Furthermore, experiments were performed to verify the optimized results. The experiments were performed in triplicates, and the standard deviation between optimized and experimental results was evaluated. The deviation must be <5% [101].

Table 2.9: RSM studies for ELM based systems

S.No.	Solute to be removed	Parameters selected	Method used	Reference
1.	Methyl violet	Surfactant concentration, internal stripping agent concentration, treat ratio	BBD	[92]
2.	Chromium	Retention time, agitation speed, treat ratio	BBD	[147]
3.	Copper	Surfactant concentration, carrier concentration, internal stripping agent concentration, phase ratio	BBD	[73]
4.	Dysprosium	Surfactant concentration, carrier concentration, internal stripping agent concentration, pH of feed phase, concentration of MWCNT	CCD	[82]

5.	Diclofenac	Surfactant concentration, carrier concentration, extraction time, feed concentration, treat ratio, stirring speed	CCD	[32]
6.	Gallilium	Surfactant concentration, carrier concentration, internal stripping agent concentration, stirring speed, phase ratio	BBD	[172]
7.	Norfloxacin	Feed concentration, internal stripping agent concentration, saponin concentration	BBD	[150]
8.	Phenol	Stirring speed, extraction time, carrier concentration, treat ratio	FFD	[173]
9.	Bisphenol	Surfactant concentration, internal stripping agent concentration, phase ratio, treat ratio	CCD	[174]
10.	Orange 3R	Extraction time, stirring speed, surfactant concentration, treat ratio	BBD	[175]

11.	Cadmium	Carrier concentration, feed phase concentration, feed pH	BBD	[149]
12.	Lactic acid	Treat ratio, internal stripping agent concentration, phase ratio, feed concentration	BBD	[167]
13.	Lactic acid	Phase ratio, treat ratio, stirring speed	BBD	[176]
14.	Amoxicillin	Carrier concentration, feed concentration, internal stripping agent concentration, treat ratio	CCD	[116]

15.	Copper	Feed concentration, carrier concentration, surfactant concentration, stirring speed, treat ratio, per traction time	CCD	[177]
16.	Neodymium, Gadolinium,	Carrier concentration, feed pH, surfactant concentration, stirring speed	CCD	[178]
17.	Phenol	Stirring speed, treat ratio, settling time		[18]
18.	Lead	Surfactant concentration, diluent concentration, internal stripping agent concentration, treat ratio, stirring time, feed pH,	Taguchi method	[179]
19.	Methylene blue	Surfactant concentration, phase ratio, treat ratio, carrier concentration, homogenization time, stirring speed	BBD	[180]
20.	Lactic acid	internal stripping agent concentration, phase ratio, treat ratio, stirring time, feed pH,	CCD	[181]

2.12 WVO-ILEM permeation and kinetics

Permeation rates through ELM have to be evaluated to allow sizing of contacting stages and agitation requirements. Because the ILEM contains a carrier, this extraction proceeds through the formation of a complex. Several models based on carrier-mediated transport via the emulsion globule have been presented. Permeation rate can be found using spherical shell model proposed by Cahn and Li [182].

Assumptions: Following assumptions were made

i. Mass transfer resistance is constant with time.

ii. There's no accumulation of BAC in the internal and membrane phase.

It was proposed that mass transfer of solute is proportional to the concentration difference through the membrane. It is represented using equation 2.7:

$$\Delta C = C_d - C_i \tag{2.7}$$

where,

C_d = concentration of BAC in external phase at a time, t

C_i =concentration of solute in the emulsion phase

The rate of permeation of solute is defined by the equation 2.8

$$-\frac{dC_d}{dt} = DA\frac{\Delta C}{\delta} \tag{2.8}$$

C_d= concentration of BAC

D= diffusivity of BAC through the membrane

A=mass transfer per unit volume of external solution

δ=thickness of membrane

For ELM, area and thickness determination is a bit difficult; hence term $DA\frac{\Delta C}{\delta}$ can be replaced by $D'\frac{Ve}{V_d}$. t

Where D'= effective diffusivity

V_e=volume of emulsion

V_d=volume of the external phase

For the carrier-mediated transport, The effective diffusivity can be calculated by integrating the equation and substituting, the equation becomes:

$$ln\frac{C_i}{C_f} = D'\frac{V_e}{V_d}\,t \tag{2.9}$$

C_i=initial concentration of BAC in the external phase

C_f=final concentration of BAC in the external phase

Based upon the above equation, permeation rates can be calculated for the BAC under study.

Also, the diffusivity of BAC in the aqueous phase and in the membrane phase i.e, BAC-ionic liquid complex, can also be evaluated using the Wilke-Chang equation:

$$D_i = \frac{117*10^{-18}\,(\Psi M_B)^{0.5}\,T}{\mu V_A^{0.6}} \tag{2.10}$$

Where,

Ψ= solvent association factor; for aqueous phase =2.26 and for oil phase =1, respectively

V_A=solute molar volume (m^3/kg-mol)

μ= viscosity of solvents (kg/m-s)

M= molecular wt. of solvent (kg/kg-mol)

In this study, kinetic analysis was conducted using first order and second order to investigate BAC extraction order of BACs extraction using WVO-ILEM [79] [76]. Table 2.10 presents the related research carried out for studying the permeation and kinetics of ELM. The value of the rate constant can be obtained using the equation.

Following equations were used to carry out the analysis

First Order

$$ln\ C_{ext} = ln\ C_{final} - k.t \quad (2.11)$$

$$ln\frac{C_f}{C_i} = -kt \quad (2.12)$$

Second order

$$\frac{1}{C_f} - \frac{1}{C_i} = -k.t \quad (2.13)$$

Table 2.10: Permeation and kinetic studies for ELM

S.No.	Solute name	Carrier	Findings	Reference
1.	Benzoic acid	[BMim][Ntf2]	The reaction followed first order kinetics with good permeation rates	[86]
2.	Dysprosium	CYANEX 272	The reaction followed first order kinetics with higher extraction+	[82]
3.	Ethylparaben	MWCNT	Extraction followed first order kinetics with higher diffusivities.	[162]

2.13 Demulsification: WVO-ILEM recycle and reuse

Demulsification is an essential process for the recovery, recycling, and reuse of the organic phase and recovery of BAC stripped by the internal agent. Demulsification is used for the breakage of emulsion, resulting in the separation of the membrane phase and internal agent. The constituents of ELM, surfactant, and carrier are costly, and hence this process makes the reuse of these chemicals possible. The emulsion recovered can be reused for the removal of BACs again. Once demulsification takes place, the emulsion breaks into two layers. The upper organic emulsion layer consists of oil, surfactant, ionic liquid, while the lower layer, consists of the entrapped BAC and internal stripping agent [104].

Several methods are being used for the demulsification process. Table 2.7 shows a few examples of research carried out using various demulsification methods. These methods are classified as physical, chemical, and biological. Microwave, heating, centrifugation, freeze-thawing, use of a membrane, application of electrical field, ultrasonication are the commonly used physical methods for demulsification. Chemical processes incorporate the additional step to separate the chemicals added to the ELM before further use. The use of chemical methods for demulsification is limited as it involves an extra cost to separate the membrane and chemicals used [104]. Biological processes involve cell dispersal into the oil phase and adsorption onto the oil-water interface [183]. But for ELM demulsification, this method is not being used.

After the separation and recovery of both phases, recovery efficiency can be calculated for the BAC using equation 2.14 [21]. The recovery efficiency will reveal how much BAC is extracted and can be recovered through ELM.

$$Recovery\ Efficiency\ (\%) = \frac{C_{fis}}{C_{ie}-C_{fe}} * 100 \qquad (2.14)$$

Where,

C_{fis}=final BAC concentration in internal stripping agent after demulsification

C_{ie}= initial concentration of BAC in the external phase

C_{fe}= final concentration of BAC in external phase after treatment

Table 2.11: Demulsification methods for the recovery of various solutes through ELM

S.No	Solute to be removed	Demulsification method	Reference
1.	Lactic acid	centrifuge	[20]
2.	Succinic acid	ultrasonic vibration	[90]
3.	Succinic acid	heating	[94]
4.	Chromium	ultrasonic	[147]
5.	Phenol	electric field	[91]
6.	Phenol	electro coalescer	[184]
7.	Pyridine	heat-induced	[185]

After the demulsification process, the organic membrane phase can be re-emulsified. This is accomplished by adding an internal stripping agent with homogenization to form a milky emulsion. The re-emulsification of the recovered membrane phase results in the formation of WVO-ILEM. This designed WVO-ILEM may be used in the extraction process again until the emulsion is stable. The benefit of this approach is that it prevents the waste of expensive materials like ILs and prevents pollution by disposing of them [85]. This process is repeated until the emulsion is stable and has high extraction efficiency.

[26]

2.14 Research Gap

Table 2.11 shows the work carried on the removal of selected BACs. Based on the literature following findings were obtained for the related research on the selected BACs.

i. There are very few researches on biologically active compounds using ELM.
ii. Most of the research works are being carried out using PBS [186][75][32][45].
iii. Only two researches incorporate vegetable oil for LA, namely sunflower oil (SFO) [26], and rice bran oil (RBO-70%) [19]. As mentioned in the preceding section, the cause of the increasing food crisis use of virgin oil is not advisable. Also the work was carried out without IL [26] and in other work [TOMAC] was used as IL [19].
iv. For Dcf and Ibf there's no literature available using VO and IL as carrier.
v. Few researches incorporated carrier, however proper screening was not made.

The instability of ELM is the only constraint that restricts its industrial application. An external agent, carrier, is used to overcome it to improve stability. ILs are an excellent alternative as carriers due to their green properties in the separation processes and hence can be employed in ELM. However, less focus has been paid to screening the best suitable IL for specific BAC. Therefore, this research has used COSMO-RS as an efficient simulation tool to select ILs for BAC. The advantage of this tool is that it gives the best possible cation-anion combination for the formation of ILs while avoiding the time consumed in screening it practically. Furthermore, the screened IL was used in the synthesis of ELM to enhance its stability and improve its efficacy.

Table 2.12: Related work on selected BACs using ELM

S.No	Solute name	Diluent	Surfactant	Stripping agent	Carrier	Efficiency (%)	Reference
1.	LA	Toluene, kerosene heptane	Span 80	Na_2CO_3	Alamine 336	91	[186]
2.	LA	SFO	Span 80	NaOH	Aliquat 336	99	[26]
3.	LA	RBO:Hexane (70:30)	Span 80	NaOH	TOMAC	90	[19]
4.	Dcf	n-heptane	Span 80	NaOH, HNO_3, HCl	TOA, D_2EHPA	95	[75]
5.	Dcf	DCM	Span 80	NaOH	[TBAm][Br]	99.65	[32]
6.	Ibf	Kerosene	Span 80	NH_4	TPA	89	[89]
7.	Ibf	Hexane	Span 80	Na_2CO_3	-	99.30	[187]
8.	Ibf	Parleam 4	Abil EM	NaOH	TOA	99	[151]

ELM used in literature is composed of PBS and VOs. As observed for Dcf and Ibf DCM, kerosene, hexane and heptane were being employed as diluent [75] [32] [188][151]. For LA the studies were carries using kerosene, hexane, toluene. Also, research reported the use of blend of RBO and hexane. Since the PBS are toxic and harmful, VOs are being used as greener alternatives. For LA there's a research utilizing SFO as diluent [26]. However, keeping in mind the food crisis and stability of ELM use of VOs is another issue. To overcome this problem, waste vegetable oil (WVO) can be used to develop ELM. An added advantage of using WVO is the prevention of waste oil from disposal and hence putting a stop to the environmental problems caused by its disposal. Therefore, in this study, WVO was used as a diluent to develop the green emulsion membrane. ILs have been applied for the removal and recovery of BACs. There is no research reported for the formulation of ELM to remove BACs from aqueous streams using WVO and ILs. Hence this work will be able to extract waste from waste material as feed. It is believed that waste vegetable oil-ionic liquid-based emulsion membrane WVO-ILEM will be highly stable with high extraction efficiency. Also, since all components are green, the developed WVO-ILEM will be less toxic, renewable, and efficient for removing biologically active compounds. This research will modestly contribute to overcoming the mentioned research gaps.

CHAPTER 3

METHODOLOGY

This chapter describes the detailed methodology for screening ILs using COSMO-RS and developing WVO-ILEM using ionic liquid as the carrier and WVO as diluent. It consists of selecting ILs using COSMO-RS for the specified BAC and developing WVO-ILEM using screened IL. Fig. 3.1 presents the step-by-step methodology adopted to remove BACs. Besides the formulation of WVO-ILEM, its characterization, optimization using RSM, permeation rates, and demulsification of WVO-ILEM have also been provided.

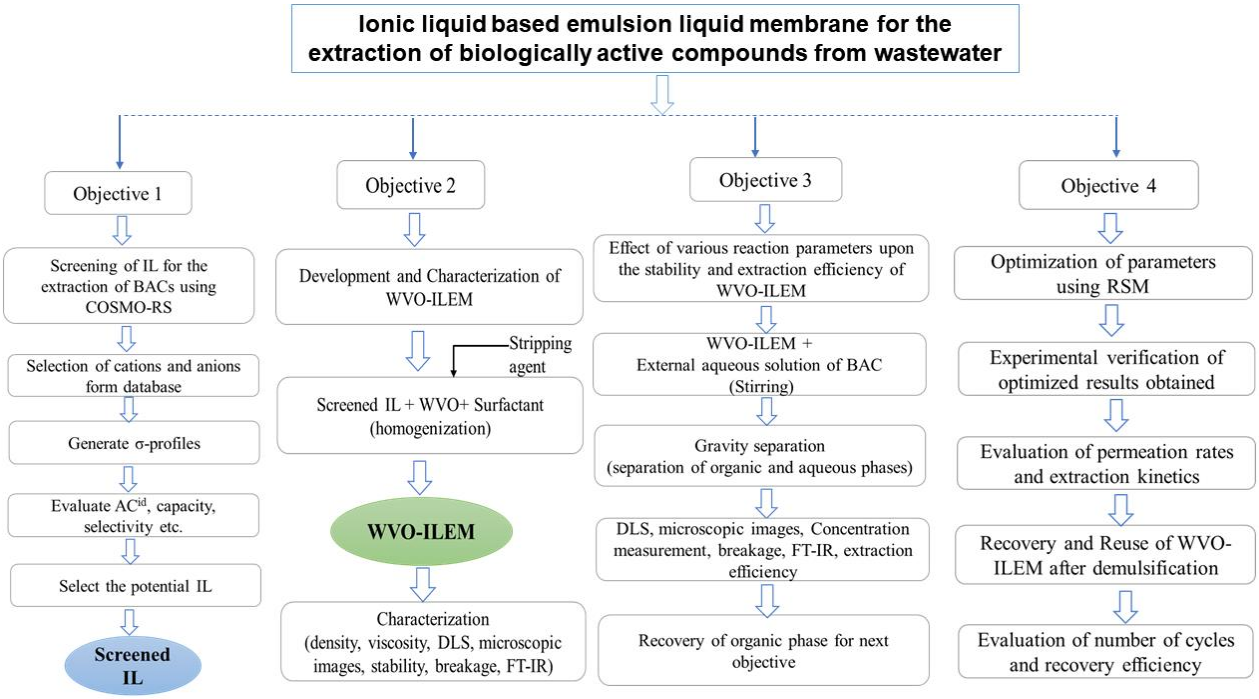


Figure 3.1: Methodology adopted for the development for WVO-ILEM and their application in the removal of BAC

3.1 Materials

Waste vegetable oil (WVO) was purchased from a local restaurant. Since the composition of WVO does not affect the emulsion formulation, and the only function of WVO is to form a barrier between internal and external phase, component analysis was not carried out. WVO was filtered to remove the solid impurities that will affect the consistency and hence homogenization process. The WVO density, viscosity, and refractive index were 0.9224 g/cm^3, 134.6 cPs, and 1.3546, respectively. . All chemicals used in this research study, including development and application, are listed in Table 3.1. All chemicals were used as received without any further purification. Stock solutions were prepared using deionized water. Model wastewater was prepared by dissolving appropriate amount of BACs in 1L deionized water [189].

Table 3.1: Chemicals and reagents used in this current research

Chemical Name	**CAS No.**	**Source**	**Purity**	**Impurities**
Tetramethylammonium acetate	10581-12-1	Sigma Aldrich	>97%	<0.5%
Tetramethylammonium chloride	56-34-8	Sigma Aldrich	>98%	<0.5%
Tributylmethylammonium chloride	1112-67-0	Sigma Aldrich	>97%	<0.5%
1-Ethyl-3-methylimidazolium chloride	65039-09-0	Sigma Aldrich	>98%	<0.5%
1-Ethyl-3-methylimidazolium acetate	143314-17-4	Sigma Aldrich	>98%	<0.5%
1-Butyl-3-methylimidazolium chloride	79917-90-1	Sigma Aldrich	>98%	<0.5%
1-Butyl-3-methylimidazolium acetate	254049-75-8	Sigma Aldrich	>96%	<0.5%
Chemical Name	**CAS No.**	**Source**	**Purity**	**Impurities**

Sodium hydroxide	1310-73-2	Sigma Aldrich	99%	<1.0% Na_2CO_3
Sodium carbonate	497-19-8	Sigma Aldrich	99.5%	0.005% silica
Ammonia	7664-41-7	Sigma Aldrich	99.98 %	
Nitric acid	7697-37-2	Sigma Aldrich		<5ppm
Diclofenac sodium	15307-79-6	Sigma Aldrich	>98%	-
Ibuprofen	15687-27-1	Sigma Aldrich	>98%	-
Lactic acid	79-33-4	Sigma Aldrich	>98%	-
Span 20	1338-39-2	Sigma Aldrich	>44%	-
Span 80	1338-43-8	Sigma Aldrich	>60%	-
Tween 80	9005-65-6	Sigma Aldrich		-
WVO	-	Rahman corner		-

3.2 Ionic liquids screening using COSMO-RS

This work aimed to screen the best suitable IL for extracting selected model compounds, diclofenac, ibuprofen, and lactic acid. COSMOtherm 18.0 was used for the computational study. Six cations from both aromatic and non-aromatic families and twenty anions, including hydrophilic and hydrophobic, were selected to check which combination gives the best results. A conductor-like screening model for real solvents (COSMO-RS) was performed for the selected BACs.

The chemical structure was drawn using the chemSketch/ChemDraw version. The quantum chemical calculations were optimized using TURBOMOLE (TMOLEX-16) software, and the files were saved in the COSMO format files. COSMO predictions were accomplished using COSMOtherm software version 18.0.2, and the thermodynamic properties were evaluated using BP_TZVP_C30_1201 parametrization. Density functional theory (DFT) was used to perform the quantum calculations using resolution identity (RI) approximations. AC^{id}, capacity, and selectivity were evaluated using COSMO-RS at room temperature. These values help in determining the efficacy of IL. Fig. 3.2 presents the COSMO-RS screening procedure for ILs. The performance index (PI) was calculated to find the best combination of cation and anion for the selection of IL. Based on literature and the nature of cations and anions, six cations and twenty anions were selected, such as aromatic, non-aromatic, hydrophobic, and hydrophilic were selected. Table 3.2 shows the list of chosen cations, and Table 3.3 shows the anions studied in this study.

3.2.1 COSMO-RS experimental validation

After screening the ILs using COSMO-RS, experimental validation was carried out for the predicted results. Two ILs were selected from the list for each model compound, and experiments were performed to extract BACs using the selected ILs as the carrier in ELM. Table A3 (Appendix A) presents the ILs selected for COSMO validation using ELM. Since the data on activity coefficient for the BACs using ILs is not available. The AC^{id} predictions by COSMO-RS for the selected ILs were compared with the extraction efficiencies obtained by the ELM approach. The theoretical efficiencies were calculated using the regression curves and compared with the experimental results for the selected ILs [190]. The mean absolute difference was calculated. The percentage absolute deviation between experimental and theoretical efficiencies was calculated. Using COSMO-RS, the best ILs screened were used to develop WVO-ILEM.

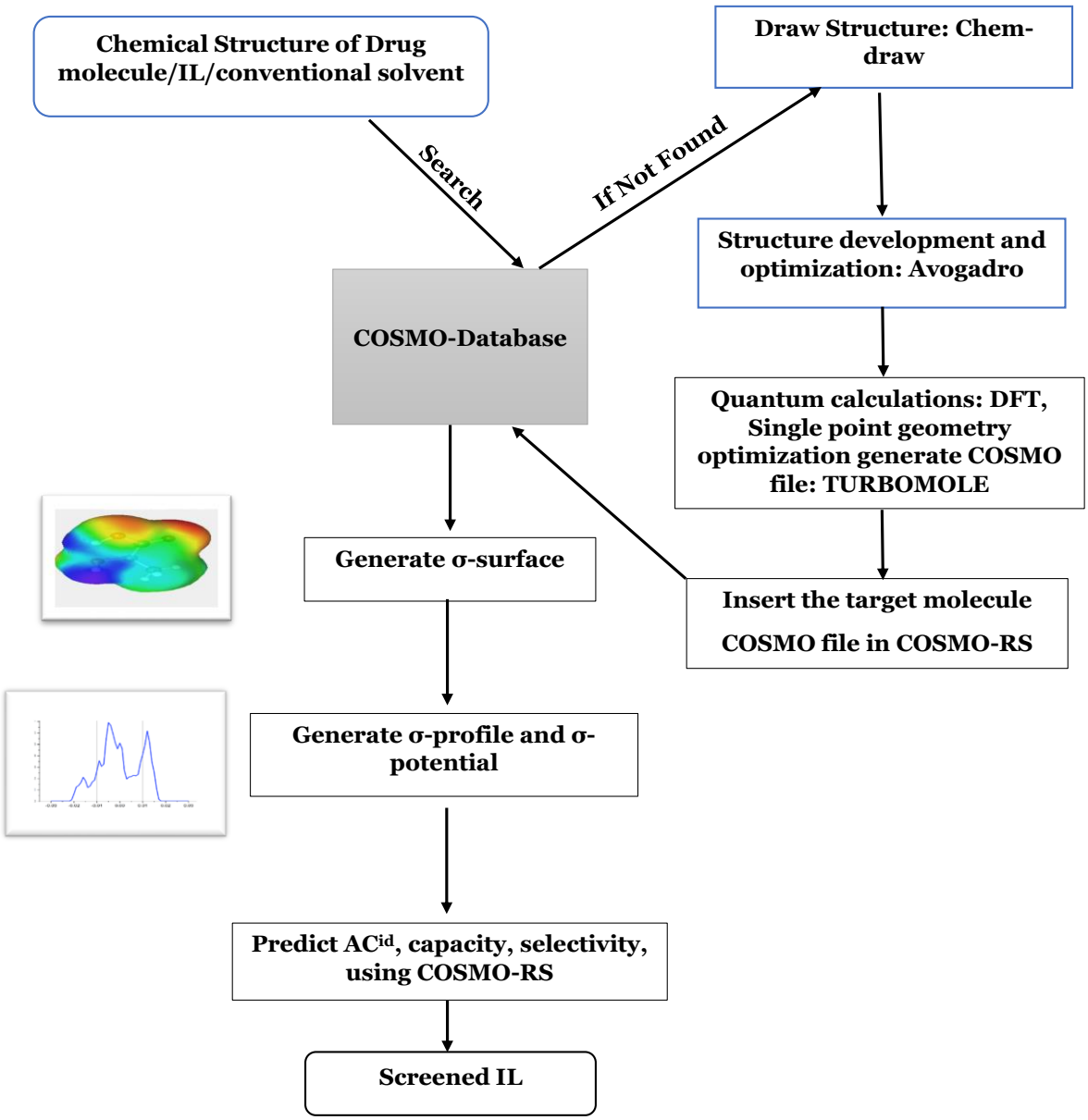


Figure 3.2: COSMO-RS step by step procedure for IL screening

Table 3.2: Cations selected for the COSMO-RS screening in increasing order of H-bond donor moment.

S. No	Abbreviation	Cation	H-Bond donor moment
1	[TBMPh]	Tributylmethylphosphonium	0.05208
2	[BMPyrro]	1-butyl-1-methyl-pyrrolidinium	0.05468
3	[BMPip]	1-butyl-1-methyl-piperidinium	0.07778
4	[TMAm]	tetramethylammonium	0.37714
5	[BMPyri]	1-butyl-3-methyl-pyridinium	0.9687
6	[BMIm]	1 butyl-3- methyl-imidazolium	1.91626

Table 3.3: Anions selected for the COSMO-RS screening in decreasing order of H-bond acceptor moment.

S. No	Abbreviation	Anion	H-bond acceptor moment
1	SO_4^{2-}	Sulphate	85.682
2	$C_6H_{14}N_2O^{2-}$	lysinate	44.3006
3	$C_5H_9NO_4^-$	glutamate	43.211
4	CH_3COO^-	acetate	38.928
5	$C_5H_{11}N_2O_3^-$	valinate	37.908
6	$C_{16}H_{34}PO_2^-$	bis(2,4,4-trimethylpentyl)phosphinate	37.4535
7	Cl^-	chloride	36.628
8	$C_7H_6O_2^-$	benzoate	32.252
9	$C_2H_6O_3S^-$	methanesulfonate	30.0845
10	Br^-	bromide	29.444
11	NO^{2-}	nitrite	25.756
12	HSO_4^-	hydrogen sulfate	19.398
13	$C_7H_5NO_3S^-$	sacchrinate	19.3244
14	$C_{16}H_{34}POS^-$	bis(2,4,4-trimethylpentyl)thiophosphinate	16.437
15	SCN^-	thiocyanate	12.291
16	$CF_3O_3S^-$	trifluoromethanesulfonate	10.684
17	ClO_4^-	perchlorate	3.8852
18	BF_4^-	tetrafluoroborate	2.487
19	Tf_2N^-	bis(trifluoromethyl)sulfonylimide	2.3103
20	PF_6^-	hexafluorophosphate	0

3.3 Synthesis of IL

Synthesis of ionic liquid was carried out by using a simple ion-exchange reaction. 10.02g of [TMAm][Cl] was dissolved in 18.28 ml of water. 2.102 g of Na_2SO_4 was added to it. The components were transferred to a beaker and stirred for 2 hrs. Methanol was added to precipitate the byproduct NaCl [191]to the solution obtained. It was followed by filtration resulting in the precipitation of NaCl. The aqueous solution obtained was rotavapor at 65^{o}C and 300 mm Hg pressure for 24 hrs. Methanol, along with water, was evaporated. The powder crystals left after evaporation in the flask were [TMAm][SO_4].

3.3.1 Characterization of IL

The characterization of synthesized IL was carried out using ^{H}NMR and FT-IR*H*

3.3.1.1 Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) is an important characterization technique that provides detailed knowledge on molecular structure and enables the study of chemical reactions. The synthesized IL was characterized using 1H NMR at room temperature. The Bruker AVANCE III 500 MHz spectrometer (Country) made all NMR measurements. Deuterium oxide (D_2O) was used as the solvent. The NMR solvent was purchased from Sigma Aldrich. The results are present in Fig. A1 (APPENDIX A)

3.3.1.2 Fourier transform infrared spectroscopy

FT-IR was carried out using thermo scientific Nicolet iS5 FTIR spectrophotometer in the wavenumber range 400-4000 cm^{-1} at 4 cm^{-1} resolutions at room temperature. A drop of solution was held on the lens with the aid of a dropper at psi pressure for study. The spectrum output was as a function of wavenumber in transmittance mode. The background spectra of Diamond-IR were measured to adjust the relative scale for absorption intensity. The real sample was compared with the baseline spectrum to achieve the resulting spectrum with no instrumental character. The results are present in Fig. A2 (APPENDIX A)

3.4 Waste vegetable oil-ionic liquid-based emulsion membrane (WVO-ILEM)

To develop WVO-ILEM initial organic phase consisted of waste vegetable oil (WVO), surfactant, and IL. Internal stripping agent solutions were prepared using different concentrations in distilled water. Initially, the emulsion was prepared using 10 mL of oil (WVO). To it 1 wt. % of Span 80 and 0.2 wt.% of IL [TMAm][SO_4] was added. The mixture was homogenized using a high-speed homogenizer at 5200 rpm for 3 min. To this 2.5 mL of stripping, agent was added dropwise, and the homogenization was carried out for 5 min [192]. A milky white WFO-ILEM was obtained. The emulsion was characterized and used for the removal of BACs.

All the extraction experiments were conducted at room temperature. The WVO-ELM (without IL)/ WVO-ILEM was added to 25 mL external solution with continuous stirring at 250 rpm for a specific time to extract selected model compounds. The BACs (Dcf, Ibf and LA) get transported from the external solute phase to the membrane phase through mass transfer. At the membrane-external phase, the solute reacts with the IL (carrier) present in the membrane, resulting in complex formation. This complex moves towards an internal stripping agent where the stripping reaction occurs. As a result, the solute is stripped off, and the carrier is regenerated.

After the extraction, the mixture (WVO-ILEM with external BAC solution) was poured into a separating funnel and allowed to separate. The upper layer consisting of the organic membrane phase extracts BAC, and the bottom layer is composed of an aqueous phase devoid of it; if present, it is in trace amounts. The collected samples were filtered using a syringe filter of 0.24 μm. The obtained results in all experiments were in terms of BAC concentration extracted from external solution (Dcf, Ibf and LA). All the experiments were performed in triplets, and the mean values were reported as the final result with error bars indicating standard deviation. The emulsion can be reused for further extraction of LA. Fig. 3.3 shows the schematic process flow of ILEM.

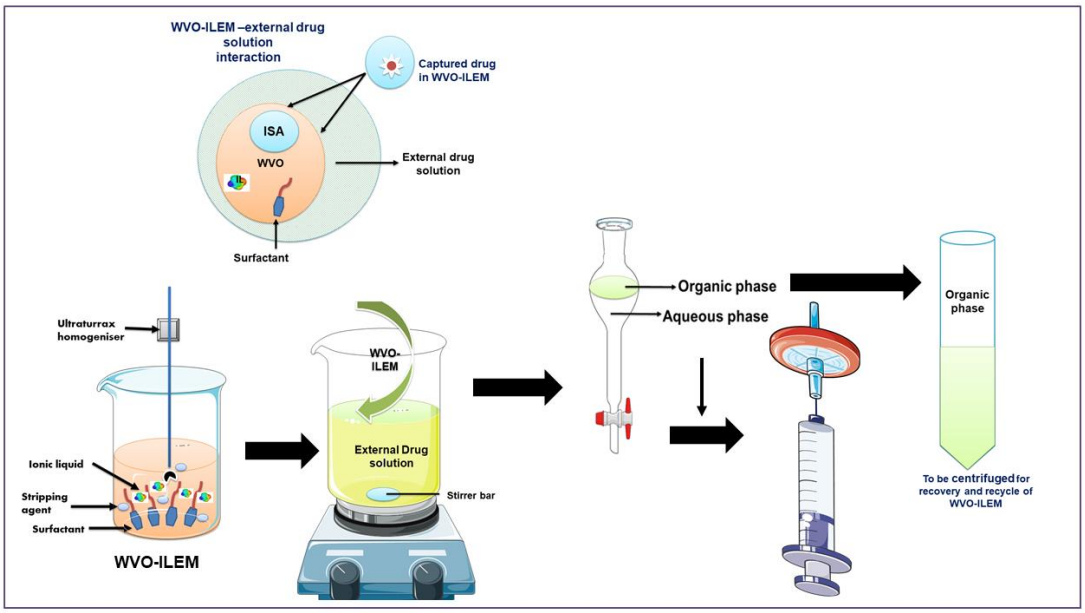


Figure 3.3: Schematic diagram of WVO-ILEM development and extraction

3.5 Characterization of WVO-ILEM

The characterization of WVO-ILEM was done before and after the extraction process. Diameter, interfacial tension, viscosity, density, breakage, pH measurement, stand-alone stability (time), concentration measurement, and efficiency were measured to

characterize WVO-ILEM. The current section describes, in brief, the characterization techniques.

3.5.1 Dynamic light scattering (DLS)

The internal droplet size and dispersed drop size of emulsions are determinant factors because of their effect on stability and hence the efficacy of WVO-ILEM [26]. Therefore, it is essential to determine the diameter of the emulsion. The diameter of the emulsion globule was measured using dynamic light scattering (DLS). The measurements were made for the freshly prepared WVO-ILEM and WVO-ILEM after being dispersed in the external BAC solution. A computerized inspection system was used to conduct dynamic light scattering (DLS) investigations (Zetasizer Nano Series, Malvern Instruments, United Kingdom). The dispersion angle was chosen to be 90 degrees. The mean was calculated using Malvern DTS software. All measurements were carried out at a temperature 25 + 0.1 °C. A thermostat was used to keep the temperature constant.

3.5.2 Microscopic imaging

Microscopic imaging was carried out as it gives detailed information on the changes in emulsion diameter, which determines the stability of WVO-ILEM [152]. The microscopic images of WVO emulsion were measured using Eclipse LV 100N Pol microscope. The microscope was equipped with a camera and toupview software for image analysis. A drop of freshly prepared ILEM was placed on a slide covered with a slide cover. The images were recorded, and the diameter was measured. Three slides were prepared for each emulsion to ensure accuracy, and the average value of diameter was reported for each case.

3.5.3 Density

Density (ρ) measurement was carried out for the WVO-ILEM, external agent, pure components, and WVOs. All measurements were conducted at 25 $\pm$ 2^{o}C using Anton Par stabinger viscometer SVM 3000, Sdn Bhd Malaysia.

3.5.4 Viscosity

Viscosity is an important parameter and plays a governing role for the emulsion's size and hence the stability of WVO-ILEM [193]. In addition, it also determines diffusivity. The viscosity of WVO-ILEM was determined using Brookfield viscometer CAP 2000+, version 1.5, purchased from Ametek Bhd Malaysia. A spindle type 5 was used for a run time of 60 seconds at rpm, and a shear rate of 3000/s to measure the viscosity. All measurements were carried out at room temperature (25 $\pm$ 2^{o}C). Viscosity was calculated by taking a rate of change of shear stress vs strain**.** The measurements were made in triplets, and an average value was reported.

3.5.5 Interfacial tension

Interfacial tension (IFT) is a critical factor governing the emulsification process [194]. Additionally, the emulsion droplet's size and stability depend upon the interfacial tension. Thus it is necessary to determine IFT for WVO-ILEM. IFT between the emulsion and external aqueous phases was measured using a spinning drop tensiometer, SVT 20 Dataphysics. The experiments proceed in a spinning horizontal glass syringe Data physics FEC 622/400 HT rapid exchange capillary containing aqueous external phase. A drop of WVO-ILEM formed was injected into the center of the syringe, which was then rotated at a speed of 4000 to 7000 rpm. All observations were repeated thrice, and the average interfacial tension value was reported at room temperature (25 $\pm$ 2^{o}C). Cold water was circulated to maintain the temperature.

3.5.6 pH measurement

WVO- ILEM stability is determined by how easily an emulsion breaks. pH levels are used to determine the extent of breakage (%). pH measurements were made using a digital pH meter with a pH electrode (ECFC7252101**)** that was calibrated at pH values of 4 and 7 for WVO-ILEM, initial external phase, and WVO-ILEM-external phase. All measurements were made in triplets and at room temperatures.

3.5.7 ILEM stand-alone stability test

Stand-alone stability, also termed static or physical stability, was determined for WVO-ILEM. It was examined by placing the freshly prepared WVO-ILEM into a 10 mL measuring cylinder and left for phase separation. The time at which the water layer has appeared was recorded, the emulsion starts to break. It thus becomes unstable, resulting in a reduction in extraction efficiency as shown in Fig. 3.4 [91]. It is also referred as "stand-alone stability" [195].

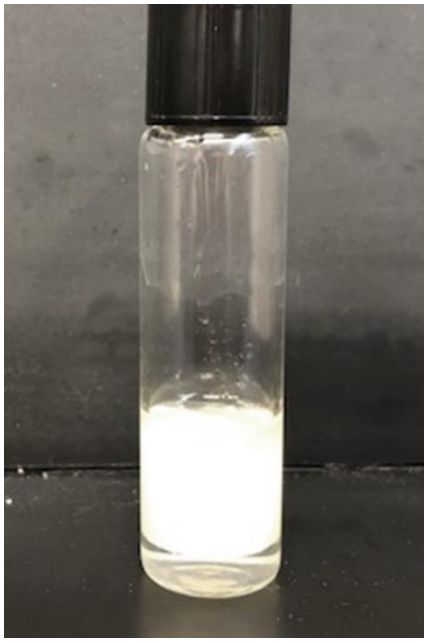


Figure 3.4: Stand-alone stability test

3.5.8 ILEM breakage

The stability of the emulsion is directly related to the breakage of WVO-ILEM. Hence it is essential to calculate the breakage (%). Since the volume of internal stripping agent leaked into external phase is very less, membrane breakage can be calculated based on $[H^+]$ ion concentration change in the external solution. This can be determined via pH meter. Breakage is calculated using the following equation 3.1 [107]

$$\epsilon(\%) = \frac{V_s}{V_i} * 100 \qquad (3.1)$$

Where

V_s= volume of internal stripping agent leaked into the external solution

V_i=volume of internal stripping agent

V_s can be calculated as follows

$$V_s = V_{ext} \frac{10^{-pH_o} - 10^{-pH}}{10^{-pH} - C_{H^+}^{int}} \qquad (3.2)$$

Where,

pH_o= pH of the external phase initially

pH = pH of the external phase with WVO-ILEM

$C_{H^+}^{int}$=concentration of H^+ in the stripping phase initially

3.5.9 FTIR Spectra

To obtain more information about the interaction of IL with the organic phase, it is necessary to characterize the organic phase before and after being in contact with WVO-ILEM [120]. Fourier transform infrared spectroscopy (FTIR) is a valuable technique for analyzing the functional groups present in the system. Nicolet iS5 FTIR spectrophotometer in the wavenumber range 400-4000 cm^{-1} at 4 cm^{-1} resolutions at room temperature was used for analysis. A drop of solution was held on the lens with the aid of a dropper at psi pressure for study. The spectrum output was as a function of wavenumber in transmittance mode.

3.5.10 UV-vis spectrophotometer

The extraction efficiency determines the efficacy of WVO-ILEM. Therefore, it is essential to find out the unknown concentration of the solute in the aqueous external phase after extraction. The extraction efficiency can be calculated using equation 3.4. The concentration of model BACs was measured using a UV-vis spectrophotometer. After separation, the BAC concentration in the aqueous solution was measured using a UV-vis spectrophotometer. The absorbance was recorded at a standard wavelength with the reference solution. The aqueous solution obtained using ILEM after extraction and separation without BAC was used as a reference solution. The removal efficiency was determined using equation 3.3.

$$\text{Extraction efficiency (\%)} = \frac{C_0 - C}{C_0} * 100 \quad (3.3)$$

where C_o = initial analyte concentration in the feed phase
C= solute concentration in the lower aqueous phase.

The calibration curves for Dcf, Ibf, and LA are shown in Fig. A3, A4, and A5, respectively (APPENDIX A). The reference solution was the aqueous solution obtained after extraction without BAC. The solution's absorbance was recorded at Dcf -270 nm, Ibf- 222 nm, and LA=390 nm, respectively.

3.5.11 High-performance liquid chromatography (HPLC)

The concentration of BAC understudy in the aqueous phase was further verified using HPLC. HPLC equipped UV-vis, and a C_{18} HPLC column (250mm * 46mm * 5m) was used. The mobile phase was acetonitrile: methanol (70:30v/v) at a flow rate of 1.0 ml/min with 20µL of the sample [196]. The measurements were done at room temperature 25^{o}C. The UV detection wavelengths for Dcf and Ibf were 276nm, 222 nm, and 390 nm, respectively. Fig. A6, A7, and A8 (APPENDIX A) present the calibration curve for Dcf, Ibf, and LAs.

3.6 Optimization using RSM

Optimization studies were carried out using Design-Expert 13.0.7 StatEase. Central Composite Design (CCD) was selected to remove BACs from aqueous solution using WVO-ILEM, as it is helpful in a situation where the response is influenced by several factors [82]. Five parameters that affect the composition, stability, and extraction efficiency were selected. The ranges were determined experimentally in the objective 3. The parameters were varied and the effect was studied upon the stability and

extraction efficiency. The ranges obtained were used for the design of DOE. Table 3.4 presents the chosen parameters for the design.

Table 3.4: Parameters selected for Dcf

Code	Parameter	Unit
A	Surfactant concentration	wt.%
B	Stripping agent concentration	M
C	Carrier concentration	wt.%
D	Phase ratio	
E	Treat ratio	

Using these ranges, the experimental design matrix was generated by RSM. Table 3.5 presents the experimental design matrix generated using RSM. A total of 50 runs were conducted using RSM-CCD. Experiments were performed in triplets to avoid error. The response was the extraction efficiency (%), and the concentration was determined using a UV-vis spectrophotometer.

Table 3.5: Design matrix developed by Response Surface Methodology

Run	Factors				
	A: Surfactant concentration (wt.%)	B:Phase ratio	C:Treat ratio	D: Stripping agent concentration (M)	E: Carrier concentration (wt.%)
1	3	0.4	4	0.05	0.1
2	0.5	0.4	4	0.3	0.1
3	1.75	0.275	2.5	0.175	0.35
4	1.75	0.275	2.5	0.175	0.35
5	1.75	0.15	2.5	0.175	0.35
6	3	0.4	1	0.3	0.1
7	3	0.15	1	0.05	0.6

8	3	0.15	1	0.05	0.1
9	1.75	0.275	2.5	0.05	0.35
10	0.5	0.4	1	0.05	0.6
11	0.5	0.4	1	0.3	0.6
12	1.75	0.275	4	0.175	0.35
13	3	0.15	4	0.3	0.6
14	0.5	0.4	1	0.3	0.1
15	1.75	0.275	2.5	0.175	0.35
16	3	0.4	1	0.05	0.1
17	1.75	0.4	2.5	0.175	0.35
18	0.5	0.4	4	0.05	0.6
19	1.75	0.275	2.5	0.175	0.35
20	3	0.4	4	0.05	0.6
21	0.5	0.15	1	0.3	0.6
22	0.5	0.4	4	0.3	0.6
23	1.75	0.275	1	0.175	0.35
24	3	0.15	4	0.3	0.1
25	0.5	0.15	1	0.05	0.6
26	1.75	0.275	2.5	0.175	0.35
27	3	0.4	4	0.3	0.6
28	3	0.15	1	0.3	0.1
29	1.75	0.275	2.5	0.175	0.35
30	3	0.15	1	0.3	0.6
31	3	0.4	1	0.3	0.6
32	3	0.15	4	0.05	0.1
33	1.75	0.275	2.5	0.175	0.6
34	0.5	0.15	4	0.05	0.1
35	1.75	0.275	2.5	0.175	0.35
36	3	0.4	1	0.05	0.6
37	0.5	0.15	1	0.05	0.1
38	0.5	0.15	4	0.3	0.1

39	0.5	0.4	1	0.05	0.1
40	0.5	0.15	1	0.3	0.1
41	3	0.4	4	0.3	0.1
42	0.5	0.15	4	0.3	0.6
43	0.5	0.275	2.5	0.175	0.35
44	1.75	0.275	2.5	0.175	0.35
45	1.75	0.275	2.5	0.175	0.1
46	0.5	0.15	4	0.05	0.6
47	3	0.15	4	0.05	0.6
48	1.75	0.275	2.5	0.3	0.35
49	0.5	0.4	4	0.05	0.1
50	3	0.275	2.5	0.175	0.35

Likewise, optimization was performed for Ibf and LA. The parameters and RSM design matrix range for Ibf and LA are presented in Table B1, Table B2, Table B3, and Table B4 (APPENDIX B).

3.7 Permeation and kinetics of WVO-ILEM

At the optimized conditions obtained, the permeation rate of BAC extraction was studied. It is a function of both chemical reaction and diffusion. Both these processes were taken into account while analyzing the kinetics of BAC. At experimentally optimized conditions, the change in concentration of BACs was observed as a function of time. Kinetic study was performed for all three BACs. Permeation rate, effective diffusivity, and rate constants were evaluated.

3.8 Demulsification for recycling and reuse of WVO-ILEM

After WVO-ILEM extraction, emulsion obtained as an upper phase with the BAC entrapped in the internal phase was demulsified. Demulsification was carried out using Hettich centrifuge ROTOFIX 32-A. The speed for agitation was 25000 rpm for ten minutes. The demulsification resulted in the separation of phases. The emulsion was split into two phases. Oil, surfactant, and IL make up the organic phase. Internal agent and BAC are both present in the aqueous phase. The recovered organic phase can be reused in the subsequent extraction processes. The BAC extracted in the internal phase can also be recovered. Fig. 3.5 shows the emulsion before and after demulsification

.

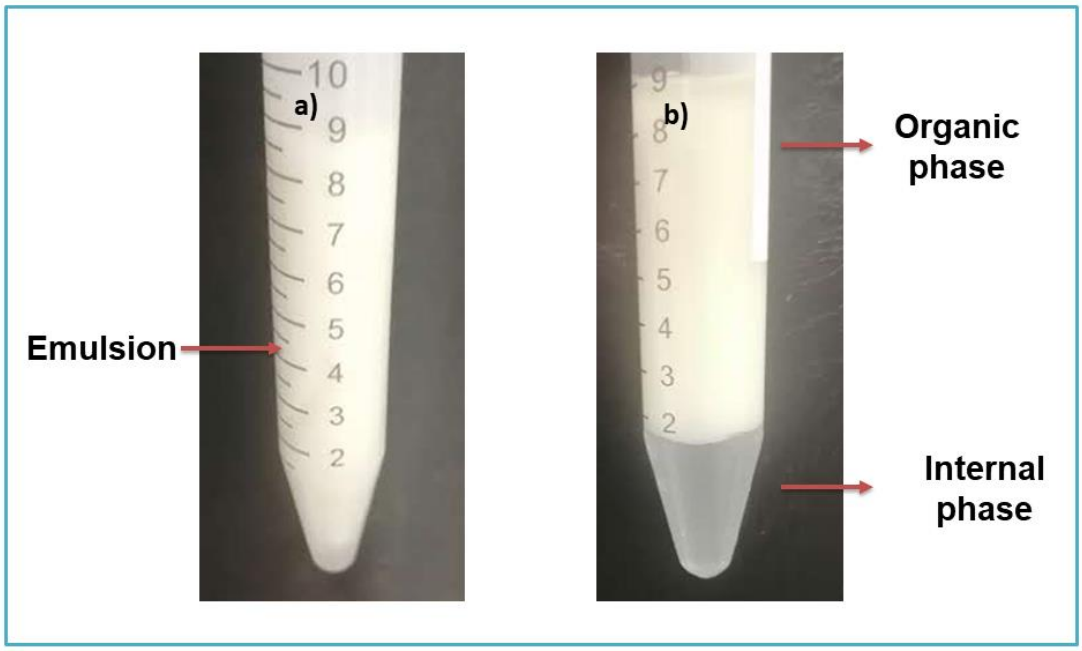


Figure 3.5: Emulsion a) before demulsification and b) after demulsification

CHAPTER 4

RESULT AND DISCUSSION

This chapter is divided into four sections. The first section presents the screening of ILs for model BACs using COSMO-RS. The second section presents the development of WVO-ILEM using screened IL. Also, a plausible reaction mechanism is proposed to extract diclofenac using WVO-ILEM. The third section explains the effect of various reaction parameters on the stability and extraction efficiency of WVO-ILEM. Also, it presents the optimization of reaction parameters for maximum extraction efficiency; a model is developed that correlates the effect of various parameters upon the extraction efficiency of WVO-ILEM. Section 4 presents the system's permeation rates and kinetics studied at the optimized results. Demulsification and stripping at the optimized conditions for the BACs under study are also present. Also, it presents the recovery efficiencies evaluated after demulsification

4.1 SECTION I COSMO-RS SCREENING

The screening of ILs for model compound diclofenac (Dcf), ibuprofen (Ibf), and lactic acid (LA) was carried out using COSMOtherm version 18.0. The sigma profiles, sigma potentials, activity coefficient at infinite dilution AC^{id}, capacity, selectivity, and performance index were predicted for selected combinations of cations and anions.

4.1.1 Sigma surface and profiles for Dcf

Polarity, charge distribution, and hydrogen bonding was assessed by three-dimensional (3D) screening charge distribution (σ-surface) using the COSMO-RS model [197]. Fig. 4.1 shows the chemical configuration and σ-surface for Dcf. Red, blue, and green signify negative, positive, and neutral charges [127]. Fig. 4.2 presents the σ profile and σ potential distributions of Dcf predicted using COSMO-RS. The σ-profile was

bifurcated into three regions, specifically H-bond donor ($\sigma < -1.0$ e/nm^2), non-polar ($-1.0 < \sigma < 1.0$ e/nm^2) and H-bond acceptor region ($\sigma > 1.0$ e/nm^2) [198]. The figure reveals that Dcf possesses both H-bond donor and acceptor sites. Dcf is highly polar due to the presence of N, O, Cl. It possesses interaction with H-bond acceptor and donor groups due to the presence of NH group that can accept and donate proton [142]. The σ-profile for Dcf reveals a series of peaks observed in both polar and non-polar regions. There are two small peaks in the H-bond donor region (at 0.17 and 0.3 e/nm^2) corresponding to NH's presence in Dcf. A slight peak can also be observed H-bond acceptor region is due to the presence of the COOH group and hence will act as an H-bond acceptor [199]. This trend is visible in the σ-potential, which shows an increasing trend in the H-bond acceptor region compared to the H-bond donor region [200] since Dcf possesses 2 H-bond donor counts and 3 H-bond acceptor counts. Dcf will be attracted by both H-bond donor and acceptor groups.

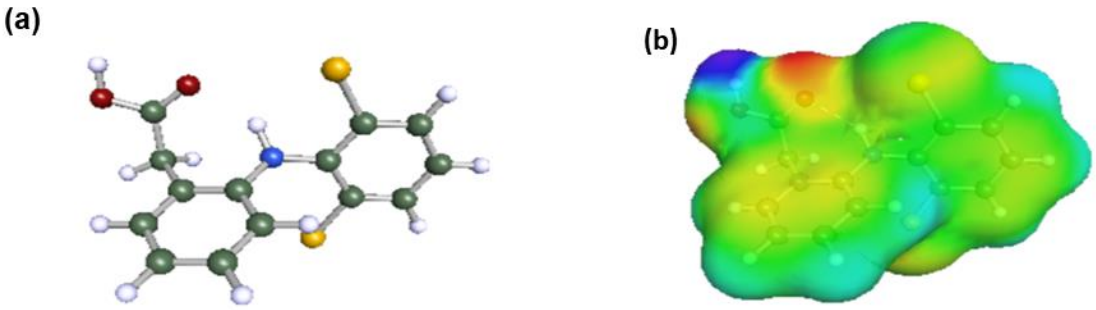


Figure 4.1: (a) Chemical configuration and (b) σ surface of Dcf using COSMO-RS model

Ibf and LA also both show a similar trend. Fig. B1 and Fig. B2 (APPENDIX B) present the chemical configuration and the σ-profiles and σ-potential for Ibf. Fig. B3 and B4 present the σ surfaces and σ-profiles for LA. The results show a similar trend like Dcf that Ibf and LA will be attracted more toward H-bond acceptor groups.

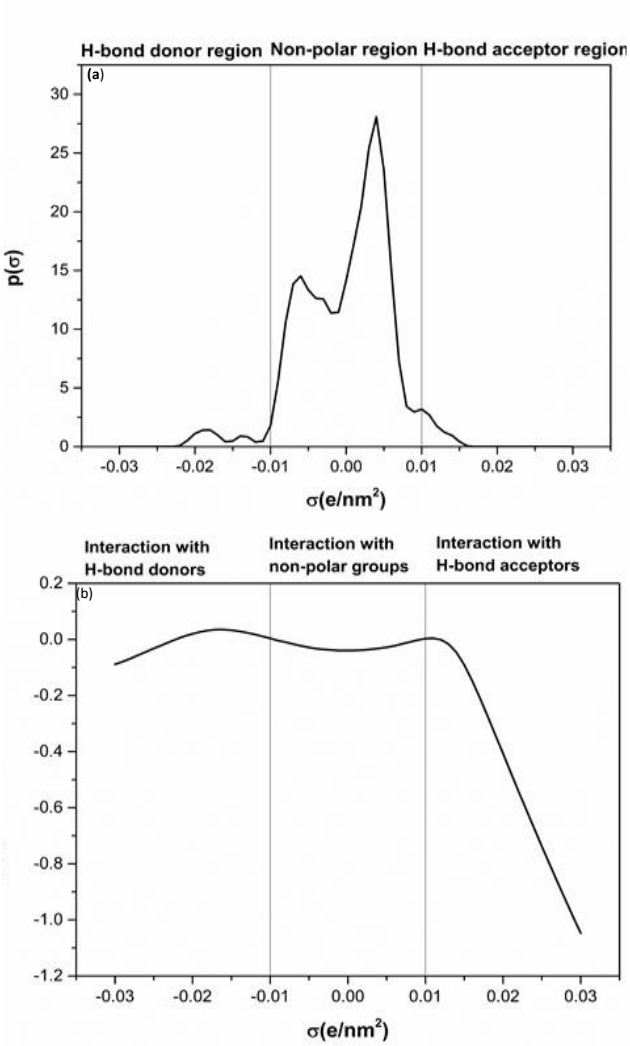


Figure 4.2: Predicted (a) σ profile and (b) σ potential distributions of Dcf using COSMO-RS

4.1.2 Activity coefficient at infinite dilution

Activity coefficient is an important property related to solubilizing power of IL, and based upon this; one can estimate whether a given IL will be effective in the separation process [129]. The more negative the AC^{id}, the better the IL to be used as a carrier for extraction purposes. Fig. 4.3 presents the result for the AC^{id} values for Dcf. The results reveal that quaternary ammonium cation and SO_4^{2-} anion possess the lowest AC^{id} values

compared to other cation-anion combinations. This is because of the extra charge on SO_4^{2-} and the highest hydrogen bond acceptor moment. Anions BF_4^- and PF_6^- showed an opposite trend due to their non-coordinating nature. Similar results were reported for the extraction of linoleic acid [201].

Also, it can be observed that the cations that do not possess π-electrons show more negative values of AC^{id} and hence will be better extracting agents for extraction of Dcf. The cations with aromatic rings are less effective for Dcf extraction because of steric hindrance in the aromatic structure resulting from delocalization. Cations show following trend: [TMAm] < [BMPyrro] < [BMPip] < [TBMPh] < [BMPyri] < [BMIm].

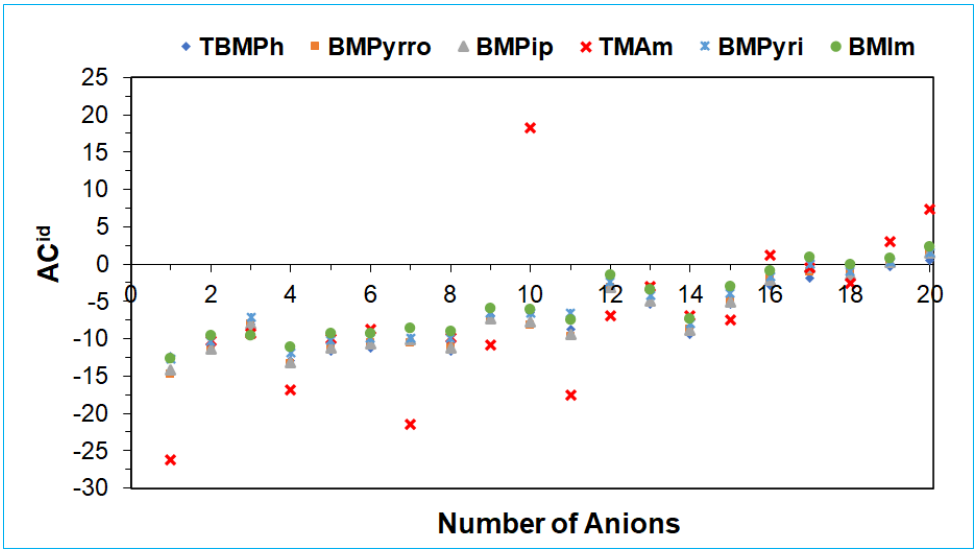


Figure 4.3: AC^{id} values predicted using COSMO-RS for Dcf

[TMAm][SO_4] and [TMAm][Cl] were found to possess lesser AC^{id} values for the extraction of eicosapentaenoic acid as well [202] . Similar results were obtained for Ibf and LA using COSMO-RS. Fig. B5 and Fig. B6 (APPENDIX B) present the AC^{id} values for Ibf and LA, respectively.

4.1.3 IL capacity towards Dcf

The capacity of IL determines the amount of IL required to remove solute from solution during extraction [203]. It signifies the ability to dissolve the maximum amount of solute [124]. The capacity of 120 cation-anion pairs forming ILs for Dcf was evaluated at 25^{o}C. Fig. 4.4 presents the ILs capacity towards Dcf and reveals the type of cation and anion effect. The cation shows the following trend for the capacity values: [TMAm]>[BMpyrro]>[BMPip]>[TBMPh]>[BMPyri]>[BMIm]

The results reveal that ILs with benzene rings have lesser capacity than cations without benzene rings. The capacity values for [Im] and [Pyri]were lower. This could be due to increased charge delocalization in [Im] and [Pyri]. Also, cations such as [Am], [Pyrro], [Pip] possess higher capacity values. This can further be explained as the π-electron cloud increased, the capacity decreased for Dcf due to steric hindrance resulting in delocalization of charges [204]. Compared to [Im] cation, [Pyrro] showed better extractability for Dcf. This is because [Pyrro] cation has no ring structure and possesses quaternary nature, allowing it to form H-bonds with Dcf relative to [Im], in which electrons are delocalized [205] [112]. [TMAm] was found to be a suitable cation for the extraction of Dcf because of the strong hydrogen bond interactions between the IL and cation and Dcf. A similar observation was made for eicosapentaenoic acid, which reveals that cations that do not possess delocalization have stronger hydrogen bonding properties and, hence, are better for extraction [206].

As shown in Fig. 4.4 the anions that give better capacity for Dcf are as follows: [SO_4^{2-}]>[Cl^-]> [CH_3COO^-] >[Br^-]>[NO_2^-]. These results reveal that anions that are good hydrogen bond acceptors are better extracting agents for Dcf. This can further be elaborated as the H-bond between (S=O----H) is stronger, enhancing its extraction ability as a carrier [199]. The anions that possess hydrophobic nature, such as [PF_6^-] and [BF_4^-], show poor capacity with Dcf as a result of shielding nature [112]. Authors reported similar results for the screening of ILs for the extraction of docosahexaenoic acid [199]. This trend is also visible by the σ-potential of Dcf; an increasing trend can be observed in the hydrogen bond acceptor region.

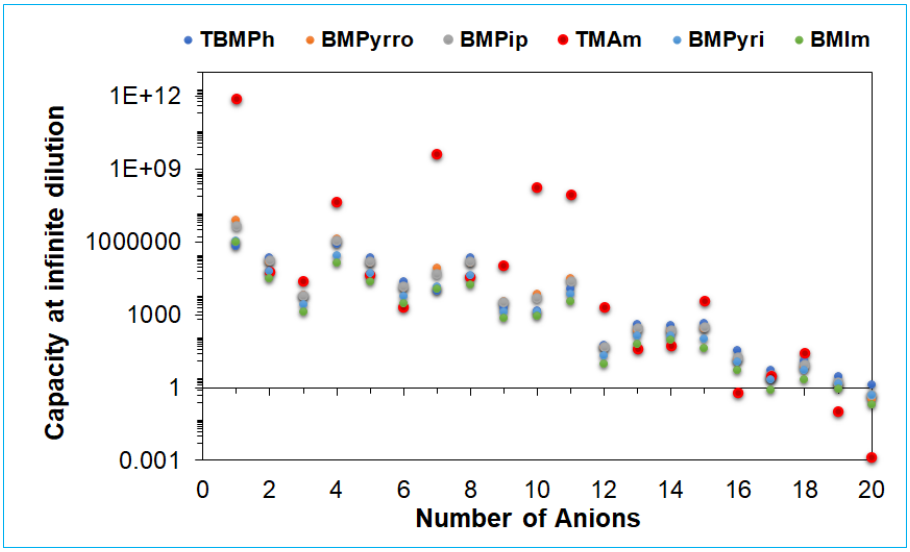


Figure 4.4: Capacity of selected ILs for extraction of Dcf from aqueous solution

Similar results were obtained for Ibf and LA for the capacity of ILs. It was found that [TMAm] with [SO_4^{2-}] possessed the highest capacity values for Ibf and LA. The results are presented in Fig. B7 and B8(APPENDIX B).

4.1.4 IL selectivity towards Dcf

Selectivity is an important parameter governing the extraction ability of ILs. Selectivity towards Dcf with ammonium, pyrrolidinium, piperidinium, phosphonium, pyridinium, and imidazolium cations along with 20 anions was estimated via COSMO-RS. Fig. 4.5 displays the selectivity of different combinations for Dcf at 25°C. The results reveal that cation containing ring structures such as [Im] and [Pyri] decreases selectivity. This was due to the presence of π-π bonds resulting from the delocalization of electrons. A similar observation was made in a recent study to extract the phenolic compound from aqueous solutions using ILs [204].

As shown in Fig. 4.5 the anions that give better selectivity for Dcf are as follows: [SO_4^{2-}]>[Cl^-] >[CH_3COO^-]>[Br^-]>[NO_2^-]. These results reveal that the anions that are good hydrogen bond acceptors are better extracting agents for Dcf. This can further be

elaborated as the H-bond between (S=O----H) is stronger, enhancing its extraction ability as a carrier [199]. The anions with non-coordinating nature showed lesser selectivity for Dcf. Hydrophobic anions such as BF_4^- and PF_6 possess a greater shielding effect near their charge centers than hydrophilic anions, thus lower selectivity value values and poor extractability of these anions for Dcf [207]. The results reveal that SO_4^{2-}, Cl^- possess higher extraction ability. The selectivity studies for Ibf and LA are present in Fig. B9 and B10 (APPENDIX B).

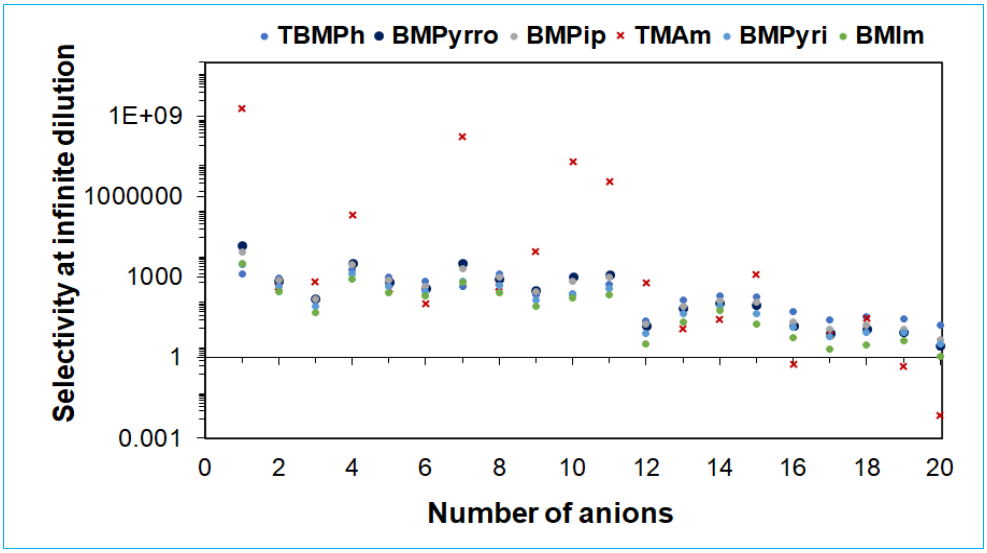


Figure 4.5: Selectivity of the ILs for the extraction of Dcf from aqueous solutions

4.1.5 Performance Index

Performance Index (P.I) is an estimate of the potency of IL for the extraction of BACs [204]. Since it's the product of capacity and selectivity, the values are pretty high. The higher the P.I value of an IL, the better the IL for extraction. It was observed that [TMAm] and [BMPyrro] cations with [SO_4^{2-}], [Cl^-] and [CH_3COO^-] anions gave higher values of P.I. This was because of significant hydrogen bonding between ammonium cation-BACs and potential acidic nature of anions. Similar results were reported for the extraction of phenolic compounds, docosahexaenoic acid, where [TMAm][SO_4] was found to be potential for the extraction of compounds under study [199][204]. Fig. 4.6

presents the values of P.I. Overall, [TMAm][SO_4] showed the highest value of PI because of hydrogen bond acceptor nature, and [TMAm][PF_6] showed the lowest value because of the steric shielding. An advantage of quaternary ammonium cation along with anions [SO_4^{2-}], [CH_3COO^-], [Cl^-] is that it will be less toxic and biodegradable than long-chain cations with hydrophobic anions [208]. Table 4.1 presents the overall COSMO-RS results.

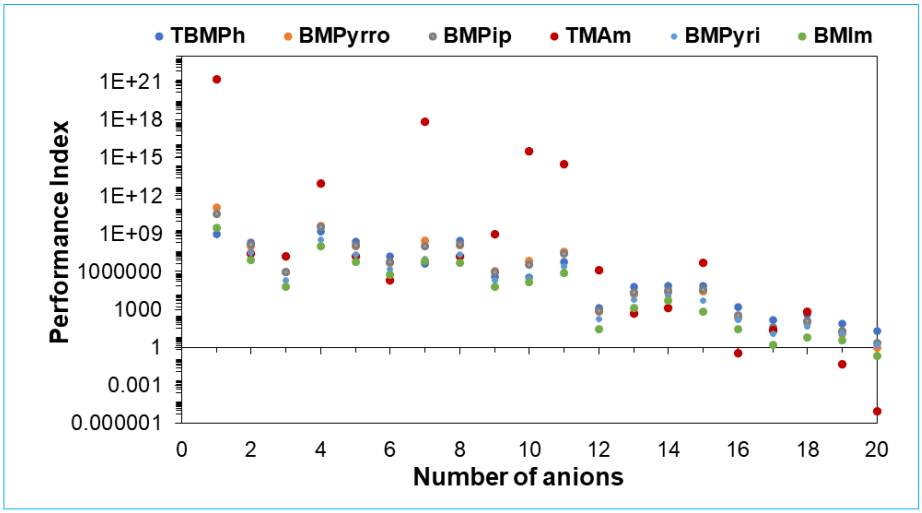


Figure 4.6: Performance Index of selected combinations evaluated using COSMO-RS Streams

Table 4.1: COSMO-RS results

IL	**AC^{id}**	**Capacity**	**Selectivity**	**P.I**
[TMAm][SO_4]	-26.22718108	7.88E+11	1.99E+09	1.56E+21
[TMAm][Cl]	17.668	7.88E+11	98.21928	7.25E+17
[BMPyrro][SO_4]	-14.7833	7896746	15883.74	1.25E+11
[BMPyrro][Cl]	-10.5828	78902.22	385.7806	2.67E+08
[TMAm][PF_6]	7.325327	0.001317	0.006825	8.99E-06

For Ibf and LA, the results are present in Fig. B11 and B12 (APPENDIX C). Since all the three model compounds were found to have a COOH group, the BACs understudy possessed a polar nature. Thus the BAC-IL association was mainly due to polar interactions [209]. COSMO-RS screening results showed the same trend. Quaternary ammonium cation and sulfate anion were most suitable for extracting Ibf and LA.

The power of extraction of ILs can also be explained based on σ-profiles of the anions. The σ-profiles are present in Fig. B13 (APPENDIX B). For SO_4^{2-} (2.5 e/nm^2), CH_3COO^- (2.25 e/nm^2), and Cl^- (2.1 e/nm^2), sharp peaks can be observed in H-bond acceptor0 regions, signifying the promising interaction with the OH^- group of Dcf. Also, it is worth mentioning that σ-profiles for anions SO_4^{2-}, CH_3COO^-, Cl^- lie in the polar region, indicating their comparable capability to form H-bonds [210]. PF_6^- and BF_4^- showed a small peak at 1.2 e/nm^2 near the non-polar area, indicating poor bonding capability by accepting hydrogen bonds. In contrast, the cations that do not possess a shielding effect hence the π-electron cloud, have better-extracting properties [206]. This could be conferred due to electron delocalization, resulting in steric hindrance in the aromatic ILs, which reduces extraction efficiency [202]. For example, imidazolium-based ILs showed lower extraction efficiency for the separation of carboxylic acid than phosphonium-based ILs [211].

4.1.6 Experimental validation of COSMO-RS results

Fig. 4.7 shows the relation between AC^{id} and extraction efficiencies evaluated using different ILs as a carrier in WVO-ILEM for Dcf, Ibf, and LA. The theoretical efficiencies were calculated using the regression equation obtained. A linear correlation was found between AC^{id} and WVO-ILEM extraction efficiency with a correlation coefficient of 0.959. The obtained relationship indicated that the values predicted by

COSMO-RS could be used to calculate the hypothetical extraction efficiency of WVO-ILEM Table 4.2 presents the COSMO-RS validation results using COSMO-RS Experimental efficiencies were determined using experiments. The average absolute deviation was found to be 3.16%. The obtained variation is well acceptable when compared to the existing method.

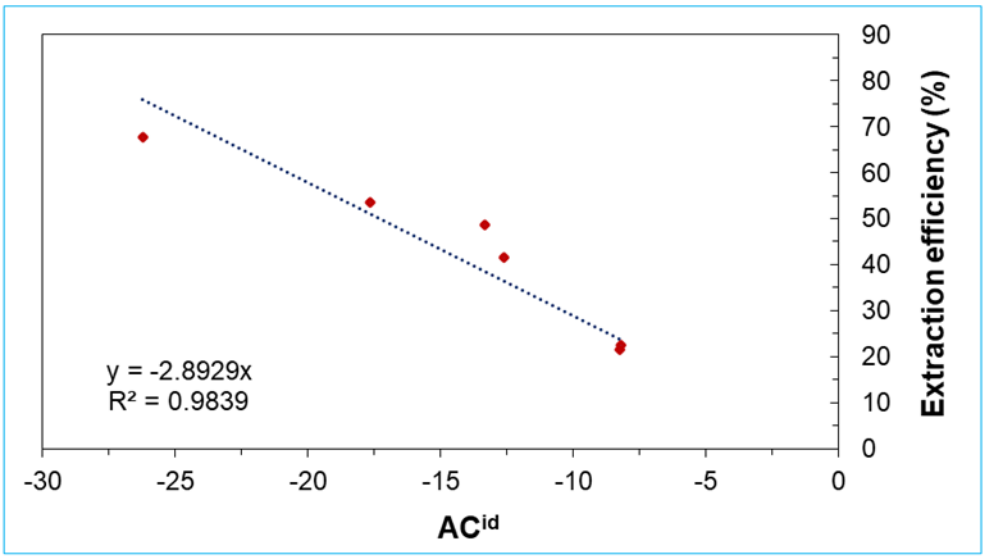


Figure 4.7: Regression curve between AC^{id} obtained using the COSMO-RS and the experimental extraction efficiency

Table 4.2: ILs selected for validation of COSMO-RS

BAC	IL	AC^{id}	Extraction efficiency (%)	Predicted Efficiency (%)
	[TMAm][SO_4]	-26.22718108	67.8	71.10791
Dcf	[BMIm][Cl]	-12.62738788	41.5	37.12452
	[TMAm][Cl]	-17.668	53.6	51.94392
Ibf	[BMIm][Ac]	-8.265	21.6	24.2991
	[TMAm][Ac]	-13.352	48.6	45.25488
LA	[BMPyrro][Cl]	-8.194	22.6	24.09036

4.2 SECTION II: WVO-ILEM DEVELOPMENT AND CHARACTERIZATION

This section deals with the development of WVO-ILEM using IL as carrier and WVO as diluent. Also, an attempt has been made to present a plausible extraction mechanism for WVO-ILEM. WVO-ILEM was characterized by investigating the viscosity, density, interfacial tension, emulsion globule diameter, breakage, and standalone stability. It also presents the stability analysis and evaluation of the extraction efficiency of WVO-ILEM for the removal of Dcf, Ibf, and LA. The stability of WVO-ILEM affects the extraction efficiency of WVO-ILEM. When water/oil WVO-ILEM disperses into the external BAC solution followed by continuous stirring, the emulsion must be highly stable for the extraction purpose. Surfactant is used to increase the stability of the emulsion. The extraction efficiency is proportional to the stability of the emulsion directly. Hence, the effect of various reaction parameters on the stability of WVO-ILEM and extraction efficiency was investigated using the one-factor approach. All the experiments were carried out in triplets, and average results were reported.

4.2.1 WVO-ILEM development and its Plausible mechanism

For the development of WVO-ILEM, Span 80 was selected as a surfactant, waste vegetable oil (WVO) as diluent, nitric acid as a stripping agent for Dcf, and sodium hydroxide as stripping agent for LA and Ibf. The mechanism for the extraction of Dcf is present in Fig. 4.8. Initially, WVO-ILEM was formulated using WVO (10 mL) as a diluent, Span 80 (1 wt.%) as a surfactant, HNO_3 (0.1 M) as internal stripping agent, [$TMAmSO_4$] (0.2 wt.%) as a carrier, at 0.25 phase ratio, 5200 rpm homogenization speed, 5 min homogenization time. Once WVO-ILEM is formulated using the procedure as described in section 3.4. The freshly prepared WVO-ILEM was added to the external solution at a treat ratio 2, stirring speed of 240 rpm, stirring time of 20 min, and settling time of 5 min. The concentration of Dcf was selected as 100 µg/L. To study the effect of various factors on stability and extraction efficiency, WVO-ILEM were freshly prepared before each experimental run.

The plausible mechanism of Dcf extraction by WVO-ILEM using [TMAm][SO_4] (tetramethylammonium sulfate) as a carrier is presented in Fig.4.7. The extraction takes place via H-bonding formation between IL-Dcf complexes. Dcf was stripped off, and the carrier was regenerated. The ion exchange mechanism is anticipated to occur at the membrane-internal phase interphase, where SO_4^{2-} is exchanged with the NO_3^{2-} group. This can be represented as:

$$2[TMAm^+SO_4^{2-}] + 2[HNO_3] \leftrightarrow 2[TMAm^+NO_3^{2-}] + [H_2S_2O_8] \quad (4.1)$$

The ion exchange generates another carrier, tetramethylammonium nitrate [TMAm][NO_3]. The system now consists of two carriers for the extraction of Dcf. This proceeds through the formation of the Dcf-IL complex resulting in polar interactions due to the H-bonding between Dcf and IL external interphase. The reaction at the feed membrane phase can be represented as eqn:

$$[TMAm^+SO_4^{2-}] + [Dcf] \leftrightarrow [TMAm^+SO_4^{2-}:Dcf] \text{ (Complex formation)} \quad (4.2)$$

$$[TMAm^+NO_3^{2-}] + [Dcf] \leftrightarrow [TMAm^+NO_3^{2-}:Dcf] \text{ (Complex formation)} \quad (4.3)$$

As shown in Fig. 4.8, the complexes diffuse through the membrane phase and enter the inner phase, where they react with HNO_3 resulting in the stripping reaction. As a result, Dcf gets stripped off. [TMAm][SO_4] releases into the external phase and subsequently regenerates. A similar mechanism was proposed to extract amoxicillin using ALIQUAT-336 and TOA as carriers [21]. Also, similar results were reported for tetracycline using tributylphosphate [TBP] as carrier [212] and for ethylparaben using TOA as carrier [213].

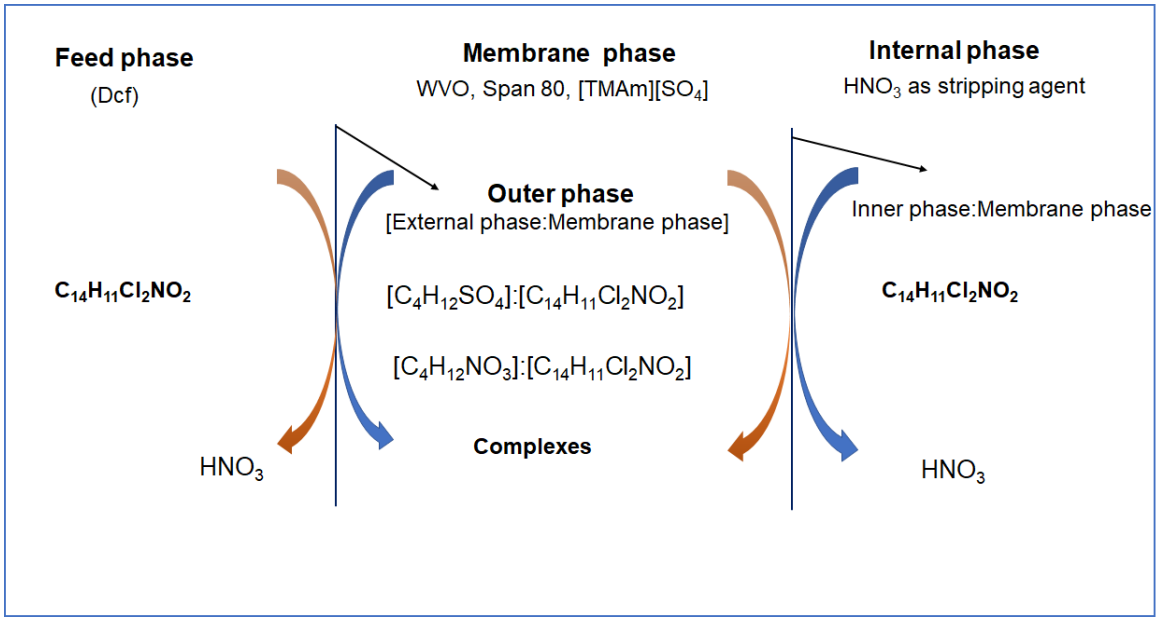


Figure 4.8:Schematic mechanism of diclofenac extraction

FTIR spectra before and after the extraction process for WVO-ILEM were investigated to confirm the bonding and existence of functional groups and identify functional group changes. The FTIR spectra of WVO-ILEM and WVO-ILEM after extraction of Dcf was compared. Fig. 4.9 presents the FTIR spectra of WVO-ILEM before and after extraction of Dcf.

The characteristic peaks in the spectra of WVO-ILEM at 3299 cm^{-1}, 2926cm^{-1}, and 1742 cm^{-1} reveal the N-H, OH stretch, and C=O stretch. The dominant peaks at 1464 $cm^{-1}$and 1374 cm^{-1} represent C-N which confirms the presence of quaternary ammonium salts [21][214]. In the spectra after treatment with external Dcf solution, the stretching of peaks at 2925 cm^{-1}, 2850 cm^{-1}, 1627 cm^{-1}, 1458 cm^{-1}, 1091 cm^{-1} were observed. Since the Dcf-IL complex gets stripped into the internal phase through the

membrane phase, there was Dcf in the membrane phase. The peaks at 2925 cm^{-1} and 2850 cm^{-1} indicated the increase of saturated C-H. The stretching at 1658 cm^{-1} represents an increase in C=O. An increased stretching of the peaks confirms the presence of Dcf. Peaks at 1464 and 1374 represent the increase in C-N. Because there were more C-H, C-N, and C=O in Dcf, the stretching of three peaks confirms the presence of Dcf. The characteristics peaks at 1228 cm^{-1} and 1153 cm^{-1} confirm the presence of nitrate and sulfate groups, signifying the presence of IL. Since the central atom of IL [TMAm][SO_4] is "N" and is positively charged. It forms a bond with the "O" in Dcf. The peak at 1094 cm^{-1} represents N-O. Small peak at 1098 cm^{-1} shows the presence of S=O due to the formation of peroxydisulfuric acid. The broad OH group in spectra of WVO-ILEM after extraction indicated that the nitrogen atom of Dcf was involved in the interaction with OH group of Dcf with the transfer of proton [215]. Similar results were reported for amoxicillin using Aliquat-336 and TOA as carrier [21]. Also, similar results were reported for methylparaben using TOA as carrier [152].

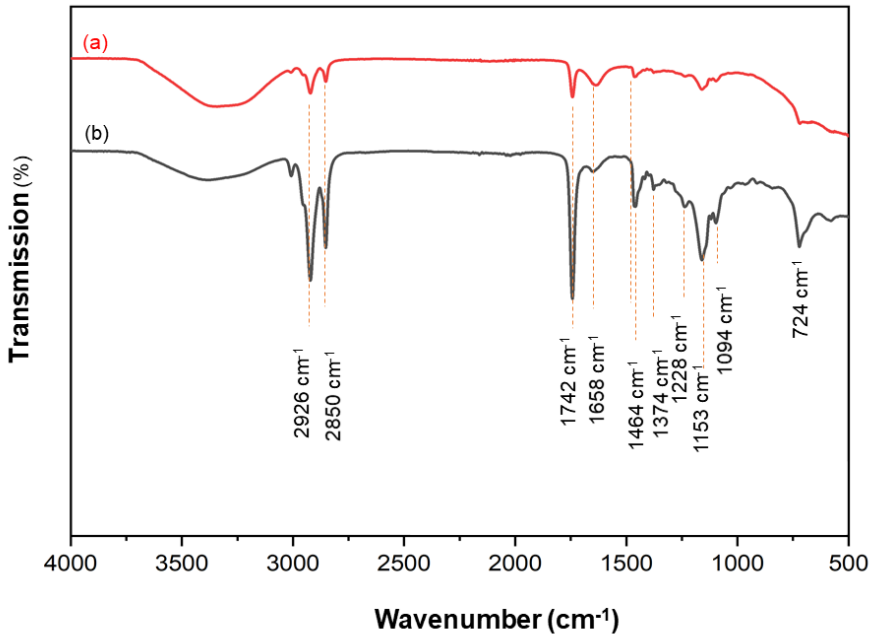


Figure 4.9: FTIR spectra for WVO-ILEM a) before extraction and b) after extraction

4.3 SECTION III: EFFECT OF VARIOUS PARAMETERS UPON THE STABILITY AND EXTRACTION EFFICIENCY OF WVO-ILEM AND OPTIMIZATION USING RSM

The effect of various reaction parameters that affect the stability and hence extraction efficiency is presented in this section. The effect of various parameters upon breakage, standalone stability, emulsion diameter, viscosity, interfacial tension, and extraction efficiency was investigated.

4.3.1 Effect of surfactant type

The selection of surfactant simplifies the choice of surfactant to develop WVO-ILEM. Selection of surfactant is essential as it directly influences the stability and hence extraction efficiency of WVO-ILEM. The addition of surfactant reduces the interfacial tension, resulting in the development of stable WVO-ILEM. To investigate this effect, water-insoluble surfactant Span-20 (HLB=8.6), Span 80 (HLB=4.3), and water-soluble surfactant Tween-80 (HLB=16.7) were selected at a constant concentration. WVO-ILEM with different surfactants was developed. Stability and the extraction efficiency for the extraction of Dcf, Ibf, and LA were investigated. Fig. 4.10 presents the emulsion breakage (%) and extraction efficiency for all different surfactants. It was observed that the extraction efficiency of WVO-ILEM increased as the HLB value decreased. The WVO-ILEM formed for high HLB surfactant was highly unstable with increased breakage and hence a larger emulsion diameter. It was found that Span-80 provided less breakage and relatively better extraction efficiency for BACs removal than Tween-80 and Span 20. This could be explained as the HLB value increases, the inversion of emulsion occurs, and emulsion diameter starts increasing, resulting in an unstable emulsion [155]. Also, Tween-80 is water-soluble and provides less stable emulsion than the emulsion formed by water-insoluble Span-80 [216]. In a study on the extraction of methylparaben, similar observations were made. At HLB>5, it was found that ELM was highly unstable, resulting in larger droplet diameter [155]. Since, the breakage of

emulsion for Tween 80 was highest, and Span 80 was lowest. Span-80 was chosen as an emulsifier in developing WVO-ILEM for the extraction of BACs under study.

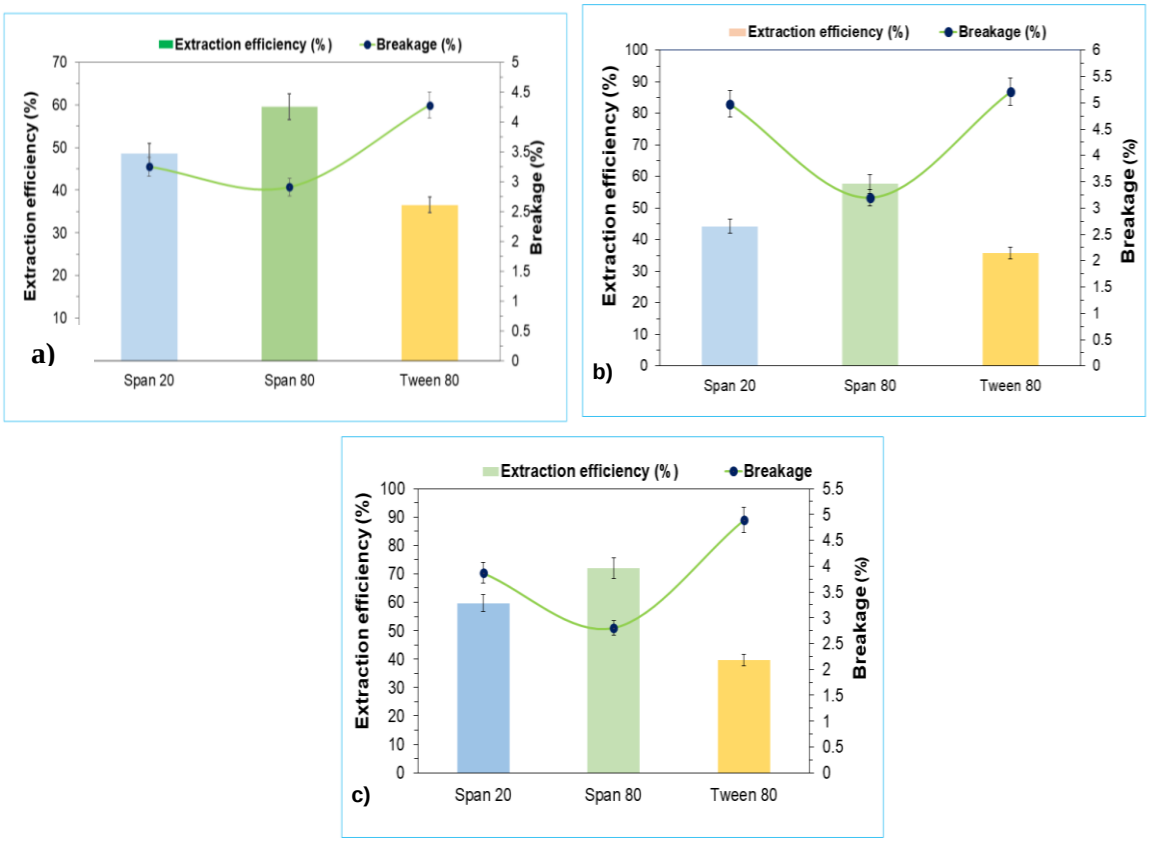


Figure 4.10: Effect of surfactant type upon breakage and extraction efficiency for (a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.2 Effect of surfactant concentration

Surfactant is an essential constituent of WVO-ILEM; hence the effect of Span 80 concentration on the stability and extraction efficiency of WVO-ILEM for the extraction of BACs was studied. Fig. 4.11 shows the effect of surfactant concentration upon the breakage and extraction efficiency of WVO-ILEM for Dcf, Ibf, and LA. The concentration of surfactant was varied from 0.5 wt.% to 2.5 wt.%. Membrane breakage, emulsion diameter, stand-alone stability, viscosity, density, interfacial tension, and extraction efficiency were measured. At low concentration, it was observed that the

efficiency was less as the interfacial tension was relatively high for Dcf extraction. At the same time, the diameter of the emulsion was significant, giving rise to a highly unstable emulsion resulting in more breakage (4.46%) and less stability. This result is because the surfactant is insufficient at a lower concentration, the interfacial tension is high, and the emulsion is highly unstable. As the concentration of Span 80 increased from 0.5-1 wt.%, breakage reduced to 2.19%, and hence the stability of WVO-ILEM increased. This can further be elaborated based upon the molecular interactions as predicted using COSMO-RS. At 1 wt.% concentration the surfactant is enough, the stripping and extraction reactions proceeds through the formation of enough complexes. At this emulsion composition, 59.05 % efficiency for Dcf was achieved. It is to be mentioned that at higher concentrations of surfactant, WVO-ILEM breakage increases, and hence the stability and efficiency were found to decrease. This is because an excess surfactant concentration results in the formation of aggregates, causing an increase in viscosity (Table 4.3), and breakage and hence affects the transport of Dcf. In a similar study on the extraction of succinic acid, it was reported that although the surfactant is adsorbed at the organic phase and internal stripping agent interphase, reducing interfacial tension. The emulsion gets destabilized cause of rapid coalescence between droplets [156]. This can further be explained as IFT decreased with the increase in surfactant concentration, and breakage increased as the low value of IFT impedes coalescence, resulting in a larger emulsion diameter and less stability. Similar results were reported in a study on the enhanced separation of water in oil emulsions [217].

Additionally, a high surfactant concentration above the optimum point tends to increase the viscosity of emulsion, which is not favored by the extraction kinetics. This affects the dispersion behavior of emulsion, thus causing a decline in the interfacial area, resulting in lower extraction efficiency. These results agree with the previous work on the extraction of succinic acid using palm oil-based ELM [218]. Maximum removal of Dcf with minimum breakage of the emulsion was observed at 1 wt.% surfactant concentration, and hence it was selected for the removal of Dcf. Likewise, a similar trend was observed for the extraction efficiency of WVO-ILEM for Ibf and LA (Fig. b and c). At 1 wt.%, the stability of WVO-ILEM was maximum with minimum breakage and hence maximum extraction efficiency for Ibf and LA. Therefore, a

concentration of 1 wt.% of Span 80 is selected to prepare WVO-ILEM for selected BACs

Table 4.3: Characterization results and efficiency of WVO-ILEM at different surfactant concentrations for Dcf

Surfactant concentration (wt.%)	**Breakage (%)**	**Diameter (µm)**	**Stand-alone stability (min)**	**Viscosity (cP)**	**Density (g/cm^3)**	**Interfacial tension (mN/m)**	**Extraction Efficiency (%)**
0.5	4.46	3.65	27	135.9	0.9363	3.31	32.65
1	2.91	2.24	65	145.6	0.9372	2.56	59.05
1.5	3.18	2.53	54	147.5	0.9381	2.49	41.59
2	3.91	2.98	32	150.3	0.9383	2.45	36.23
2.5	4.11	3.82	18	151.5	0.9386	2.39	25.6

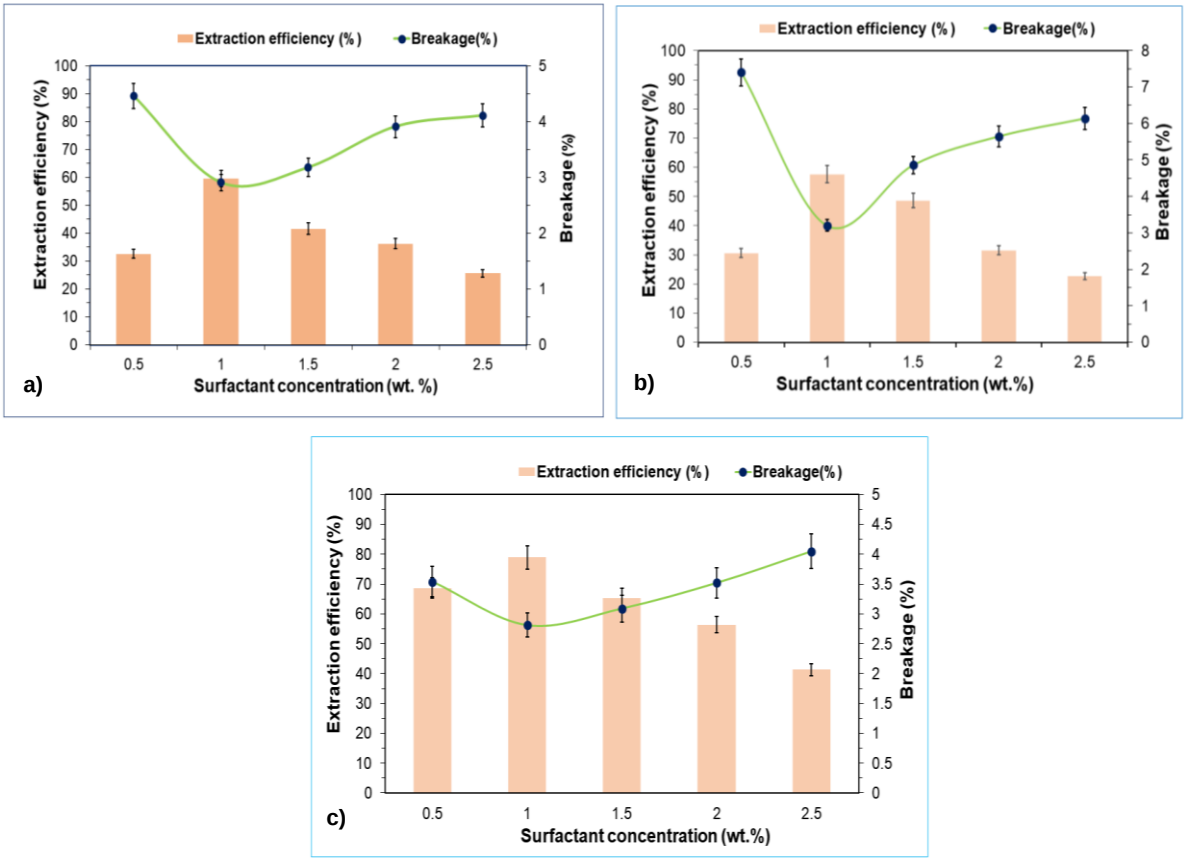


Figure 4.11: Effect of surfactant concentration upon breakage and extraction efficiency a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.3 Effect of internal stripping agent concentration

The stripping of solute is an essential step in emulsion stability that helps to improve WVO-ILEM extraction efficiency. As a result, an integral component of WVO-ILEM is the internal stripping agent. For Dcf, HNO_3 was found to be a better stripping agent, whereas, for Ibf and LA, NaOH was found to be a suitable stripping agent. The influence of HNO_3 concentration on the stability and performance of WVO-ILEM was investigated and is present in Fig. 4.12. At low concentrations of stripping agents,

WVO-ILEM was unstable with breakage of 4.15% for Dcf extraction. The stability and extraction efficiency improved for the removal of Dcf as the concentration of HNO_3 was increased to 0.1 M. At this concentration, minimum breakage and emulsion diameter were observed. The predominant driving force between the exterior and internal phases was [H^+] ions. Similar observations were reported on the extraction of ciprofloxacin from an aqueous solution, where HCl was chosen as a stripping agent. It was reported that 0.1 M HCl gives the lowest breakage and high extraction efficiency. [85]. Also, the stripping agent was inadequate; it could not disperse nicely in the oil phase. HNO_3-Dcf complexes formed are not enough for the stripping of the Dcf. As the concentration of HNO_3 increases, the emulsion thickens, and the viscosity rises. This could be explained by the loss of surfactant characteristics of Span 80 as the stripping agent concentration is raised. As a result, the breakage increases; hence efficiency declines. These results correlate with the removal of acetaminophen from the aqueous stream where 0.1 M NaOH was found to form highly stable and effective ELM [107]. The emulsion diameter and breakup were also measured to verify this. The diameter was increased to 3.62 μm, with breakage of 4.56 %. Finally, 0.1 M HNO_3 was chosen since it had negligible breakage and was the most stable with maximum efficiency. Likewise, for Ibf and LA, an optimum amount of stripping agent was required for the formulation of stable WVO-ILEM. The reason underlying is the molecular interactions between stripping agent and model BACs. For Ibf, less concentration of NaOH (0.02M) was required to formulate a stable emulsion. This was because a very high concentration of NaOH results in an increased viscosity of WVO-ILEM that was unfavorable for Ibf extraction. Also, the stripping agent is excess, as a result the external agent is not sufficient for the reaction to proceed. In contrast, for LA, the concentration of NaOH was 0.15 M for the formulation of a stable WVO-ILEM.

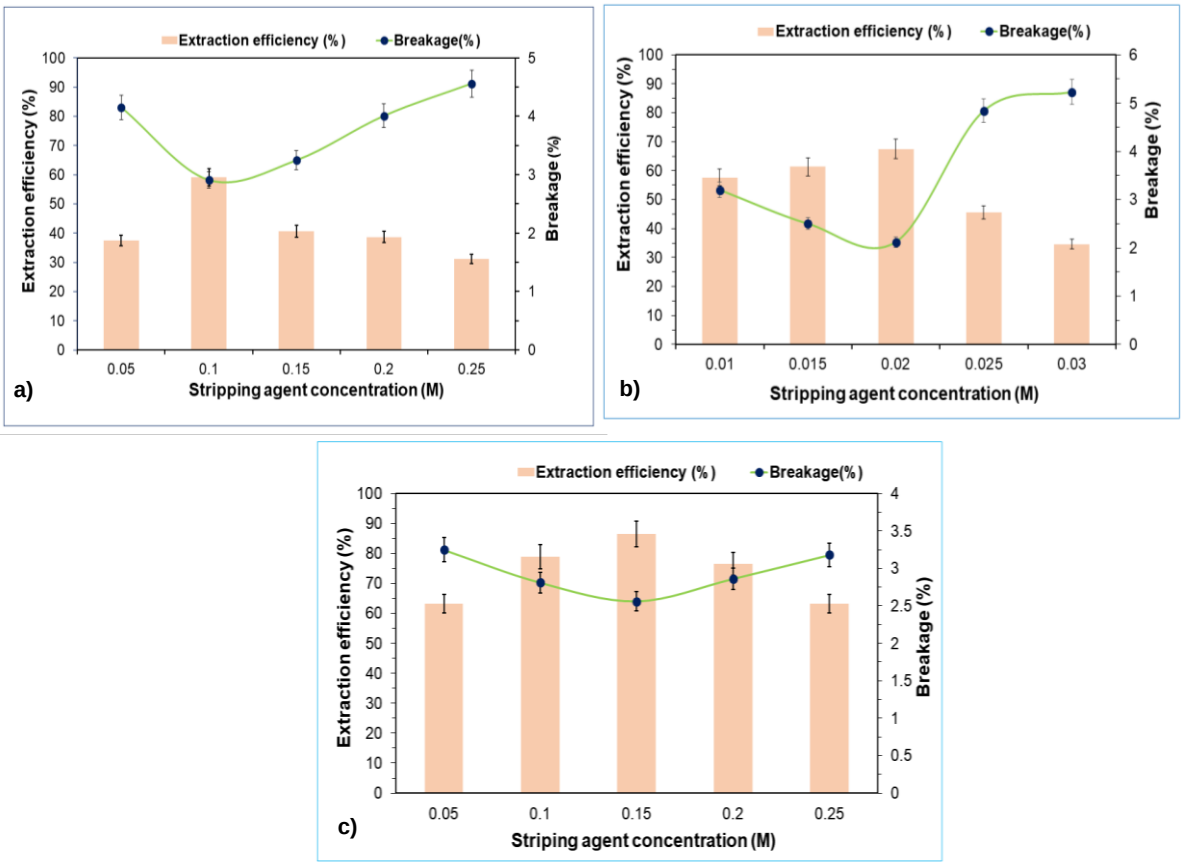


Figure 4.12: Effect of stripping agent concentration upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.4 Effect of IL concentration

The only constraint in ELM is the instability of WVO-ILEM. IL was used as a carrier to improve stability, resulting in enhanced stability and extraction efficiency. IL works by generating an IL-BAC complex and enhances separation [219], which is then broken down by reacting with the internal stripping agent, stripping off BACs, and the IL enhances mass transfer. [TMAm][SO_4] was used as a carrier of 0-0.5 wt.%. Fig. 4.13 shows the effect of varying IL concentration as a carrier upon the emulsion breakage and extraction efficiency of WVO-ILEM for Dcf, Ibf, and LA. It was observed that without the use of IL (0 wt.% IL), the emulsion was highly unstable, with breakage of

5.8% for Dcf. The stability began to improve after the addition of [TMAm][SO_4]. Furthermore, at 0.3 wt.% of [TMAm][SO_4], the WVO-ILEM was steady for 98 min with minimum breakage of 0.89%. Increasing the amount of IL improves mass transfer through the formation of complexes, enhancing stability and efficiency. Similar observations were reported for the extraction of acetaminophen using TOA as a carrier. The authors reported that 4 wt.% of TOA was adequate for developing highly stable ELm with maximum efficiency [41]. Further increase in [TMAm][SO_4] concentration causes an increase in leakage of internal stripping agent as a result of breakage of WVO-ILEM (2.72 % breakage at 0.6 wt.% IL). Also, the viscosity and interfacial tension increased with IL, further responsible for decreased efficiency (Table 4.4). As a result, large emulsion globule size and maximum breakage (2.86 μm at 0.6 wt.% of IL). Similar results were reported for recovery of Ibf using TOA as the carrier. The results suggest that 1 wt.% of TOA resulted in the development of highly stable ELM resulting in effective removal of Ibf [151]. Hence 0.3 wt.% of [TMAm][SO_4] was chosen as the best value for developing WVO-ILEM with maximum stability. A similar observation was made for the extraction of Ibf and LA. IL resulted in forming a sable WVO-ILEM to extract Ibf and LA.

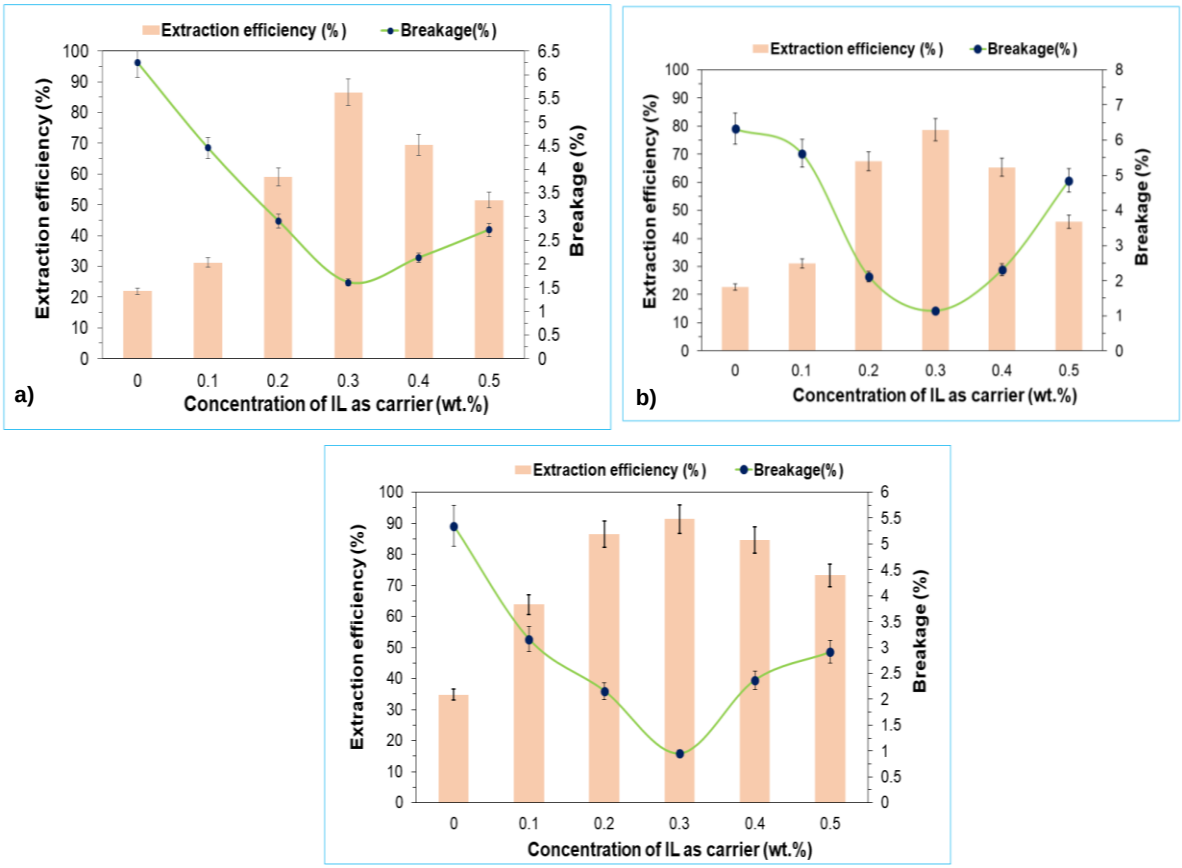


Figure 4.13: Effect of carrier concentration upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

Table 4.4: Characterization results and efficiency of WVO-ILEM at different carrier concentrations for Dcf

Carrier concentration (wt.%)	**Diameter (µm)**	**Stand-alone stability (min)**	**Viscosity (cP)**	**Density (g/cm^3)**	**Interfacial tension (mN/m)**	**Efficiency (%)**
0	4.9	15	116.5	0.9310	4.55	21.9
0.1	2.24	24	136.5	0.9369	3.98	31.2
0.2	1.58	65	145.6	0.9372	2.56	59.05
0.3	0.244	136	153.7	0.9387	1.25	86.5
0.4	2.18	69	159.5	0.9391	1.58	69.4
0.5	2.86	46	163.5	0.9406	2.01	51.5

4.3.5 Effect of phase ratio

Phase ratio is the amount of stripping agent required to formulate stable WVO-ILEM. The ideal emulsion composition plays an essential role in the formulation of stable WVO-ILEM to extract Dcf, Ibf, and LA. Any change in phase ratio significantly impacts its stability and hence extraction efficiency. The effect of variation in phase ratio on the stability and extraction efficiency of WVO-ILEM was studied. The phase ratio was varied from 0.15 to 0.35. The profiles of breakage and extraction efficiency are shown in Fig. 4.14 a for Dcf. At 0.15 phase ratio, the efficiency was poor. The changing ratio from 0.15 to 0.25 increased the efficiency to 86.5%. The stability of WVO-ILEM improved with the increase in the volume of HNO_3. The emulsion was highly stable, with minimum breakage of 1.61%. This could be explained as the volume of HNO_3 increased the amount of internal stripping agent is sufficient for the stripping of Dcf; as a result, high efficiency, standalone stability, smaller emulsion diameter, and minimum breakage. Similar results were reported for the extraction of ciprofloxacin, 0.25 phase ratio resulted in the development of highly effective and stable ELM [85].

When the phase ratio exceeds 0.25, WVO-ILEM becomes unstable, so efficiency decreases significantly. The droplet diameters increased with the excess stripping agent (2.8 μm at 0.4 phase ratio), and the droplets agglomerated and broke, increasing breakage (2.96% at 0.4 phase ratio). Furthermore, too much internal stripping agent causes an increase in viscosity which reduces the organic phase's holding ability, resulting in a less stable emulsion (Table C2-APPENDIX C). Similar observations were made for the extraction of amoxicillin, where NaCl was used as an internal stripping agent [116]. Similar observations were found for the extraction of Ibf and LA. A phase ratio of 0.25 was chosen for the formulation of efficient WVO-ILEM.

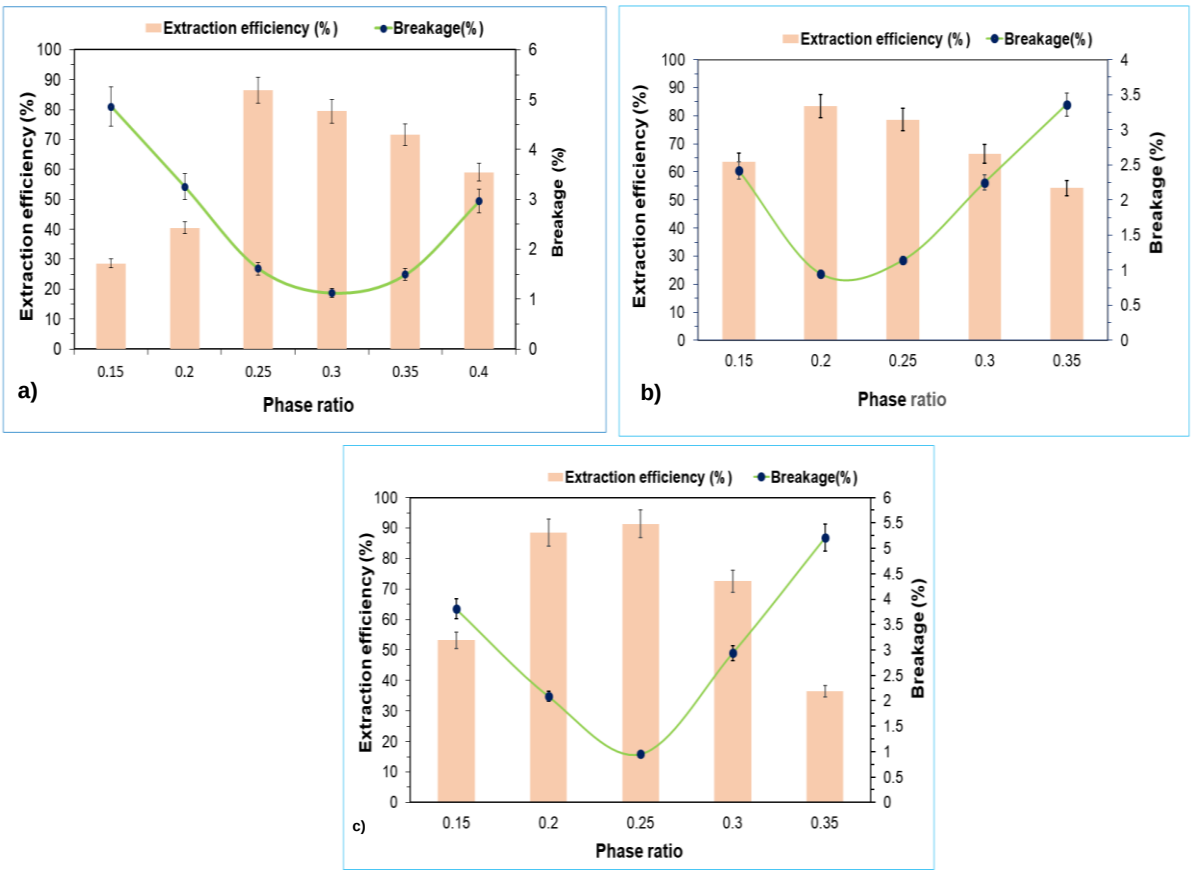


Figure 4.14: Effect of phase ratio upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.6 Effect of homogenizer speed

Homogenizer speed is another essential factor that significantly impacts the static stability and hence the extraction efficiency of WVO-ILEM. It is crucial for the stability of WVO-ILEM and BAC transfer across the membrane. Homogenization is a method of poly-dispersion of tiny droplets of stripping agent (HNO_3) in the organic phase (WVO as a diluent, Span 80 as surfactant). The homogenizer speed strongly influences the size and distribution of the tiny droplets of the internal stripping reagent. It is evident from Fig. 4.15 that the extraction efficiency rises with the rise in homogenizer speed from 3200 to 5200 rpm. This is because the shear force imparted by the homogenizer

on the emulsion globule rises, aiding the production of tiny droplets. As a result, it takes longer for WVO-ILEM to break, resulting in maximum stability time, minimum breakage, and smaller emulsion globule size. These results are in good agreement with similar work on the stability and extraction of ciprofloxacin. A high homogenizer speed of 12700 rpm was adequate for forming stable ELM [85].

At 5200 rpm, ILEM was stable for 144 min, with a breakage of 1.61% and 0.342 μm globule size. According to a study, faster homogenization is desirable to achieve a smaller droplets size; hence a more significant number of droplets will be generated per unit volume, raising the mass transfer area [220]. However, it was observed that an increase in homogenizer speed above 5200 rpm results in decreased efficiency. This was because the large shear force causes rapid coalescence resulting in a larger emulsion globule diameter and hence fast membrane breakage (at 7200 rpm, 1.5 μm diameter, and 2.12 % breakage). Also, at 7200 rpm, the viscosity of WVO-ILEM was relatively high (172.5 cP) due to larger emulsion droplets resulting in reduced membrane stability (89 min) and efficiency. Similar variations in results were observed for the extraction of phenol. The authors reported that an optimum homogenizer speed of 8000 rpm was required to develop stable ELM. At this speed, ELM was stable with a small emulsion diameter [155]. Almost the same variations were obtained for Ibf and LA; hence 5200 rpm was selected for the formulation of WVO-ILEM.

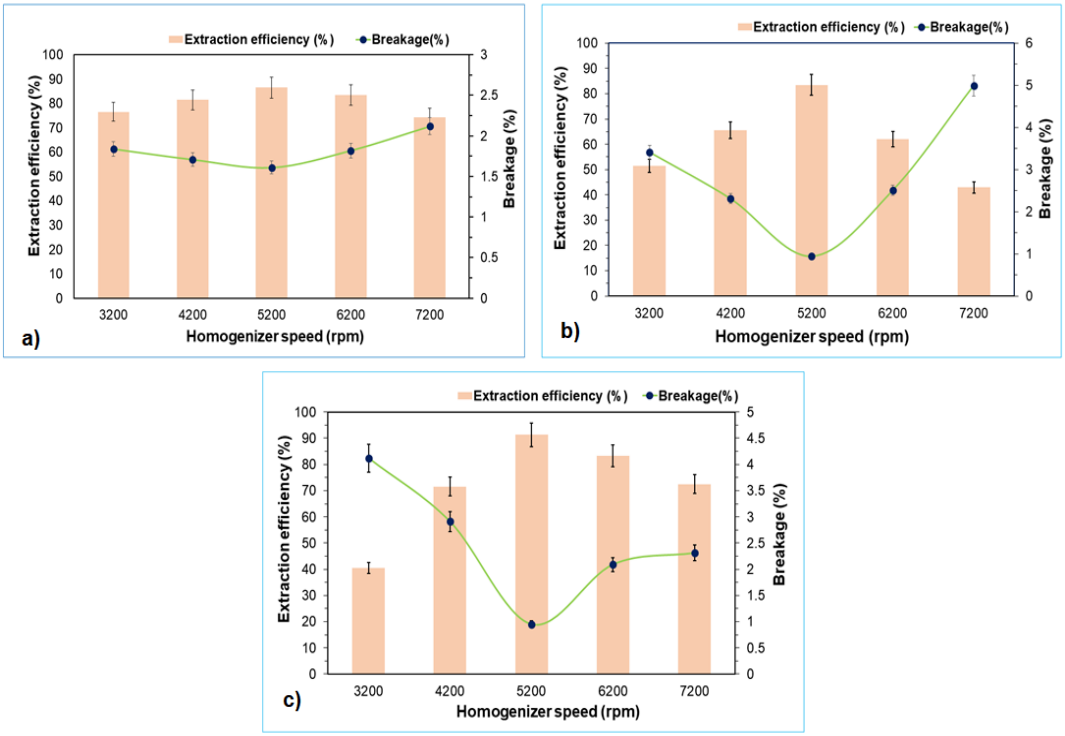


Figure 4.15: Effect of homogenization speed upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.7 Effect of homogenization time

Homogenization time is another crucial factor governing the stability, hence WVO-ILEM stability and efficacy. For the internal phase to encapsulate in the WVO phase, the time required to generate a homogeneous and stable emulsion is essential. At various homogenization time, the stability and extraction efficiency of WVO-ILEM was investigated. Variations in emulsion diameter and breakage were also observed at various times. The time it took to homogenize the samples ranged from 1 to 13 min. The emulsion remained stable for 88 minutes for a shorter homogenization time (1 min). It was investigated that at 5 minutes of homogenization, a highly stable WVO-ILEM with an extraction efficiency of 86.5% (Fig. 4.16) was observed. The emulsion starts to break after 144 minutes as the homogenization time increases to 5 minutes. With membrane breakage of 1.61 %, the emulsion formed was smaller in diameter (0.342 µm). The surfactant had enough time to completely adsorb on the oil-water

interphase, lowering the interfacial tension and generating a stable emulsion, promoting smaller droplets. Homogenization time of 3-5 min was found to be adequate in a similar study for the extraction of phenol. The emulsion was found to be highly stable for 2h [155]. Breakage increases from 1.61 to 2.72 % as the homogenization time increases from 5 to 13 min. As a result of the strong internal shearing, globules formed quickly and coalesced, resulting in a greater emulsion diameter and membrane breakage. Similar observations were reported in a study on ciprofloxacin extraction [85]. Therefore, 5 min of homogenization time was selected throughout the study. Fig. 4.17 shows the DLS results and the microscopic images of the emulsion diameter of the WVO-ILEM prepared using the above-optimized conditions for Dcf, Ibf, and LA.

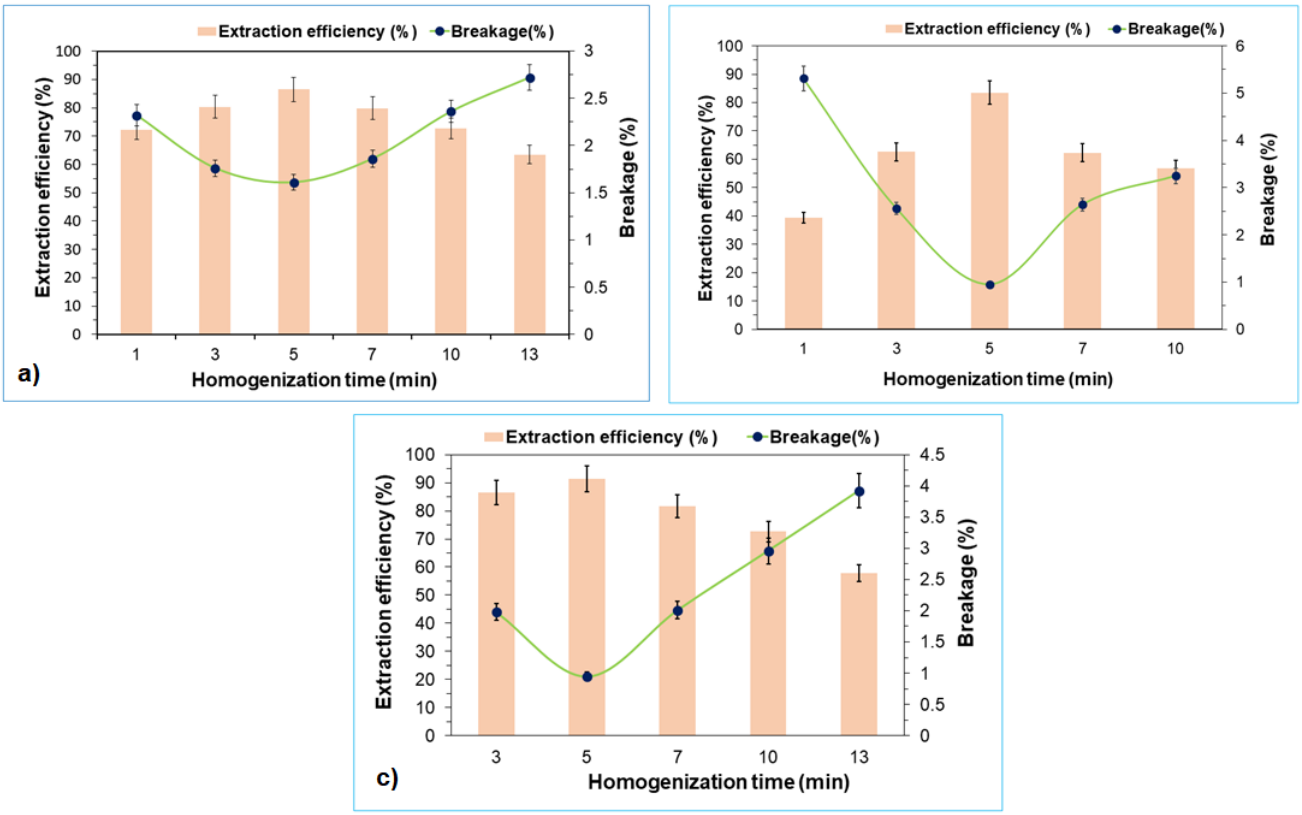
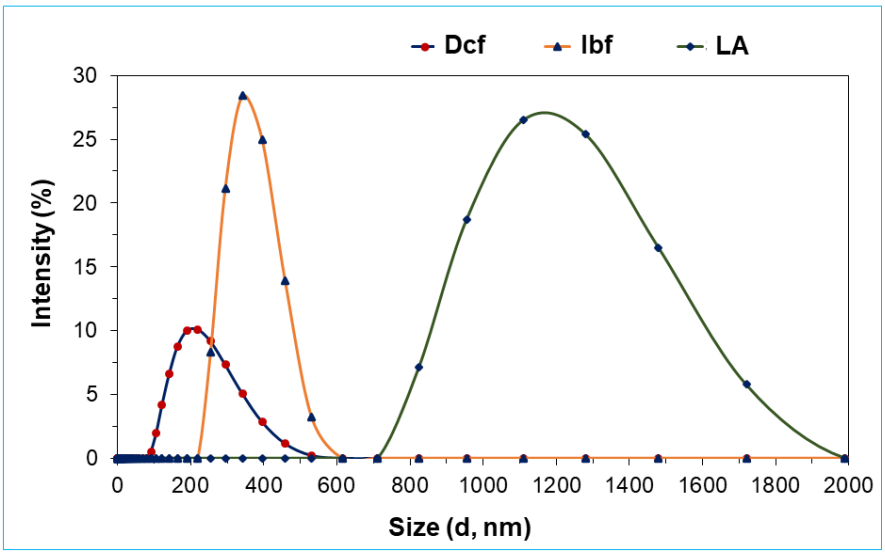


Figure 4.16: Effect of homogenization time upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL



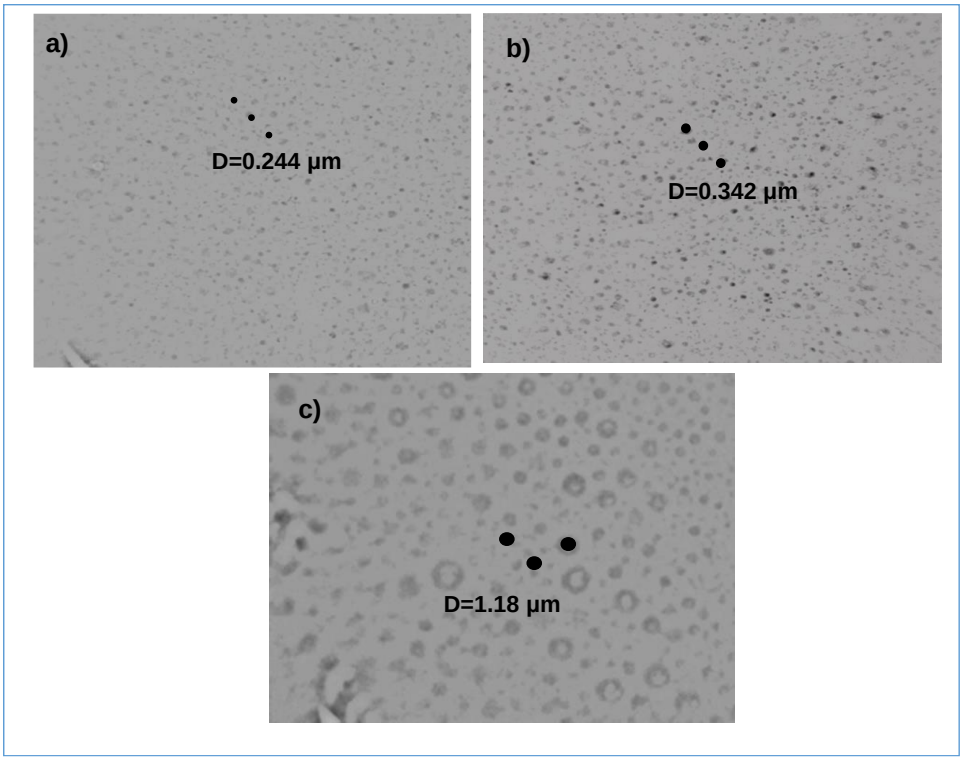


Figure 4.17: i) Size of emulsion globule before exposure to external solution and ii) microscopic images a) Dcf HNO_3=0.1 M (b) Ibf, NaOH=0.02 M M(c) LA=5000 µg/mL, NaOH=0.15 M) ii.) microscopic images for Surfactant concentration 1 wt.%, IL [$TMAmSO_4$] 0.3 wt.% as carrier, HNO_3=0.1 M, phase ratio=0.25

4.3.8 Effect of treat ratio

After synthesizing stable WVO-ILEM, an essential parameter in determining the efficacy is the treat ratio. Treat ratio estimates how much external solution can be treated to obtain maximum efficiency. An optimum treat ratio is required for the stripping and extraction of Dcf. The treat ratio was varied from 1:1 to 5:1 to investigate the effect of varying treat ratios upon the efficacy of WVO-ILEM. The freshly prepared ILEM was poured into the vessel containing Dcf. Fig. 4.18 a shows the effect of different treat ratio upon the breakage and extraction efficiency for the removal of Dcf. At 1 treat ratio, the emulsion was dispersed into Dcf solution. The amount of Dcf treated was low, and the viscosity of the combination was relatively high; the emulsion could not disperse properly. The aggregates were detected on the vessel wall. When the treat ratio was raised to 3:1, the WVO-ILEM diffused effectively, and the extraction efficiency rose from 52.3 to 91.5 %. This may be because, with the increase in treat ratio, WVO-ILEM diffuses uniformly, resulting in increased efficiency [147]. Similar observations were made for the extraction of acetaminophen. The authors reported that at treat ratio 3, a stable emulsion was formed cause of increased mass transfer due to high interfacial area [107]. On the other hand, any further rise in the treat ratio of 4 or 5 reduces the efficiency. As a result, the stripping agent becomes inadequate, leading to reduced emulsion globule capacity, increased emulsion diameter, and breakage. This results from swelling of emulsion and hence reduced efficiency. Amoxicillin extraction from an aqueous solution shows similar results. It was observed that beyond treat ratio 5, the mass transfer area declines as a result ELM effectiveness reduces [116]. At treat ratio 3, maximum extraction efficiency was obtained for Ibf and LA. Hence treat ratio 3 was selected for carrying out further experiments.

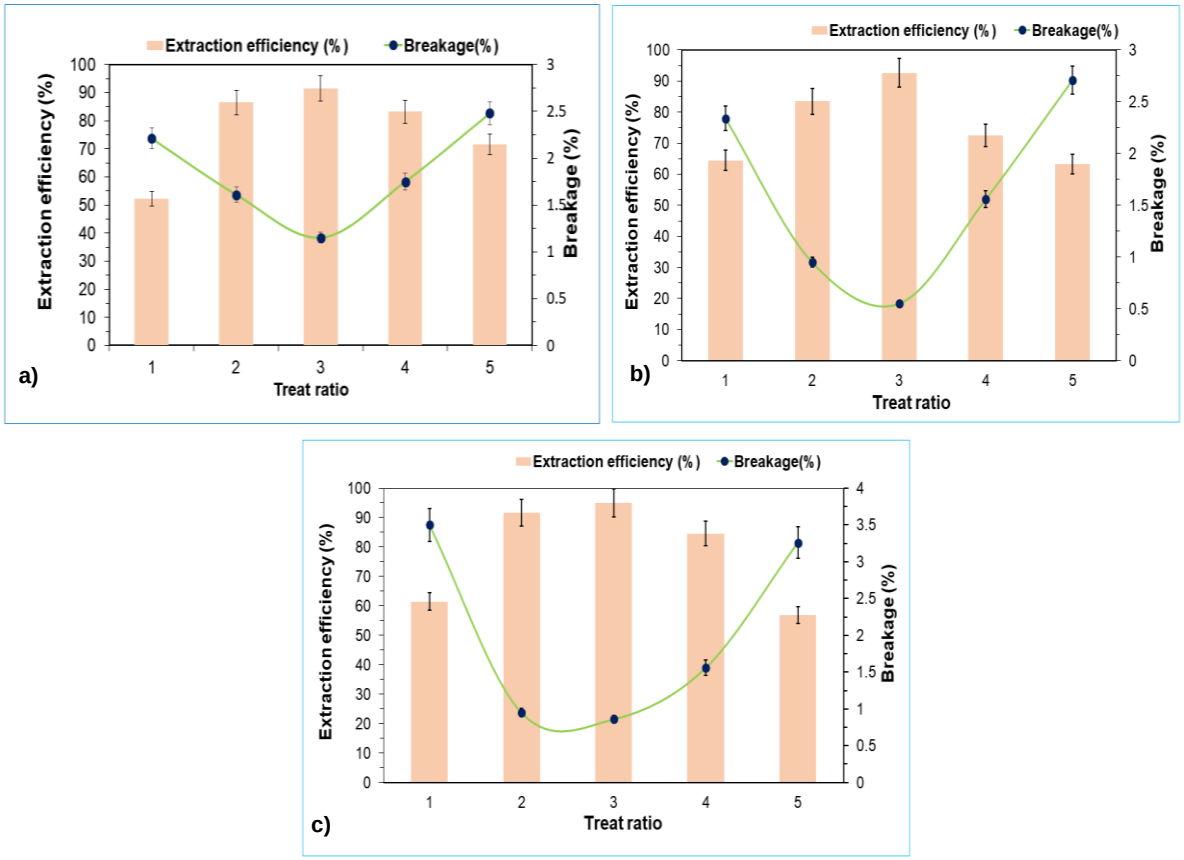


Figure 4.18: Effect of treat ratio upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.9 Effect of stirring speed

Stirring speed is critical for evaluating breakage and WVO-ILEM performance since it is responsible for emulsion dispersion to the external aqueous phase. It also plays a key function in membrane rupturing and governs extraction behavior. Emulsion globule formation is affected by stirring speed for the extraction of Dcf. The impact of changing the stirring speed was investigated (Fig. 4.19). With a 40-rpm interval, the stirring speed was adjusted from 160 to 320 rpm. The extraction efficiency was 71.6 % with 2.45 % WVO-ILEM breakage at a stirring speed of 160 rpm. Because of the low shear energy, the dispersion of emulsion droplets is not uniform. The globules coalesce, as a result,

resulting in a greater diameter and less mass transfer. As the speed increased to 240 rpm, higher shear energy to scatter the globules was provided, and hence, greater extraction was achieved. At this speed, the maximum extraction efficiency of 91.5 % was achieved. Increasing the interfacial area between the feed solution and the WVO-ILEM solution using a high agitation speed creates fine droplets with a higher surface area. Membrane stability improves as a result. However, the extraction efficiency drops as the stirring speed exceeds 240 rpm. An unstable primary emulsion is created by increasing agitation speed, which promotes the internal dispersed phase to leak into the external aqueous phase. The emulsion globule was smaller, but the coalescence happened faster due to the greater energy, resulting in bigger globules and membrane rupture. Similar results were reported for the extraction of ibuprofen [187]. Stirring speed of 240 rpm for selected for further experiments.

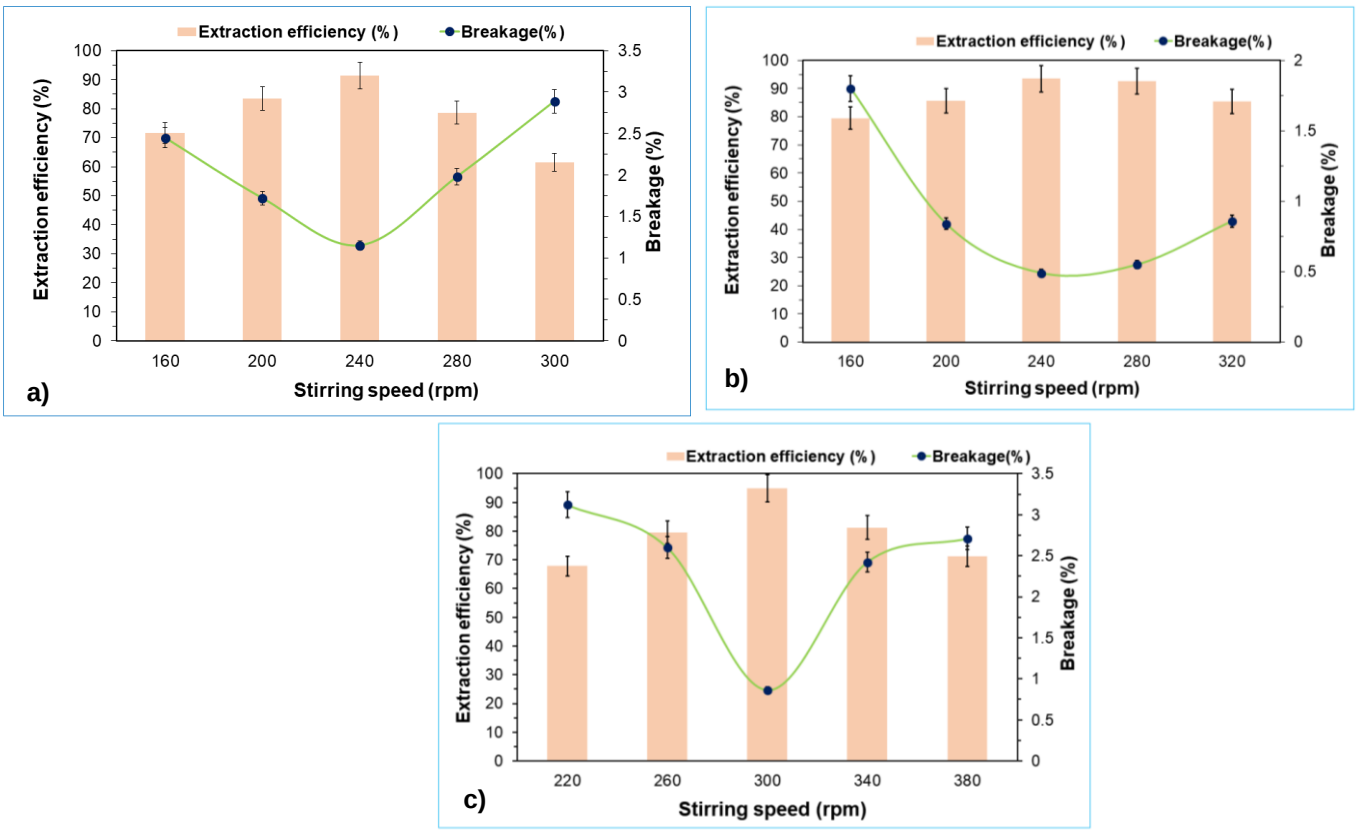


Figure 4.19: Effect of stirring speed upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.10 Effect of stirring time

The time duration for which WVO-ILEM and external Dcf solution are in contact with each other while the combination is stirring is referred to as stirring time. The permeation rate and, as a result, the extraction performance of WVO-ILEM is governed by this time. While all other parameters were kept constant, the effect of stirring duration on WVO-ILEM extraction efficiency was investigated. The impact of stirring time on Dcf elimination is present in Fig. 4.20. For Dcf under optimum ILEM conditions, 76.5 % of WVO-ILEM extraction efficiency occurs within 15 min. It was observed that extraction efficiency increased and reached 95.6 % at 25 min with minimum breakage. This may be because with an increase in stirring time the size of droplets and leakage decreases resulting in better dispersion and hence maximum stability and efficiency. Also, at the same time more mass transfer area is available between the external phase and membrane phase. However, a longer contact time 30 or 35 min caused the extraction efficiency to decrease. For higher extraction time the leakage of internal stripping agent starts from membrane phase to external phase. The Dcf molecules leak from the internal stripping phase into the external aqueous phase [19]. A similar observation was made for Ibf and LA. For Ibf extraction, 7 min of stirring time was enough for maximum extraction efficiency. For LA, maximum extraction efficiency was observed at 20 min of extraction time.

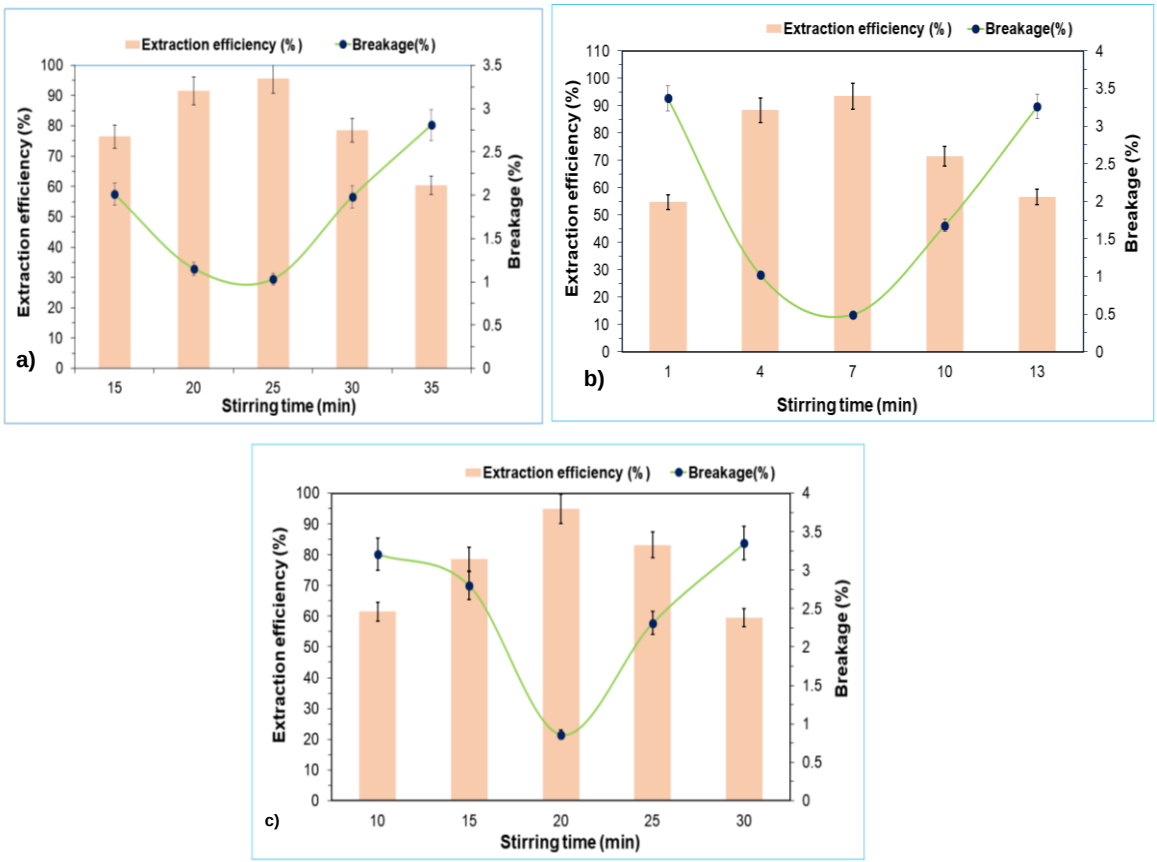


Figure 4.20: Effect of stirring time upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.11 Effect of settling time

The settling time was a key parameter for the extraction of Dcf after the extraction had taken place. The contents of the WVO-ILEM + external phase was poured into the separating funnel. The contents were allowed to separate by gravity. The aqueous phase was collected from the bottom of the funnel every 2 minutes, filtered, and evaluated the extraction efficiency. Settling time was varied from 1 to 10. Fig. 4.21 presents the effect of settling time on the breakage and extraction efficiency. It was discovered that initially, the aqueous phase was hazy and separation was poor, and as a result, the removal efficiency was less (30.5%) for Dcf. However, by the time it had reached 5

minutes, 95.6 % efficiency was accomplished. This was the outcome of appropriate organic and aqueous phase settling with minor WVO-ILEM breakage. Furthermore, as time increased, efficiency was reduced (52.5%) due to Dcf leakage from the internal phase to the aqueous phase (breakage of 2.21%). The leakage causes an increase in Dcf concentration in the aqueous phase. At the optimized conditions obtained, the diameter of WVO-ILEM dispersed in an external solution was studied using DLS is present in Fig. C5 (APPENDIX D) presents the dia of dispersed WVO-ILEM for Dcf, Ibf and LA.

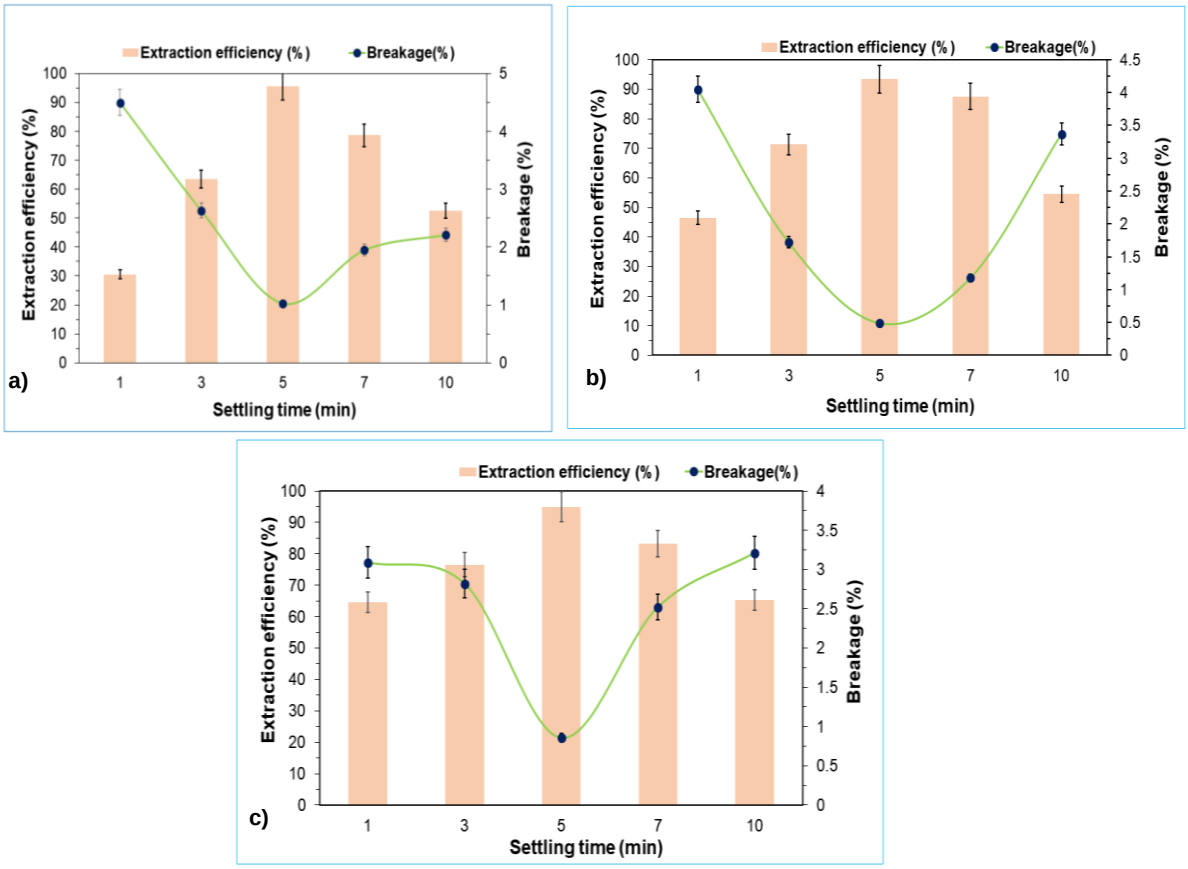


Figure 4.21: Effect of settling time upon breakage and extraction efficiency of WVO-ILEM from aqueous streams a) Dcf =100µg/mL (b) Ibf=100µg/mL (c) LA=5000 µg/mL

4.3.12 Effect of Feed concentration

The benefit of WVO-ILEM is that it can remove even small quantities of the solute; therefore, the influence of feed concentration on WVO-ILEM performance was investigated. The Dcf concentration was changed between 50 and 150 μg/mL. The effect of Dcf concentration on WVO-ILEM extraction efficiency was observed in Fig. 4.22. The results show that ILEM proved highly efficient at removing Dcf at lower concentrations and at optimal circumstances. Initially, the extraction efficiency was high when the concentration was low, and the stripping agent was sufficient to form complexes. As the concentration increases, the stripping agent becomes saturated, resulting in lesser extraction efficiency. However, when the concentration exceeds optimum, the amount of Dcf removed is reduced. Excess Dcf depletes the stripping agent, resulting in fewer complexes and reduced efficiency. Similar observations were reported for lactic acid extraction [19] and bismuth [221]. A similar observation was made for Ibf and LA.

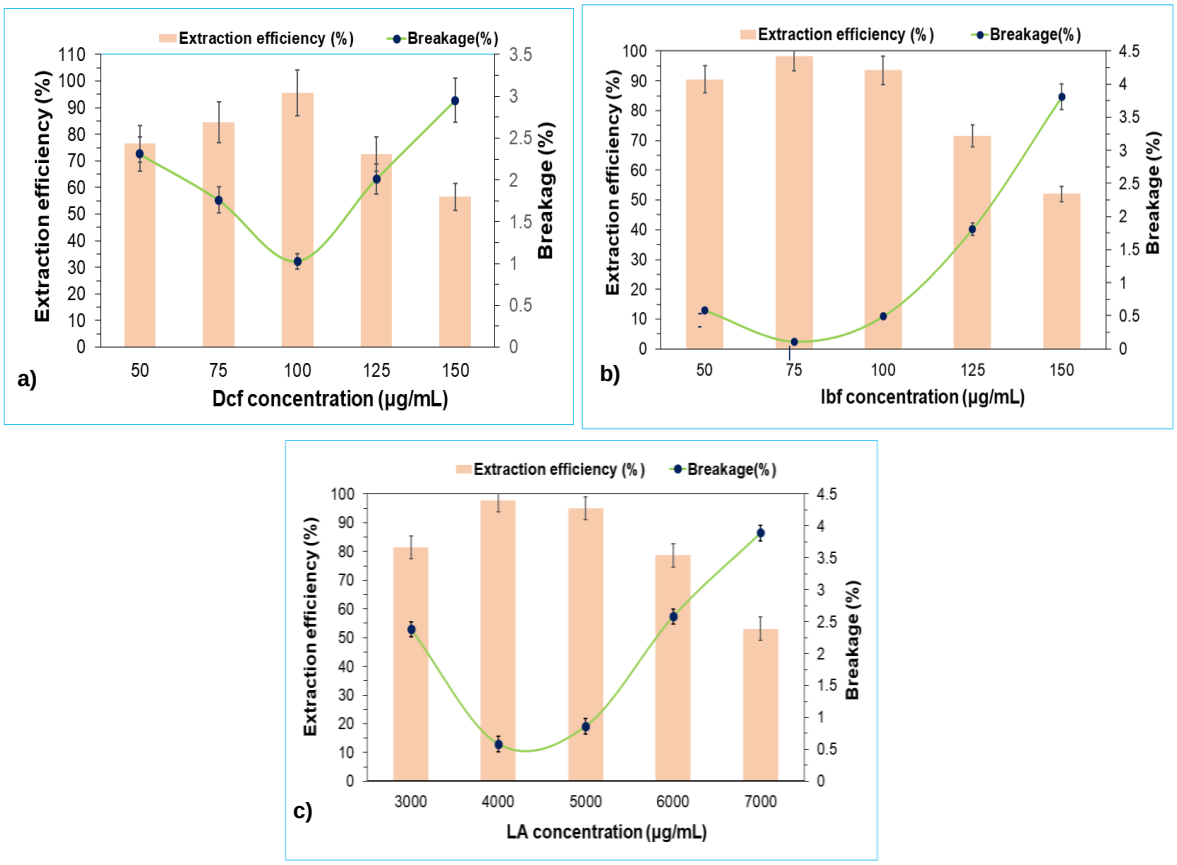


Figure 4.22: Effect of feed concentration upon breakage and extraction efficiency of WVO-ILEM from aqueous (a) Dcf (b) Ibf (c) LA

4.3.13 Optimization of process parameters using RSM for removal of BACs using WVO-ILEM

Since there are many factors affecting the stability and efficacy of WVO-ILEM, optimization was carried out using DOE. Although earlier studies evaluated optimized composition but using WVO-ILEM there's no reported study. The present study investigated promising factors (surfactant concentration, internal striping agent concentration, IL concentration, phase ratio, and treat ratio) that affect emulsion development. These factors affect the stability of WVO-ILEM and hence extraction

efficiency. Optimizing the selected factors is essential to achieve maximum extraction efficiency, resulting in highly stable WVO-ILEM. Table 4.5 presents the factors and their selected ranges using OFAT.

Table 4.5: Parameters and their ranges for Dcf

Code	Parameter	Unit	Range	
			Low	high
A	Surfactant concentration	wt.%	0.5	3.0
B	Stripping agent concentration	M	0.05	0.3
C	Carrier concentration	wt.%	0.1	0.6
D	Phase ratio		0.15	0.4
E	Treat ratio		1	4

As discussed in the section 3.9, fifty experimental runs were developed using Design-Expert software. Experimental and predicted results using the response surface model for the extraction of Dcf are present in Table D1 (APPENDIX D). For Ibf and LA, the results are present in Tables D2 and D3 (APPENDIX D). After getting every run's response value, the next step is developing and analyzing the response prediction model followed by optimization to achieve maximum extraction efficiency. The regression computation suggested a quadratic model. The quadratic model was statistically significant because it captured most of the variations in their subject response, which was not aliased, and the p-value was observed to be <0.0001.

4.3.13.1 Analysis of variance

Analysis of variance (ANOVA) was performed to evaluate the significance of the quadratic model and the effect of individual terms and their interaction on the response. ANOVA results are presented in Table 4.6. Results show the most significant factors that influence extraction efficiency. In this case, the only insignificant factor was AC, AE, and BC. The obtained F value 499.0 and p<0.0001 indicated that the model is

significant. The lack of fit value of 0.0630 shows that it is not significant compared to the pure error.

Table 4.6: ANOVA analysis for Response surface quadratic model for Dcf removal (%) using WVO-ILEM

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	5407.28	20	270.36	499.00	< 0.0001	significant
A-Surfactant concentration	120.66	1	120.66	222.70	< 0.0001	
B-Phase ratio	248.35	1	248.35	458.36	< 0.0001	
C-Treat ratio	60.65	1	60.65	111.94	< 0.0001	
D-Stripping agent	1262.58	1	1262.58	2330.30	< 0.0001	
E-IL concentration	128.93	1	128.93	237.97	< 0.0001	
AB	1213.77	1	1213.77	2240.21	< 0.0001	
AC	1.28	1	1.28	2.36	0.1351	
AD	34.20	1	34.20	63.12	< 0.0001	
AE	0.0512	1	0.0512	0.0945	0.7607	
BC	0.5151	1	0.5151	0.9507	0.3376	

BD	80.58	1	80.58	148.73	< 0.0001	
BE	91.87	1	91.87	169.56	< 0.0001	
CD	241.67	1	241.67	446.04	< 0.0001	
CE	32.93	1	32.93	60.77	< 0.0001	
DE	637.07	1	637.07	1175.81	< 0.0001	
A^2	315.56	1	315.56	582.43	< 0.0001	
B^2	14.07	1	14.07	25.97	< 0.0001	
C^2	792.01	1	792.01	1461.79	< 0.0001	
D^2	248.10	1	248.10	457.90	< 0.0001	
E^2	8.60	1	8.60	15.87	0.0004	
Residual	15.71	29	0.5418			
Lack of Fit	14.26	22	0.6483	3.13	0.0630	not significant
Pure Error	1.45	7	0.2072			
Cor Total	5422.99	49				

Table 4.7 shows the fit statistics. Standard deviation, coefficient of variation (C.V), and mean were 0.7361, 68.01, and 1.08%. The R^2 value was found to be 0.9971, adjusted

R^2=0.9951, and predicted R^2=0.9914 are in good agreement as the difference between the two is less than 0.2. This result shows that the selected model is 99% reliable [94]. Also, the signal-to-noise ratio, i.e adequate precision, was 97.708, which was quite higher than 4. The value indicates that the model is appropriate for the statistical design and data analysis. This model can be employed for the removal of Dcf using WVO-ILEM.

Table 4.7: Fit statistics of the regression model

Std. Dev.	0.7361	**R^2**	0.9971		
Mean	68.01	**Adjusted R^2**	0.9951		
C.V. %	1.08	**Predicted R^2**	0.9914	**Adeq Precision**	97.7087

The regression equation for the quadratic model for the extraction efficiency (response) for Dcf is represented by the equation 4.1

$$\textit{Extraction Efficiency } (Y) = +65.33 + 1.88A - 2.70B + 1.34C - 6.09\,D - 1.95E + 6.16\,AB + 0.2000A + 1.03\,AD + 0.0400\,AE - 0.1269\,BC + 1.59\,BD - 1.69\,BE - 2.75\,CD + 1.01\,CE + 4.46\,DE + 11.30\,A^2 + 2.39\,B^2 - 17.89\,C^2 + 10.02\,D^2 - 1.86\,E$$

Where,

A=surfactant concentration (wt.%), B=Phase ratio, C=Treat ratio, D=stripping agent concentration, E=IL concentration

The ANOVA results for Ibf are present in table D4 and for in table D5 respectively (APPENDIX D). Fit statistics are present in Table-D6 for Ibf. The result reveal R2 0.9948 and adjusted R^2 0.9931 for Ibf with a C.V of about 0.939. For LA the R^2 value as predicted by ANOVA was found to be 0.9978 and adjusted R^2 0.9921 with a C.V of 1.689. The predicted and adjusted R^2 for Ibf and LA are in good agreement. Also, the adequate precision was >4. Hence, the model can be employed for the removal of Ibf and LA. The regression equation for Ibf and LA are present in equation 4.2 and 4.3 respectively.

For Ibf

$$Extraction\ Efficiency\ (Y) = 84.38 - 3.09A - 0.73B + 0.80C - 3.17D + 4.39E + 1.47AB + 1.61AC - 1.73AD + 1.41AE + 1.043BC - 4.046BD - 1.68BE + 0.25CD + 1.01CE - 0.30DE - 23.7A^2 + 10.56B^2 + 1.26C^2 - 4.26D^2 - 20.00E^2 \quad (4.2)$$

For LA

$$Extraction\ Efficiency\ (Y) = +80.82 - 5.91A - 4.43B + 1.37C - .38D + 9.00E - 3.06AB - 1.98AC - 1.59AD - 1.54AE - 0.5269BC - 2.36BD - 3.17BE - 0.328CD + 1.36CE - 2.73DE + 9.59A^2 + 3.43B^2 - 20.01C^2 - 25.27D^2 + 1.20E^2 \quad (4.3)$$

4.3.13.2 Interactive effects of different parameters upon WVO-ILEM extraction efficiency

The reliability of the model and the combined effect of different parameters upon WVO-ILEM were investigated. Fig. 4.23 shows the plot between the obtained actual results using experiments and the model's predicted results for Dcf, Ibf and LA. It was found that the experimental and predicted response (extraction efficiency) are in good agreement.

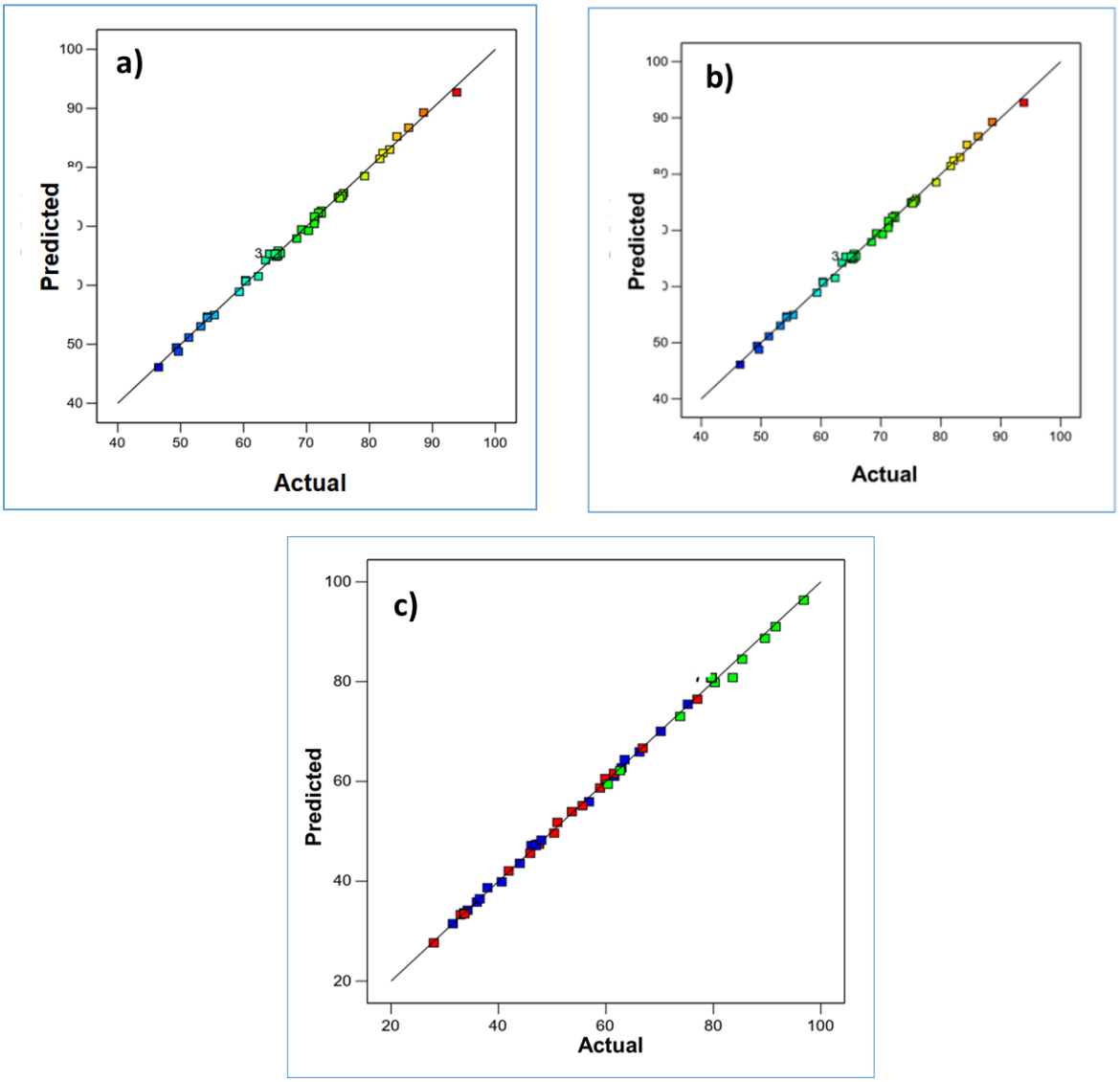


Figure 4.23: WVO-ILEM effectiveness diagnostics plots predicted vs. actual for a) Dcf b) Ibf and c) LA

The 3D plots of response curves are present in Fig 4.24, illustrating the effect of interaction parameters on the extraction efficiency of WVO-ILEM. The interactive effect between the surfactant concentration and treat ratio upon extraction efficiency is present in Fig. 4.24 a. The results reveal that extraction efficiency increased with increased surfactant concentration and treat ratio. It is to be mentioned that the emulsion formed becomes stable as interfacial tension decreases with the increase in surfactant concentration. However, an increase in surfactant beyond an optimum value result in a

decrease in extraction efficiency. This is because the emulsion gets destabilized by the addition of increased surfactant. Also, the extraction efficiency increased with the increase in treat ratio up to a specific limit. With the rise in treat ratio, proper dispersion of emulsion droplets in the external phase occurs. After that, the extraction efficiency reduces. It occurs because of the formation of tiny emulsion globules that undergo rapid coalescence giving rise to emulsion breakage and decreasing efficiency. Similar results were reported for the extraction of succinic acid using palm oil based ELM [94]. Fig. 4.24 b shows the combined effect of surfactant concentration and carrier concentration upon the extraction efficiency. An optimum concentration of surfactant and carrier is desired for the formation of stable WVO-ILEM. Since surfactant lowers the interfacial tension, the carrier increases the interfacial tension simultaneously. It was observed that the extraction efficiency increased with an increase in carrier concentration because an improved carrier concentration results in the formation of enough Dcf-IL complexes; as a result, better efficiency. However, an increase in carrier concentration beyond an optimum value causes the efficiency to decline. This is because too high carrier concentration (>0.35 wt.%) causes the viscosity of emulsion to increase, hence unstable WVO-ILEM and reduced efficiency. Therefore, the emulsion will be highly unstable if the carrier concentration exceeds the optimum value and extraction efficiency declines. Optimization of dysprosium extraction using ELM reported similar results [82].

Fig. 4.24 c shows the combined effect of phase ratio and treat ratio. The results reveal that maximum efficiency was achieved at 0.16 phase ratio and 2.56 treat ratio. This could be because any variation in the stripping agent changes the WVO-ILEM composition and affects the stability and hence extraction efficiency. It is to be mentioned that an increase in phase ratio results in a stable WVO-ILEM, and thus the extraction efficiency increases. A stripping agent less than the optimum amount is insufficient to form stable WVO-ILEM. However, if it exceeds the optimum value, the viscosity increases, and WVO-ILEM is highly unstable, resulting in increased emulsion diameter, breakage, and reduced efficacy [172]. Fig. 4.24 d shows the effect of carrier concentration and treat ratio. Carrier is essential for the stability of WVO-ILEM formulation. It was found that the efficiency increases with an increase in carrier concentration and treat ratio. This is because the stability of WVO-ILEM increased with an increase in carrier concentration. The dispersion is proper at higher treat ratios

and with stable WVO-ILEM, resulting in higher extraction efficiency. However, an increase in carrier concentration above the optimum limit, reduces the stability of WVO-ILEM as a result of high viscosity. Also, when WVO-ILEM gets dispersed at too higher treat ratio, is unable to form enough complexes and hinders stripping. Hence the extraction efficiency reduces. An optimum value of both parameters is necessary to form enough complexes that help extract Dcf. Similar observations were reported to optimize phenol removal from aqueous streams [95].

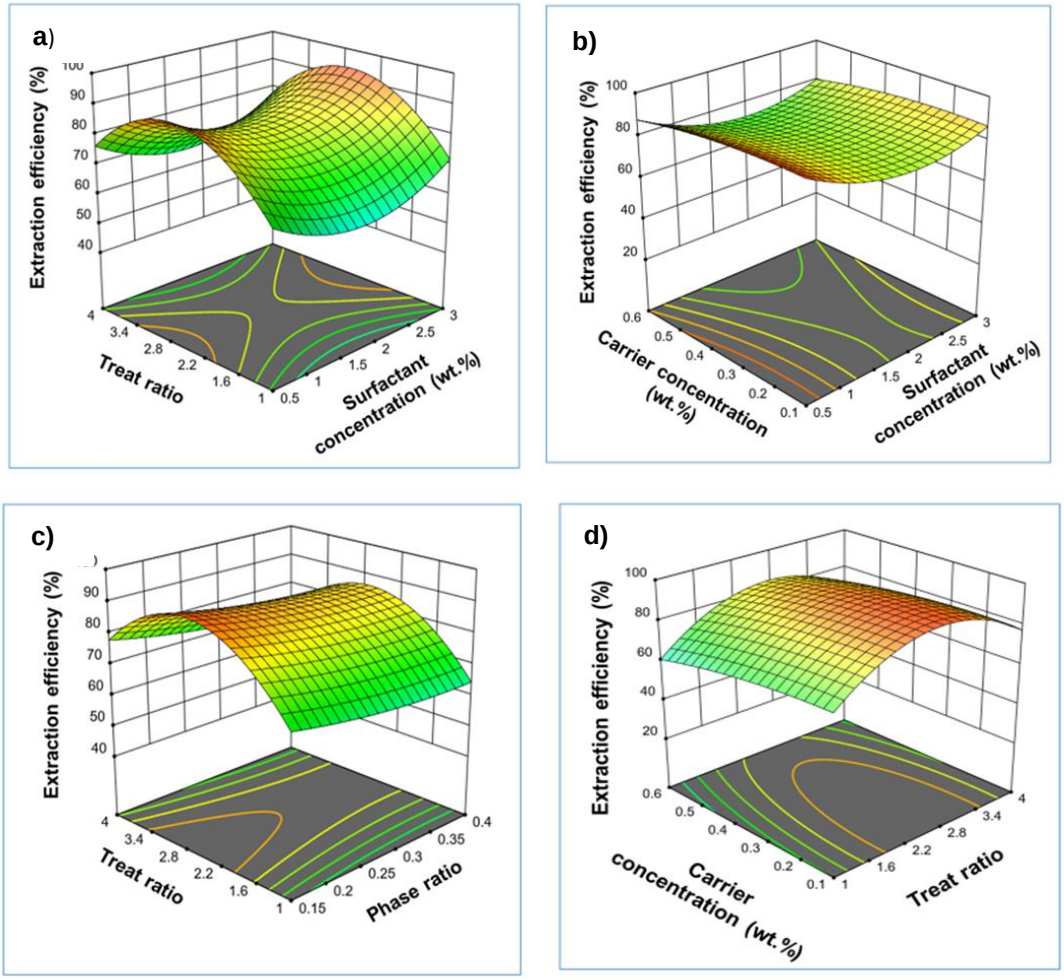


Figure 4.24: Response surface plot of the interaction between various parameters for Dcf (a) surfactant concentration and treat ratio (b) surfactant concentration and carrier concentration (c) phase ratio and treat ratio (d) treat ratio and carrier concentration

In a similar manner Fig. 4.25 presents the interactive effects for Ibf extraction. The results reveal that an optimum amount of surfactant concentration, treat ratio, carrier concentration, stripping agent concentration and phase ratio are needed to form a stable emulsion. The reason can be because of the molecular interactions and proper reactions to proceed optimum values are required.

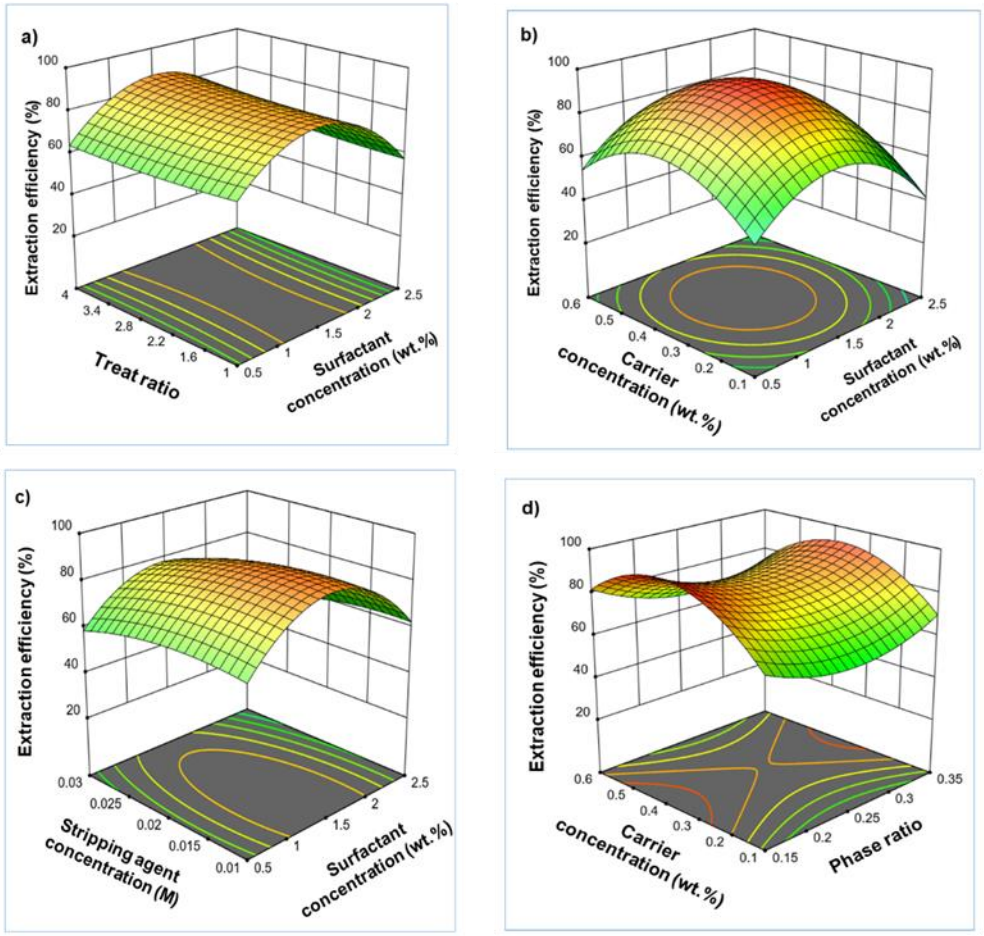


Figure 4.25: Response surface plot of the interaction between various parameters for Ibf (a) surfactant concentration and treat ratio (b) surfactant concentration and carrier concentration (c) Surfactant concentration and striping agent concentration (d) phase ratio and carrier concentration

A similar trend was observed for the extraction of LA. Fig. 4.26 presents the interactive effects of the parameters for stable WVO-ILEM formulation and dispersion. The results reveal that the composition of emulsion affects the stability and hence extraction efficiency. Hence and adequate amount of surfactant concentration, stripping

agent concentration, phase ratio and carrier concentration are needed for stable emulsion formulation. Furthermore, to disperse this WVO-ILEM an optimum amount of treat ratio is required to form enough complexes between LA and IL. Also, for proper stripping of these complexes, an adequate amount of treat ratio is required.

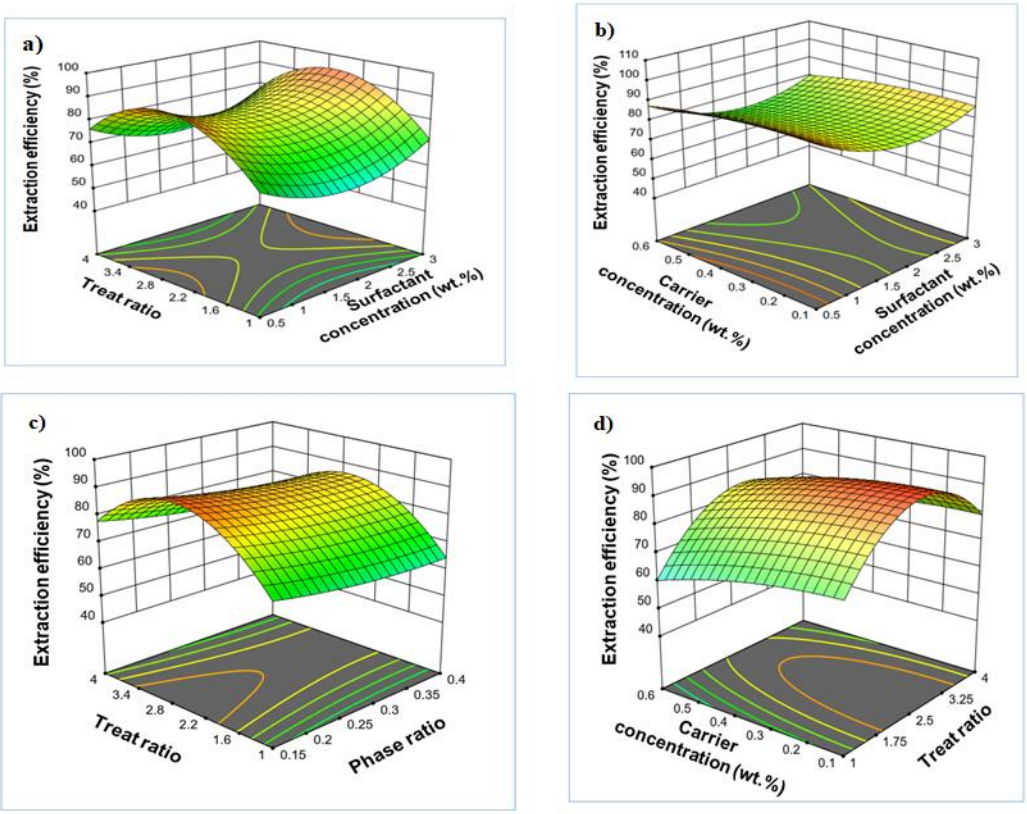


Figure 4.26: Response surface plot of the interaction between various parameters for LA (a) surfactant concentration and treat ratio (b) surfactant concentration and carrier concentration (c) phase ratio and treat ratio (c) treat ratio and carrier concentration

4.3.13.3 Optimization of process parameters vis RSM and model validation

Optimization of process parameters for maximizing the extraction efficiency of WVO-ILEM was carried out. One hundred different solutions were obtained. The solution with maximum treat ratio and optimum value of IL was chosen. The results obtained are present in Table 4.8. The main objective was to maximize the extraction efficiency with minimum error. Desirability (0.95) suggests that the estimated function can be utilized to predict the desired conditions for the extraction of Dcf using WVO-ILEM.

Table 4.8: Optimized results obtained using RSM for Dcf

Parameters	Optimized values	Predicted efficiency (%)	Desirability
Surfactant concentration (wt.%)	0.964		0.952
tripping agent concentration (M)	0.05		
IL concentration (wt.%)	0.32	97.93	
Phase ratio	0.21		
Treat ratio	3.2		

Table 4.9 presents the optimized results for Ibf. The predicted results suggest 95.68% of extraction efficiency can be obtained at optimized conditions with desirability 0.954.

Table 4.9: Optimization results obtained for Ibf by using CCD-RSM

Parameters	Optimized values	Predicted efficiency	Desirability
Surfactant concentration (wt.%)	1.0		0.954
Stripping agent concentration (M)	0.02		
IL concentration (wt.%)	0.35	95.68	
Phase ratio	0.275		
Treat ratio	4.0		

Likewise, Table 4.10 presents the optimized results for LA. 97.88% extraction efficiency can be obtained for LA at optimized conditions.

Table 4.10: Optimization results obtained for LA by using CCD-RSM

Parameters	**Optimized values**	**Predicted efficiency**	**Desirability**
Surfactant concentration (wt.%)	0.987		0.947
Stripping agent concentration (M)	0.15		
IL concentration (wt.%)	0.35	97.88	
Phase ratio	0.188		
Treat ratio	4.0		

The optimized values obtained using CCD model were further verified experimentally. The experiments were repeated four times to minimize error while comparing the predicted results. It was found that the WVO-ILEM prepared at optimized conditions was stable for about 144 minutes, with minimum breakage of 0.5 %. Emulsion diameter was observed to be 0.296 μm and 0.669 μm after the dispersion of WVO-ILEM in external solution Fig. D1 (APPENDIX D). The obtained experimental results were compared to predicted outcomes. Table 4.11 presents the experimental verification of RSM results along with the calculated error for Dcf. The results show that the error was less than 3%, and the standard deviation was 0.83. Hence it can be concluded that the predicted model is accurate and efficient for removing Dcf for the environmentally friendly WVO-ILEM.

Table 4.11: Experimental verification of optimized obtained results for Dcf

Run No.	Extraction Efficiency (%)		% Error
	Predicted	Experimental	
1		96.48	1.49
2		96.38	1.59
3	97.93	96.04	1.94
4		96.12	1.86
Mean		96.25	1.73
Standard deviation			0.83

At the optimized conditions obtained experiments were performed for Ibf extraction. Table 4.12 presents the predicted and experimental efficiencies It was found that WVO-ILEM developed was highly stable with minimum breakage at these conditions. Standard deviation between experimental and predicted results was found to be less than 3%.

Table 4.12: Experimental verification of results at optimum conditions or Ibf

Run No.	Extraction Efficiency (%)		% Error
	Predicted	Experimental	
1		94.3	1.14
2		94.8	1.96
3	95.68	93.6	2.17
4		94.12	1.63
Mean		94.95	1.8
Standard deviation			0.86

At the optimized conditions obtained experiments were performed for LA extraction. Average efficiency of 96.07% was obtained. Table 4.13 presents the predicted and experimental efficiencies for LA. It was found that WVO-ILEM developed was highly stable with minimum breakage at these conditions. Standard deviation between experimental and predicted results was found to be less than 3%.

Table 4.13: Experimnetal verification of results at optimum conditions for LA

Run No.	**Extraction Efficiency (%)**		**% Error**
	Predicted	**Experimental**	
1		96.23	1.68
2		96.15	1.76
3	97.88	96.26	1.66
4		95.67	2.25
Mean		96.07	1.841
Standard deviation			0.87

4.4 SECTION IV: PERMEATION, KINETICS AND DEMULSIFICATION OF WVO-ILEM

This section presents the permeation rate, kinetics of WVO-ILEM formed at optimized results obtained in objective 3. Also, the kinetics was studied using first and

second order rate equations. Furthermore, demulsification was carried out to check how many times the WVO-ILEM can be reused. Also, recovery efficiency was calculated for the target BAC removed.

4.4.1 Rate equation for WVO-ILEM permeation

At the optimized conditions obtained for the removal of Dcf using RSM, the permeation rates and kinetics of WVO-ILEM were studied. The fixed conditions were 5200 rpm, homogenization speed, 5 min homogenization time, 240 rpm stirring speed, and 5 min settling time. Experiments were performed at different stirring times. Permeation rates were evaluated as discussed in section 2.14. Table 4.14 presents the permeation rate constants values at the different stirring times. At 20 min of extraction time, it was found that the permeation rate was maximum. The highest permeation rate was $7.93*10^{-3}$ sec^{-1} at 20 min of extraction time. The diffusivity value obtained using the Wilke-Chang equation was $1.19* 10^{-11}$ m^2/s. The Dcf rates indicate a drop as extraction approached completion. Similar observations were reported to extract organic pollutants, mainly benzoic acid using ELM [86].

Additionally, the rate constant was also evaluated. Fig. 4.27 presents the first-order kinetics analysis for Dcf. A high R^2 (0.9266) value implies that WVO-ILEM follows the first-order model, and the rate constant for the first-order model was 0.151 min^{-1} [222]. Fig. 4.27 suggests that the extraction rate increases and reaches a maximum value beyond which it declines. This could be explained on the basis of emulsion breakage. The breakage of WVO-ILEM increased beyond the optimum extraction time, affecting the kinetics [223]. Fig. 4.28 presents the second-order kinetic analysis. A low value of R^2 (0.6043) was obtained.

Table 4.14: Dcf removal using WVO-ILEM at optimized conditions

Time (min)	**C_o/C_t**	**D' (sec^{-1})**
10	1.95	$4.7*10^{-3}$
15	3.58	$4.8*10^{-3}$
20	20.53	$7.93*10^{-3}$
25	7.88	$4.7*10^{-3}$
30	6.41	$2.8*10^{-3}$

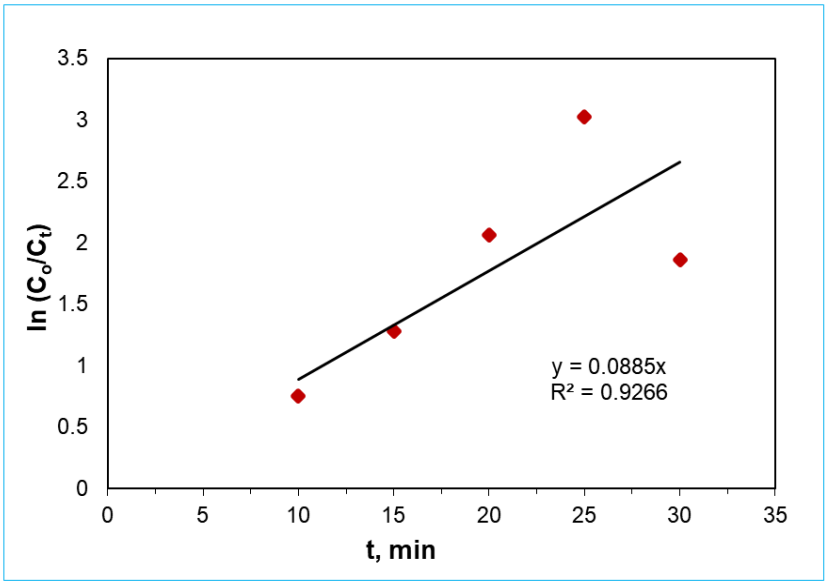


Figure 4.27: First-order kinetic analysis for Dcf removal using WVO-ILEM

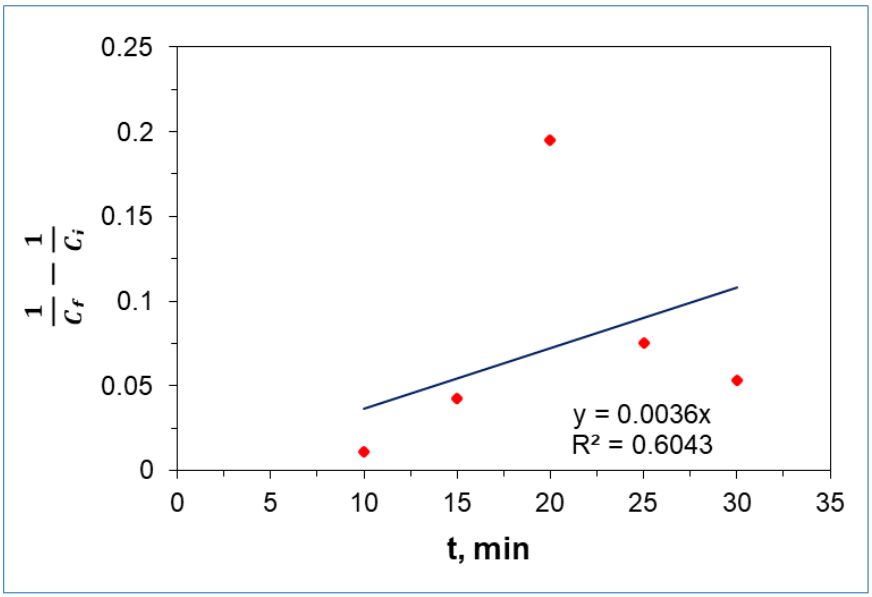


Figure 4.28: Second order kinetic analysis for Dcf removal using WVO-ILEM

Table 4.15 presents the kinetics for Ibf removal. The results suggest that a highly stable WVO-ILEM with maximum efficacy and hence permeation was obtained at 7 min of extraction time. An increase in extraction time beyond that cause the emulsion to break and hence larger diameter, reduced permeation. The highest permeation rate was $2.61*10^{-2}$ $sec^{-1}$and diffusivity was $1.76*\ 10^{-11}$ m^2/s. Fig. 4.29 presents the kinetics of Ibf removal using WVO-ILEM first order and Fig. 4.30 presents kinetic of Ibf removal using second order kinetics. The results reveal that extraction of Ibf follows first order kinetics using WVO-ILEM.

Table 4.15: Ibf removal by WVO-ILEM at optimized conditions

Time (min)	**C_o/C_t**	**D' (sec^{-1})a**
1	1.48	$1.8*10^{-2}$
4	2.76	$1.6*10^{-2}$
7	15.62	$2.61*10^{-2}$
10	8.84	$1.4*10^{-2}$
13	7.63	$1.04*10^{-2}$

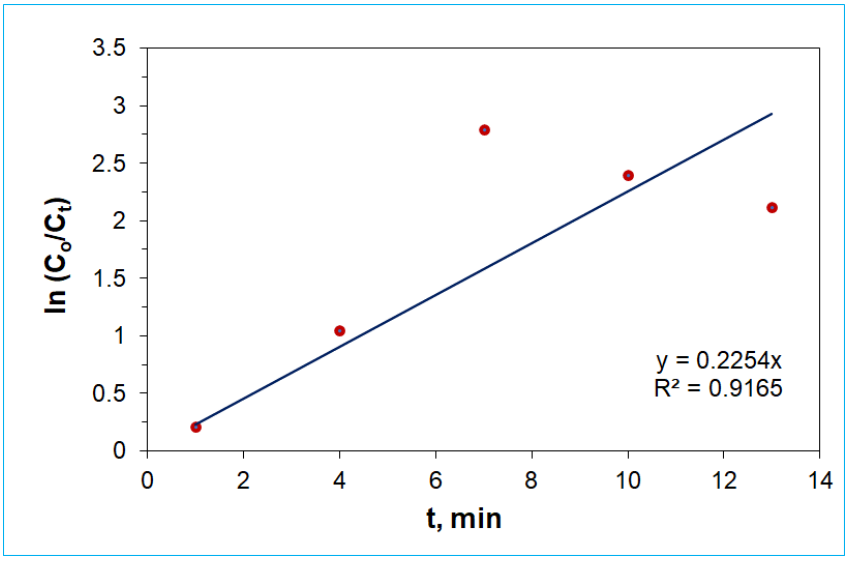


Figure 4.29: First order kinetic analysis for Ibf removal using WVO-ILEM

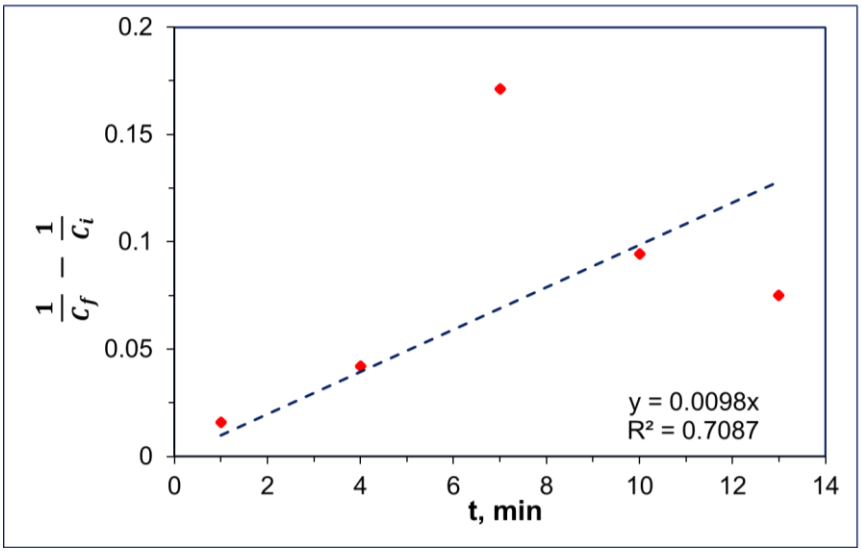


Figure 4.30: Second order kinetic analysis for Ibf removal using WVO-ILEM

The kinetic study was performed for LA as well. The results suggest that maximum permeation was obtained at 20 min of contact time between WVO-ILEM and external phase. After which the stripping agent leaks into external solution declining peremation. Table 4.16 presents kinetics for LA removal. The highest permeation rate was obtained as $9.9*10^{-3}$ sec^{-1} and diffusivity were found to be $3.28 * 10^{-11}$ m^2/s. Fig. 4.31 and 4.32 presents the first and second order kinetics for LA. The results reveals that extraction of LA using WVO-ILEM follows first order kientics as R^2 value was higher for first order than second order.

Table 4.16: LA removal by WVO-ILEM at optimized conditions

Time (min)	**C_o/C_t**	**D' (1/sec)**
10	2.59	$6.36*10^{-3}$
15	4.31	$6.49*10^{-3}$
20	19.92	$9.9*10^{-3}$
25	10.86	$6.36*10^{-3}$
30	5.430.	$3.76*10^{-3}$

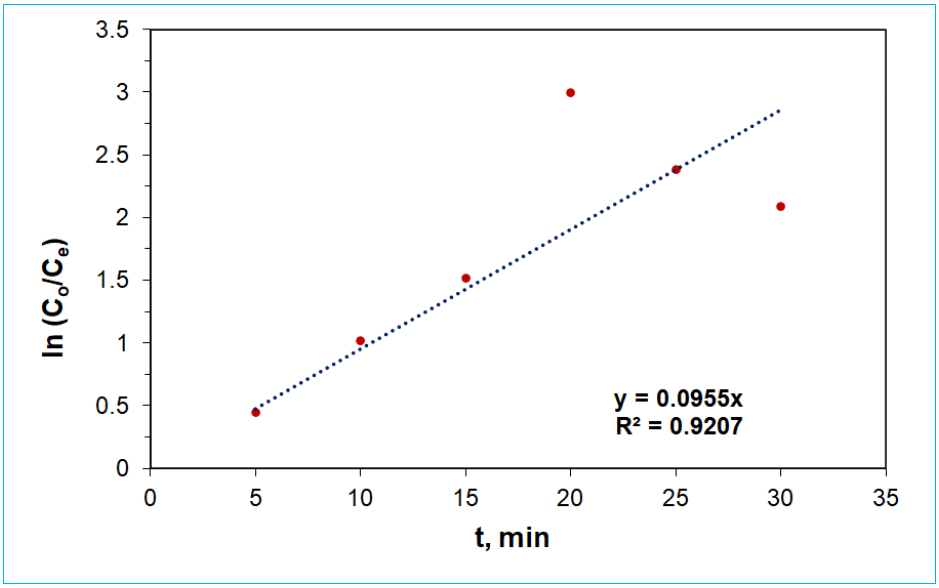


Figure 4.31 First order kinetic analysis for LA removal using WVO-ILEM

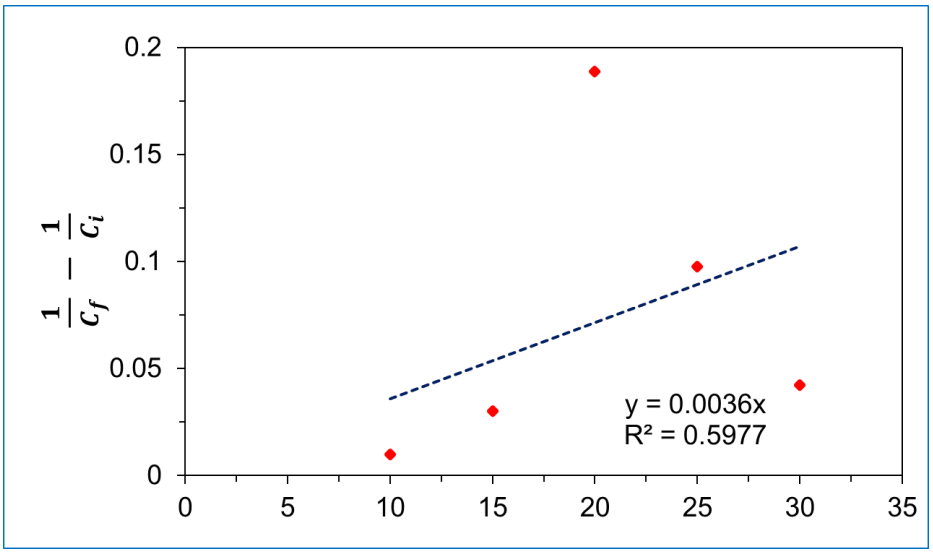


Figure 4.32 Second order kinetic analysis for LA removal using WVO-ILEM

4.4.2 Demulsification for the recycling and reuse of WVO-ILEM

At optimized conditions of WVO-ILEM formulation, demulsification was carried out. After separation and settling, the organic phase was poured into the test tube for centrifugation. The WVO-ILEM separated after demulsification was recovered. The emulsion was re-emulsified so that it could be reused for the extraction of model BACs after the addition of an internal stripping agent. The WVO-ILEM was re-emulsified by adding 0.05 M HNO_3 dropwise at a phase ratio of 0.15 for Dcf. To achieve this, the mixture was homogenized at 5200 rpm for 5 min. WVO-ILEM was used for the extraction of Dcf. It was found that WVO-ILEM was efficient up to five cycles. After the fifth cycle, the stability of WVO-ILEM was decreased as breakage increased, and hence the extraction efficiency was found to be reduced. This could be explained that since after each cycle the organic phase is recovered after demulsification. The organic phase is then re-emulsified by the addition of stripping agent. Since 100% extraction is never achieved. Some stripping agent along with the external phase is always presents in organic phase. With continuous re-emulsification the organic phase becomes saturated with stripping agent. After five cycles the concentration of stripping agent is

quite high and further emulsification results in highly viscous in unstable WVO-ILEM. Also some Dcf-IL complexes were still present after demulsification and increased with the number of cycles, resulting in instability and reduced efficiency [79]. In a study on the removal of methylparaben using ELM, heptane was used as diluent, Span 20 as emulsifier and TOA was as carrier. The author's reported ELM was stable upto four cycles after which the ELM was saturated with the stripping phase [152]. Table 4.17 shows the WVO-ILEM reusability results for Dcf.

Table 4.17: Effect of reuse cycles upon the extraction efficiency and other properties of WVO-ILEM for Dcf.

Cycle No.	**Static stability (min)**	**Emulsion diameter (µm)**	**Viscosity (cP)**	**Breakage (%)**	**Extraction efficiency (%)**	**Recovery efficiency (%)**
1	141	0.342	151.5	0.72	96.23	97.8
2	136	0.85	155.3	0.93	92.35	89.6
3	128	1.18	159.2	1.58	88.62	75.6
4	118	1.28	161.9	1.92	82.64	71.6
5	94	2.96	163.7	2.81	78.91	60.3
6	79	3.73	167.5	4.28	58.36	31.3

Similarly, emulsification was carried out for Ibf. The WVO-ILEM recovered was emulsified by the addition of 0.15 M NaOH in dropwise manner at a phase ratio of 0.3. The mixture was homogenized at 5200 rpm for 5 min. The prepared emulsion was used for further extraction of Ibf. Table 4.18 shows number of times emulsion can be reused along with extraction efficiency and other properties.

Table 4.18: Effect of reuse cycles upon the extraction efficiency and other properties of WVO-ILEM for Ibf

Cycle No.	**Static stability (min)**	**Emulsion diameter (µm)**	**Viscosity (Cp)**	**Breakage (%)**	**Extraction efficiency (%)**	**Recovery efficiency (%)**
1	144	0.269	147.5	0.42	94.24	95.6
2	136	0.398	151.3	0.94	89.65	80.6
3	126	0.486	154.8	1.05	82.5	70.3
4	114	0.983	158.2	1.14	76.08	56.5
5	86	1.32	161.3	1.72	70.54	49.5
6	79	2.76	165.4	3.06	55.23	32.6

In a similar way number of cycles were evaluated for LA. The WVO-ILEM recovered was emulsified by the addition of 0.15 M NaOH in dropwise manner at a phase ratio of 0.188. The mixture was homogenized at 5200 rpm for 5 min. The prepared emulsion was used for further extraction of LA. Table 4.19 shows number of times emulsion can be reused along with extraction efficiency and other properties. It can be observed that initially good extraction efficiency was achieved which decline with the increase in number of cycles. The decline in the extraction efficiency was due to the WVO-ILEM and carrier being saturated with LA molecules and cannot transport anymore. Also the emulsion becomes saturated with internal striping agent, increasing viscosity and hence increase in globule diameter and breakage

Table 4.19: Effect of reuse cycles upon the extraction efficiency and other properties of WVO-ILEM for LA

Cycle No.	Stand alone stability (min)	Emulsion diameter (µm)	Viscosity (Cp)	Breakage (%)	Extraction efficiency (%)	Recovery efficiency (%)
1	136	0.394	146.4	0.72	95.6	94.7
2	126	0.689	151.5	0.95	90.5	88.6
3	118	0.94	154.3	1.26	86.5	73.5
4	105	1.09	157.6	1.89	81.59	69.5
5	90	1.18	161.6	2.18	77.06	40.6
6	72	1.89	165.4	2.56	56.5	32.5

4.4.3 Recovery efficiency for removed BAC

Since the main objective was to extract BAC from wastewater, Recovery efficiency was calculated at the optimized conditions. The recovery efficiency for Dcf was found to be 97.25%. Table 4.10 shows the recovery efficiency along with breakage viscosity, density, and emulsion diameter for Dcf, Ibf and LA.

Table 4.20: Recovery efficiency at optimized conditions

BAC	Extraction efficiency (%)	Recovery efficiency (%)	Breakage (%)	Emulsion diameter (µm)	Viscosity (cP)
Dcf	96.3	97.25	0.45	0.292	148.6
Ibf	94.24	93.84	0.52	0.269	149.3
LA	95.6	94.8	0.72	0.394	146.4

CHAPTER 5

CONCLUSION AND FUTURE RECOMMENDATIONS

5.1 Conclusion

The present work aimed to develop an emulsion liquid membrane (ELM) using ionic liquids (ILs) and waste vegetable oil (WVO) for the removal of biologically active compounds (BACs) such as diclofenac (Dcf), ibuprofen (Ibf) and lactic acid (LA). ILs were employed as a carrier to improve the only drawback of ELM, i.e., instability, and hence increase efficiency. Since thousands of cation-anion combinations can form innumerous ILs because of their tunable nature, the selection of specific IL for the target molecule is backbreaking; hence an efficient simulation tool conductor like a screening model for real solvents (COSMO-RS) was used for screening of IL. The cations that do not possess ring structure and anions that have hydrogen bond acceptor regions were better extracting agents. Screened IL tetramethylammonium sulfate [TMAm][SO_4], was used as a carrier to remove Dcf, Ibf, and LA.

Using screened IL [TMAm][SO_4] as a carrier and waste vegetable oil (WVO) as a diluent, a waste vegetable oil ionic liquid-based emulsion liquid membrane (WVO-ILEM). was developed. The other components of WVO-ILEM were Span 80 as the surfactant, internal stripping agent (nitric acid for Dcf, sodium hydroxide for Ibf, and LA). A highly stable WVO-ILEM was developed using these components to extract BACs under study.

The effect of various parameters on the stability of WVO-ILEM was investigated. WVO-ILEM developed using [TMAm][SO_4] was highly stable and efficient for removing Dcf, Ibf, and LA. Using the one-factor approach, the extraction efficiency was about 95.6%, 93.48%, and 94.98% for Dcf, Ibf, and LA. The results obtained suggest that WVO-ILEM can be used to remove stubborn BACs from aqueous streams. Since many factors hindered the extraction efficiency, optimization of parameters that

affect the composition and hence stability and extraction efficiency was carried out using RSM. Upon optimization, the maximum removal efficiency of up to 96.25%, 95.68%, and 97.88% for Dcf, Ibf, and LA was attained. The results were verified experimentally. The error was observed to be less than 3%. Overall, WVO-ILEM was highly efficient for the removal of BACs under study.

The permeation and kinetics showed that WVO-ILEM followed first-order kinetics with high diffusivity. To reuses and recycle WVO-ILEM, demulsification was done. The WVO-ILEM obtained was reused again and again for extraction purposes. It was found that recovered WVO-ILEM can be reused for up to five cycles to extract BACs, after which the efficacy started declining.

5.2 Recommendations

The core issues that could be addressed in future research incorporating WVO-ILs for the formulation of ELM include:

1. [TMAm][SO_4] showed excellent capability for the extraction of BACs under study (Dcf, Ibf and LA). The mechanism of extraction using WVO as diluent and IL as carriers should be studied using a computational chemistry approach to see how cation and anion play their role in the extraction of BACs using WVO-ILEM

2. Toxicity and biodegradability studies for WVO-ILEM can be performed using various methods.

3. Future research can use plant-based surfactants such as lecithin, etc., to formulate bio-waste vegetable oil-ionic liquid-based emulsion liquid membrane.

4. Since this is the first study and there are no other researches on the screening of ILs using COSMO-RS for ELM, it would be interesting to screen some new and better ILs such as surfactant-based ILs, IL derived from natural

sources such as amino acids, etc., Also, new ILs-DES can be tailored for the extraction of BACs.

5. Ionic liquid-based emulsion membrane (ILEM) can be developed using non-edible oils such as jatropha, neem, Karanja, etc. to extract BACs. Since non-edible oils are also cheap and readily available, future work can use them as diluent.

6. To scale up this study on an industrial scale continuous waste vegetable oil ionic liquid emulsion membrane must be developed. This can be accomplished by using a continuous process instead of the batch process.

7. A separate study on the rheological behaviors of WVO-ILEM can be conducted to explain in detail the rheology of WVO-ILEM.

8. Mathematical modeling in WVO-ILEM for BACs extraction should be considered as a further extension of this work. Proposing a new model based upon the membrane breakage, emulsion diameter, standalone stability would be of great interest in the area of ELM for separation applications.

PUBLICATIONS

1. H.W. Khan, M. Moniruzzaman, M. M. E. Nasef, M. A. Bustam, M. Goto, Ionic liquid assisted cellulose aerogels for cleaning an oil spill, Materials today: Proceedings 2020, 31, pp. 217-220

2. H.W. Khan, A. V. B. Reddy, M. M. E. Nasef, M. A. Bustam, M. Goto, M. Moniruzzaman, Screening of ionic liquids for the extraction of biologically active compounds using emulsion liquid membrane: COSMO-RS prediction and experiments, Journal of Molecular liquids, 2020, 309 (113122). (I.F: 6.165)

3. H. W. Khan, A. A. M. Elgharbawy, M. A. Bustam, Muhammad Moniruzzaman, Design and Selection of Ionic Liquids Via COSMO for Pharmaceuticals and Medicine, In *Application of Ionic Liquids in Drug Delivery*, (2021) 137-164. Springer, Singapore.

4. H. W. Khan, A. V. B. Reddy, M. A. Bustam, M. Goto, M. Moniruzzaman Development and optimization of an ionic liquid-based emulsion liquid membrane process for the efficient recovery of lactic acid: An eco-friendly approach, Biochemical Engineering Journal, 2021, 176 (108216) (IF=3.475) .

5. H. C. Ting, H. W. Khan, A. V. B. Reddy, M. Goto, M. Moniruzzaman, Extraction of salicylic acid from wastewater using ionic liquid-based green emulsion liquid membrane: COSMO-RS prediction and experimental verification, Journal of Molecular Liquids, 2021, (118280) (IF=6.165)

6. H. W. Khan, A. Elgharbawy, M. A. Bustam, M. Goto, M. Moniruzzaman, Vegetable oil- ionic liquid based emulsion liquid membrane for the removal of lactic acid from aqueous streams: Emulsion size, membrane breakage, and stability study. -Submitted to ACS Omega, (I.F=4.132)

BIBLIOGRAPHY (OR REFERENCES)

1. J. A. Rivera-Jaimes, C. Postigo, R. M. Melgoza-Alemán, J. Aceña, D. Barceló, and M. López de Alda, Study of pharmaceuticals in surface and wastewater from Cuernavaca, Morelos, Mexico: occurrence and environmental risk assessment, *Science of the Total Environment,* 613 (2018): 1263-1274
2. E. Gracia-lor, J. V Sancho, R. Serrano, and F. Hernández, Occurrence and removal of pharmaceuticals in wastewater treatment plants at the Spanish Mediterranean area of Valencia, *Chemosphere*, 87, 5 (2012): 453-462
3. K. Y. Andrew Lin, H. Yang, and W. Der Lee, Enhanced removal of diclofenac from water using a zeolitic imidazole framework functionalized with cetyltrimethylammonium bromide (CTAB), *RSC Advances,* 5(2015): 81330-81340
4. C. Gadipelly, A. Pérez-González, G. D. Yadav, I. Ortiz, R.l Ibáñez, V. K. Rathod, and K. V. Marathe, Pharmaceutical industry wastewater: review of the technologies for water treatment and reuse, *Industrial & Engineering Chemistry Research,* 53 (2014): 11571-11592
5. W. Zhao, G. Yu, L. Blaney, B. Wang, Development of emission factors to estimate discharge of typical pharmaceuticals and personal care products from wastewater treatment plants, *Science of the Total Environment,* 769 (2021): 144556.
6. L. M. Madikizele, Determination of selected acidic pharmaceutical compounds in wastewater treatment plants, PhD thesis, University of the Witwatersrand 2017.
7. L. Lonappan, S. K. Brar, R. K. Das, M. Verma, and R. Y. Surampalli, Diclofenac and its transformation products: environmental occurrence and toxicity-a review, *Environment Internationaml* 96 (2016): 127-138.
8. P. Sathishkumar, R. A. A Meena, T. Palanisami, V A. Kumar, T. Palvannan, F. L. Gu, Occurrence, interactive effects and ecological risk of diclofenac in environmental compartments and biota-a review, Science of The Total Environment 698 (2020): 134057
9. S. Chopra, D. Kumar, Ibuprofen as an emerging organic contaminant in environment, distribution and remediation, *Heliyon,* 6 (2020): e04087.
10. A. Kumar, A. Thakur, P. Singh Panesar, Lactic acid and its separation and purification techniques: A review, *Reviews in Environmental Science and Bio/Technology,* 4 (2019): 823-853.

11. M. A. Hossain, J. S. Lee, D. H. Kim, D. Q. Nguyen, M. S. Cheong, H. S. Kim, Ionic liquids as benign solvents for the extraction of aromatics, *Bulletin of the Korean Chemical Society*, 33(2012): 3241-3247.
12. D. Cherik, M. Benali, and K. Louhab, Occurrence, ecotoxicology, removal of diclofenac by adsorption on activated carbon and biodegradation and its effect on bacterial community: A review, World Scientific News 10 (2015): 116-144.
13. J. Garcia-Ivars, L. Martella, M. Massella, C. Carbonell-Alcaina, M. I. Alcaina-Miranda, M. I. Iborra-Clar., Nanofiltration as tertiary treatment method for removing trace pharmaceutically active compounds in wastewater from wastewater treatment plants, *Water research*, 125 (2017): 360-373.
14. M. Leeman, F. Vossebeld, T. J. Visser, B. Schuur, Novel extractants for the recovery of fermentation derived lactic acid, *Separation and purification technology,* 111 (2013): 82-89.
15. N. F. M. Noah, N. Jusoh, N. Othman, R. N. R. Sulaiman, N. A. M. K. Parker, Development of stable green emulsion liquid membrane process via liquid–liquid extraction to treat real chromium from rinse electroplating wastewater, *Journal of Industrial and Engineering Chemistry*, 66 (2018): 231-241
16. S. B. M. Najib, K. S. N. Kamaruddin, Removal of Carbon Dioxide by Emulsion Liquid Membrane Containing Blended Amine, In Advanced Materials Research, vol. 1113, pp. 481-485. Trans Tech Publications Ltd, 2015.
17. O. Hamdaoui, Extraction of organic pollutants from water by emulsion liquid membrane, *Process Engineering Journal,* 1(2014): 19-27.
18. R. N. R. Sulaiman, N. Othman, N. H. Harith, H. A. Rahman, N. Jusoh, N. F. M. Noah, and M. B.Rosl, Phenol recovery using continuous emulsion liquid membrane (CELM) process, *Chemical Engineering Communications,* 208 (2021): 483-499.
19. A. Kumar, A. Thakur, and P. S. Panesar, Lactic acid extraction using environmentally benign Green emulsion ionic liquid membrane, *Journal of Cleaner Production,* 181 (2018): 574-583
20. H. W. Khan, A. V. B. Reddy, M. A. Bustam, M. Goto, and M. Moniruzzaman, Development and optimization of ionic liquid-based emulsion liquid membrane process for efficient recovery of lactic acid from aqueous streams, *Biochemical Engineering Journal,* 176 (2021)108216.

21. B. Yan, X. Huang, K. Chen, H. Liu, S. Wei, Y. Wu, Li Wang, A study of synergetic carrier emulsion liquid membrane for the extraction of amoxicillin from aqueous phase using response surface methodology, *Journal of Industrial and Engineering Chemistry*, (2021).
22. S. P. M. Ventura, F. A. e Silva, M. V. Quental, D. Mondal, M. G. Freire, J.A.P. Coutinho, Ionic-liquid-mediated extraction and separation processes for bioactive compounds: past, present, and future trends, *Chemical Reviews*, 117 (2017): 6984-7052.
23. H. W. Khan, A. A. M. Elgharbawy, M. A. Bustam, Muhammad Moniruzzaman, Design and Selection of Ionic Liquids Via COSMO for Pharmaceuticals and Medicine, *In Application of Ionic Liquids in Drug Delivery*, (2021) 137-164. Springer, Singapore.
24. P. Isosaari, V. Srivastava, M. Sillanpaa, Ionic liquid-based water treatment technologies for organic pollutants: Current status and future prospects of ionic liquid mediated technologies, *Science of the Total Environment* 690 (2019): 604-619.
25. J. Claus, F. O. Sommer, and U. Kragl, Ionic liquids in biotechnology and beyond, *Solid State Ionics*, 314 (2018): 119-128
26. F. Garavand, S. H. Razavi, and I. Cacciotti, Synchronized extraction and purification of L-lactic acid from fermentation broth by emulsion liquid membrane technique, *Journal of Dispersion Science and Technology*, 39 (2018): 1291-1299
27. A. Kumar, A. Thakur, and P. S. Panesar, Recent developments on sustainable solvents for emulsion liquid membrane processes, *Journal of Cleaner Production*, 240 (2019): 118250
28. A. Kumar, A. Thakur, and P. S. Panesar, A review on emulsion liquid membrane (ELM) for the treatment of various industrial effluent streams, *Reviews in Environmental Science and Bio/Technology*, 18 (2019): 153-182
29. D. Zheng, D. Hua, Y. Hong, A. R. Ibrahim, A. Yao, J. Pan, and G. Zhan, Functions of Ionic Liquids in Preparing Membranes for Liquid Separations: A Review, *Membranes*, (2020): 395.
30. G. Mascolo, L. Balest, D. Cassano, G. Laera, A. Lopez, A. Pollice, and C. Salerno, Biodegradability of pharmaceutical industrial wastewater and formation of

recalcitrant organic compounds during aerobic biological treatment, *Bioresource technology*, 101 (2010): 2585-2591.

31. N. Othman, N. F. M. Noah, R. N. R. Sulaiman, N. Jusoh, W. T. Tan, Emulsion liquid membrane modeling for chromium removal from electroplating wastewater using TOMAC as a carrier, *Water Environment Research*, 93 (2021):1669-1679.
32. Z. Seifollahi and A. Rahbar-Kelishami, Diclofenac extraction from aqueous solution by an emulsion liquid membrane: parameter study and optimization using the response surface methodology, J*ournal of Molecular Liquids*, 231 (2017): 1-10.
33. M. A. D. Sawsan, N. Zouli, M. A. Dahhan, Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane stabilized by the combination of surfactant and ionic liquid, *Desalination, 110* (2018): 168-179.
34. D. C. Panadare, V. K. Rathod, Applications of Waste Cooking Oil Other Than Biodiesel: A Review, *Iranian Journal of Chemical Engineering*, 12 (2015). 55–76, 2015.
35. M. Patel, R. Kumar, K. Kishor, T. Mlsna, C. U. Pittman Jr, D.Mohan, Pharmaceuticals of emerging concern in aquatic systems: chemistry, occurrence, effects, and removal methods, *Chemical reviews* 119 (2019): 3510-3673.
36. M. Ariffin, T. S. T Zakili. Household pharmaceutical waste disposal in Selangor, Malaysia—policy, public perception, and current practices, *Environmental management*, 64 (2019): 509-519.
37. J. Heo, S. Kim, N. Her, C. M. Park, M. Yu, Y. Yoon, Removal of contaminants of emerging concern by FO, RO, and UF membranes in water and wastewater, *Contaminants of Emerging Concern in Water and Wastewater* (2020): 139-176.
38. B. M. Sharma, J. Bečanová, M. Scheringer, A. Sharma, G. K. Bharat, P. G. Whitehead, J. Klánová, L. Nizzetto, Health and ecological risk assessment of emerging contaminants (pharmaceuticals, personal care products, and artificial sweeteners) in surface and groundwater (drinking water) in the Ganges River Basin, India , *Science of the Total Environment*, 646 (2019): 1459-1467.
39. S. M. Praveena, S. N. M.Shaifuddin, S. Sukiman, F. A. M. Nasir, Z. Hanafi, N. Kamarudin, T. H. T. Ismail, A. Z. Aris, Pharmaceuticals residues in selected tropical surface water bodies from Selangor (Malaysia): Occurrence and potential risk assessments, *Science of the total environment*, 642 (2018): 230-240. 37

40. J. Rivera-Utrilla, M. Sánchez-Polo, M. Á.s Ferro-García, G. Prados-Joya, R.Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, *Chemosphere*, 93 (2013): 1268-1287.
41. A. L. Ahmad, N. D. Zaulkiflee, A. Kusumastuti, M. M. H. Shah Buddin, Removal of acetaminophen from aqueous solution by emulsion liquid membrane: emulsion stability study, *Industrial & Engineering Chemistry Research*, 58 (2018): 713-719.
42. Y. Ji, Z. Du, H. Zhang, Y. Zhang., Rapid analysis of non-steroidal anti-inflammatory drugs in tap water and drinks by ionic liquid dispersive liquid–liquid microextraction coupled to ultra-high performance supercritical fluid chromatography, *Analytical Methods*, 6 (2014): 7294-7304.
43. T. Lin, S.Yu, Wei Chen, Occurrence, removal and risk assessment of pharmaceutical and personal care products (PPCPs) in an advanced drinking water treatment plant (ADWTP) around Taihu Lake in China, *Chemosphere*, 152 (2016): 1-9.
44. O. M. Rodriguez, J. N. Peralta-Hernandez, A. Goonetilleke, E.R. Bandala. Treatment technologies for emerging contaminants in water: A review, *Chemical Engineering Journal*, 323 (2017): 361-380.
45. H. F. D. Almeida, I. M. Marrucho, M. G. Freire, Removal of nonsteroidal anti-inflammatory drugs from aqueous environments with reusable ionic-liquid-based systems, *ACS Sustainable Chemistry & Engineering* 5 (2017): 2428-2436.
46. K. Balakrishna, A. Rath, Y. Praveenkumarreddy, K. S. Guruge, B. Subedi, A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies, *Ecotoxicology and environmental safety* 137 (2017): 113-120.
47. M. Parolini, Toxicity of the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) acetylsalicylic acid, paracetamol, diclofenac, ibuprofen and naproxen towards freshwater invertebrates: A review, *Science of the Total Environment* 740 (2020): 140043.
48. T. Xiong, X. Yuan, H. Wang, Z. Wu, L. Jiang, L. Leng, K. Xi, X.Cao, G. Zeng, Highly efficient removal of diclofenac sodium from medical wastewater by Mg/Al layered double hydroxide-poly (m-phenylenediamine) composite, *Chemical Engineering Journal*, 366 (2019): 83-91.

49. C. Toledo-Neira, A. Álvarez-Lueje. Ionic liquids for improving the extraction of NSAIDs in water samples using dispersive liquid–liquid microextraction by high performance liquid chromatography-diode array–fluorescence detection., *Talanta*, 134 (2015): 619-626.
50. K. D. Rainsford, Ibuprofen: pharmacology, efficacy and safety, *Inflammopharmacology* 17 (2009): 275-342.
51. R. Davarnejad, B. Soofi, F. Farghadani, R. Behfar, Ibuprofen removal from a medicinal effluent: A review on the various techniques for medicinal effluents treatment, *Environmental Technology & Innovation*, 11 (2018): 308-320.
52. L. Moulahcene, O. Kebiche-Senhadji, M. Skiba, M. Lahiani-Skiba, F. Oughlis-Hammache, M. Benamor, Cyclodextrin polymers for ibuprofen extraction in aqueous solution: recovery, separation, and characterization, *Desalination and Water Treatment*, 57, (2016): 11392-11402.
53. L. Rafati, M. H. Ehrampoush, A. A. Rafati, M. Mokhtari, A. H. Mahvi, Removal of ibuprofen from aqueous solution by functionalized strong nano-clay composite adsorbent: kinetic and equilibrium isotherm studies, *International Journal of Environmental Science And Technology*, 15 (2018): 513-524.
54. V. D. Talnikar, Y.S. Mahajan, Recovery of acids from dilute streams: A review of process technologies, *Korean Journal of Chemical Engineering*, 31 (2014): 1720-1731.
55. G. Du, L. Liu, J. Chen, White biotechnology for organic acids, *In Industrial Biorefineries & White Biotechnology*, (2015): 409-444.
56. J. Wang, S. Wang, Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review, *Journal of Environmental Management*,182 (2016): 620-640.
57. L. M. Madikizela, and L. Chimuka, Simultaneous determination of naproxen, ibuprofen and diclofenac in wastewater using solid-phase extraction with high performance liquid chromatography, *Water Sa* 43, (2017): 264-274.
58. M. A. Oturan, J. J Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, *Critical Reviews in Environmental Science and Technology*, 44 (2014): 2577-2641.

59. L. Mzukisi, N. Tawanda, L. Chimuka, Applications of molecularly imprinted polymers for solid-phase extraction of non-steroidal anti-inflammatory drugs and analgesics from environmental waters and biological samples, *Journal of Pharmaceuticals and Biomedical Analysis*, 147 (2018): 624–633, 2018.
60. M. Zawadzki, F. A. e Silva, U. Domańska,J. A. P Coutinho, S. P.M. Ventura, Recovery of an antidepressant from pharmaceutical wastes using ionic liquid-based aqueous biphasic system, *Green Chemistry,* 18 (2016): 3527-3536.
61. S. Álvarez-Torrellas, J. A. Peres, V. Gil-Álvarez, G. Ovejero,, J. García, Effective adsorption of non-biodegradable pharmaceuticals from hospital wastewater with different carbon material, *Chemical Engineering Journal*, 320 (2017): 319-329.
62. M. Chakraborty, C. Bhattacharya, and S. Datta, Emulsion liquid membranes: Definitions and classification, theories, module design, applications, new directions and perspectives, *Liquid membranes, Principles and Applications in Chemical Separations and Wastewater Treatment, (*2010):141-199. Elsevier
63. M. Ahmad, M. Ali, F. Nabi, Ionic liquids in supported liquid membrane technology, *Chemical Engineering Journal,* 171, (2011): 242-254.
64. T. Eljaddi, L.Laurent, H. Miloudi, Review on mechanism of facilitated transport on liquid membranes, *Journal of Membrane Science and Research*, 3 (2017): 199-208.
65. R. D. Noble, J. Douglas Way, Applications of liquid membrane technology, Liquid membranes, ACS publications (1987):110-122
66. M. Peng, L. M. Vane, and S. X. Liu, Recent advances in VOCs removal from water by pervaporation, *Journal of Hazardous Materials*, 98 (2003): 69-90.
67. A. M. Sastre, A. Kumar, J. P. Shukla, aR. K. Singh, Improved techniques in liquid membrane separations: an overview, *Separation and Purification Methods,* 27, (1998): 213-298.
68. G. Zante, M. Boltoeva, A. Masmoudi, and R. Barillon, Supported ionic liquid and polymer inclusion membranes for metal separation, *Separation & Purification Reviews*, (2021):1-17.
69. B. Keskin, B. Z. -Gökoğlu, I. Koyuncu, Polymer inclusion membrane applications for transport of metal ions: A critical review, *Chemosphere*, (2021): 130604.

70. A. Kargari, Simultaneous extraction and stripping of 4-chlorophenol from aqueous solutions by emulsion liquid membrane, *Desalination and Water Treatment,* 51(2013):2275-2279.
71. V. S. Kislik, Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment, (2010):1-15, Burlington, Elsevier.
72. K. Anarakdim, G. Gutiérrez, Á. Cambiella, O. S. -Kebiche, M. Matos, The effect of emulsifiers on the emulsion stability and extraction efficiency of Cr (VI) using emulsion liquid membranes (ELMs) formulated with a green solvent. *Membranes,* 10 (2020)
73. S. Zereshki, A. Shokri, A. Karimi, Application of a green emulsion liquid membrane for removing copper from contaminated aqueous solution: Extraction, stability, and breakage study using response surface methodology, *Journal of Molecular Liquids* 325 (2021): 115251.
74. S. H. Chang, Vegetable oil as organic solvent for wastewater treatment in liquid membrane processes, *Desalination and Water Treatment*, 52(2014) 88–101.
75. S. Gupta, Pritam B. Khandale, M. Chakraborty, Application of emulsion liquid membrane for the extraction of diclofenac and relationship with the stability of water-in-Oil emulsions, *Journal of Dispersion Science and Technology*, (2019):1579655.
76. X. Feng, S. Toufouki, Z. Li, Y. Li, and S. Yao, A highly hyphenated preparative method with emulsion liquid membrane extraction-in situ magnetization-magnetic separation for bioactive constituents from typical medicinal plant, *Separation and Purification Technology*, 275 (2021): 119249.
77. Q. Al-Obaidi, M. Alabdulmuhsin, A. Tolstik, J. G. Trautman, and M. Al-Dahhan, Removal of hydrocarbons of 4-nitrophenol by emulsion liquid membrane (ELM) using magnetic Fe_2O_3 nanoparticles and ionic liquid, *Journal of Water Process Engineering,* 39 (2021): 101729.
78. J. Tang, S. Liang, B. Dong, Y. Li, and S. Yao, Extraction and quantitative analysis of tropane alkaloids in Radix physochlainae by emulsion liquid membrane with tropine-based ionic liquid, *Journal of Chromatography A,* 1583 (2019): 9-18.
79. A. A. Mohammed, M. A. Atiya, M. A. Hussein, Removal of antibiotic tetracycline using nano-fluid emulsion liquid membrane: Breakage, extraction and stripping

studies, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 595 (2020): 124680.

80. P. Zaheri, R. Davarkhah, Rapid removal of uranium from aqueous solution by emulsion liquid membrane containing thenoyltrifluoroacetone, *Journal of Environmental Chemical Engineering*, 5 (2017): 4064-4068.
81. H. M. Salman and A. A. Mohammed, Extraction of lead ions from aqueous solution by co-stabilization mechanisms of magnetic Fe_2O_3 particles and nonionic surfactants in emulsion liquid membrane, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 568 (2019): 301-310.
82. M. Raji, H. Abolghasemi, J. Safdari, and A. Kargari, Response Surface Optimization of Dysprosium Extraction Using an Emulsion Liquid Membrane Integrated with Multi-Walled Carbon Nanotubes, *Chemical Engineering & Technolog*, 41 (2018): 1857-1870.
83. N. D. Zaulkiflee, M. M. Shah Buddin, A. L. Ahmad, Extraction of acetaminophen from aqueous solution by emulsion liquid membrane using taylor-couette column, International Journal of Engineering, 31(2018): 1413-1420.
84. A. L Ahmad, Z. M. H. M. Shafie, N. D. Zaulkiflee, W. Y.Pang, Preliminary study of emulsion liquid membrane formulation on acetaminophen removal from the aqueous phase, *Membranes*, 9 (2019): 133.
85. A. A. Mohammed, M. A. Atiya, M. A. Hussein, Studies on membrane stability and extraction of ciprofloxacin from aqueous solution using Pickering emulsion liquid membrane stabilized by magnetic nano-Fe_2O_3, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 585 (2020): 124044.
86. S. A. M. Mohammed, Investigating the performance of ELM systems in separating organic pollutants from industrial wastewater, *Journal of Water Process Engineering*,13 (2016): 79-87.
87. N. Jusoh, M. B.Rosly, N. Othman, H. A. Rahman, N. F. M. Noah, R. N. R Sulaiman, Selective extraction and recovery of polyphenols from palm oil mill sterilization condensate using emulsion liquid membrane process, *Environmental Science and Pollution Research* 27 (2020): 23246-23257.

88. P. D. Nasab, A. R. Kelishami, J. Safdari, H. Abolghasemi, Selective separation and enrichment of neodymium and gadolinium by emulsion liquid membrane using a novel extractant CYANEX, *Minerals Engineering*, 117 (2018): 63-73.
89. A. L. Ahmad, M. H. Z. M. Harun, M. K. A. Jasni, N. D. Zaulkiflee, Removal of Ibuprofen at Low Concentration Using a Newly Formulated Emulsion Liquid Membrane, *Membranes*, 11 (2021): 740.
90. N. Jusoh, R. N. R. Sulaiman, N. Othman, N. F. M. Noah, M. B. Rosly, H. A. Rahman, Development of vegetable oil-based emulsion liquid membrane for downstream processing of bio-succinic acid, *Food and Bioproducts Processing*, 119 (2020): 161-169.
91. N. Othman, N. F. M Noah, L. M. Shu, Z. Y. Ooi, N. Jusoh, M. Idroas, M. Goto, Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process, *Chinese Journal of Chemical Engineering*, 25 (2017): 45-52
92. P. Daraei, S. Zereshki, A. Shokri, Application of nontoxic green emulsion liquid membrane prepared by sunflower oil for water decolorization: process optimization by response surface methodology, *Journal of Industrial and Engineering Chemistry*, 77 (2019): 215-222.
93. N. Jusoh, N. Othman, N. A. Nasruddin, Emulsion liquid membrane technology in organic acid purification, *Malaysian Journal of Analytical Sciences*, 20 (2016): 436-443.
94. N. Jusoh, N. F. M. Noah, N. Othman, Extraction and recovery optimization of succinic acid using green emulsion liquid membrane containing palm oil as the diluent, *Environmental Progress & Sustainable Energy*, 38 (2019): e13065.
95. M. B. Rosly, N.Jusoh, N.Othman, H. A. Rahman, N. F. M. Noah, R. N. R. Sulaiman, Effect and optimization parameters of phenol removal in emulsion liquid membrane process via fractional-factorial design, *Chemical Engineering Research and Design*, 145 (2019): 268-278.
96. S. Björkegren, R. F. Karimi, A. Martinelli, N. S. Jayakumar, M. A. Hashim, A new emulsion liquid membrane based on a palm oil for the extraction of heavy metals, *Membranes* 5(2015): 168-179.

97. N. Othman, R. N. Raja Sulaiman, H. A. Rahman, N. F. M. Noah, N. Jusoh, M. Idroas, Simultaneous extraction and enrichment of reactive dye using green emulsion liquid membrane system, *Environmental Technology*, 40 (2019): 1476-1484.
98. P. Davoodi-Nasab, A. Rahbar-Kelishami, M. Raji-Asadabadi, Fast and efficient chromium (VI) pertraction with Aliquat 336 in emulsion liquid membrane using sunflower oil as a high potential solvent, *Desalination and Water Treatment*, 80 (2017): 234-246.
99. A. Orjuela, J. Clark, Green chemicals from used cooking oils: Trends, challenges, and opportunities, Current opinion in green and sustainable chemistry 26 (2020): 100369
100. S. Samantam, R. R. Sahoo, Waste Cooking (Palm) Oil as an Economical Source of Biodiesel Production for Alternative Green Fuel and Efficient Lubricant, *Bioenergy Research,*14 (2021) 163–174,
101. E. K. Sachin, A. Ramachandran, K. Palanivelu, D. A. Syrtsova, V. V. Teplyakov, S. Kunalan, Waste cooking oil as an efficient solvent for the production of urea precursor ammonium carbamate from carbon dioxide, Greenhouse Gases, *Science and Technology*, 11 (2021): 222-231.
102. W. Li, R. Guan, X. Yuan, H. Wang, S. Zheng, L. Liu X.Chen, Product Soap from Waste Cooking Oil, In IOP Conference Series: *Earth and Environmental Science*, 510 (2020): 042038.
103. A. Shokri, P. Daraei, S. Zereshki. Water decolorization using waste cooking oil: An optimized green emulsion liquid membrane by RSM, *Journal of Water Process Engineering*, 33 (2020): 101021.
104. M. M. H. Shah Buddin, A. L. Ahmad, A. T. A.Khalil, S. W. Puasa. A review of demulsification technique and mechanism for emulsion liquid membrane applications, *Journal of Dispersion Science and Technology,* (2020): 1-18.
105. G. Villora, Liquid membranes, Supported and Emulsion, *Membrane Materials, Characterization and Module Design,* (2013) 1-45.
106. R. M. Pfeiffer, A. L. Bunge, Calculating leakage in emulsion liquid membrane systems from pH measurements, *Separation and Purification Technology*, 235 (2020): 116162.

107. N. D. Zaulkiflee, A. L. Ahmad, J. Sugumaran, N. Fahanis C. Lah, Stability Study of Emulsion Liquid Membrane via Emulsion Size and Membrane Breakage on Acetaminophen Removal from Aqueous Solution Using TOA, *ACS Omega* , (2020): 23892-23897.

108. Y. Wan, X. Zhang, Swelling determination of W/O/W emulsion liquid membranes, *Journal of Membrane Science*, 196 (2002) 185-201

109. B. Khadem, M. Khellaf, N. Sheibat-Othman, Investigating swelling-breakdown in double emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 585 (2020): 124181

110. Y. Park, Development and optimization of novel emulsion liquid membranes stabilized by non-Newtonian conversion in Taylor Couette flow for extraction of selected organic and metallic contaminants, Ph.D thesis, Georgia Institute of Technology, 2006.

111. J. Wang, J. Luo, S. Feng, H. Li, Y. Wan, X. Zhang, Recent development of ionic liquid membranes, *Green Energy & Environment*, 1(2016):43–61.

112. H. W. Khan, A. V. B. Reddy, M. M. E. Nasef, M. A. Bustam, M. Goto, M. Moniruzzaman, Screening of ionic liquids for the extraction of biologically active compounds using emulsion liquid membrane: COSMO-RS prediction and experiments, *Journal of Molecular Liquids*, 309 (2020): 113122.

113. A. Pozarska, C. Da Costa Mathews, M. Wong, and K. Pencheva, Application of COSMO-RS as an excipient ranking tool in early formulation development, *European Journal of Pharmaceutical Sciences,* 49 (2013): 505-511.

114. N. Adawiyah, M. Moniruzzaman, S. Hawatulaila, and M. Goto, onic liquids as a potential tool for drug delivery systems, *MedChemComm* 7 (2016): 1881-1897.

115. M. Smiglak, J. M. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D.. R. Macfarlane, and R.D. Rogers, Ionic liquids for energy, materials, and medicine, *Chemical Communications,* 66 (2014): 9228-9250.

116. Z. Seifollahi, A. R. Kelishami, Amoxicillin extraction from aqueous solution by emulsion liquid membranes using response surface methodology, *Chemical Engineering & Technology,* 42 (2019): 156-166.

117. S. Chaouchi, O. Hamdaoui, Acetaminophen extraction by emulsion liquid membrane using Aliquat 336 as extractant, *Separation and Purification Technology*, 129 (2014): 32-40.

118. A. B. Lende, M. K. Dinker, V. K. Bhosale, S. P. Kamble, P. D. Meshram, P. S. Kulkarni., Emulsion ionic liquid membranes (EILMs) for removal of Pb (II) from aqueous solutions, *RSC Advances*, 94 (2014): 52316-52323.

119. R. N. R. Sulaiman, N. Othman, N. A. S. Amin, Emulsion liquid membrane stability in the extraction of ionized nano silver from wash water, *Journal of Industrial and Engineering Chemistry*, 20 (2014): 3243-3250.

120. A. Balasubramanian, S. Venkatesan, Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid [BMIM]+[PF_6]− in Tributyl phosphate, *Desalination*, 289 (2012): 27-34

121. R. K. Goyal, N. S. Jayakumar, M. A. Hashim, Chromium removal by emulsion liquid membrane using $[BMIM]^+[NTf2]^-$ as stabilizer and TOMAC as extractant, *Desalination*, 278 (2011): 50-56

122. S. Venkatesan, K. M. Meera Sheriffa Begum, Emulsion liquid membrane pertraction of benzimidazole using a room temperature ionic liquid (RTIL) carrier, *Chemical Engineering Journal*, 148 (2009): 254-262.

123. A. L. Ahmad, M. M. H Shah Buddin, B. S. Ooi, Adhi Kusumastuti, Utilization of environmentally benign emulsion liquid membrane (ELM) for cadmium extraction from aqueous solution, *Journal of Water Process Engineering*, 15 (2017): 26-30.

124. R. Anantharaj, T. Banerjee, COSMO-RS-based screening of ionic liquids as green solvents in denitrification studies, *Industrial & Engineering Chemistry Research*, 49 (2010): 8705-8725.

125. P. Cysewski, Prediction of ethenzamide solubility in organic solvents by explicit inclusions of intermolecular interactions within the framework of COSMO-RS-DARE, *Journal of Molecular Liquids*, 290 (2019): 111163.

126. A. Klamt, M. Diedenhofen, COSMO-RS as a tool for property prediction of IL mixtures-A review, *Fluid Phase Equilibria*, 294 (2010): 1-2.

127. Z. Rashid, C. D. Wilfred, N. Gnanasundaram, A. Arunagiri, T. Murugesan, Screening of ionic liquids as green oilfield solvents for the potential removal of

asphaltene from simulated oil: COSMO-RS model approach, Journal *of Molecular Liquids*, *255* (2018): 492-503.

128. A. Klamt, Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena, *Journal of Physical Chemistry*. 99 (1995), 2224-2235.

129. K. Paduszyński, An overview of the performance of the COSMO-RS approach in predicting the activity coefficients of molecular solutes in ionic liquids and derived properties at infinite dilution, Physical Chemistry Chemical Physics 19 (2017): 11835-11850.

130. A. Klamt, F. Eckert, COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids, *Fluid Phase Equilibria*, 172 (2000): 43-72.

131. E. Mullins, R. Oldland, Y. A. Liu, S. Wang, S. I. Sandler, C. C. Chen, M. Zwolak, K. C. Seavey, Sigma-profile database for using COSMO-based thermodynamic methods, *Industrial & Engineering Chemistry Research*, 45 (2006): 4389-4415.

132. G. Oliveira, J. P. Wojeicchowski, F. O. Farias, L. I. Mafra, R. P. Soares, M. R. Mafra, Enhancement of biomolecules solubility in aqueous media using designer solvents as additives: An experimental and COSMO-based models approach, *Journal of Molecular Liquids*, 318 (2020): 114266.

133. S. Fernandez, V. P. Esteiro, R. Santiago, D. Moreno, J. Palomar, and E. Tojo, Design and synthesis of alverine-based ionic liquids to improve drug water solubility, *New Journal of Chemistry*, 44 (2020): 20428-20433.

134. J. Esteban, A. J. Vorholt, W. Leitner, An overview of the biphasic dehydration of sugars to 5-hydroxymethylfurfural and furfural: a rational selection of solvents using COSMO-RS and selection guides, *Green Chemistry*, 22(2020): 2097-2128

135. K. A. Kurnia, S. Harimurti, H. K Yung, A. Baraheng, M. A. S. Alimin, N. S. M.Dagang, A. Fadhilah, R. Rosyadi, W. Z. N.Yahya, M. A.Bustam, Understanding the effect of pH on the solubility of Gamavuton-0 in the aqueous solution: Experimental and COSMO-RS modelling, *Journal of Molecular Liquids*, 296 (2019): 111845.

136. N. Andreas, N. Wyttenbach, M. Kuentz, New prediction methods for solubility parameters based on molecular sigma profiles using pharmaceutical materials, *International Journal of Pharmaceutics*, 546 (2018): 137-144.

137. M. Lotfi, M. Moniruzzaman, M. Sivapragasam, S. Kandasamy, M. I. A. Mutalib, N. B. Alitheen, M. Goto, Solubility of acyclovir in nontoxic and biodegradable ionic liquids: COSMO-RS prediction and experimental verification, *Journal of Molecular Liquids*, 243 (2017): 124-131.

138. M. Lotfi, M. Moniruzzaman, M. I. A. Mutalib, C. D.Wilfred, N. B. Alitheen, M. Goto, Analysis of multiple solvation interactions of methotrexate and ammonium based ionic liquids using COSMO-RS, *Procedia Engineering*, 148 (2016): 459-466.

139. B. Bouillot, S. Teychené, B. Biscans, An evaluation of thermodynamic models for the prediction of drug and drug-like molecule solubility in organic solvents, *Fluid Phase Equilibria*, 309 (2011): 36-52.

140. I. Hahnenkamp, G. Graubner, J. Gmehling, Measurement and prediction of solubilities of active pharmaceutical ingredients, *International Journal of Pharmaceutics*, *388* (2010): 73-81.

141. B. Burghoff, E. L. V. Goetheer, A. B. de Haan, COSMO-RS-based extractant screening for phenol extraction as model system, *Industrial & Engineering Chemistry Research*, 47 (2008): 4263-4269.

142. L. F. Žilnik, A. Jazbinšek, A. Hvala, F. Vrečer, A. Klamt, Solubility of sodium diclofenac in different solvents, *Fluid Phase Equilibria*, 261, (2007): 140-145.

143. H. Ikeda, K.Chiba, A. Kanou, N.Hirayama, Prediction of solubility of drugs by conductor-like screening model for real solvents, *Chemical and Pharmaceutical Bulletin*, 53 (2005): 253-255.

144. H. Palmelund, M.P. Andersson, C. J. Asgreen, B. J. Boyd, J. Rantanen, K. Löbmann, Tailor-made solvents for pharmaceutical use? Experimental and computational approach for determining solubility in deep eutectic solvents (DES), *International Journal of Pharmaceutics*: 1 (2019): 100034.

145. K. Abbassian, A. Kargari, Modification of membrane formulation for stabilization of emulsion liquid membrane for extraction of phenol from aqueous solutions, *Journal of Environmental Chemical Engineering*, 4 (2016): 3926-3933.

146. L. Boyadzhiev, “MEMBRANE SEPARATIONS | Liquid Membranes,” in Encyclopedia of Separation Science, 2000, pp. 1739–1748.

147. N. F. M. Noah, R. N. R. Sulaiman, N. Othman, N. Jusoh, M. B. Rosly, Extractive continuous extractor for chromium recovery: Chromium (VI) reduction to chromium (III) in sustainable emulsion liquid membrane process, *Journal of Cleaner Production*, 247 (2020): 119167.

148. N. Othman, K. H. Chan, M. Goto, H. Mat, Emulsion liquid membrane extraction of silver from photographic waste using CYANEX 302 as the mobile carrier, *Solvent Extraction Research and Development*, 13 (2006): 191-202.

149. A. Benderrag, B. Haddou, M. Daaou, H. Benkhedja, B. Bounaceur, M. Kameche, Experimental and modeling studies on Cd (II) ions extraction by emulsion liquid membrane using Triton X-100 as biodegradable surfactant, *Journal of Environmental Chemical Engineering*, 7 (2019): 103166.

150. S. Muthusaravanan, S. v. Priyadharshini, N. Sivarajasekar, R. Subashini, S. Sivamani, S. Dharaskar, N. Dhakal, Optimization and extraction of pharmaceutical micro-pollutant-norfloxacin using green emulsion liquid membranes, *Desalination and Water Treatment*, 156 (2019): 238-244.

151. T. A. Razo Alejandra, M. Stambouli, M. del P. González-Muñoz, D. Pareau, M. Ávila-Rodríguez, Emulsion liquid membranes for recovery of ibuprofen from aqueous solutions, *Journal of Chemical Technology & Biotechnology*, 89 (2014): 890-898

152. R. Shirasangi, H. P. Kohli, S.Gupta, Chakraborty, Separation of Methylparaben by emulsion liquid membrane: Optimization, characterization, stability and multiple cycles studies, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 597 (2020): 124761.

153. B. Sumalatha, A. V. Narayana, K. K. Kumar, D. J. Babu, T. C. Venkateswarulu. Phenol Removal from Industrial Effluent Using Emulsion Liquid Membranes, *Journal of Pharmaceutical Sciences and Research*, 8 (2016): 307

154. R. M. Pfeiffer, A. L. Bunge, Leakage and swell in emulsion liquid membrane systems: Comparing continuous stirred-tank reactor and batch experiments, *Journal of Industrial and Engineering Chemistry*, 87 (2020): 68-77.

155. M. B. Rosly, N. Jusoh, N.Othman, H. A. Rahman, R. N. R. Sulaiman, N. F. M. Noah, Stability of emulsion liquid membrane using bifunctional diluent and blended nonionic surfactant for phenol removal, *Chemical Engineering and Processing-Process Intensification*, 148 (2020): 107790.

156. A. Kumar, A. Thakur, P. S. Panesar, Stability analysis of environmentally benign green emulsion liquid membrane, *Journal of Dispersion Science and Technology*, 39 (2018): 1510-1517.

157. N. Jusoh, N. Othman, Stability of palm oil-based emulsion liquid membrane for succinic acid extraction from aqueous solution, *Journal of Applied Membrane Science & Technology*, 19 (2016).

158. A. L. Ahmad, M. M. H. Shah Buddin, B. S. Ooi, A. I. Kusumastuti, Cadmium removal using vegetable oil-based emulsion liquid membrane (ELM): Membrane breakage investigation, *Jurnal Teknologi*, 75 (2015).

159. M. Djenouhat, O.Hamdaoui, M.i Chiha, M. H. Samar, Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane: Part 2. Permeation and stripping, *Separation and Purification Technology*, 63 (2008): 231-238

160. S. Zereshki, P. Daraei, A. Shokri, Application of edible paraffin oil for cationic dye removal from water using emulsion liquid membrane, *Journal of Hazardous Materials*, 356 (2018): 1-8.

161. A. L. Ahmad, A. Kusumastuti, C. J. C. Derek, B. S. Ooi, Emulsion liquid membrane for cadmium removal: Studies on emulsion diameter and stability, *Desalination*, 287 (2012): 30-34.

162. H. P. Kohli, S. Gupta, M. Chakraborty, Stability and performance study of emulsion nanofluid membrane: A combined approach of adsorption and extraction of Ethyl paraben, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 579 (2019): 123675.

163. N. Othman, O. Z. Yi, S. N. Zailani, E. Z. Zulkifli, S. Subramaniam, Extraction of Rhodamine 6G dye from liquid waste solution: Study on emulsion liquid membrane stability performance and recovery, *Separation Science and Technology* 48 (2013): 1177-1183.

164. T. A. Razo, M. del Pilar González, M. Stambouli, D. Pareau, L. Hernández-Perales, M. A. Rodriguez, Chlorpheniramine recovery from aqueous solutions by emulsion liquid membranes using soy lecithin as carrier, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 536 (2018): 68-73.

165. A. Balasubramanian, S. Venkatesan, Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid [BMIM]+[PF6]− in Tributyl phosphate, *Desalination* 289 (2012): 27-34.

166. M. Yusuf, A. S. Farooqi, M. A. Alam, L. K. Keong, K. Hellgardt, B. Abdullah, Response surface optimization of syngas production from greenhouse gases via DRM over high performance Ni–W catalyst, *International Journal of Hydrogen Energy* (2021).

167. A. Kumar, A. Thakur, P. S. Panesar, Statistical optimization of lactic acid extraction using green emulsion ionic liquid membrane (GEILM), *Journal of Environmental Chemical Engineering*, 6 (2018): 1855-1864.

168. F. S. Hoseinian, B. Rezai, E. Kowsari, Optimization and separation mechanism of Ni (II) removal from synthetic wastewater using response surface method, *International Journal of Environmental Science and Technology*, 16 (2019): 4915-4924.

169. J. Zhou, X. M. Ma, B. H. Qiu, J. X Chen, L. Bian, L. M. Pan, Parameter's optimization of supercritical fluid-CO_2 extracts of frankincense using response surface methodology and its pharmacodynamics effects, *Journal of Separation Science*, 36 (2013): 383-390.

170. A. A. H. Saeed, , N. Y. Harun, M. M. Nasef, H. K. Afolabi, A. A. S. Ghaleb, Removal of Cadmium from Aqueous Solution by Optimized Magnetic Biochar Using Response Surface Methodology, *In Proceedings of the International Conference on Civil, Offshore and Environmental Engineering*, 119-126. Springer, Singapore, 2021.

171. M. S. Rajabi, M. Moniruzzaman, H.Mahmood, M. Sivapragasam, M. A. Bustam, Extraction of β-carotene from organic phase using ammonium based ionic liquids aqueous solution, Journal of Molecular Liquids 227 (2017): 15-20.

172. H. Asadian, A. Ahmadi, The extraction of gallium from chloride solutions by emulsion liquid membrane: Optimization through response surface methodology, *Minerals Engineering,* 148 (2020): 106207

173. M. B. Rosly, N. Jusoh, N.n Othman, H. A.Rahman, N. F. M. Noah, R. N. R. Sulaiman, Effect and optimization parameters of phenol removal in emulsion liquid membrane process via fractional-factorial design, Chemical Engineering Research and Design 145 (2019): 268-278.

174. H. Jiao, W. Peng, J. Zhao, C.n Xu, Extraction performance of bisphenol A from aqueous solutions by emulsion liquid membrane using response surface methodology, Desalination 313 (2013): 36-43.

175. R. N. R. Sulaiman, H. A. Rahman, N. Othman, M. B. Rosly, N. Jusoh, N. F. M. Noah, Extraction of reactive dye via synergistic Aliquat 336/D2EHPA using emulsion liquid membrane system, Korean Journal of Chemical Engineering 37 2020): 141-150.

176. A. Kumar, A. Thakur, P. S. Panesar, A comparative study on experimental and response surface optimization of lactic acid synergistic extraction using green emulsion liquid membrane, Separation and Purification Technology 211 (2019): 54-62.

177. A. Azarang, A. R. Kelishami, R. Norouzbeigi, H.Shayesteh, Modeling and optimization of pertraction performance of heavy metal ion from aqueous solutions using M2EHPA/D2EHPA: Application of response surface methodology." Environmental Technology & Innovation 15 (2019): 100432.

178. P. Davoodi-Nasab, A.Rahbar-Kelishami, J. Safdari, H. Abolghasemi, Selective separation and enrichment of neodymium and gadolinium by emulsion liquid membrane using a novel extractant CYANEX® 572, *Minerals Engineering,* 117 (2018): 63-73.

179. E. A. Fouad, A. Farooq, A. Naveed, Optimization of chromium extraction from aqueous solutions by emulsion liquid membrane, *Desalination and Water Treatment,* 65 (2017): 428-434.

180. M. Djenouhat, F. Bendebane, L. Bahloul, M. E. H Samar, F. Ismail, Optimization of methylene blue removal by stable emulsified liquid membrane using Plackett–

Burman and Box–Behnken designs of experiments, *Royal Society Open Science,* 5 (2018): 171220,

181. B. S. Chanukya, M. Kumar, N. K. Rastogi, Optimization of lactic acid pertraction using liquid emulsion membranes by response surface methodology, *Separation and Purification Technology*, 111. (2013) 1-8.

182. R. P. Cahn, N. N. Li, Separation of phenol from waste water by the liquid membrane technique, *Separation Science*, 9 (1974): 505-519.

183. Y. Wen, H.Cheng, L Lu, J.Liu, Y. Feng, W. Guan, Q. Zhou, X. Huang, Analysis of biological demulsification process of water-in-oil emulsion by Alcaligenes sp. S-XJ-1, *Bioresource technology, (*2010): 8315-8322.

184. M. T. A. Reis, O. M. F. Freitas, S.Agarwal, L. M. Ferreira, M. Rosinda C. Ismael, Remígio Machado, J. M. R. Carvalho, Removal of phenols from aqueous solutions by emulsion liquid membranes, *Journal of Hazardous Materials*, 192 (2011): 986-994.

185. W. Peng, H. Jiao, H.Shi, Chunjian Xu, The application of emulsion liquid membrane process and heat-induced demulsification for removal of pyridine from aqueous solutions, Desalination, 286 (2012): 372-378

186. A. Manzak, O. Tutkun, The extraction of lactic acid by emulsion type of liquid membranes using alamine 336 in escaid 100, Canadian Journal of Chemical Engineering, 89 (2011) 1458-1463.

187. A. Dâas, O. Hamdaoui, Removal of non-steroidal anti-inflammatory drugs ibuprofen and ketoprofen from water by emulsion liquid membrane., Environmental Science and Pollution Research 21, (2014): 2154-2164

188. Y. Liu, Y. Sun, Z. Peng, Evaluation of bipolar membrane electrodialysis for desalination of simulated salicylic acid wastewater, *Desalination* 537 (2022): 115866.

189. T. Jeliński, P. Cysewski, Screening of ionic liquids for efficient extraction of methylxanthines using COSMO-RS methodology, *Chemical Engineering Research and Design* 122 (2017): 176-183.

190. M. Markowitz, A convenient method for preparation of quaternary ammonium salts, *The Journal of Organic Chemistry*, 22 (1957): 983-984.

191. H. Zhang, M. Shang, C. Shen, G. Li, Y. Su, Continuous Extraction of Gold (III) Using Pyridine Ionic Liquid-Based Water-in-Oil Microemulsion in Microreactors, *Industrial & Engineering Chemistry Research* 58 (2019): 12729-12740.

192. Y. Long, Q. Sang, M. Dong, Y. Yuan, Effects of interfacial tension and droplet size on the plugging performance of oil-in-water emulsions in porous media., *Industrial & Engineering Chemistry Research*, 56(2017): 9237-9246.

193. N. Politova, S. Tcholakova, N. D. Denkov, Factors affecting the stability of water-oil-water emulsion films, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 522 (2017): 608-620.

194. S. Samsnavith, A. Varun, N. Gowtham, S. Samdavid, Removal of phenol from aqueous phenol solution using bio-emulsion, *Separation and Purification Technology*, 275 (2021): 119138.

195. S. S. Bhattacharya, S. Banerjee, A. K. Ghosh, P. Chattopadhyay, A. Verma, A. Ghosh, A RP-HPLC method for quantification of diclofenac sodium released from biological macromolecules, International Journal of Biological Macromolecules, 58 (2013): 354-359.

196. L. Y. Garcia-Chavez, A. J. Hermans, B. Schuur, A. B. de Haan, COSMO-RS assisted solvent screening for liquid–liquid extraction of mono ethylene glycol from aqueous streams, *Separation and Purification Technology*, 97 (2012): 2-10.

197. Y. Chu, X. He, MoDoop: an automated computational approach for COSMO-RS prediction of biopolymer solubilities in ionic liquids, *ACS omega* 4 (2019): 2337-2343.

198. S. R. Motlagh, R. Harun, D. R. A.Biak, S. A.Hussain, A. A. Elgharbawy, Ramin Khezri, and C. D.Wilfred, Prediction of Potential Ionic Liquids (ILs) for the Solid–Liquid Extraction of Docosahexaenoic Acid (DHA) from Microalgae Using COSMO-RS Screening Model, Biomolecules, 10 (2020): 1149

199. N. I. M. F. Hilmy, W. Z.N. Yahya, K. A.Kurnia, Eutectic ionic liquids as potential electrolytes in dye-sensitized solar cells: Physicochemical and conductivity studies, *Journal of Molecular Liquids*, 320 (2020): 114381.

200. S. R. Rezaei, R. Harun, D. R. A. Biak, S. A. Hussain, R. Omar, A. A. Elgharbawy, COSMO-RS based prediction for alpha-linolenic acid (ALA)

extraction from microalgae biomass using room-temperature ionic liquids (RTILs), *Marine drugs*, 18 (2020): 108.

201. S. R. Motlagh, R.Harun, D. R. A. Biak, S. A. Hussain, W. A. W. Wan Ab Karim Ghani, R.Khezri, C. D. Wilfred, A. A. M Elgharbawy, Screening of suitable ionic liquids as green solvents for extraction of eicosapentaenoic acid (EPA) from microalgae biomass using COSMO-RS model, *Molecules* 24 (2019): 713.
202. R. Anantharaj, Tamal Banerjee, COSMO-RS based predictions for the desulphurization of diesel oil using ionic liquids: Effect of cation and anion combination, *Fuel Processing Technology*, 92(2011): 39-52.
203. A. S. Khan, T. H. Ibrahim, Z. Rashid, M. I. Khamis, P. Nancarrow, N. A. Jabbar, COSMO-RS based screening of ionic liquids for the extraction of phenolic compounds from aqueous media, *Journal of Molecular Liquids*, 328 (2021): 115387.
204. B. Baek, S. Lee, C.Jung, Pyrrolidinium cation-based ionic liquids with different functional groups: butyl, butyronitrile, pentenyl, and methyl butyrate, *International Journal of Electrochemistry*, Sci 6 (2011): 6220-6234.
205. S. R. Motlagh, A. A. Elgharbawy, R. Harun, D. R. A. Biak, S. A.Hussain, Ionic liquid method for the extraction of lipid from microalgae biomass: a review, *Biomass Conversion Biorefinery* (2021): 1-23.
206. L. Kumar, T. Banerjee, K. Mohanty, Prediction of selective extraction of cresols from aqueous solutions by ionic liquids using a theoretical approach, *Separation Science and Technology*, 46 (2011): 2075-2087.
207. M. Gras, L. Duclos, N. Schaeffer, V. Mogilireddy, L. Svecova, E. Chainet, I. Billard, N. Papaiconomou, A Comparison of Cobalt and Platinum Extraction in Hydrophobic and Hydrophilic Ionic Liquids: Implication for Proton Exchange Membrane Fuel Cell Recycling, *ACS Sustainable Chemistry & Engineering*, 42 (2020): 15865-15874.
208. S. Schlosser, J. Marták, M. Blahušiak, Specific phenomena in carboxylic acids extraction by selected types of hydrophobic ionic liquids, Chemical Papers, 72 (2018): 567-584.
209. C. U. Mussagy, N. L. Tabanez, F. O. Farias, K.A. Kurnia, M. R.. Mafra, J. F. B Pereira, Determination, characterization, and modeling of aqueous biphasic

systems composed of propylammonium-based ionic liquids and phosphate salts, *Chemical Physics Letters*, 754 (2020): 137623.

210. C. L. S Louros, A. F. M. Cláudio, C. M. S. S. Neves, Mara G. Freire, I. M. Marrucho, J. Pauly, J. A. P Coutinho, Extraction of biomolecules using phosphonium-based ionic liquids+ K_3PO_4 aqueous biphasic systems, *International Journal of Molecular Sciences*, 11 (2010): 1777-1791

211. A. A. Mohammed, M. A. Atiya, M. A. Hussein, Simultaneous studies of emulsion stability and extraction capacity for the removal of tetracycline from aqueous solution by liquid surfactant membrane, *Chemical Engineering Research and Design*, 159 (2020): 225-235.

212. H. P. Kohli, S. Gupta, M. Chakraborty, Extraction of Ethylparaben by emulsion liquid membrane: Statistical analysis of operating parameters, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 539 (2018): 371-381.

213. A. Dawelbeit, M. Yu, Transient Confinement of the Quaternary Tetramethylammonium Tetrafluoroborate Salt in Nylon 6, 6 Fibres: Structural Developments for High-Performance Properties, *Materials*, 14, 11 (2021): 2938.

214. Y. Pore. V. Mangrule, M.Mane, A. Chopade, Preparation, characterization and physicochemical studies of diclofenac ionic liquids, *Asian Journal of Pharmacy and Pharmacology*, (3 (2017): 208-214.

215. K. Abbassian, A. Kargari, Modification of membrane formulation for stabilization of emulsion liquid membrane for extraction of phenol from aqueous solutions, 4 (2016): 3926-3933.

216. X. Luo, H. Gong, J. Cao, H. Yin, Y. Yan, Limin He, Enhanced separation of water-in-oil emulsions using ultrasonic standing waves, *Chemical Engineering Science*, 203 (2019): 285-292.

217. N. Jusoh, Palm oil-based emulsion liquid membrane formulation for succinic acid extraction performance, Ph.D thesis, *Universiti Teknologi Malaysia, Malaysia* (2017),

218. L. Zheng, B. Onghena, X. Li, Z. Zhang, K. Binnemans, enhancing metal separations using hydrophilic ionic liquids and analogues as complexing agents in the more polar phase of liquid–liquid extraction systems, *Industrial & Engineering Chemistry Research*, 34 (2019): 15628-15636.

219. M. S. Gasser, N. E. El-Hefny, A. Daoud, Extraction of Co (II) from aqueous solution using emulsion liquid membrane, *Journal of Hazardous Materials*, 151 (2008): 610-615.

220. B. Mokhtari, K. Pourabdollah, Emulsion liquid membrane for selective extraction of Bi (III), *Chinese Journal of Chemical Engineering*, 23 (2015): 641-645.

221. S. Sujatha, M. Rajasimman, Development of a green emulsion liquid membrane using waste cooking oil as diluent for the extraction of arsenic from aqueous solution – Screening, optimization, kinetics and thermodynamics studies, *Journal of Water Process Engineering*, 41(2021):102055

222. S. Sujatha, N. Rajamohan, Y. Vasseghian, M. Rajasimman, Conversion of waste cooking oil into value-added emulsion liquid membrane for enhanced extraction of lead: Performance evaluation and optimization, Chemosphere 284 (2021): 131385.

APPENDIX A

METHODOLOGY

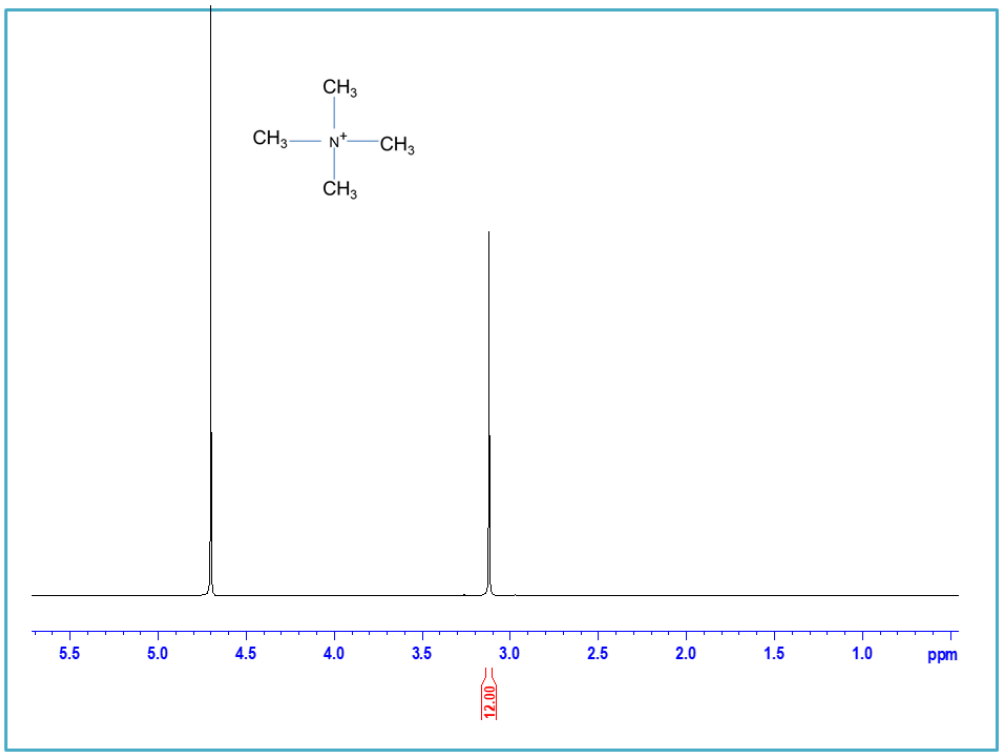


Figure A1 H NMR of tetramethylammonium sulfate

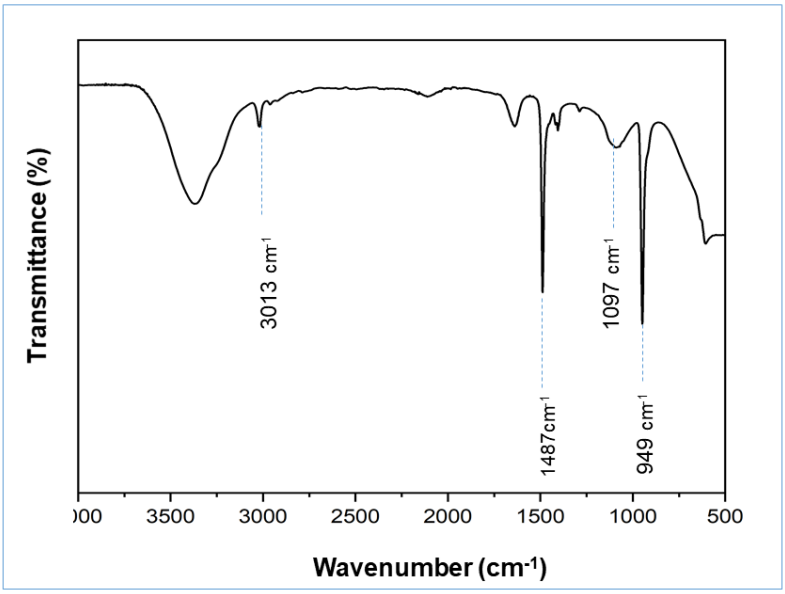


Figure A2 FTIR for tetramethylammonium Sulfate

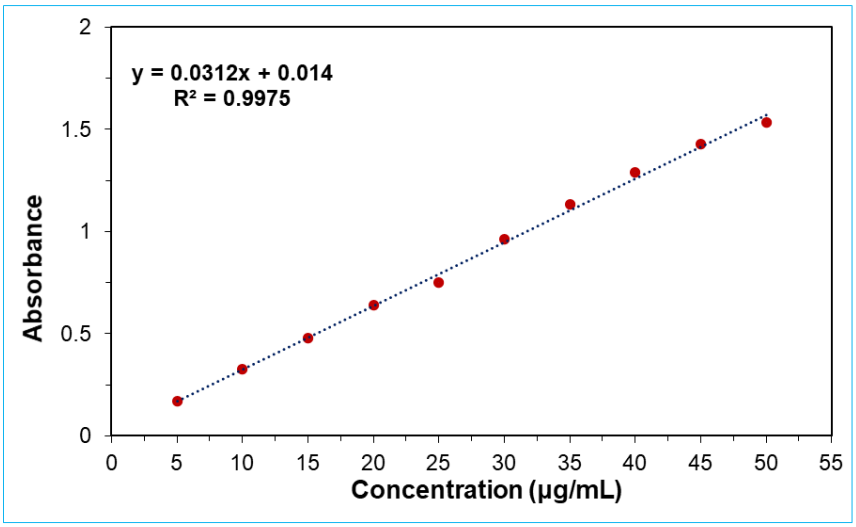


Figure A3 Calibration curve for Diclofenac

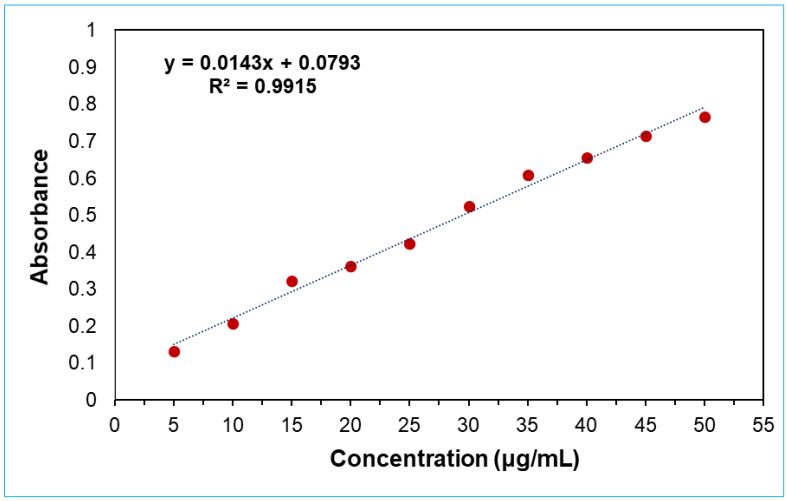


Figure A4 Calibration curve for Ibuprofen

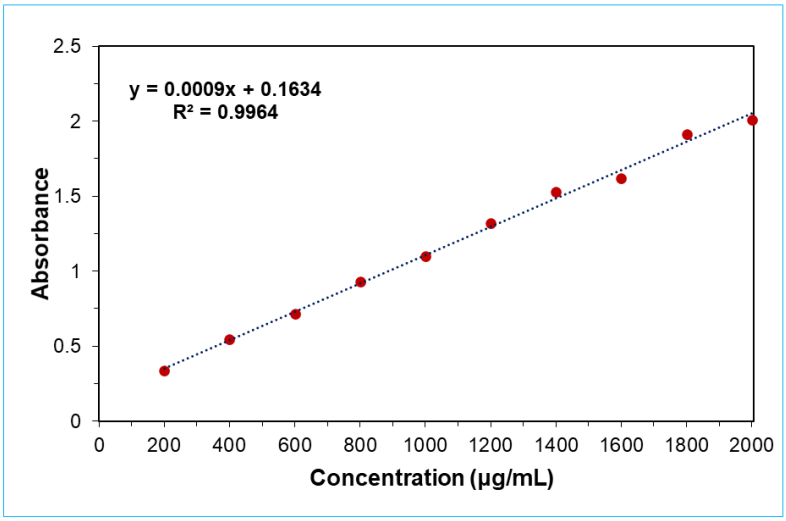


Figure A5 Calibration curve for LA-UV-vis

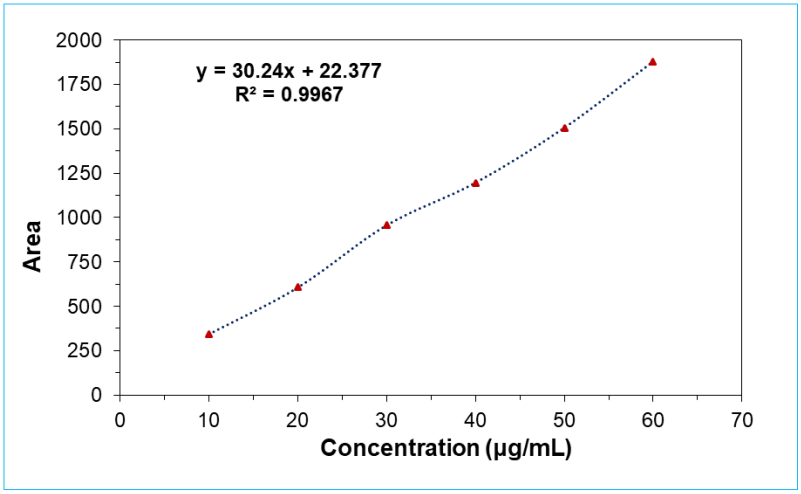


Figure A 6 HPLC calibration curve for Dcf

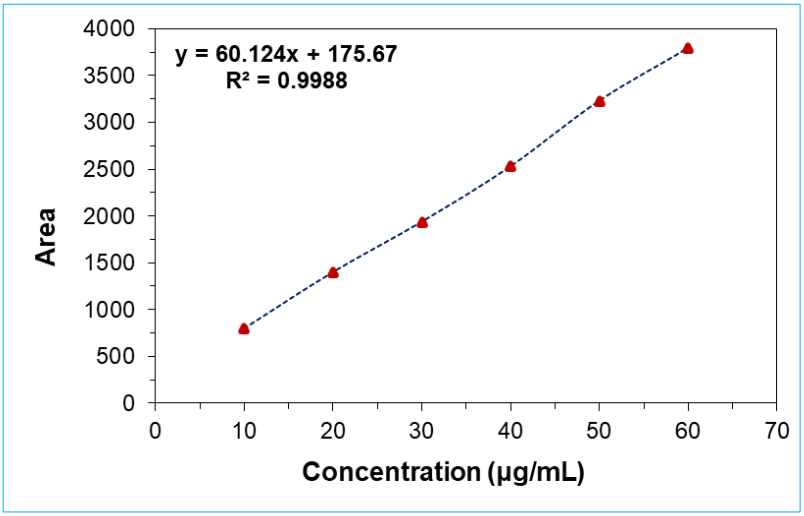


Figure A 7 HPLC calibration curve for Ibf

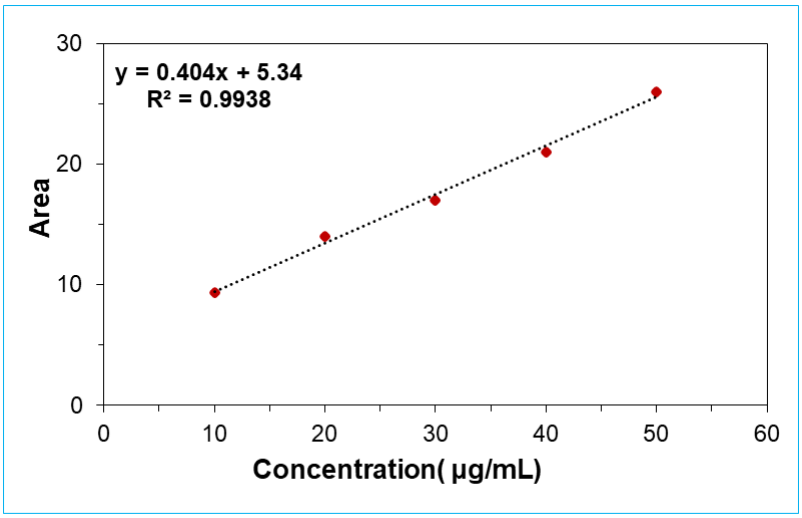


Figure A 8 HPLC calibration curve for LA

Table A1 Parameters and their ranges for Ibf

Code	**Parameter**	**Unit**	**Range**	
			Low	**high**
A	Surfactant concentration	wt.%	0.5	2.0
B	Stripping agent concentration	M	.005	.025
C	Treat ratio		2	6
D	Phase ratio		0.15	0.35
E	Extraction time	min	1	13

Table A2 Design matrix developed for Ibf removal using Response Surface Methodology

Run	**Factors**				
	A:Surfactant conccentration	B:Phase ratio	C:Treat ratio	D:Stripping agent	E:IL conc.
	wt.%			M	wt.%
1	2.5	0.35	1	0.03	0.6
2	1.5	0.25	2.5	0.02	0.35
3	0.5	0.15	1	0.01	0.6
4	2.5	0.35	4	0.03	0.1
5	0.5	0.35	4	0.03	0.1
6	1.5	0.25	4	0.02	0.35
7	0.5	0.15	4	0.01	0.6
8	2.5	0.25	2.5	0.02	0.35
9	0.5	0.35	1	0.01	0.6
10	2.5	0.35	1	0.01	0.1
11	2.5	0.15	4	0.01	0.6
12	0.5	0.15	4	0.01	0.1
13	2.5	0.15	1	0.01	0.1
14	0.5	0.15	4	0.03	0.6
15	0.5	0.15	1	0.03	0.6
16	0.5	0.35	4	0.01	0.1

17	1.5	0.25	2.5	0.02	0.35
18	1.5	0.25	2.5	0.02	0.6
19	0.5	0.25	2.5	0.02	0.35
20	2.5	0.35	4	0.01	0.6
21	2.5	0.15	1	0.01	0.6
22	1.5	0.25	1	0.02	0.35
23	2.5	0.15	4	0.03	0.6
24	2.5	0.15	1	0.03	0.1
25	0.5	0.15	1	0.03	0.1
26	1.5	0.25	2.5	0.02	0.35
27	1.5	0.25	2.5	0.01	0.35
28	0.5	0.35	1	0.01	0.1
29	0.5	0.35	4	0.03	0.6
30	0.5	0.15	1	0.01	0.1
31	1.5	0.15	2.5	0.02	0.35
32	1.5	0.25	2.5	0.02	0.35
33	1.5	0.25	2.5	0.02	0.1
34	0.5	0.35	1	0.03	0.1
35	0.5	0.35	1	0.03	0.6
36	1.5	0.35	2.5	0.02	0.35
37	1.5	0.25	2.5	0.02	0.35

38	2.5	0.35	1	0.03	0.1
39	2.5	0.35	4	0.01	0.1
40	1.5	0.25	2.5	0.03	0.35
41	2.5	0.15	4	0.01	0.1
42	1.5	0.25	2.5	0.02	0.35
43	0.5	0.15	4	0.03	0.1
44	2.5	0.35	4	0.03	0.6
45	1.5	0.25	2.5	0.02	0.35
46	2.5	0.35	1	0.01	0.6
47	1.5	0.25	2.5	0.02	0.35
48	2.5	0.15	1	0.03	0.6
49	2.5	0.15	4	0.03	0.1
50	0.5	0.35	4	0.01	0.6

Table A3 Parameters and their ranges for LA

Code	Parameter	Unit	Range	
			Low	high
A	Surfactant concentration	wt.%	0.5	2.5
B	Stripping agent concentration	M	.05	.025
C	Carrier concentration	wt.%	0.1	0.5
D	Phase ratio		0.15	0.35
E	Treat ratio		1	4

Table A4 Design matrix developed by Response Surface Methodology for LA

Run	**Factors**				
	A:Surfactant concentration wt.%	B:Stripping agent concentration (M)	C:Carrier concentration (wt.%)	D:Phase ratio	E:Ttreat ratio
1	2.5	0.05	0.5	0.15	4
2	0.5	0.25	0.5	0.35	1
3	2.5	0.05	0.1	0.35	1
4	2.5	0.25	0.1	0.35	4
5	0.5	0.25	0.1	0.15	1
6	2.5	0.05	0.5	0.15	1
7	1.5	0.05	0.3	0.25	2.5
8	0.5	0.25	0.5	0.15	1
9	2.5	0.05	0.1	0.15	4
10	2.5	0.25	0.5	0.35	1
11	0.5	0.05	0.1	0.15	4
12	0.5	0.25	0.5	0.15	4
13	2.5	0.05	0.5	0.35	4
14	0.5	0.25	0.1	0.15	4
15	2.5	0.25	0.1	0.35	1

16	0.5	0.25	0.1	0.35	4
17	1.5	0.15	0.3	0.25	1
18	0.5	0.05	0.5	0.35	1
19	2.5	0.25	0.5	0.15	4
20	1.5	0.15	0.3	0.25	4
21	1.5	0.15	0.3	0.25	2.5
22	1.5	0.15	0.3	0.25	2.5
23	0.5	0.05	0.1	0.35	4
24	0.5	0.15	0.3	0.25	2.5
25	0.5	0.25	0.5	0.35	4
26	2.5	0.25	0.5	0.15	1
27	1.5	0.15	0.5	0.25	2.5
28	0.5	0.05	0.1	0.35	1
29	1.5	0.15	0.3	0.25	2.5
30	2.5	0.05	0.1	0.35	4
31	0.5	0.05	0.5	0.15	1
32	2.5	0.05	0.5	0.35	1
33	1.5	0.15	0.3	0.25	2.5
34	0.5	0.05	0.5	0.35	4
35	0.5	0.25	0.1	0.35	1
36	1.5	0.15	0.3	0.25	2.5

37	1.5	0.25	0.3	0.25	2.5
38	2.5	0.15	0.3	0.25	2.5
39	1.5	0.15	0.3	0.15	2.5
40	2.5	0.25	0.1	0.15	1
41	0.5	0.05	0.1	0.15	1
42	2.5	0.05	0.1	0.15	1
43	1.5	0.15	0.3	0.35	2.5
44	1.5	0.15	0.3	0.25	2.5
45	1.5	0.15	0.3	0.25	2.5
46	2.5	0.25	0.1	0.15	4
47	2.5	0.25	0.5	0.35	4
48	1.5	0.15	0.1	0.25	2.5
49	0.5	0.05	0.5	0.15	4
50	1.5	0.15	0.3	0.25	2.5

APPENDIX B

COSMO-RS SCREENING FOR BACS

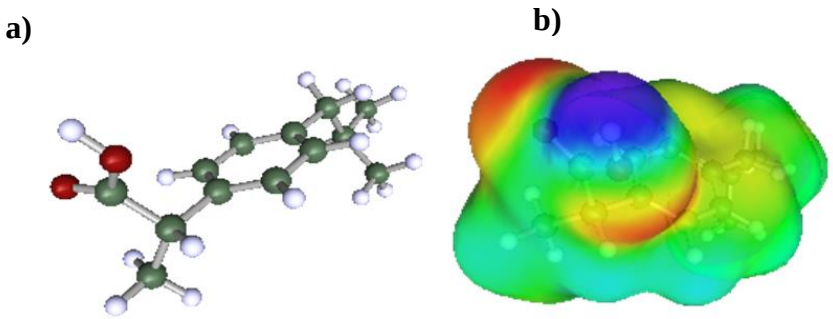


Figure B1 a) Chemical configuration and b) σ surface of Ibf using COSMO-RS model

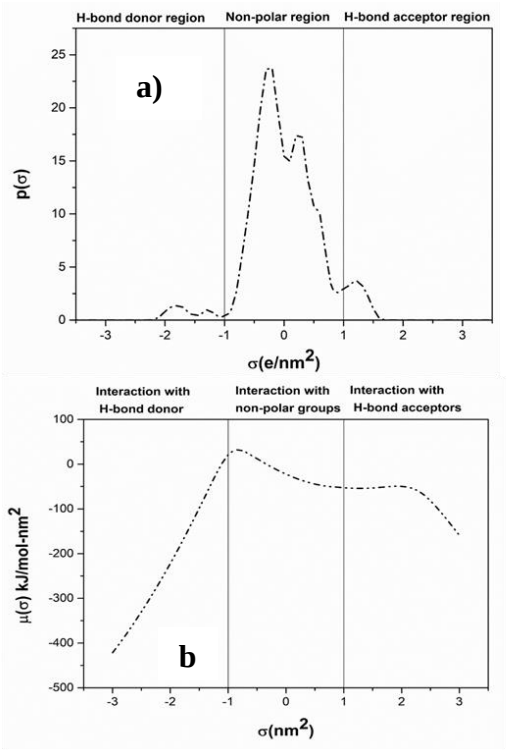


Figure B2 Predicted (a) σ profile and (b) σ potential distributions of Ibf using the COSMO-RS model

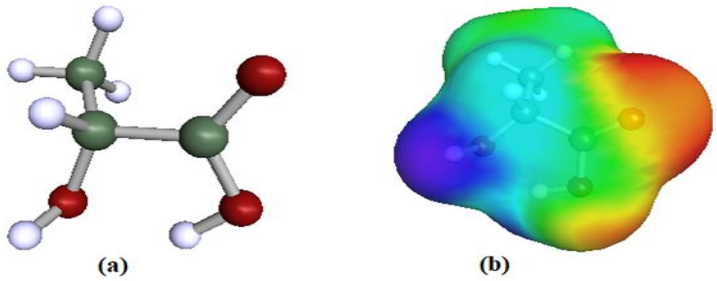


Figure B3 a) Chemical configuration and b) σ surface of LA using COSMO-RS model

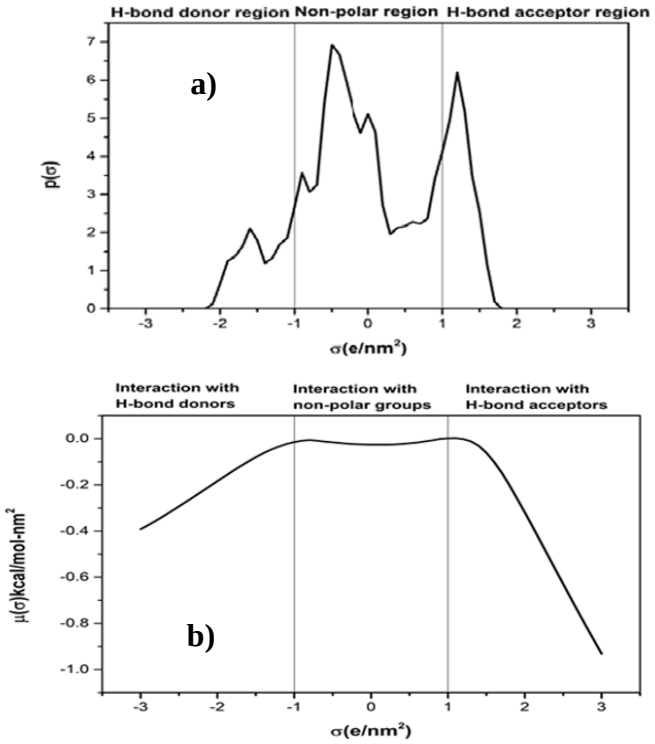


Figure B4 Predicted (a) σ profile and (b) σ potential distributions of LA using the COSMO-RS model

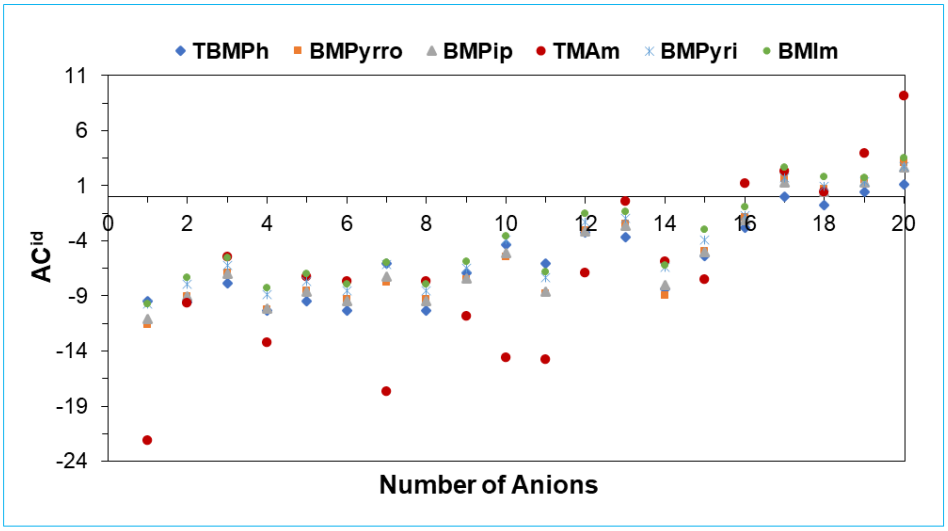


Figure B5 AC^{id} values predicted using COSMO-RS for Ibf

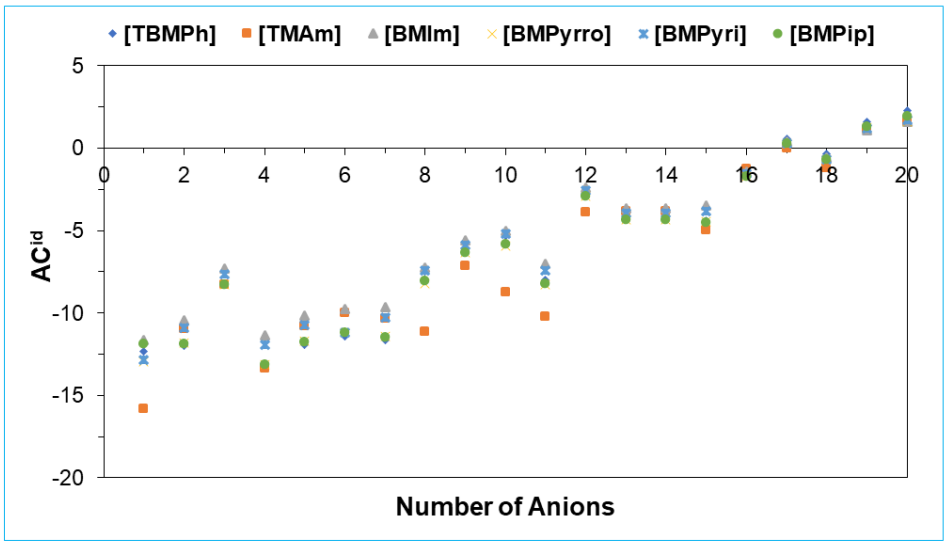


Figure B6 AC^{id} values predicted using COSMO-RS for LA

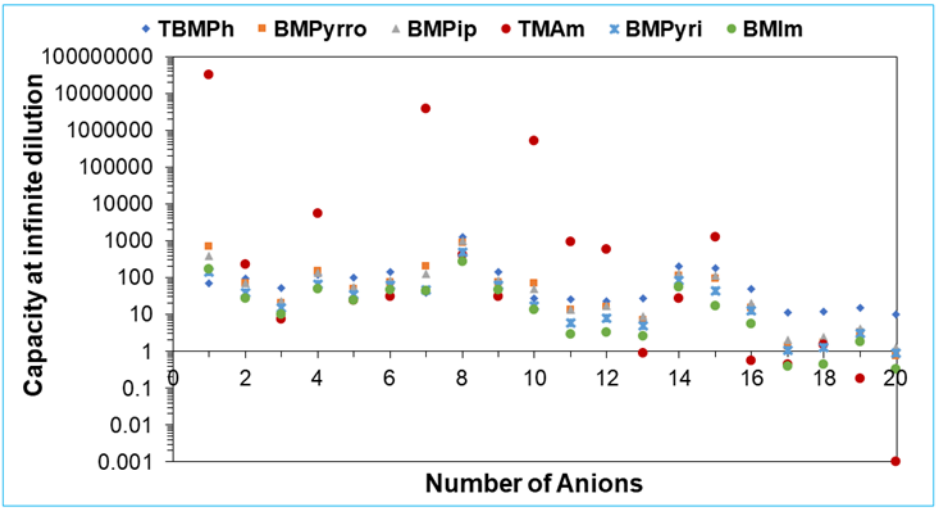


Figure B7 Capacity of selected ILs for extraction of Ibf from aqueous solution

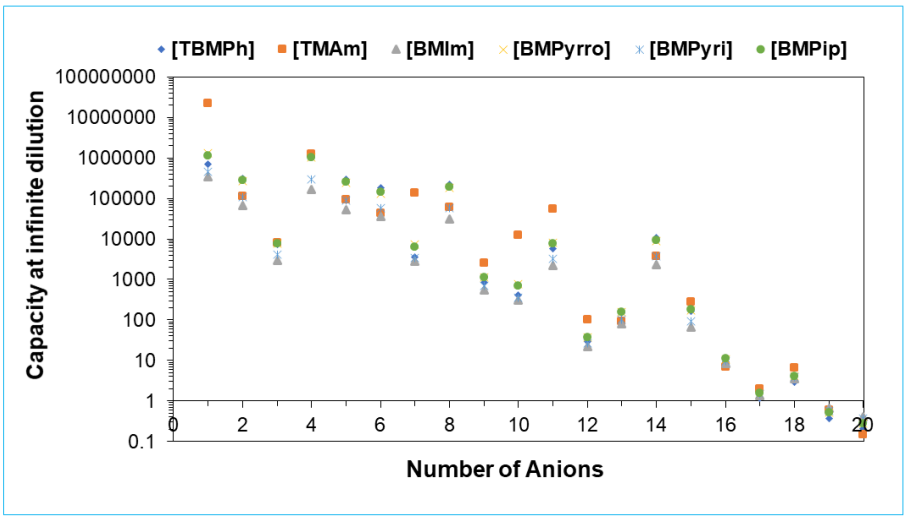


Figure B8 Capacity of selected ILs for extraction of LA from aqueous solution

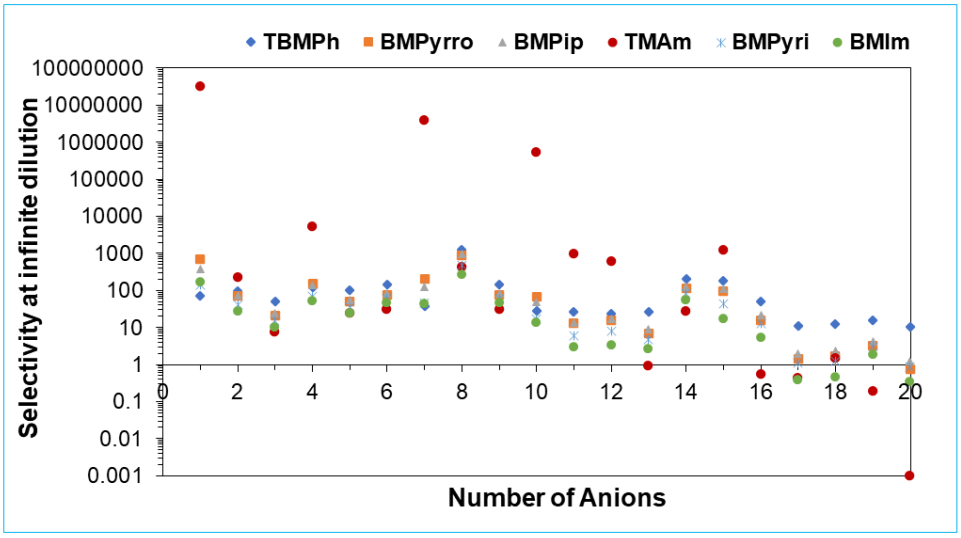


Figure B9 Selectivity of selected ILs for extraction of Ibf from aqueous solution

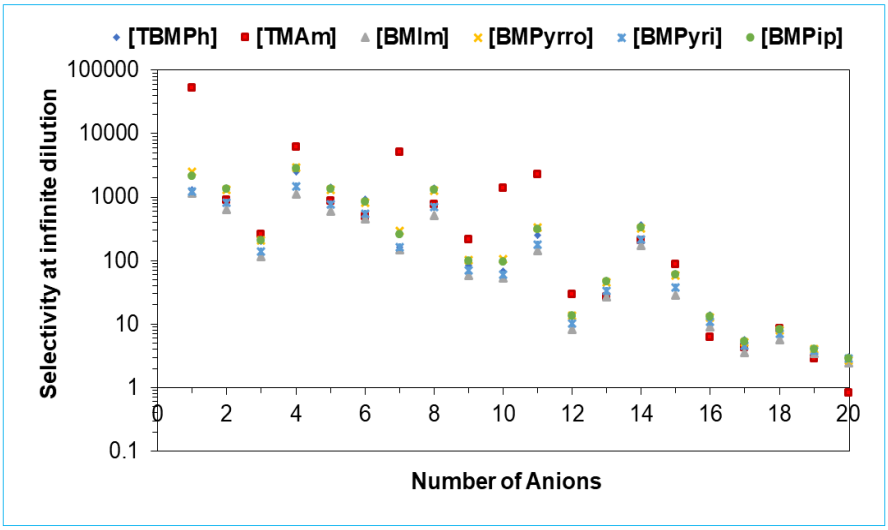


Figure B10 Selectivity of selected ILs for extraction of LA from aqueous solution

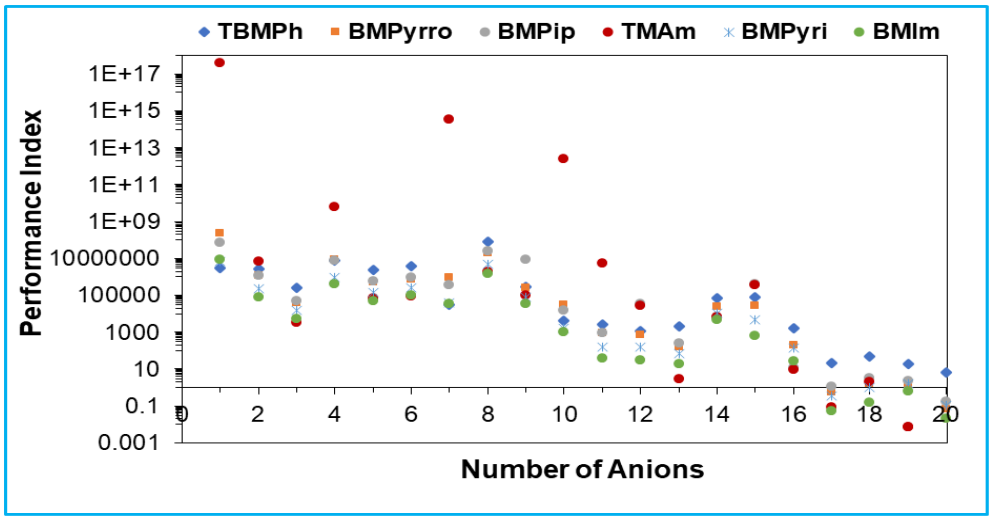


Figure B11 Performance Index selected ILs for extraction of Ibf from aqueous solution

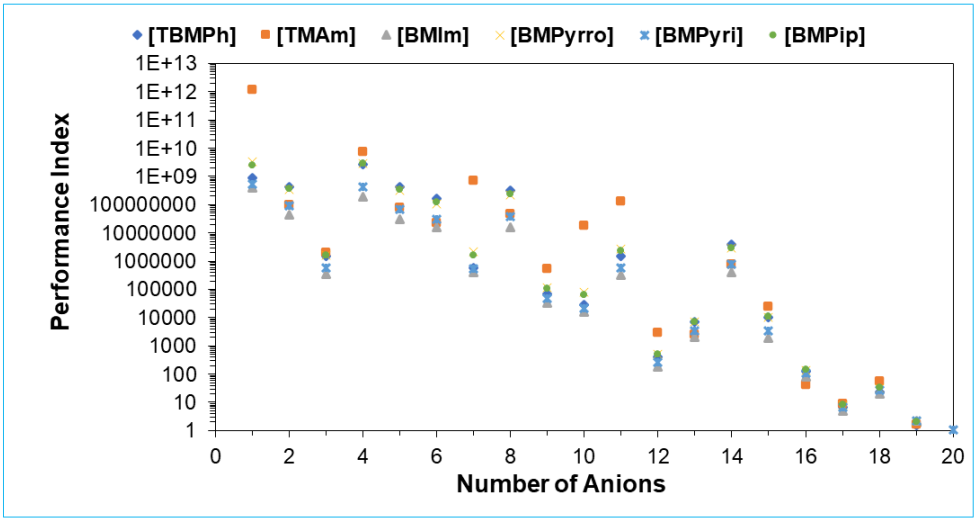


Figure B12 Performance index of selected ILs for extraction of LA from aqueous solution

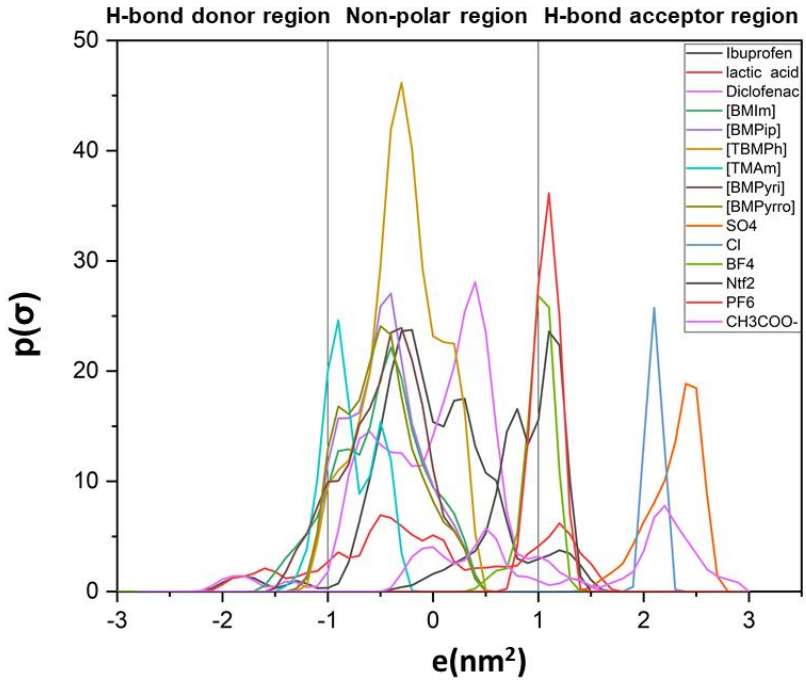


Figure B13 Sigma profiles of cations, Dcf, Ibf and LA

APPENDIX C

EXTRACTION OF BACS USING WVO-ILEM

Table C1 Emulsion characterization for Dcf

Parameter		**Breakage (%)**	**Diameter (µm)**	**Stand alone stability (min)**	**Viscosity (cPs)**	**Density (g/cm^3)**	**Interfacial tension (mN/m)**	**Extraction Efficiency (%)**
	0.05	4.15	3.01	34	138.6	0.9367	3..27	37.5
HNO_3 concentration M	0.1	2.91	2.24	65	145.6	0.9372	2.56	59.05
	0.15	3.25	2.54	55	146.5	0.9382	2.47	40.7
	0.2	4.01	2.85	48	143.3	0.9385	2.43	38.6
	0.25	4.56	3.62	29	135.9	0.9371	2.39	31.2
phase ratio	0.15	4.86	2.83	38	131.4	0.9363	2.34	28.6
	0.2	3.25	1.78	49	142.7	0.9366	2.27	40.5
	0.25	1.61	0.244	136	147.6	0.9375	1.25	86.5
	0.3	1.12	1.08	92	154.6	0.9388	1.21	79.5
	0.35	1.49	1.29	86	159.6	0.9391	1.19	71.6
	0.4	2.96	2.8	65	162.5	0.9394	1.16	59.05
	3200	1.74	1.31	94	134.6	0.9365	1.52	76.5

Homogenization speed rpm	4200	1.69	0.79	118	136.5	0.9369	1.41	81.5
	5200	1.61	0.244	136	147.6	0.9374	1.25	86.5
	6200	1.82	0.91	102	151.9	0.9379	1.23	83.5
	7200	2.12	1.5	89	154.5	0.9381	1.21	74.3
Homogenization time min	1	2.32	1.18	88	132.9	0.9362	1.47	72.3
	3	1.76	0.86	118	136.7	0.9369	1.42	80.35
	5	1.61	0.244	136	147.6	0.9374	1.25	86.5
	7	1.86	0.91	105	149.6	0.9377	1.22	79.8
	10	2.36	1.09	93	152.7	0.9381	1.19	72.6
	13	2.72	1.59	72	155.4	0.9385	1.15	63.5

Table C2 Characterization of WVO-ILEM emulsion for Ibf

Parameter		**Breakage (%)**	**Diameter (µm)**	**Stand alone stability (min)**	**Viscosity (cP)**	**Density (g/cm3)**	**Interfacial tension (mN/m)**	**Extraction Efficiency (%)**
Internal Stripping agent concentration (M)	0.05	4.15	3.01	34	138.6	0.9367	2.98	37.5
	0.1	2.91	2.6	65	145.6	0.9372	2.56	59.05
	0.15	3.25	2.54	55	146.5	0.9382	2.48	40.7
	0.2	4.01	2.85	48	153.3	0.9385	2.34	38.6
	0.25	4.56	3.62	29	155.9	0.9387	2.14	31.2
Phase ratio	0.15	4.86	3.73	38	131.4	0.9323	1.98	28.6
	0.2	3.25	2.85	49	142.7	0.9356	1.67	40.5
	0.25	1.61	0.342	136	147.6	0.9387	1.25	86.5
	0.3	1.12	1.08	92	154.6	0.9391	1.21	79.5
	0.35	1.49	1.29	86	159.6	0.9395	1.16	71.6
	0.4	2.96	2.8	65	162.5	0.9398	1.05	59.05
Homogenization Speed (rpm)	3200	1.74	1.31	94	134.6	0.9378	1.56	76.5
	4200	1.69	0.79	118	136.5	0.9384	1.38	81.5
	5200	1.61	0.342	136	147.6	0.9387	1.25	86.5
	6200	1.82	0.91	102	151.9	0.9391	1.18	83.5
	7200	2.12	1.5	89	157.5	0.9396	1.06	74.3

Homogen ization time (min)	1	2.32	1.18	88	141.6	0.9381	1.45	72.3
	3	1.76	0.79	118	144.5	0.9384	1.36	80.35
	5	1.61	0.342	136	147.6	0.9387	1.25	86.5
	7	1.86	0.91	105	149.5	0.9392	1.18	79.8
	10	2.36	1.09	93	152.6	0.9395	1.07	72.6
	13	2.72	1.59	72	157.4	1.00	63.5	

Table C3 Characterization of WVO-ILEM emulsion for LA

Parameter		**Breakage (%)**	**Diameter (μm)**	**Stand alone stability (min)**	**Viscosity (cP)**	**Density (g/cm^3)**	**Interfacial tension (mN/m)**	**Extraction Efficiency (%)**
Surfactant concentration (wt.%)	0.5	3.54	3.4	58	135.6	0.9053	3.51	68.6
	1.0	2.81	2.96	72	138.5	0.9196	2.86	78.9
	1.5	3.09	3.18	69	141.6	0.9213	2.82	65.3
	2.0	3.52	3.45	56	145.4	0.9245	2.63	56.4
Internal stripping agent concentration M	0.05	3.25	3.1	65	133.6	0.9156	2.76	63.2
	0.1	2.81	2.9	72	138.5	0.9196	2.86	78.9
	0.15	2.56	2.51	86	141.3	0.9154	2.79	86.5
	0.2	2.86	2.75	83	145.7	0.923	2.72	76.5
	0.25	3.18	3.09	68	148.9	0.9245	2.65	63.2
Carrier concentration (wt.%)	0.1	2.79	2.95	74	137.6	0.9132	2.89	34.8
	0.2	2.56	2.51	86	141.3	0.9154	2.79	63.8
	0.3	2.09	1.18	108	144.6	0.9196	2.69	91.3
	0.4	2.46	2.48	82	148.6	0.9236	2.64	86.5
	0.5	3.38	3.36	53	151.6	0.9256	2.61	74.6
	0.15	3.81	3.65	72	133.2	0.9114	2.98	53.2
	0.2	2.09	3.12	108	135.4	0.9123	2.78	88.5

Phase ratio	0.25	0.95	1.18	136	141.3	0.9196	2.69	91.3
	0.3	2.94	2.81	76	143.3	0.9213	2.65	72.6
	0.35	5.21	4.6	32	146.5	0.9134	2.58	36.5
	3200	4.12	3.85	47	135.6	0.9136	2.76	40.5
Homogenization	4200	2.91	2.86	72	138.6	0.9157	2.72	71.5
speed	5200	0.95	1.18	136	141.3	0.9196	2.69	91.3
(rpm)	6200	2.09	1.81	106	144.1	0.9121	2.62	83.2
	7200	2.15	1.95	91	146.5	0.9126	2.58	72.5
	3	1.98	1.86	95	136.5	0.9135	2.72	86.5
Homogenization	5	0.95	1.18	136	141.3	0.9196	2.69	91.3
time	7	2.01	1.86	102	143.2	0.9124	2.64	81.7
min	10	2.96	2.89	76	146.5	0.9131	2.59	72.6
	13	6.8	4.23	28	151.3	0.9139	2.55	57.8

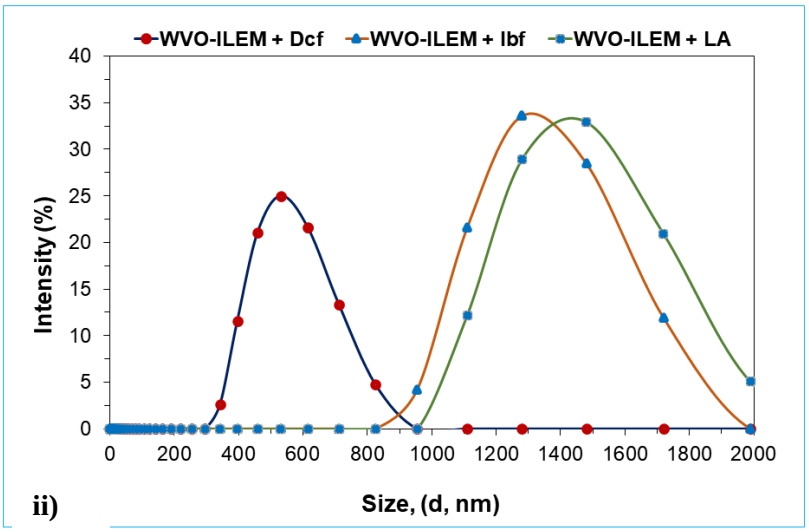


Figure C1 Size of emulsion globule before exposure to external solution. a) Dcf HNO_3=0.1 M (b) Ibf, NaOH=0.02 M M(c) LA=5000 µg/mL, NaOH=0.15 M

APPENDIX D

OPTIMIZATION RESULTS USING RSM

Table D1: Experimental design matrix and response results for Dcf

Run	**Factors**					**Extraction Efficiency (%)**	
	A:Surfactant concentration (wt.%)	B:Phase ratio	C:Treat ratio	D: Stripping agent concentration (M)	E: carrier concentration (wt.%)	Actual value	Predicted Value
1	3	0.4	4	0.05	0.1	88.6	89.29
2	0.5	0.4	4	0.3	0.1	49.32	49.45
3	1.75	0.275	2.5	0.175	0.35	64.35	65.33
4	1.75	0.275	2.5	0.175	0.35	64.35	65.33
5	1.75	0.15	2.5	0.175	0.35	71.23	70.42
6	3	0.4	1	0.3	0.1	72.35	72.63
7	3	0.15	1	0.05	0.6	63.5	64.24
8	3	0.15	1	0.05	0.1	75.9	75.62
9	1.75	0.275	2.5	0.05	0.35	81.65	81.44
10	0.5	0.4	1	0.05	0.6	51.3	51.15
11	0.5	0.4	1	0.3	0.6	54.21	54.49
12	1.75	0.275	4	0.175	0.35	49.65	48.77
13	3	0.15	4	0.3	0.6	65.35	65.23
14	0.5	0.4	1	0.3	0.1	55.36	54.96
15	1.75	0.275	2.5	0.175	0.35	64.12	65.33
16	3	0.4	1	0.05	0.1	83.21	83
17	1.75	0.4	2.5	0.175	0.35	65.48	65.02
18	0.5	0.4	4	0.05	0.6	60.36	60.69
19	1.75	0.275	2.5	0.175	0.35	64.89	65.33

20	3	0.4	4	0.05	0.6	75.65	75.19
21	0.5	0.15	1	0.3	0.6	72.36	72.17
22	0.5	0.4	4	0.3	0.6	53.21	53.04
23	1.75	0.275	1	0.175	0.35	46.5	46.1
24	3	0.15	4	0.3	0.1	54.26	54.7
25	0.5	0.15	1	0.05	0.6	75.69	75.18
26	1.75	0.275	2.5	0.175	0.35	64.98	65.33
27	3	0.4	4	0.3	0.6	71.23	71.67
28	3	0.15	1	0.3	0.1	59.32	58.9
29	1.75	0.275	2.5	0.175	0.35	64.35	65.33
30	3	0.15	1	0.3	0.6	65.31	65.37
31	3	0.4	1	0.3	0.6	71.9	72.32
32	3	0.15	4	0.05	0.1	82.13	82.41
33	1.75	0.275	2.5	0.175	0.6	62.35	61.52
34	0.5	0.15	4	0.05	0.1	93.86	92.71
35	1.75	0.275	2.5	0.175	0.35	65.21	65.33
36	3	0.4	1	0.05	0.6	65.21	64.85
37	0.5	0.15	1	0.05	0.1	86.23	86.72
38	0.5	0.15	4	0.3	0.1	60.31	60.86
39	0.5	0.4	1	0.05	0.1	69.21	69.47
40	0.5	0.15	1	0.3	0.1	65.48	65.86
41	3	0.4	4	0.3	0.1	68.45	67.92
42	0.5	0.15	4	0.3	0.6	71.32	71.23
43	0.5	0.275	2.5	0.175	0.35	75.3	74.74
44	1.75	0.275	2.5	0.175	0.35	65.31	65.33
45	1.75	0.275	2.5	0.175	0.1	65.86	65.42
46	0.5	0.15	4	0.05	0.6	84.36	85.23
47	3	0.15	4	0.05	0.6	75.36	75.09
48	1.75	0.275	2.5	0.3	0.35	70.32	69.25
49	0.5	0.4	4	0.05	0.1	75.03	74.95
50	3	0.275	2.5	0.175	0.35	79.23	78.51

Table D2 Experimental design matrix and response results for Ibf

Run	**Factors**					**Extraction Efficiency**	
	A:Surfactant conccentration (wt.%)	B:Phase ratio	C:Treat ratio	D:Stripping agent (M)	E:IL conc. (wt.%)	Actual	Predicted
1	2.5	0.35	1	0.03	0.6	32.7	33.04
2	1.5	0.25	2.5	0.02	0.35	84.76	84.38
3	0.5	0.15	1	0.01	0.6	53.54	53.96
4	2.5	0.35	4	0.03	0.1	33.27	32.74
5	0.5	0.35	4	0.03	0.1	44.91	44.96
6	1.5	0.25	4	0.02	0.35	86.18	86.45
7	0.5	0.15	4	0.01	0.6	52.27	51.82
8	2.5	0.25	2.5	0.02	0.35	56.81	57.5
9	0.5	0.35	1	0.01	0.6	58.24	58.15
10	2.5	0.35	1	0.01	0.1	45.32	45.23
11	2.5	0.15	4	0.01	0.6	58.16	58.11
12	0.5	0.15	4	0.01	0.1	40.14	39.86
13	2.5	0.15	1	0.01	0.1	40.61	40.19

14	0.5	0.15	4	0.03	0.6	56.9	56.95
15	0.5	0.15	1	0.03	0.6	58.6	58.05
16	0.5	0.35	4	0.01	0.1	54.81	54.8
17	1.5	0.25	2.5	0.02	0.35	84.76	84.38
18	1.5	0.25	2.5	0.02	0.6	68.09	68.78
19	0.5	0.25	2.5	0.02	0.35	63.63	63.7
20	2.5	0.35	4	0.01	0.6	60.81	60.43
21	2.5	0.15	1	0.01	0.6	53.63	53.78
22	1.5	0.25	1	0.02	0.35	84.36	84.85
23	2.5	0.15	4	0.03	0.6	55.9	56.28
24	2.5	0.15	1	0.03	0.1	39.06	38.54
25	0.5	0.15	1	0.03	0.1	50.76	51.35
26	1.5	0.25	2.5	0.02	0.35	84.76	84.38
27	1.5	0.25	2.5	0.01	0.35	83.21	83.29
28	0.5	0.35	1	0.01	0.1	57.19	56.95
29	0.5	0.35	4	0.03	0.6	48.63	48.97
30	0.5	0.15	1	0.01	0.1	45.67	46.04
31	1.5	0.15	2.5	0.02	0.35	95.5	95.68
32	1.5	0.25	2.5	0.02	0.35	84.76	84.38
33	1.5	0.25	2.5	0.02	0.1	59.91	59.98
34	0.5	0.35	1	0.03	0.1	46.36	46.08

35	0.5	0.35	1	0.03	0.6	46.36	46.06
36	1.5	0.35	2.5	0.02	0.35	93.63	94.21
37	1.5	0.25	2.5	0.02	0.35	84.76	84.38
38	2.5	0.35	1	0.03	0.1	26.88	27.39
39	2.5	0.35	4	0.01	0.1	49.08	49.54
40	1.5	0.25	2.5	0.03	0.35	76.27	76.94
41	2.5	0.15	4	0.01	0.1	40.16	40.49
42	1.5	0.25	2.5	0.02	0.35	84.76	84.38
43	0.5	0.15	4	0.03	0.1	46.28	46.21
44	2.5	0.35	4	0.03	0.6	42.99	42.42
45	1.5	0.25	2.5	0.02	0.35	84.76	84.38
46	2.5	0.35	1	0.01	0.6	52.27	52.09
47	1.5	0.25	2.5	0.02	0.35	84.76	84.38
48	2.5	0.15	1	0.03	0.6	51.09	50.91
49	2.5	0.15	4	0.03	0.1	39.81	39.88
50	0.5	0.35	4	0.01	0.6	59.63	60.03

Table D3 Experimental design matrix and response results for LA

Run	**Factors**					**Extraction efficiency (%)**	
	A:Surfactant concentration (wt.%)	B: Striping agent concentration (M)	C: carrier concentration wt.%	D:phase ratio	E:treat ratio	Actual	Predicted
1	2.5	0.05	0.5	0.15	4	66.26	65.92
2	0.5	0.25	0.5	0.35	1	50.36	49.65
3	2.5	0.05	0.1	0.35	1	45.92	45.60
4	2.5	0.25	0.1	0.35	4	33.6	33.70
5	0.5	0.25	0.1	0.15	1	43.96	43.59
6	2.5	0.05	0.5	0.15	1	36.5	36.48
7	1.5	0.05	0.3	0.25	2.5	89.6	88.67
8	0.5	0.25	0.5	0.15	1	46.12	47.15
9	2.5	0.05	0.1	0.15	4	62.9	62.71
10	2.5	0.25	0.5	0.35	1	27.96	27.66
11	0.5	0.05	0.1	0.15	4	63.5	64.37
12	0.5	0.25	0.5	0.15	4	70.2	70.05
13	2.5	0.05	0.5	0.35	4	59.86	60.58
14	0.5	0.25	0.1	0.15	4	61.56	61.05
15	2.5	0.25	0.1	0.35	1	32.96	33.31

16	0.5	0.25	0.1	0.35	4	53.65	53.95
17	1.5	0.15	0.3	0.25	1	73.81	73.02
18	0.5	0.05	0.5	0.35	1	50.98	51.80
19	2.5	0.25	0.5	0.15	4	47.98	48.25
20	1.5	0.15	0.3	0.25	4	91.6	91.01
21	1.5	0.15	0.3	0.25	2.5	79.63	80.82
22	1.5	0.15	0.3	0.25	2.5	79.63	80.82
23	0.5	0.05	0.1	0.35	4	66.85	66.69
24	0.5	0.15	0.3	0.25	2.5	96.84	96.32
25	0.5	0.25	0.5	0.35	4	61.5	61.64
26	2.5	0.25	0.5	0.15	1	31.5	31.51
27	1.5	0.15	0.5	0.25	2.5	62.65	62.18
28	0.5	0.05	0.1	0.35	1	47.56	47.44
29	1.5	0.15	0.3	0.25	2.5	79.63	80.82
30	2.5	0.05	0.1	0.35	4	58.9	58.69
31	0.5	0.05	0.5	0.15	1	40.58	39.88
32	2.5	0.05	0.5	0.35	1	41.9	42.06
33	1.5	0.15	0.3	0.25	2.5	79.63	80.82
34	0.5	0.05	0.5	0.35	4	77.02	76.49
35	0.5	0.25	0.1	0.35	1	46.98	47.39
36	1.5	0.15	0.3	0.25	2.5	79.63	80.82

37	1.5	0.25	0.3	0.25	2.5	80.27	79.82
38	2.5	0.15	0.3	0.25	2.5	85.36	84.50
39	1.5	0.15	0.3	0.15	2.5	56.84	55.93
40	2.5	0.25	0.1	0.15	1	35.98	35.84
41	0.5	0.05	0.1	0.15	1	34.26	34.20
42	2.5	0.05	0.1	0.15	1	37.95	38.71
43	1.5	0.15	0.3	0.35	2.5	55.63	55.16
44	1.5	0.15	0.3	0.25	2.5	79.63	80.82
45	1.5	0.15	0.3	0.25	2.5	79.63	80.82
46	2.5	0.25	0.1	0.15	4	46.95	47.15
47	2.5	0.25	0.5	0.35	4	33.65	33.48
48	1.5	0.15	0.1	0.25	2.5	60.35	59.45
49	0.5	0.05	0.5	0.15	4	75.23	75.48
50	1.5	0.15	0.3	0.25	2.5	83.6	80.82

Table D4 ANOVA analysis for Response surface quadratic model for Ibf removal (%) using WVO-ILEM

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	16206.98	20	810.35	3296.83	< 0.0001	significant
A-Surfactant conc.	326.50	1	326.50	1328.32	< 0.0001	
B-Phase ratio	18.37	1	18.37	74.73	< 0.0001	
C-Treat ratio	21.89	1	21.89	89.06	< 0.0001	
D-Stripping agent	342.93	1	342.93	1395.16	< 0.0001	
E-IL conc.	658.07	1	658.07	2677.30	< 0.0001	
AB	69.21	1	69.21	281.57	< 0.0001	
AC	83.72	1	83.72	340.63	< 0.0001	
AD	96.81	1	96.81	393.86	< 0.0001	
AE	64.13	1	64.13	260.91	< 0.0001	
BC	32.28	1	32.28	131.34	< 0.0001	
BD	523.90	1	523.90	2131.44	< 0.0001	
BE	90.45	1	90.45	367.98	< 0.0001	
CD	2.15	1	2.15	8.76	0.0061	
CE	32.52	1	32.52	132.31	< 0.0001	
DE	2.95	1	2.95	12.01	0.0017	
A^2	1398.91	1	1398.91	5691.33	< 0.0001	
B^2	275.96	1	275.96	1122.71	< 0.0001	
C^2	3.98	1	3.98	16.17	0.0004	

D^2	44.93	1	44.93	182.80	< 0.0001	
E^2	989.56	1	989.56	4025.92	< 0.0001	
Residual	4.16	29	0.1435			
Lack of Fit	3.28	22	0.1493	1.19	0.434	not significant
Pure Error	0.8783	7	0.1255			
Cor Total	16214.11	49				

Table D5 ANOVA analysis for Response surface quadratic model for LA removal (%) using WVO-ILEM

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	169s7.75	20	845.89	842.61	< 0.0001	significant
A-Surfactant concentration	1188.50	1	1188.50	1183.90	< 0.0001	
B-Striping agent concentration	666.98	1	666.98	664.40	< 0.0001	
C-carrier concentration	63.38	1	63.38	63.13	< 0.0001	
D-phase ratio	4.96	1	4.96	4.94	<0.0001	
E-treat ratio	2752.74	1	2752.74	2742.08	< 0.0001	
AB	299.88	1	299.88	298.72	< 0.0001	
AC	124.90	1	124.90	124.42	< 0.0001	
AD	80.52	1	80.52	80.21	< 0.0001	
AE	75.89	1	75.89	75.60	< 0.0001	
BC	8.88	1	8.88	8.85	0.0059	
BD	177.66	1	177.66	176.97	< 0.0001	
BE	322.58	1	322.58	321.33	< 0.0001	
CD	3.45	1	3.45	3.43	0.0741	
CE	59.02	1	59.02	58.80	< 0.0001	

DE	238.27	1	238.27	237.35	< 0.0001	
A^2	227.69	1	227.69	226.81	< 0.0001	
B^2	29.09	1	29.09	28.98	< 0.0001	
C^2	989.86	1	989.86	986.03	< 0.0001	
D^2	1579.45	1	1579.45	1573.33	< 0.0001	
E^2	3.56	1	3.56	3.55	0.0697	
Residual	29.11	29	1.00			
Lack of Fit	15.32	22	0.6965	0.3535	0.9709	not significant
Pure Error	13.79	7	1.97			
Cor Total	16946.86	49				

Table D6 Fit statistics for Ibf and LA

BAC	**Std Dev**	**Mean**	**C.V %**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**Adequate precision**
Ibf	0.4958	59.75	0.839	0.9948	0.9936	0.9931	212.52
LA	0.4785	59.70	1.68	0.9948	0.9971	0.9963	105.7446

For Ibf

Extraction Efficiency (Y) =84.38 - 3.09 A - 0.73 B + 0.80 C - 3.17 D + 4.39 E + 1.47 AB + 1.61 AC - 1.73 AD + 1.41 AE + 1.043 BC - 4.046 BD - 1.68 BE + 0.25 CD + 1.01 CE -0.30 DE - 23.7 A^2 + 10.56 B^2 + 1.26 C^2 - 4.26 D^2 - 20.00 E^2

For LA

Extraction Efficiency (Y)=+ 80.82 – 5.91 A – 4.43 B +1.37 C – .38 D +9.00 E -3.06 AB – 1.98 AC – 1.59 AD – 1.54 AE – 0.5269 BC – 2.36 BD – 3.17 BE - 0.328 CD + 1.36 CE – 2.73 DE + 9.59 A^2 + 3.43 B^2 - 20.01 C^2 - 25.27 D^2 + 1.20 E^2

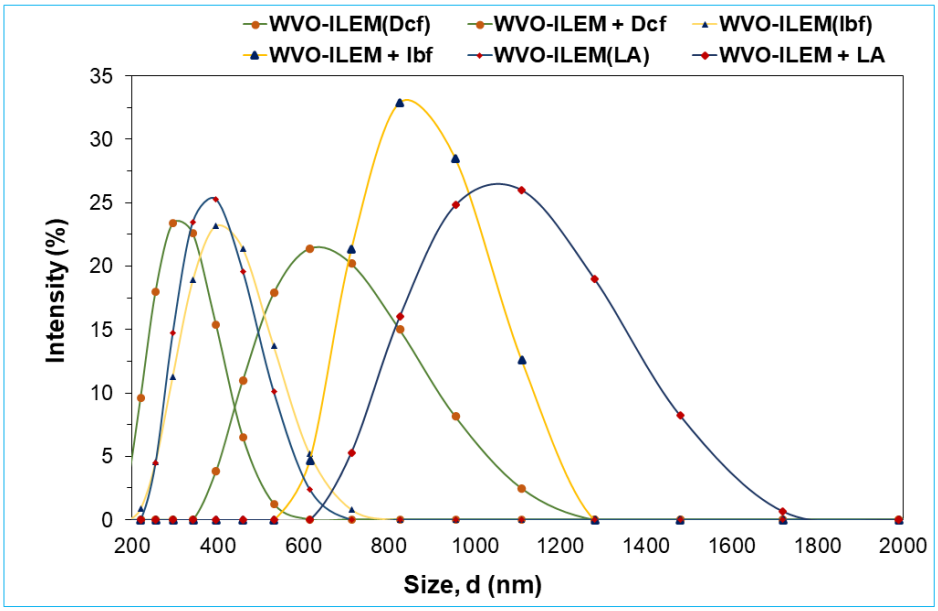


Figure D1 Emulsion diameter using DLS at optimised conditions obtained for WVO-ILEM before and after extraction for Dcf, Ibf and LA