

INVESTIGATION AND OPTIMIZATION OF INTENSIFIED SEPARATION PROCESSES: TREATMENT OF AQUEOUS ORGANIC MIXTURES USING REACTIVE EXTRACTION AND EMULSION LIQUID MEMBRANE TECHNIQUES

By

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As the candidate's Supervisor I agree to the submission of this thesis.



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DECLARATION 2 – Publications

This section presents the articles that form part and/or include the research presented in this thesis. The following international peer-reviewed book chapter and journals have been published or are under review:

ISI/SCOPUS/DoHET Book Chapter

Inyang, Victoria M. and Lokhat, David (2019). Separation of Carboxylic Acids: Conventional and Intensified Processes and Effects of Process Engineering Parameters. *Valorization of Biomass to Value-added Commodities, 475990, Springer Nature*. Published: DOI: 10.1007/978-3-030-38032-8; ISBN: 978-3-030-38032-8.

ISI/SCOPUS/ DoHET Accredited Journals

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The candidate for all the publications is the main and corresponding author respectively while Professor David Lokhat is the supervisor.

DEDICATION

Dedicated to my late father, who inspired me so much for academic excellence and encouraged me to get to the zenith of my career.

May his gentle soul continue to rest in the bosom of the Most High God.

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ABSTRACT

The application of intensified processes of reactive extraction and emulsion liquid membrane technique for the separation of various low molecular weight carboxylic acids (propionic acid, malic acid and butyric acid) from very dilute aqueous solution was undertaken. The aqueous phase feed concentration ranges of the different carboxylic acids for reactive extraction [propionic, butyric (0.4-1 kmol/m^3), malic (0.1-1 kmol/m^3) acids] and emulsion liquid membrane (propionic and malic acid (0.05 – 0.1 k mol/m^3) were chosen to simulate the actual aqueous waste streams and fermentation conditions encountered in industry. Trioctylamine extractant in 1-decanol as active diluent was used as the extractant (organic) phase to perform the experiment. The effect of different process variables on the extraction efficiency expressed in terms of distribution coefficient (K_D) and degree of extraction (%E) was systematically determined.

Three independent process variables were chosen, including temperature (298.15-313.15 K for propionic acid and malic acid and 298.15-318.15 K for butyric acid), initial organic acid concentration in the aqueous phase and trioctylamine composition (10-30 %) in the organic phase for the reactive extraction technique. The interactive effects and optimum values of these process design variables were determined using response surface methodology (RSM) for the reactive extraction process. The statistical design analysis demonstrated that the acid concentration and trioctylamine composition had significant effect while temperature had an insignificant effect on the response value as well as interactive and quadratic effect on the response. The optimum solution led to an experimentally determined extraction efficiency of 89.79% for propionic acid, 93.25% for malic acid and 96.45% for butyric acid.

The extraction efficiency in the emulsion liquid membrane process is dependent on the studied parameters such as initial acid concentration, sodium carbonate concentration, trioctylamine concentration, treat ratio and extraction time. The formulation of the liquid membrane consists of trioctylamine as carrier, 1-decanol as modifier, sorbitan monooleate (Span 80) as surfactants in heptane and sodium carbonate (Na_2CO_3) as a stripping agent. Response surface methodology (RSM) and artificial neural network (ANN) was employed for experimental design, optimization, construction and interpretation of response/output surface plots so as to show the effect of input variables on extraction efficiency in addition to the combined effects between variables. The optimum solution achieved by RSM led to an experimentally determined extraction efficiency of 92.28% and 85.91% in the propionic and malic acid extraction respectively by (emulsion liquid membrane) ELM process.

The intrinsic kinetic studies of reactive extraction were determined for propionic and malic acid extraction using dilute solutions of the acids with concentration range of 0.2 to 0.6 kmol/m^3 and trioctylamine (10 %v/v) in 1 decanol as extractant at 303.15 K. The kinetic process parameters such as reaction order, mass

transfer coefficient and rate constant were evaluated using the experimental data. From the results obtained, the reaction was found to be an instantaneous second-order chemical reaction occurring in the organic diffusion film. The values of the rate constants were found to be 0.430 m^3/mol s and 0.332 m^3/mol s respectively for propionic acid and malic acid while the mass transfer coefficient, k_m was also obtained for propionic acid (9 x 10^{-6} m/s) and malic acid (3x10^{-6} m/s). From the results obtained, these intensified technique represents an effective method for the recovery of low concentrations of carboxylic acids from aqueous waste streams and fermentation broths, with emulsion liquid membrane offering significant properties/characteristics like small quantity of organic phase and extractant, very fast extraction time, increased solute transfer rate and selectivity through the membrane, high selectivity and applicability in specie removal from very low to high concentrations and governed by a non-equilibrium mass transfer. It is therefore worth investing in this process or alternatively a hybrid of both reactive extraction and emulsion liquid membrane processes.

Chapter ONE

Introduction and Background of Study

Chapter ONE

INTRODUCTION

1.1 Background of Study

The chemical industry is faced with the challenge of producing chemicals with low energy consumption, waste generation and in an eco-friendly manner due to rapid competitiveness and industrialization. To overcome these challenges, development and sustainable bio-based technologies (biorefinery creation) have been highlighted as a major potential requirement. To achieve this objective, an integrated economic strategy taking into account health, safety and environmental (HSE) benefits need to be considered. The biorefinery development would require cheap and renewable chemical feedstock (such as biomass). This trend in the utilization of renewable feedstocks, wastes and by-products and studies in general green chemistry makes the production of chemicals through integrated biological route (bio-refining) more competitive (López-Garzón and Straathof, 2014, Huang and Ramaswamy, 2013a, Huang et al., 2008).

Carboxylic acids are weak organic acids and a promising versatile green platform feedstock with a potential chemical application for various industries. They are generally present in very dilute aqueous industrial waste streams (less than 10% w/w) which are generated from fermentation broth. Despite challenges in the optimization of fermentation and production processes of value-added products, it is necessary to formulate cost and energy-effective approach in the downstream processes in order to improve the prevailing processing approach (Kurzrock et al., 2011, López-Garzón and Straathof, 2014, Wasewar and Yoo, 2012, Straathof, 2011). Many biorefinery processes employing especially the biochemical approach have challenges in separation and purification owing to some factors including product inhibition, low concentration feed and product yields. The traditional approaches need to be replaced with novel separation techniques to overcome these challenges. The development of this efficient and effective separation technique is necessary to reduce the downstream processing cost of product recovery (Datta et al., 2015b, Wasewar, 2005).

Among the several separation methods (ion exchange, adsorption, electrodialysis, liquid extraction, precipitation, etc.) as described in paper 2 (Chapter 2), reactive extraction and emulsion liquid membrane (ELM), found to be a promising technique for carboxylic acids recovery from a very dilute aqueous solution was explored in this work. These separation methods have several advantages such as removal of the product as soon as it is produced leading to enhanced reaction rates, increased feed conversions, reduced reaction severity and provide operation under milder conditions, reduction in equipment size, elimination

of recyclable streams and reduction in capital and operating costs (Wasewar et al., 2004, Wasewar and Yoo, 2012, Cascaval and Galaction, 2004, Kumar et al., 2019b, Jusoh et al., 2016).

In the reactive extraction, the conventional extractants (aliphatics, aromatics, ketones, alcohols, etc.) have very slight capacity to extract acids from their aqueous solutions because of their low distribution coefficients (lower than 1). So, an extractant (phosphorous and amine-based) is usually employed with diluent to get better separation of acid and appropriate physical properties of the organic phase. Reactive extraction strongly depends on various parameters such as aqueous and organic phase concentration, types of complexes (1:1, 2:1, etc.) formed, type of solvent and their properties (extractant and diluent), temperature, pH and so on (KAHYA et al., 2001). The extraction yield in the emulsion liquid membrane (ELM) process depends on the operation conditions in addition to the solvent properties, surfactant, carrier type (extractant) and concentration, among others (Berrios et al., 2010, Kumar et al., 2019a). Thus, the emulsion liquid membrane efficiency can be presumed to be influenced by the inherent properties of the membrane and operating process parameters (Ng et al., 2010).

1.2 Research Motivation

Low molecular weight carboxylic acids (propionic, butyric acids and so on) and their derivatives are attracting considerable attention for their presence in chemical, pharmaceuticals, food, flavour and fragrance industries and many other natural products. Although significant research work has been carried out on carboxylic acid recovery, experimental and theoretical studies are essential using the best extractant/diluent system, operating conditions and biocompatible system for these acids. To date, there has been no comprehensive study of the effect of operating conditions on the performance of reactive extraction processes for malic and butyric acid systems, in particular the optimization of these processes. Studies on emulsion liquid membrane using different statistical techniques, artificial neural network (ANN) and response surface methodology (RSM) for carboxylic acid recovery are scarce in the literature. These techniques may be useful to find out optimum operating conditions of the reactive extraction system and the interactive effects of the process parameter on the reaction performance which is lacking in the literature. The optimization technique for the determination of reactive extraction parameters and efficiency is studied for propionic, malic, and butyric acids which are still at the research stage. Also, literature is devoid of kinetic information regarding reactive extraction studies for these acids and their useful applications in process intensification. The knowledge of kinetics and optimized conditions of process variables will aid in large scale process design, and possibly feasibility studies.

1.3 Statement of Research Problems

In recent years, interest in the manufacture of fermentation-based chemicals has increased in an effort to replace fossil resources and reduce emissions of carbon dioxide and other greenhouse pollutants. However, an economically viable fermentation process needs to be combined with cost-efficient and effective product recovery and purification approach. About 40% of the production cost of carboxylic acids are incurred by downstream processes. This problem needs to be surmounted so as to develop a cost-effective route in the separation and purification of valuable finished products. It is imperative to study the recovery of carboxylic acids using reactive extraction and emulsion liquid membrane, process intensification methods, which is economically attractive compared to other separation methods. This work therefore, seeks to develop cost-effective and energy-efficient process for low-molecular weight carboxylic acids (propionic, malic and butyric acid) recovery from very dilute aqueous solutions. In addition, there has been no quantitative information on the yields, parametric optimization, kinetics of the studied acids including amounts of solvents, temperatures, initial acid concentrations involved in the separation process. Therefore, in solving these inherent research problems, this research develops a generally applicable platform for efficient carboxylic acid recovery and/or their products, on the models of the studied acids. The integration of bio-based production processes with these recovery operations can pave the way for more successful biorefinery processes currently under development the world over. Based on the research problems, the following research questions were addressed in the present work:

- How efficient is the tri-Octyl Amine (TOA) +1-decanol system in the extraction of propionic, malic and butyric acid from very dilute aqueous solutions?
- What are the most significant operating parameters and their interactive effects on the extraction yield of these acids?
- What are the effects of the reaction kinetics on the overall reactive extraction performances and the reaction regime?
- What are the mathematical relationships between operating parameters and the process performance for reactive extraction and emulsion liquid membrane techniques?
- Which technique is most efficient and effective in the recovery of these acids?

1.4 Aim and Objectives of Research

The purpose of the current research study was to generate fundamental data/information on the application of these intensified separation processes for carboxylic acid recovery. The overall objective of this study was to employ high selective extractant and diluent with different process parameters in order to achieve a

high distribution coefficient giving a higher extraction efficiency and selectivity. In order to achieve this aim, the following specific objectives were outlined:

- To study the efficiency of the intensified processes in the recovery of these carboxylic acids:
  Propionic acid;
  Malic acid; and
  Butyric acid
- To investigate and quantify the effect of operating parameters on carboxylic acid extraction using reactive extraction and emulsion liquid membrane technique.
- Optimization of reaction conditions for the intensified reactive extraction process and emulsion liquid membrane with regard to maximizing the yield.
- To extract kinetic data for the reactive extraction process of propionic and malic acids.
- To formulate and develop mathematical models that relate the process parameters to the extraction efficiency for carboxylic acid recovery.

Each of these objectives was accomplished in the publications as outputs emanating from this study.

1.5 Research Goals Achieved

These specific goals were accomplished by adopting a formal approach. An appropriate organic phase extractant/diluent system for the separation process was carefully selected for optimal selectivity based on a comprehensive literature review. Thus, trioctylamine in 1-decanol met the requirements and was selected for this study. A three-level Box-Behnken design (BBD) was used to carry out the different experimental runs for the optimization of the process variables used in the extraction process. Therefore, high selectivity extractant and diluent with different conditions of process parameters were employed. The purpose of these experiments was to study how the combined effects of the initial concentration of acid in the aqueous phase, initial extractant concentration in the organic phase and temperature influenced the distribution coefficients and extraction yield. Subsequently, the statistical experimental design was used to investigate the optimum conditions of the process parameters on the extraction yield. The intrinsic kinetics of reactive extraction for propionic and malic acid was described and the values of physical mass transfer coefficient, orders of extraction, and rate constants were experimentally determined. Lastly, the application of emulsion liquid membrane for propionic and malic acid extraction was studied. The different parameters investigated were the acid concentration, sodium carbonate concentration, trioctylamine concentration, treat ratio and extraction time on the propionic acid extraction efficiency to study the effects on the percentage of extraction. Response surface methodology (RSM) and artificial neural network (ANN) were employed for experimental design, optimization, interpretation of response/output surface plots and comparison of

predicted response with the experimental results. It was believed that the development of these downstream separation strategies for carboxylic acid recovery using these techniques and adequate mathematical model would contribute to knowledge in this field of study and constitute a novel work.

1.5 Thesis Overview

In this thesis which consists of eight (8) chapters and appendices, the first chapter is a general introduction to the entire work, including the background of the study, rationale and motivation for the research project. An overall aim and objectives and the scope of the project. Description is made on the research goals achieved in line with the statement of research problems. The thesis as a whole is a research outcome of publications as required by the University of KwaZulu-Natal for the award of the prescribed degree. Six research papers emanated from the study each addressing the specific objective of the entire study. They have been submitted to relevant accredited journals, some have been peer-reviewed, accepted and published, while others are under peer-reviews.

In Chapter Two, which is the first contribution that presents an exhaustive literature review on studies relating to carboxylic acid separation. The different conventional and intensified processes are discussed. An overview of the effects of various process parameters, equilibrium and reaction kinetics of carboxylic acid recovery are also presented. The chapter closes with a summary and discussion on industrial applications of intensified separation processes.

Chapters Three, Four and Five are the second, third and fourth contributions on reactive extraction of 3 different acids (propionic, malic and butyric acids) respectively using trioctylamine in 1-decanol by response surface methodology (RSM). The details of the experimental materials, apparatus, procedures, analytical techniques and optimization methodologies are described. Experimental results are presented and discussed. The mathematical model (theoretical) studies for the determination of the optimum equilibrium parameters are also given.

Chapter Six is the fifth contribution and presents the experimentally determined kinetics of reactive extraction of propionic and malic acids.

Chapters Seven and Eight highlight the sixth and seven contributions which were the application of emulsion liquid membrane technique in propionic and malic acid extraction using these statistical techniques: response surface methodology (RSM) and artificial neural network (ANN). The details of the experimental materials, apparatus, procedures including preparation of aqueous and membrane phase, the theory of extraction mechanism, analytical techniques and optimization methodologies are described.

The concluding remarks of this thesis, major contributions, and recommendations for further research are highlighted for the present study in the final chapter, Chapter Nine.

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Chapter TWO

LITERATURE STUDY

Paper 1, SCA: ConIntPro, Accepted and Published

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Inyang, Victoria M. and Lokhat, David (2019)

Separation of Carboxylic Acids: Conventional and Intensified Processes and Effects of Process Engineering Parameters

This chapter represents the literature review of this study which has been peer reviewed, accepted in the form of a book chapter and published: DOI: 10.1007/978-3-030-38032-8; ISBN: 978-3-030-38032-8.

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PAPER ONE

Separation of Carboxylic Acids: Conventional and Intensified Processes and Effects of Process Engineering Parameters

Abstract

Recent research thrust and industrial focus have been directed towards the production of platform chemicals and value-products from biomass-derived materials. However, downstream separation of these bio-based chemicals particularly organic acids such as carboxylic acids poses a great challenge due to low concentration in aqueous solutions. Various conventional separation processes have been proposed, but limitations from waste generation, large energy input and material requirements leading to high costs remain a challenge. Improved sustainability can be attained through intensified process separation with a reduction in production cost, equipment sizes, energy consumptions and flexibility of the process. The direct conversion of the acid in aqueous solutions to esters using hybrid reactors, wherein reaction and separation occur in one single process unit have distinct but significant benefits to comparable applications. Future research on its operational performance requires attention to obtain parameters for process design and consequent corresponding scale-up to commercial production. Good knowledge of reaction kinetics is necessary to enhance process chemistry analysis, reaction parameter optimization, process efficiency and equilibrium studies of the separation process. This information will allow an assessment on the potential industrial applicability of the overall design and development of a sustainable biorefinery approach to value-added production.

Keywords: Carboxylic acid, Process Intensification, biorefinery, reactive separation, reactive distillation.

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1.0 Introduction

The recent global research agenda highlighted industrial system development via process intensification in various sectors vis à vis chemical, water, and food production as being crucial to achieving technological milestones in the envisaged 2050 (Górak and Stankiewicz, 2012). The new trend in the utilization of renewable feedstock, wastes and by-products and studies in general green chemistry has made the production of chemicals through a bio-based route using cheap and available biomass materials to receive increasing attention. Many bio-refinery processes employing especially the biochemical approach have challenges in the downstream separation and purification processes due to some factors such as product inhibition, low concentration feed and product yields (Huang and Ramaswamy, 2013b). Use of biomass materials which are cheap and abundantly available contributes to reducing the costs in producing desired products. Biotechnology is potentially presenting new, efficient and low-cost fermentation processes using biomass feedstock for chemical production. The economic impact of fermentation bio-products is presently limited due to challenges in the recovery of products from aqueous solution. Therefore, the development of recovery techniques is essential to allow for chemicals obtained by fermentation to further penetrate into the industry (Datta et al., 2015b).

Currently, acids derived from petrochemicals are produced at a cheaper rate compared to those derived through bio-based route. Therefore, research efforts must be expanded to discover more effective ways to decrease the cost of processing bio-based acids. More importantly, in the downstream processing as a significant amount of the final processing costs are taken into account in the separation and purification of the required products (Kurzrock and Weuster-Botz, 2010, Rackemann and Doherty, 2011). While several attempts have been made to improve bio-based separation processes to source different acids, no adequately successful technologies have been developed to industrial production level. In spite of the several separation processes proposed (chromatography, liquid-liquid extraction, ion-exchange resins, precipitation, membrane separation) to overcome this bottleneck, limitations still remain in terms of lean production, waste generation, large energy input and material consumption (López-Garzón and Straathof, 2014, Rackemann and Doherty, 2011, Wasewar, 2005).

A potential alternative process is using hybrid reactors in the direct conversion of acids in aqueous solutions to esters, where reaction and separation occur simultaneously. This intensified process has clear advantages over conventional processes by reducing the cost of production and providing esters as intermediates for other chemical syntheses. Although esterification is a well-known technology, focus on its operational performance still needs to be better understood to generate the necessary design model tools, and consequently its scale-up to commercial production. Thus, a major requirement for making the reactive separation process viable is the identification of suitable catalysts with high stability and activity, easy separation and recovery of products, and avoidance of equipment corrosion. Besides catalyst development, a better understanding of esterification reaction kinetics is necessary to enhance process chemistry analysis, reaction parameter optimization, and equilibrium studies of the separation process. This information, in

turn, will allow an assessment to be made on the potential industrial applicability of the overall design and development of a sustainable bio refinery approach to value-added production.

The development and implementation of these separation strategies are required for optimum and successful commercialization of biorefineries. Biorefineries are essentially the upstream, midstream and downstream processing of biomass to bio-based products including a collection of co-products and bioenergy (including chemicals and other materials) (Huang et al., 2008, Huang et al., 2012). Before any industrial commercialization can succeed, some technical challenges need to be overcome for the full utilization of bio-based products. Biomass feedstocks for production of chemicals and energy include starchy biomass (cassava, wheat/corn), sugarcane, lignocellulose biomass like agricultural residues (crop residues) such as barley straw and sugarcane bagasse), municipal solid wastes refined materials, such as fructose, glucose, and sucrose, mixtures of these materials, post-fermentation liquor and the likes. In general, biomass-based industries have been moving towards the integrated biorefinery approach employing the three necessary sequential approach/stages which include (Girisuta, 2007):

1. Biomass separation into different components in the fractionation unit.

2. Conversion of fractions into useful products. For these secondary processes, three so-called platforms can be applied: chemical, biochemical and thermochemical processes (gasification and liquefaction).

3. Further downstream processing to value-added products. This can be achieved through three different platforms.

1.1 Biochemical Platform

The biochemical platform includes all biochemical conversion processes, including the production of fermentable sugars by saccharification of cellulose and starch, and the fermentation of sugars obtained from lignocellulosic biomass. One of the many biochemical conversions deals with sugars, where biomass is initially pre-treated and hydrolysed to mono-sugars that on further processing, are fermented to biofuels (ethanol and butanol), or chemicals (example succinic, butyric, lactic, malic, propionic, acid) depending on the biocatalysts that are employed.

1.2 Thermo-chemical Platform

Thermo-chemical platform biomass conversion includes biomass combustion for heat generation, bio-oil and bio-char, hydrothermal liquefaction to bio-oils as a key product, and biomass gasification to syngas. Syngas (CO and H_2) from biomass gasification can be converted further into a variety of diverse chemicals and fuels using appropriate catalysts and appropriate operating conditions.

1.3 Chemical Platform

Bio-refinery comprises several other chemical conversion processes. For example, the manufacture of value-added chemicals such as butyric, succinic, malic, propionic acids; formic, acetic and lactic acids (de Souza et al., 2014). A biorefinery can also utilize both thermochemical and biochemical or chemical and biochemical conversion approaches. Therefore, the chemical industry based on biomass derived-materials will be developed on selective platform chemicals other than the petrochemical-based industry. There is no standard solution to define the ‘optimum’ bio-refinery, but a highly efficient, economically viable and sustainable one can be realized by efficient downstream conversion processes, flexibility in equipment design, maximizing chemical energy utilization from feedstock, and development of conversion capacities, that are independent of specific fuels, materials and chemicals (Corma et al., 2007).

The implementation of the biorefinery concept brings about several advantages at various levels and for multiple stakeholders: From a national perspective, it may help to meet national energy needs, while reducing greenhouse gas (GHG) emissions (Naik et al., 2010). From the industrial point of view, an integrated biorefinery reduces the risk of operation by increasing the number of products produced, aiming at various markets. Additionally, the return on investment is significantly improved when the processing plant operates continuously throughout the year. In this article, the status and different recovery and purification process for carboxylic acids, a platform chemical that can be obtained from biomass-derived materials are summarized and presented. Conventional separation processes of carboxylic acid, which include membrane separation, precipitation, liquid-liquid extraction, distillation, chromatography, and crystallization have been reviewed and discussed. Each technology has its own limitation and no single method has proved to be simple, efficient and effective with regards to yields, purity, energy consumption and scale-up to commercial production. Therefore, improvements are still needed in the development of separation and purification processes which deserves utmost attention for the promising biorefinery industry.

Thus, the need for the intensified separation process and enhancement mechanisms with particular focus on Process Intensification of reactive extraction and reactive distillation processes as the most significant separation methods. Additionally, the reliability and potential of reactive separation processes which is promising and will enable higher efficiency and capacity are discussed. Downstream processing of carboxylic acids with different extractant types and diluent used, equilibrium and kinetic studies and models which is necessary for the overall process design of the reactive separation process and the effects of process parameters on the separation and purification of carboxylic acids are also discussed.

2.0 Carboxylic Acids/Platform Chemicals

Carboxylic acids such as butyric, lactic, malic, propionic, citric, lactic, succinic and itaconic acids and others are important chemicals products and are often recovered from fermentation broths. Historically, raw materials for the production of carboxylic acids include animal fats, petroleum and vegetable oil sources in largely non-aqueous systems. In recent times, these carboxylic acids have been listed among the most desirable products which are manufactured from biomass feedstock through fermentation routes. In the later processing, it is produced from fermentation broths of dilute aqueous solutions (King and Poole, 1995). A drawback of using fermentation of bio-based feedstocks for the production of chemicals is that an aqueous solution with inherently low product concentrations is achieved, and above 40% of the cost stems from downstream processing according to Straathof (2011). This has led to the advancement of existing processes as well as the development of new processes due to the current interest in bio-based economy (López-Garzón and Straathof, 2014). Thus, the need for an overview of recovery alternatives.

Most carboxylic acids have extensive applications in food, pharmaceuticals, detergents, surfactants, and green solvent industries and as raw materials for eco-friendly polymers (Hong et al., 2001). Carboxylic acids are favorable intermediates in a bioprocessing multifaceted complex because the oxygen of the biomass is placed in a form that is useful for further reaction with many other products (King, 1992). Typical carboxylic acids with early stage process development are shown in Table 2.1.

Table 2.1 Typical carboxylic acids of commercial interest for production by fermentation (López-Garzón and Straathof (2014)

Molecular formula	Carboxylic acid	Status biochemical production	Main application
$C_2H_4O_2$	Acetic	Industrial	Vinegar
$C_3H_4O_2$	Acrylic	Research	Polymers
$C_3H_6O_2$	Pyruvic	Research	Chemicals

$C_3H_6O_2$	Propionic	Design stage	Chemicals
$C_3H_6O_3$	$_{D/L}$- Lactic	Industrial	Food, polymers
$C_3H_6O_3$	3 – Hydroxy-propionic	Research	Polymers
$C_4H_4O_4$	Fumaric	Formerly industrial	Food, polymers
$C_4H_6O_4$	Succinic	Industrial	Polymers, chemicals
$C_4H_6O_5$	$_{L}$- Malic	Research	Chemicals
$C_4H_8O_2$	Butyric	Design stage	Chemicals
$C_5H_6O_4$	Itaconic	Industrial	Polymers
$C_5H_8O_4$	Glutaric	Research	Polymers
$C_6H_4O_5$	2,5-Furan-dicarboxylic	Research	Polymers
$C_6H_8O_7$	Citric	Industrial	Food
$C_6H_{10}O_4$	Adipic	Design stage	Polymers
$C_6H_{10}O_7$	2-Keto-$_{L}$-gulonic	Industrial	Vitamin C precursor
$C_6H_{12}O_7$	$_{D}$-Gluconic	Industrial	Food

2.1 Dissimilar Property Nature of Various Carboxylic Acids

Physical properties of carboxylic acids are dissimilar and so recovery processes are different. But those carboxylic acids grouped on the basis of physical properties have a similar way of recovery. These dissimilar physical properties of various carboxylic acids are shown in Table 2.2. It is one of the bases for employing intensified separation approach, recovery and purification involving carboxylic acids. There is no particular recovery process for all carboxylic acid. Some carboxylic acids may be grouped based on their physical properties and they should be recoverable in a similar way, for example acetic, itaconic, propionic, succinic acids and butyric acids.

Table 2.2 Dissimilar properties nature of various carboxylic acids (López-Garzón and Straathof (2014)

Acid name	pK_a values	Solubility in water (g/L)	Melting point (°C)	Boiling point (°C)
Acetic	4.75	Miscible	17	118
Butyric	4.81	Miscible	-8	163
Citric	3.14;4.77;6.39	~600	153	Decomposes
Fumaric	3.03;4.44	6.3	Sublimes	200
Gluconic	3.60	Good	131	Decomposes
3-Hydroxypropionic	4.51	High	<25	Decomposes
Itaconic	3.85;5.45	80-95	165(decomp.)	
Lactic	3.86	High	53	Decomposes
Malic	3.40;5.11	558	130	Decomp.>140
Propionic	4.87	Miscible	-21	141
Pyruvic	2.50	Miscible	12	Decomp. 165
Succinic	4.16;5.61	77	185-187	235

2.2 Conventional Processes for Downstream Recovery of Carboxylic Acid

Downstream processing accounts for a substantial part of the overall cost of production and requires a large amount of energy. To achieve optimum techno-economic feasibility and a functioning but sustainable bio-refinery, a good knowledge of current and alternative separation techniques and generation of novel method approach is required. Most carboxylic acids are generated by solvent extraction from dilute aqueous solutions. They are also obtained as products from stable oxidation and by-products from organic wastes and aqueous streams. There are several potential environmental and industrial applications where carboxylic acids can be recovered from aqueous solutions. These include citric and lactic acid production

by fermentation and carboxylic acids recovery from aqueous waste streams (King and Poole, 1995). An important aspect of chemical industries and fermentation technology is efficient carboxylic acids separation from aqueous solution utilizing different solvents with attendant significant improvements. Extractions are carried out using different organic solvents and these are grouped into three types:

Conventional solvents with oxygen and hydrocarbon content;

Oxygen-bearing extractants bonded with phosphorus; and

Aliphatic amines with high molecular weight.

Low distribution coefficients are obtained when the conventional solvents are employed for the extraction of carboxylic acid thus leading to inefficient extraction (Juang and Wu, 1996). Organophosphates solvents such as trioctylphosphine oxide, tri-*n*-butyl phosphate and aliphatic amines for carboxylic acid extraction gives higher distribution coefficient. A number of aliphatic amines have been employed in carboxylic acid extractions(Ingale and Mahajani, 1996, Luque et al., 1995).

To obtain an efficient and effective recovery process at an industrial level, the following requirements must be met (López-Garzón and Straathof, 2014):

Specified purity (99.5%) for dicarboxylic acids for polymerization use (Musser, 2005), since polymerization can be terminated using monocarboxylic acid.

High yields (90–100%) in the recovery process of the downstream processing.

Minimal energy utilization and waste production while recovering products and low chemical use.

Moderate cost of investment in the recovery equipment as a result of heat and mass transfer efficiency.

Fermentation-derived chemicals such as carboxylic acids have difficulties related to the high recovery cost. Similar to those derived through chemical routes, final product purity and co-production prevention are key influencing factors. Also, an energy-efficient way of managing the dilute fermentation broth must be developed to enable scale up to commercial production of carboxylic acid (Huh et al., 2006).

Various separation methods are used in the production of high-valued co-products from different feed streams in bio-refineries. Huang and Ramaswamy (2013b) in their study articulated the fact that separation and purification processes are vital features of bio-refinery operations; their optimum selection and design are catalysts in maximising product yields and the improvement of overall process efficiencies. Modern biorefineries approach employed various methods of separation and purification to generate co-products of high value from input feed streams and finally end-products. The different conventional methods of separation are discussed in the following sections.

2.2.1 Membrane Separation

Because of its adaptability, selectivity, high purity and yields obtainable, membrane technology is another separation process used in the recovery of organic acids. With material technology and recovery process development, more attention has been given to membrane separation, particularly in the *in-situ product recovery* (ISPR) technology. Membranes are basically a thin natural or artificial impediment, which permits selective solvent or solute mass transport through the barrier, in order to attain enrichment objectives and physical separation. The major established membrane purification/filtrations for carboxylic acids separation utilized for wastewater treatment include pervaporation, microfiltration, nanofiltration, ultrafiltration, electrodialysis and reverse osmosis (Cheng et al., 2012, Vane, 2005, Mao et al., 2014). For example, nanofiltration was employed in succinate recovery from replicated broth and a lower rejection to monovalent than the divalent ions were observed with the nanofiltration membrane (Hyeon Kang and Keun Chang, 2005).

González et al. (2008) also employed nanofiltration to recover lactic acid from the clarified broth, the lactate ions to non-ionized lactic acid ratio have a significant effect on the permeate flux and rejection of the nanofiltration membrane. Lactate permeation decreased with pH and increased with pressure while an increase in pH and pressure also increased with the lactate rejection. Other methods for membrane separation can also be employed to recover organic acids from aqueous solution. The drawback for using membrane separation is the high consumption of energy with the attendant high cost of membranes although the method is highly efficient. In addition, the efficiency of membrane separation decreases with increase in the concentration of organic acids. Another drawback is membrane pollution which occurs during the process of ion exchange which also leads to the formation of unwholesome by-products (Boonkong et al., 2009, Wasewar, 2005).

2.2.2 Precipitation

This is a traditional method for organic acid recovery from the broth, which has been used for industrial separation of lactic and citric acids in the past century. It can efficiently recover organic acids from the bulk of fermentation broths making it quite competitive particularly in primary purification. Considering precipitation of calcium as an example, there are four steps used to separate organic acids. Firstly, the filtration of fermentation liquid to remove impurities and obtaining the mother liquor then the addition of $Ca(OH)_2$ or $CaCO_3$ to the liquor with agitation. Secondly is the filtration of calcium salts of organic acid from the broth. Thirdly, treatment of calcium salt with sulphuric acid follows and further purification to obtain the acid required (Wasewar, 2005, Lee and Kim, 2011). In the study to improve the conditions of citric acid recovery from fermentation mash, the optimum conditions were found to be 50°C for 20 min with almost 100% yield (Heding and Gupta, 1975, Max et al., 2010). In another study, for isolation of lactic acid, it was observed that calcium lactate to sulphuric acid molar ratio played a vital role in the yield improvement. About 92% yield of lactic acid was obtained at optimized conditions (Min et al., 2011). As merit, precipitation has a preference for high selectivity and purity, no phase transition necessary as the main advantage which hovers mainly on establishing the right product precipitant. The underlining factor is mainly the search for the right product precipitants. High consumption makes cost reduction difficult, thus the development of reusable precipitant is needed for competitiveness.

2.2.3 Chromatography

The method mainly focuses on the adsorption properties or ion exchange products from resin. Chromatography is an established method for purification of organic acids from the aqueous medium, specifically in the product refining. Insolubility in acids or organic solvents, the stability of resins are some of the physical and chemical properties of resins. Resins have good organic acids selectivity and low energy consumption selectivity with no phase transition (Park et al., 2014). The most used resins in recovery processes are mainly ion exchange resin and macroporous adsorption resin (Bishai et al., 2014). Increased capacity, quicker recovery, low consumption regeneration, and specificity of desired products are characteristics of resin sorbents (Li et al., 2010). In the study by Tong et al. (2004), resins having weak anion exchange was employed in lactic acid purification. The result showed that yield improvement was optimum between pH of 5.0 and 6.0. The purity and yield of the recovery process were 92.2% and 82.6% respectively. Poly (4-vinylpyridine) resin was also employed in lactic acid recovery and the purity and yield obtained were 88% and 95%, respectively (Zhou et al., 2011). XUS 40285 resin from 25 different sorbents showed outstanding performance with succinic acid stability either at neutral or acidic pH (H Davison et al., 2004). Co-products are not produced using this method and product yields are high. However, a significant quantity of waste liquor is usually produced while the elution process demands high salt consumption. Additionally, the ion exchange ability of the resin are usually weakened at the long run (Aljundi et al., 2005, Cao et al., 2002).

2.2.4 Distillation

Distillation is a technique used in the separation of mixtures with differences in their component volatility or boiling points. It can be utilized both at the initial or final stage of separation and purification combined with crystallization hence it remains an important technology according to (Errico and Rong, 2012). Generally, at low organic acid concentrations, effective distillation is carried out but at high concentration or at the azeotropic point, it becomes inefficient (Huang et al., 2008).

2.2.4.1 Extractive Distillation

Extractive distillation using ionic liquid solvent was employed to separate organic acids typically carboxylic acids (Blahušiak et al., 2012). Phosphonium IL was used in the extraction of butyric acid with up to 89% yield followed by regeneration using a short-path distillation carried out in two stages. The process offers a significant advantage in product recovery where a free acid is obtained instead of its salt. Distillation which is a known separation method for volatile components is often used in separation since the carbonyl group has a strong effect on the adsorb-electron and the boiling points of most organic acids are higher than water.

2.2.4.2 Molecular Distillation

Molecular (vacuum distillation), a distinct distillation process suitable for fractionation and chemical separation from pyrolysis of bio-oils and is performed below high-vacuum conditions (Wang et al., 2009b, Guo et al., 2010, GUO et al., 2009). Wang et al. (2010) investigated crude biodiesel purification using molecular distillation and established a high yield result of up to 98.32%. The molecular distillation condensation efficiency was enhanced using traditional vacuum distillation to eliminate a greater percentage of the water in the unrefined bio-oil followed by fractionation of molecular distillation. From the obtained results, the fractions that was distilled were rich in low molecular weight ketones and carboxylic acids; the residual fraction has little or no water with improvement in heating values of 21.29 MJ/kg and 22.34 MJ/kg for two different operating conditions (80 ◦C, 1600 Pa and 80 ◦C, 340 Pa), respectively. Vacuum distillation is generally employed in carrying out experiments and in industrial manufacturing in order to accrue high-level savings in general cost of production.

2.2.5 Liquid-liquid Extraction

Liquid-liquid extraction is a standard operation in chemical engineering discipline for the separation of mixtures based on their comparative solubility in two immiscible liquids in chemical and biochemical industries (Cheng et al., 2012, Kurzrock and Weuster-Botz, 2010). It can be employed in carboxylic acids separation (Aşçi and Inci, 2012, Redhi et al., 2015, Maurer, 2006, Oliveira et al., 2012) from aqueous solutions and extracting compounds (toxic to microorganisms) from biomass hydrolyzates (Grzenia et al., 2012). Considerable research studies on liquid-liquid extraction have been conducted for the separation of carboxylic acids from aqueous solutions (Huang et al., 2008). Chen et al. (2012) developed an innovative recovery and purification process to obtain L-lactic acid with high quality without very low pressure. There was a significant improvement in the L-lactic acid yield and purity of about 61.73% and 91.6% respectively. Advantages of liquid-liquid extraction includes: short cycle, a rapid mass transfer which occurs between phases. For effective and green separation, the required properties in solvent selection and formulation must be considered.

2.2.5.1 Solvent Selection Criteria

The criteria of effective solvent selection are (Huang et al., 2008) the solvent:

be non-toxic to the microbes;

have high stability, distribution coefficient and product selectivity;

should have aqueous phase low solubility;

possesses different broth density for easy phase separation;

must have low viscosity, low broth emulsification tendency, large interfacial tension; and of minimal costs.

2.2.5.2 Ionic liquid extraction

Ionic liquids are salts consisting of ions which have developed rapidly in recent times (Lateef et al., 2012, Sun et al., 2011, Wang et al., 2005). Most of them are imidazolium (Wang et al., 2005, Lateef et al., 2012), quaternary phosphate (Marták and Schlosser, 2007, Oliveira et al., 2012), or quaternary ammonium salt (Mikkola et al., 2006), which are non-flammable and non-volatile and liquids at different temperatures (Domańska et al., 2012). Ionic liquids are promising alternatives to conventional organic solvents because of the advantageous extractabilities of organic compounds (Lateef et al., 2012, Sun et al., 2011). Oliveira et al. (2012) employed phosphonium-based hydrophobic ionic liquids for f L-lactic, succinic, and L-malic acid separation from aqueous solutions. The results showed that the extraction ability of the ionic liquids was better than the traditional extractions using organic compounds. About 73% recoveries were achieved. Marták and Schlosser (2007) demonstrated that industrially processed phosphonium-based ionic liquids have an improved performance than the conventional organic solvents used in lactic acid separation. Though many signs of progress were made using ionic liquids extraction, the only limitations have been that of the high cost of ionic liquids.

3.0 Process Intensification (PI)

Due to its sustainable and innovative potential for process improvement, studies on process intensification has received considerable attention in a chemical engineering discipline. Chemical processes with large equipment size lead to a large amount of energy consumption for process operation. The conventional processes often consist of large and cumbersome processes due to their old chemical engineering design (Stankiewicz and Moulijn, 2002) and can be replaced with the most efficient small unit operation (Stankiewicz and Moulijn, 2002, Reay et al., 2013). Thus, to achieve this, some unit operations can be integrated, combined and intensified for higher efficiency. For example, the reduction in the equipment size of methyl acetate production with 28 pieces of equipment to 3 pieces of equipment by combining reaction and separation thus leading to decrease in energy consumption and cost of manufacturing by as much as 80%. Furthermore, since the intensified process has lower energy consumption than the conventional processes, there is a reduction on acidification pollution, global warming and depletion of fossil fuel and carbon emissions by a factor of 5 and 7 respectively (Harmsen et al., 2004). Since the early introduction of process intensification in the 1970s, significant attempt has been made in the definition, application and development of process intensification by chemical engineers. Different definitions are occasionally mentioned in different studies. However, Van Gerven and Stankiewicz (2009b) opined that a universally accepted definition may be quite difficult to attain since it is a continuous growing field in chemical engineering (Stankiewicz, 2003, Yildirim et al., 2011) and should answer to the current needs of the global market and different stakeholders as well as pertained to other fields.

Process intensification can be summarized as process development involving equipment (unit operation) size reduction which leads to enhancement in chemical reaction kinetics, energy efficiency, process safety, minimization of waste generation and overall capital cost reduction. Process Intensification offers the most important drifts in recent process technology and chemical engineering. One fundamental component of Process Intensification is multifunctional reactors which combine unit operations that would traditionally be carried out separately in different equipment. Reaction and separation integration offer multifunctional reactors with significant refinement. This integration is mainly at the level of equipment; no additional functional interrelations are introduced between the operations and the fact that reactions are unaffected by the separation and vice versa. This combination is specifically aimed at improving energy management, reduced inventory and plant design. An example of process intensification is hybrid distillation at the plant level with different unit operations integration comprising of at least one unit operation, a conventional

distillation column, so as to satisfy the separation job (Babi et al., 2014). Membrane separation integration with conventional distillation can be considered to overcome certain barriers in thermodynamics such as azeotrope formation (Lutze and Gorak, 2013). Another example of process intensification is the divided wall columns (Halvorsen and Skogestad, 2011, Madenoor Ramapriya et al., 2014) and process intensification that enhance the reaction conversion through in situ product removal are membrane reactors (Van Baelen et al., 2005, Inoue et al., 2007), reactive distillation columns (Shah et al., 2013, Holtbruegge et al., 2013) and reactive extraction (Wasewar and Yoo, 2012)

Chemical product manufacturing and processing requires intensified process development and improvement by reconsidering existing operation designs into more precise and efficient options. This process intensification encompasses combining distinct unit operations into one single unit such as reaction and separation; thus, resulting in a simpler, more economical, efficient and cleaner production process. There is significant mixing improvement which enhances reaction kinetics, heat and mass transfer, selectivity and yields of the overall process. This leads to equipment size reduction, the complexity of the process, facility footprints thus minimizing risk and cost in chemical production facilities. Process performance optimization is the crux of PI and the focus is on reaction kinetics, mass and heat transfer and thermodynamics. The four fundamental principles for Process Intensification presented by Van Gerven and Stankiewicz (2009a) include:

Effectively maximizing intramolecular and intermolecular outcomes (for instance: attaining kinetic regimes through a rigorous change of conditions to achieve higher selectivity and conversions).

Uniform process occurrence for all molecules (for instance plug flow reactor conversion with minimal and uniform heating)

Optimize the driving force while maximizing their individual surface areas (for instance using microchannel designs to increase the surface area).

Maximize combined effects resulting from partial processes (for instance product removals when formed thus altering the equilibrium of reaction).

Process Intensification designs and strategies that successfully attain some/all of these optimal conditions at a molecular level will possibly be transformative. Reactors with adequate environment monitoring could considerably improve conversion, yield and also selectivity, which correspondingly would decrease energy, material requirements and carbon concentrations, reduce demands of purification, and minimize generation of wastes. In addition, PI technology know-how could facilitate product manufacture that could not be successfully achieved. PI approaches involve a combination of various steps of processing (e.g., reactive extraction and reactive distillation). Process intensification through reactive separation processes could be successfully applied to esterification with overwhelming results and outputs.

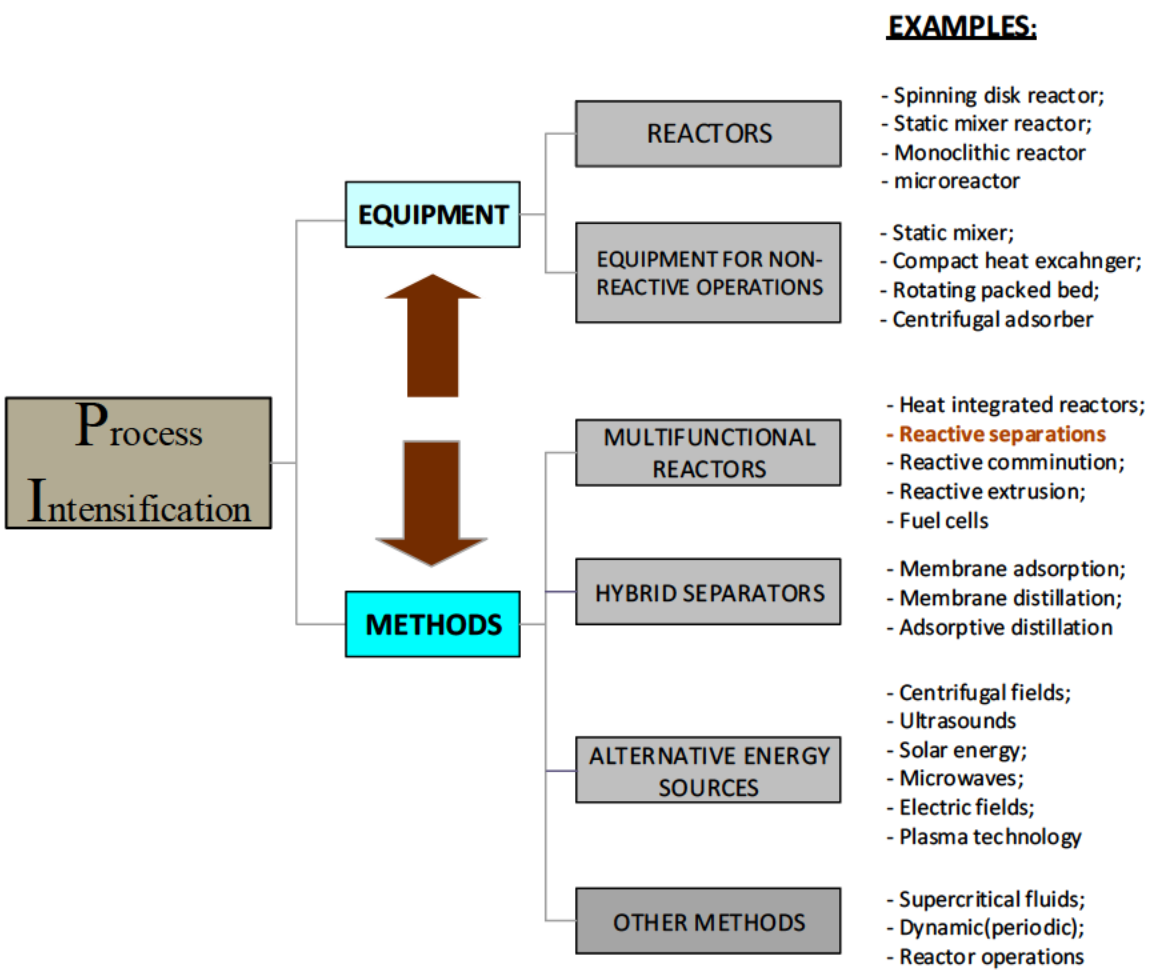

Fig 3.1: Process Intensification and successive components. Stankiewicz and Moulijn (2000)

3.1 Separation through Process Intensification

Several unit operations have been applied by various researchers for carboxylic acids (example lactic acid) recovery through fermentation routes such as membrane separation, precipitation, chromatography, distillation and extraction (Hábová et al., 2004, Ren et al., 2011, Zhou et al., 2011). Process intensification can be used to improve separation processes which account for up to 60-80% of processing cost in chemical processes (Ragauskas et al., 2006). The following section is aimed at reviewing some of the intensified separation processes with major focus on reactive separation process intensification.

3.1.1 Reactive Extraction

Reactive extraction is the combination of reaction and separation in one single unit operation. This leads to the effectiveness of the operation either when the reaction significantly enhances separation through improved mass transfer rates or when the separation propels the reaction to higher conversions or both. This fusion of reaction and separation as a single unit operation is esteemed for its novelty and easiness. The low operating and investment cost also makes the operation desirable which is accumulated on the commercial operation (Wasewar and Yoo, 2012). The processes associated with reactive extraction include the following; hydrolysis, ion complexation, dissociation and two-phase association and finally phase equilibrium.

Reactive extraction methods have gained much attention due to development of new improved processes and the decline of existing ones, demand of low cost, high purity and environmentally safe products in response to excessive economic industrial pressure (Keshav et al., 2009a). Reactive extraction also connects sources and sinks in chemical processes to improve reaction rates, selectivity and conversions. Since most of these chemical processes are driven by equilibrium, product removal as produced enhances reaction rates, increases conversion of feed, reduces the severity of reactions and provides milder operational conditions. Furthermore, reaction and separation processes increase separation driving forces, equipment size reduction, utility cost reduction, safer equipment and removal of recyclable streams. The coupling also inhibits by-product reactions capable of exhibiting runaway behaviour and separator design leads to inherent safety against serious process setbacks. The combination offers low equipment cost through recycle streams process elimination and merging of various process of pieces of equipment (Wasewar et al., 2004).

Reactive extraction with the required high distribution coefficient extractant is a promising technique in the carboxylic acid recovery. Reactive extraction is a clean process, since the extractant can be recovered and reused, has spawned a wide scope as an effective and efficient separation process. The main difficulty is in the search for an effective and selective extractant (Wasewar et al., 2010, Wasewar et al., 2002b, Keshav et al., 2009a). The development of reactive extraction is to help intensify separation and exemplifies the chemical connection between (extractant and solute) and physical (solubility and diffusion) phenomena. Thus, the reactive separation process has been positioned as an effective recovery step for carboxylic acids from dilute aqueous solutions (Cascaval and Galaction, 2004) which hitherto is quite herculean.

3.1.2 Selected extractants for Carboxylic Acid Recovery

Several extractants have been proposed by many authors for the extraction of organic acids with the aim of increasing extraction yields and selectivity. Primary amines can be used for extraction of organic acids and are characterised by aqueous phase high solubility. Secondary amines give maximum distribution coefficients but the downstream regeneration obtained by distillation has the tendency to form amides. The most attractive extractive agents for carboxylic acids are the tertiary amines and only the undissociated acid can be extracted by primary, secondary and tertiary amines. Extraction of undissociated acid can be done using primary, secondary or tertiary amines while the dissociated and undissociated acid can be extracted using quaternary amines though regeneration by back extraction is difficult.

The extractant is the active constituent primarily responsible for carboxylate transfer to the diluent/solvent phase. Extractants having hydrophilic functional groups are designed with hydrophobic substituents, for example, long alkyl chains, to minimize their solubilities in water. Also, the alkyl substituents properties influence the chemistry of interaction, transport properties and extractant phase behaviour. Therefore, undesired mass transfer properties would be present if used pure. Hence, properties such as viscosity and interfacial tension can be improved by using a diluent with a positive impact on the mass transfer and phase separation. Examples of diluents include alcohols, halogenated hydrocarbons and alkanes.

Some extractants form complexes with acids which needs to be solvated. If the diluent has no required solvation power as presented in Table 3.1, there will be the formation of complexes in a different third phase thus leading to difficulties in separation. A modifier, which generally improves complex solvation is used in some cases. Modifiers are less cost-effective than diluents and insufficient transport properties to be used exclusively with extractant (López-Garzón and Straathof, 2014). The most commonly used modifiers are long chain alcohols. Modifiers enhance extraction and additionally influence the amine basicity thereby improving phase separation (Keshav et al., 2009f, Marinova et al., 2005). Table 3.2 shows some extractants used in acid recovery together with their respective solvents/modifiers.

Table 3.1 Decreasing Solvation power of extraction systems diluents (Tamada and King (1990b), Wang et al. (2009a)

Solvent type/class	Diluents
Alkanols	1-octanol, 1-decanol, 2-Ethyl-1-hexanol
Halogenated proton donors	Dichloromethane, chloroform, 1,2-dichloroethane
Ketone and esters	Diisobutyl ketone, methyl isobutyl ketone.butyl acetate
Aliphatic hydrocarbons	Hexane, octane, dodecane
Alkyl aromatics	Xylene and toluene
Halogenated aromatics	Dichlorobenzene, chlorobenzene

3.1.3 Reactive Distillation

Reactive distillation, a coupling of reaction and distillation in a single unit operation offers multiple advantages over normal successive method of reaction and distillation in different units or other separation processes. This combination is an important concept in industrial applications of the multifunctional reactor. Some of the advantages offered by reactive distillation include enhanced selectivity, increase in conversion yields, heat control improvements, prevention of azeotropes and ease of separation, energy consumption reduction and separation of components with close boiling point resulting in a reduction in operating costs and capital investments. Integrating more functions into a single unit creates beneficial synergy for separations as the products are isolated and produced *in situ* (pulling the equilibrium conversion to completion). This *in situ* product recovery leads to complexation interactions between the vapour-liquid equilibrium, rates of mass transfer, chemical reaction kinetics and diffusion, posing a great design challenge and process synthesis of the system.

There are ongoing research efforts on process modelling and simulation, process synthesis, hardware column design due to RD being a new field. Reactive distillation in a continuous process was used for lactic acid recovery and consumes less energy with higher selectivity than conventional processes with discontinuity (Kumar et al., 2006b). Process intensification using reactive extraction and reactive distillation approach for recovery of carboxylic acids have been studied by various researchers in literature in Table 3.3. The techniques, solvents used, catalyst type, studies conducted and resultant outcomes/applications have been reviewed and summarised in Table 3.3 while Table 3.4 summarizes the various methods of recovery and their benefits and constraints.

Table 3.2 Primary recovery of carboxylic acids and selected extractants (López-Garzón and Straathof (2014)

System	Extractant name	Functional group	Structure characteristics	Solvent (modifier)
Amine-based	N1923	Primary amine	Methyloctadecyl amine	1-octanol Butyl acetate Hexane
	Primene ®JM-T	Primary amine	Branched alkyl chains C16-C22	Kerosene
	Amberlite ® LA-2	Secondary amine	Asymmetric alkyl chains C12-C15	Diethyl carbonate
				Methyl isobutyl ketone 1-Hexanol Kerosene (1-octanol)
	Tris(2-ethylhexyl)amine	Tertiary amine	2-Ethylhexyl alkyl chains	Kerosene
	Trihexylamine	Tertiary amine	Hexyl alkyl chains	1-Octanol
	Tri-n-octylamine (Alamine® 300)	Tertiary amine	Straight octyl chains	Kerosene Dodecane (1-decanol) n-Paraffins (isodecanol) Heptane (1-octanol, tripropylamine) Methyl isobutyl ketone Methyl isobutyl ketone (1-octanol) 1 – Octanol
	Triisooctylamine	Tertiary amine	Isooctyl alkyl chains	Chloroform Heptane 1 – Octanol
	Alamine® 336	Tertiary amine	Straight alkyl chains C8-C10	2-Octanol Kerosene 1 – Octanol Decanol Cyclohexanone
Ionic liquids	Aliquat® 336	Quaternary ammonium salt	Linear alkyl chains C8-C10 and methyl substituent	2-Octanol Kerosene 1-Octanol Shellsol ® A Dodecane (1-decanol) 1 – Hexanol Hexane
	[Bmim][PF6]	Imidazolium salt	Butyl and methyl substituents	None, tributylphosphate
	[Bmim][BF4]	Imidazolium salt	Butyl and methyl substituents	None

	Trioctylamine-bis(2-ethylhexyl)phosphoric acid	Tertiary amine-organophosphate salt	Linear octyl chains mostly	Xylene
	Aliquat® 336 – bis(2-ethylhexyl)phosphoric acid	Quaternary ammonium-organophosphate salt	Linear alkyl chains C8-C10-C16 phosphate	Isopar®K
	Cyphos®IL104	Phosphonium-alkylphosphinate salt	Linear alkyl chains C10-C16 phosphinate	Dodecane
Neutral/solvating	Tributylphosphate	Phosphate ester	Linear butyl chains	Dodecane Hexane Sunflower oil
	Tri-n-octylphosphine oxide	Organophosphorus oxide	Linear octyl chains	1 – Octanol Hexane

Table 3.3 Some carboxylic acids recovery processes using reactive separation as process intensification approach developed by researchers

Carboxylic acid	Process Intensification Technique	Solvent Employed	Catalyst	Comments/Remarks	References
Lactic acid	Reactive Distillation-Integration of reaction and distillation in one single piece of equipment	n-Butanol Methanol	Amberlite Catalyst, Ion exchange resin	The Study focused on the effect of feed concentration, mole ratio and catalyst loading/weight on water removal from the aqueous lactic acid solution.	Rao et al. (2014), Komesu et al. (2015) Kumar et al. (2006a)
Succinic acid	Reactive Extraction	Tri-N-Octylamine, TOA in 1-Decanol, 1-Octanol		The Study focused on equilibria and temperature effect on succinic acid extraction, extraction efficiency and Initial acid concentration	Eda et al. (2016), Eda et al. (2015), Umpuch et al. (2016), Orjuela et al. (2011)

Acetic acid	Reactive Distillation	Methanol	Ion exchange resin	Effect of changing various designs and operating parameters was studied, valid kinetic expression was developed and catalyst loading insensitivity of reaction rate was addressed.	Singh et al. (2006), Grzenia et al. (2008)
Itaconic acid	Reactive Extraction	Amine-diluent combination		Equilibrium studies were conducted to evaluate extraction performance, the effect of medium components on extraction performance were also performed.	Kaur and Elst (2014)
Citric acid	Reactive extraction	Tri-n-butyl phosphate TBP, Tri-n-octylamine, (TOA), and Aliquat 336 dissolved in three different diluents: butyl acetate, decanol, and benzene		Isothermal batch experiments were performed for the equilibrium and kinetic studies. Kinetics of extraction of citric acid was performed. Extraction parameters were estimated by a differential evolution optimization technique.	Thakre et al. (2016), Thakre et al. (2018)
Formic acid		Tri octyl amine TOA dissolved in various alcohols isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol as diluents Alamine 336 Sunflower oil		The difference between the physical extraction and reactive extraction were studied. Equilibrium studies were also conducted. .	Uslu (2009), Martı (2017)
Propionic acid	Reactive extraction	tri-*n*-butyl phosphate TBP in petroleum ether, Aliquat 336 in n-dodecane and 1-decanol		Equilibrium studies on distribution Coefficient, equilibrium complexation constant, loading ratio and extraction efficiency were conducted.	Keshav et al. (2008b), Keshav et al. (2009c), Keshav et al. (2009d), Kumar and Babu (2008)
Levulinic acid		Tri-N-Octylamine TOA in 1-Octanol		Studies focused on kinetics and extraction model development comprising of equilibrium complexation constant.	Kumar et al. (2010)

3.1.4 In Situ Product Removal (ISPR)

ISPR is an express removal of organic acids as they are formed thus preventing subsequent holdups with medium components. It combines separation with fermentation, incorporating extraction, membrane and resin to achieve a continuous process. Furthermore, product removal can reduce toxicity to any microorganisms. The ISPR investigation focuses widely on inorganic acid separation from fermentation broths (Cheng et al., 2012, Kurzrock and Weuster-Botz, 2010, Peterson and Daugulis, 2014). *In situ* lactic acid removal from fermentation broth was carried out by (Ataei and Vasheghani-Farahani, 2008) using ion exchange resin and the extractive fermentation productivity was about 4.3 times greater than the conventional processes at a higher temperature. Several other studies are listed in table 3.5. *In situ* product recovery makes continuous fermentation possible by instant acid removal from the broth. The pH is controlled and product inhibition minimized, leading to high feedstock utilization, product improvement, load and ideal cost reduction of downstream processing. An ideal *in situ* product recovery needs minimal chemical addition and energy consumption. ISPR and Continuous fermentation are more cost-efficient and cost-effective than the conventional batch production and therefore require more research attention and possible adaptation (Cheng et al., 2012).

Table 3.4 Comparison of benefits and constraints of conventional and intensified process recovery of carboxylic acids

S/N	Process Recovery	Benefits	Constraints	References
1	Solvent extraction	No further processing step is required	The quantified requirement of solvent is heeded at a higher cost, solvent toxicity, compound extraction, increased energy requirement and by-product formation	Seibert (2010)
2	Vacuum distillation	Easy, simplified and well-established technology	Extensive energy requirement, the formation of by-products	Carlson (1962)
3	Steam stripping	High purity is achieved	The energy requirement is extensive	Rackemann and Doherty (2011), Carlson (1962)
4	Membrane separation	Continuous separation, mono-step separation of by-products creates room for enhanced productivity while minimizing undesirable by-product formation	Costly, membrane fouling	Den Boestert et al. (2009)
5	Adsorption	Simple Ease of the auxiliary phase removal	Low adsorbent capacity limits use at industrial level and the susceptibility of adsorbents fouling leading to the limitation in lifetime operation of materials.	Rackemann and Doherty (2011)
6	*In situ* product removal (ISPR)	Improves the final acid concentration Base addition for controlled fermentation on the addition of base is prevented. Reduction in waste generation Reduces end product inhibition	A large quantity of acid is needed	López-Garzón and Straathof (2014), Ayoub (2008)

7	Reactive Extraction	Simple, efficient, high product yield, low energy consumption economic and clean process	Search for efficient and selective extractant	Datta et al. (2015b), Hong et al. (2001), Wasewar et al. (2010), Wasewar et al. (2011), Wasewar et al. (2004)
8	Reactive distillation	High purification levels, low energy consumption, reduction in the number of equipment	Corrosion problems when using a homogeneous catalyst, search for efficient catalyst, applied to reversible chemical reactions.	Rao et al. (2014), Kumar et al. (2006a), Kumar et al. (2006b)
9	Precipitation	Easy operation and applicable in chemical and industrial plants	The purity of product is low, consumption of a large amount of sulphuric acid, landfill disposal due to gypsum generation.	Wasewar (2005)

Table 3.5 Literature data on intensified process separation of carboxylic acid from biomaterials with process performance at optimized conditions

Carboxylic acid produced	**Separation type employed in the study**	**Process performance at optimized conditions**	**References**
Lactic acid	In situ separation using reactive extraction. Sunflower oil and Alamine-336 in oleyl alcohol solvent was employed	25.59g/dm^3 maximum yield was obtained using 15%(v/v) of the solvent at 37°C with immobilized cells.	Tik et al. (2001)
Lactic acid	In situ extraction using Alamine 336 in oleyl alcohol with kerosene as a diluent (20:40:40 wt%)	Lactate maximum yield of 67% that of theoretical yield (pH 5.0 at 43°C)	Chen and Lee (1997)
Butyric acid	Integrated extraction and pertraction using 20%w/w Hostarex A327 in oleyl alcohol	Up to 0.30g/g sugar with 0.21g/L/h productivity with a pH of 5.2 at 37°C	Zigová et al. (1999)
Propionic acid	Extractive separation using Adogen 283 (ditridecylamine) in oleyl alcohol	Propionate yield of 0.66g/g substrate with 75g/L product concentration and 90% purity (pH of 5.3 at 30°C)	Jin and Yang (1998)
Hexanoic and Butyric acids	Pertraction with oleyl alcohol using 10% v/v trioctylamine	Increased productivity and conversion rates of the studied carboxylic acid studied by 3-fold when compared to the batch conventional process.	Nelson et al. (2017)
Acetic, propionic, valeric and butyric acid	In situ separation using conventional electrodialysis	Removal of about 99% volatile fatty acid from the broth containing up to 1200 mg/l each of the acid within 1 hour	Jones et al. (2015)
Lactic acid	Integrated process operation of electrodialysis with bipolar membranes (EDBM)	Up to 69.5% lactate recovery under an initial concentration of no less than 1mol/L	Wang et al. (2013)

Lactic acid	In situ separation with ion exchange resin using Amberlite IRA-96 combined with Amberlite IR-120	98.9% recovery of lactate with 99.17% purity, maximum loading of 210.46mg/g	Bishai et al. (2015)
Lactic, butyric and acetic acid	In situ separation using Amberlite IRA-67	Up to 74% acid removal from the Amberlite IRA-67 at pH of 3.3.	Yousuf et al. (2016)
Lactic acid	In situ lactic acid separation using ion exchange resin – Amberlite IRA-400, CL^-	A maximum yield of 0.85g lactate/g substrate with the productivity of 0.984g/L/h. The concentration of 37.4g/L at 37°C and pH of 6.1.	Ataei and Vasheghani-Farahani (2008)

3.2 Equilibrium Studies Relating to Carboxylic Acid Separation

The modelling of phase equilibria or general thermodynamic properties of systems of components such as alkanols and acids with potential for association via hydrogen bonding or normal dipole-dipole interaction remains a daunting challenge. Systems of this nature exhibit complex non-ideal aggregation behaviours which are complicated. Several descriptions for liquid-liquid equilibrium (LLE) and vapour liquid equilibria (VLE) of the alkanols-containing composition of mixtures have been presented using multi-scale associated concepts employing a generalised solvatochromic approach that uses linear solvation energy relationship (LSER). Other theoretical methods/approaches like activity coefficient model of UNIFAC (universal functional group activity coefficient), NTRL (Non-Random Two-Liquid), NRTL-HOC (Hayden O'Connell), Rellich Kwong Soave (RKS-EOS) equation of state, cubic equation of state respectively have been applied widely to these systems. Senol (2013b) presented another group contribution method which has been used in the chemical industries extensively and successfully. It has been of interest in the development of several chemical processes. But in all these applications and adaptation, UNIFAC aboriginal model has been the most fascinating of the comprehensive nature of these parametric matrixes which are significantly and easily obtained.

The prediction of LLE data by the UNIFAC method is the most effective even as UNIQUAC (universal quasichemical) and NRTL models have been employed in correlating experimental data. Uslu et al. (2008)) reported in their study that the model neither fitted the data qualitatively nor quantitatively despite the different techniques of iterations used with different values of correlation. So far, UNIFAC is the only model which has been reported to indicate the suitability of this model for these thermodynamic systems. The UNIFAC approach applies the activity coefficients, Y_i for prediction. In liquid-liquid equilibria, the actions of component *i* in the mutual phases are equivalent and the mole fractions, X_i^E , X_i^R of conjugate phases may be computed using Equation (1):

$$\gamma_i^E X_i^E = \gamma_i^R X_i^R \quad (1)$$

Wherein γ_i^E and γ_i^R are the equivalent activity coefficients of component, i, in both raffinate and extract phases. The interface parameters amongst each of the main groups are employed in calculating component i activity coefficients. UNIFAC no doubt predicts temperately accurate the extraction equilibria of ternary systems and schemes. The procedure of LLE is dependent on the solubility of solutes in different organic solvents and for a specified system, the solute distribution between different solvents is determined at a partition ratio. This ratio invariably will not change if the system remains in equilibrium. The overall LLE system properties can be evaluated using the equilibrium partition ratio, distribution coefficient, separation factor and extraction factor.

4.0 Effects of Process Variables

This section explores the various effects of process parameters in process intensification of biomass-derived materials. Some of the process parameters of interest are physical equilibrium, chemical equilibrium, extraction kinetics, the effect of temperature, substrate, pH, back extraction equilibrium and kinetics, back extraction or regeneration, water-coextraction and toxicity. These are discussed and analysed.

4.1 Physical Extraction

Physical extraction (dimerization and ionization) involves the separation of solutes into substituted hydrocarbons (SHC) and non-reacting hydrocarbons (NHC) which are free of complexities. In physical extraction, factors responsible and considered according to some authors (Wasewar et al., 2010, Keshav et al., 2009e) are: Aqueous phase ionization of acids; Organic phase acid dimerization; and Partial acids dissociation between phases.

Conventional solvents used for physical extraction can be polar or non-polar diluents, protic-aprotic diluents, inorganic-organic diluents such as polar-non-polar, protic-aprotic, inorganic-organic, natural solvents and so on. Distribution coefficient is presented with respect to dimerization coefficients according to the following equation (Keshav et al., 2008a)

$$K_D^{diluent} = P + 2P^2 D[HA\}_{aq} \quad (2)$$

Where $P = {[HA]_{org}}/{[HA]_{aq}}$ D $= {[HA]_{2,org}}/{[HA\}_{org}^2}$

4.2 Chemical Extraction

In chemical extraction (diffusion and solubility), the process involves the contacting of a second phase extractant that will reversibly react with the solute. The option of the complexing agent is dependent its strength, specificity and yet reactively reversible with the solute. These complexing agents are usually viscous or solid in nature and so, they are dissoluble in low viscous and low molecular weight diluents. Equilibrium is attained and improved by the diluents through complex solvation and density control; also, interfacial tension and viscosity of the mixed solvent play crucial roles. To explain and describe the mechanism of chemical extraction using equation (3), the equilibrium constant according to Wasewar et al. (2010) is presented in Equation as:

$$Solute + n.Extractant \leftrightarrow Complex \quad (3)$$

$$K_c = \frac{[Complex]}{[Solute][Extractant]^n} \quad (4)$$

4.3 Extraction Kinetics

The design of an efficient extraction process necessitates the knowledge and application of extraction reaction kinetics. The importance of which is predicated that extractant depends on extractant type, diluents and the nature of the process which are explainable by the kinetic study (Wasewar et al., 2002b, Keshav et al., 2009c). (Keshav et al., 2008a) studied the reaction in a solution of two molecules and presented the three important steps involved: Reactant molecules diffusion to one another; Product diffusion away from each other; and Actual product diffusion from each other.

4.4 Temperature Effect

Study on the effect of temperature important in considering back extraction/regeneration step and operating temperatures. Commercial/Industrial scale fermenters for carboxylic acids production are usually conditioned to operate in within the temperature regime of between 305 K to 313 K. It is therefore, possible for an extractant to be able to efficiently operate within this operating regime. As extraction is generally an exothermic process with the liberation of heat, a reduction in extraction (to about 50%) is anticipated as the temperature is intensified. However, the works of several authors have presented the fact that general decrease/step down in extraction is primarily a function of the extractant and the choice of diluents involved (Keshav et al., 2009d, Keshav et al., 2009b).

4.5 pH Effect

Product inhibition is the main drawback in the fermentation of carboxylic acids. Simultaneous fermentation with end-product inhibition decreases the medium pH due to end production of acid. Hence, the need to add a neutralizing agent for optimal maintenance of the fermentation process to cancel out the presence of acid. Alternatively, product removal as they are formed (*in situ*) is a second important alternative which also increases the bioreactor performance and productivity. In reactive extraction, maintenance of high pH is achieved by *in situ* acid removal (Wasewar et al., 2002a, Wasewar et al., 2010). Increase in pH decreases the extraction power in the case of tertiary amines with high molecular weight for example alamine 336 and phosphorus-based extractant, another example tri-n-octyl phosphoric acid in the case of phosphorus-based extractant while optimum pH is obtained with quaternary amine (Wasewar et al., 2004, Keshav et al., 2009d, Keshav et al., 2009b).

4.6 Effect of a Mixed System

Increase in acid extraction yield can be achieved by mixed extractant using synergetic extraction principle whereby the presence of one extractant can affect the increased performance of the other (Keshav et al., 2009f). Several research studies have been carried out with the aim of improving the extraction of organic acids especially, in dilute media. These comprise using mixed extractant system with a single diluent or mixed diluent system in a single extractant system. To increase the stripping efficiency of carboxylic acids, mixed polar and nonpolar diluent have been employed in the reactive extraction of these acids. A modifier can also be added as the active diluent which has the advantage of preventing the formation of a third phase which occurs generally when an extractant is used with an inert diluent. The extraction power of the extractants depends largely on the type of modifier used. Generally, polar diluents favour an increase in extraction since they help stabilize the formation of ion-pair formed by solvation (Keshav et al., 2009f).

4.7 Effect of Substrates

In reactive extraction, it is necessary to explore the effect of substrate concentrations since 100% feed conversion is not achieved in the fermentation broth which usually contains around 40 g/l substrate source. Increase in viscosity can lead to a corresponding decrease in K_D value of the dilute aqueous phase that could change the interface surface tension leading to low complexation and hence low efficiency in extraction. However, when unconverted substrate conversion is left in the bioreactor (>40 g/l), lower K_D value would likely be expected (Keshav et al., 2009b). It was observed that certain substrates for example lactose at any given concentration showed an insignificant decrease in K_D value. Thus basically, acid extraction is unaffected by the source of substrates (Wasewar et al., 2004).

4.8 Water (polar component) Co-extraction

The type of acid and its concentration affects the mutual solubility between a particular solvent and an aqueous solution at a stable temperature. There is a substantial change in volume with weak organic acids caused by mutual solubility and the extent of the volume change is related to the water co-extraction and the acid. The increase in organic phase volume for aliquat 336 was about 2-5% with a corresponding decrease in the dilute aqueous phase while for tertiary amines and Tributyl phosphate, no significant change in the volume was observed (Keshav et al., 2009d, Wasewar et al., 2004). For high concentration extraction with (>25%) amine in a diluent, an observation of a third phase was also made between the surface of the aqueous and organic phase. The change in volume is related to water co-extraction and depends on temperature, concentration and diluent type thus may affect the overall process economics. For example, during regeneration, pure acid is recovered from a dilute aqueous solution generated from the extract. The solubility of the acid is decreased by the stripping method. Generally, extraction using amine extractants gives higher selectivity of the acid over water as compared with conventional solvents. There is a minimum amount of water in the extract phase compared to that in an aqueous back extraction, therefore there is little or no effect on the viability of the process (Keshav et al., 2009d, Wasewar et al., 2004).

4.9 Regeneration of Acid and Back Extraction

The realisation of the process of reactive extraction depends on complete acid recovery from the loaded organic phase. Next is the regeneration phase, which involves reaction reversal to recover the acid into a product phase and the recycling of free acid extractant. Various regeneration methods can be employed to back-extract the acid from the loaded organic phase using NaOH, HCl or trimethylamine (TMA) or by diluent and temperature swing (Keshav et al., 2009a, Wasewar et al., 2004, Wasewar and Yoo, 2012). TMA was found to be better amongst all, yielding approximately complete acid regeneration. Kinetics of acid regeneration was also analysed and a fast reaction was observed which indicates that TMA was effective (Wasewar et al., 2004).

4.10 Toxicity

Toxicity of both the extractants and organic solvents to microbes is a problematic issue in extractive fermentation. The organic solvent can lead to physical biochemical and microbial effects on the catalytic activity of the microorganisms. As microbes are key agents and are always present during fermentation. The degree of toxicity of the extractants and organic solvents to microbes depends on the different combination used. Toxic effects can be considerably reduced by avoidance of direct contact of the organism with the extractants (Wasewar et al., 2011, Waghmare et al., 2011).

5.0 Kinetic Studies on Reactive Extraction of some Carboxylic Acids

The overall design and modelling of a reactive extraction unit require both equilibrium and kinetic studies. A number of kinetic and equilibrium studies for carboxylic acid extractions are available in the literature with only limited kinetic studies. Jun et al. (2005),Jun et al. (2007), Eda et al. (2016) conducted kinetic ad equilibrium studies for succinic acid extraction from aqueous solution with 1-octanol solutions of tri-n-octyl-amine (TOA) using a stirred cell with a microporous hydrophobic membrane. A Lewis-type stirred cell was used in equilibrium and kinetic studies on reactive extraction of Pyruvic Acid with Trioctylamine in 1-Octanol (Marti et al., 2011). Kinetic measurements of citric acid extraction from aqueous solutions with trioctylamine in mixtures of isodecanol/*n*-paraffins were conducted in a cylindrical stirring vessel with a highly agitated system (Poposka et al., 1998). These investigative studies aimed at describing and analysing the kinetic mechanism of reactive extraction using basic reaction kinetic model, the reaction mechanism of acid-amine complexation and extraction theory. The intrinsic kinetic parameter estimation for example reaction rate constants and the order of reaction were obtained from experimental analysis.

From the investigations, the reaction involving the carboxylic acid and the type of extractant does not depend only on the extract or organic phase and aqueous phase compositions, but also on the system hydrodynamic parameters (phases volume ratio, temperature, agitation speed and interfacial area). In the study conducted by Jun et al. (2007), it was observed in the aqueous phase that the rates of reaction were affected by pH and contamination present. At a pH greater than the acid pKa, more dissociation occurred thus leading to reduced extraction efficiency. Therefore, an effective acid separation with the fermentation pH kept at a value less than the acid pKa was recommended.

5.1 Kinetic Model

Doraiswamy (1984) recommended an all-inclusive study on extraction theory in a stirred cell accompanied by chemical reaction to establish its effect on the specific reaction rate. A reactive system together with the aid of film and renewal theories with physicochemical and hydrodynamic parameters have been classified into four reaction regimes (very slow, slow, fast, and instantaneous) subject to their relative diffusion and reaction rates. The value of physical mass transfer coefficient (kL) is essential in verifying the regime of reaction. This is achieved by performing physical extraction of acid with pure diluent from the aqueous phase. For a batch process, a differential mass balance yields equation (5):

$$V_{aq}\frac{dC_{org}}{dt}=K_l A_c\left(C^*_{org}-C_{org}\right) \quad (5)$$

Where A_c is the interfacial area (m^2); V_{aq} is the aqueous phase volume (m^3); C^*_{org} is the equilibrium acid concentration in the organic phase.

The time-dependent acid concentration in the organic phase is obtained by integrating (6) as

$$\ln\left(\frac{C^*_{org}}{C^*_{org}-C_{org}}\right)=\frac{K_l A_c}{V_{org}}t \quad (6)$$

A plot of $\ln\left(C^*_{org}/(C^*_{org}-C_{org})\right)$ versus time (t) yields a straight line and the slope is used to estimate the coefficient of physical mass transfer (K_l).

A reversible reaction occurs between acid and extractant and can be avoided by measuring the initial reaction rate governed by the forward reaction. Thus, the initial rate of reaction, $R_{HC,0}\ mol.m^{-2}S^{-1}$is calculated using the following equation:

$$R_{HC,0}=\frac{V_{org}}{A_c}\left(\frac{dC_{HC,org}}{dt}\right)_{t=0} \quad (7)$$

$\left(\frac{dC_{HC,org}}{dt}\right)_{t=0}$ represents the initial slope of curve which represents the concentration in the organic phase versus time (t). The values of $R_{HC,0}$ are determined with different experimental conditions and used to determine the possible effect of the important process variables and to make a suitable deduction on the suitable reactive extraction kinetics. Consequently, to control the reaction regime, the effects of agitation speed (N) and the ratio of the volume of the phases $\left(\frac{V_{org}}{V_{aq}}\right)$ on the initial extraction rate must be examined. Following the suggestion by Doraiswamy (1984), the reactive extraction of acid with an extractant in different diluent is governed by equation (8):

$$R_{HC,0}=K_{\alpha'\beta'}[\overline{HC}]^{\alpha'}[\bar{S}]^{\beta'} \quad (8)$$

Where $\alpha'$and β' are the orders of the reaction with respect to acid and extractant, respectively, and $K_{\alpha'\beta'}$ is the reaction rate constant.

For a (α', β') reaction occurring in the organic phase with a rate law shown in equation (9), and with a high excess of extractant, Hatta number (Ha) is given as a general expression:

$$\text{Ha} = \frac{\sqrt{(2/(\alpha'+1))K_{\alpha'\,\beta'}[\overline{HC}]^{\alpha'-1}[\bar{S}]^{\beta'}D_{HC}}}{K_L} \quad (9)$$

D_{HC} represents the diluent acids diffusion coefficient. D_{HC} value is estimated using Equations 10 and 11

$$D_{HC} = 7.4 \times 10^{-12} \frac{T\sqrt{M\psi}}{\eta\left(\forall^{acid}\right)^{0.6}} \quad (10)$$

$$D_{HC} = 10^{-11} \frac{T\sqrt{M}}{\eta\left(\forall^{diluent}\forall^{acid}\right)^{1/3}} \quad (11)$$

Where ψ connotes diluent association factor; while ∀ denotes the component molar volume; T is equal to temperature (in ^{o}K); M and η represent molecular weight (kg·kmol^{-1}) and viscosity (kg·m^{-1}·s^{-1}) of the diluent, respectively.

6 Industrial Applications of Intensified Separation Processes

Process Intensification (PI) has a wide range of application owing to the fact that it can reduce the cost of inventory, improve energy utilization and heat management. This application ranges from fine chemical and pharmaceutical industries to biofuels, petrochemicals and bulk chemicals, offshore processing and carbon capture. Improvement in yield, selectivity and processing time are of utmost importance for pharmaceuticals and chemical and due to low cost of energy which constitutes an insignificant percentage compared to production costs. Since petrochemicals and bulk chemicals are produced in large amounts, environmental impact and energy consumption reduction are significant incentives for technology innovation. Several applications of process intensification technologies are adopted in bulk chemicals, agro-allied production and petrochemicals have been reviewed in this work particularly focusing on reactive distillations which have been implemented on large and commercial scales. Fine chemicals, often labelled as resource raw materials for speciality chemicals, such as renewables and allied chemicals are manufactured in limited quantities, mostly batch-based processes. Despite the fact that the trend is drastically changing to continuous processes, the technologies of process intensification in these diverse areas have been successfully implemented. Potential benefits, however, are significant with a compelling overall reduction in general costs which are constantly decreasing with time. The application of intensified distillation systems should be favourable with the continual development of the biorefineries concept away from single to multiple product systems. Additionally, bio-based raw material integration into an existing typical plant will eventually promote hybrid processing or intensified systems. However, the implementation challenges of distillation systems to bio-based processes persist with respect to the operating conditions, such as systems with high viscosity, and solid systems handling (e.g., enzymes, cells), and requires new intensified process development.

7 Conclusion and Outlook

Recovery of carboxylic acids from aqueous solutions, specifically of bio-based materials and processes are herculean tasks for bulk product implementation from renewable and green resources. It is the recurrent developmental progress for all industries to attain and be able to operate at low costs and higher efficiencies. There are economic considerations for these. Despite the diverse opportunities and options available, most processes of separation in the chemical industries have diverted attention to the innovative solution based

on process intensification (PI). Reactive separation no doubt provides the most appropriate and strategic approach for separation of multicomponent mixtures, especially at dilute concentrations. In distillation-based separation processes, the use of alternative energy sources or the coupling of reaction and separation into one unit of reactive separation are the most fundamental methods of PI applications. Particularly, improvements in reactive separation processes have several advantages in green technology. These include reduction in energy requirements, improvement of the reaction rate, and productivity and selectivity enhancement which eventually leads to high effectiveness and efficiency of the separation processes. Several challenges still need to be overcome for these promising technologies to realize their full potential. Other separation technologies combined with reactive distillation with more integrated hybrid configurations offer great potential for future considerations of complementing the potential of the respective units. To realise the smooth and efficient development of separation processes, other factors such as new and effective solvents and catalysts, membrane materials, enhanced rotary machines, dependable control systems and inexpensive fabrication of equipment needs utmost consideration.

To improve yields, productivity and subsequent scale up to commercial scale, an intensified separation system needs to be adopted for carboxylic acid synthesis. An optimized reactive separation process, with a selection of appropriate extracting solvent in the separation process, which can be recycled efficiently, is promising for industrial production of carboxylic acids. Future research should be focused on energy input minimization, wastewater generation and improvement in carboxylic acid yields which will pave the way for optimal recovery. Kinetic and equilibrium studies are necessary to substantiate the chemical reaction pathways. Equilibrium data on chemical compounds and their mixtures play a significant role in separation processes in chemical industries as they are needed for efficient and effective design and operation of chemical processing plants. This information is limited in the literature. Process integration, recovery and purification of the product should be conducted to improve yield while minimizing the energy consumption. Finally, a thorough techno-economic analysis, for sustainable process will be pivotal to successful process commercialization.

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Public Interest Statement

Recovery of carboxylic acids from dilute aqueous solutions, specifically of bio-based materials and processes are herculean tasks for bulk product implementation from renewable and green resources. Conventional and intensified processes for carboxylic acid have been presented with its associated challenges. Before any industrial commercialization can succeed, some of these technical challenges need to be overcome for the full utilization of bio-based products. Studies focused on the development and implementation of these separation strategies are required for optimum and successful commercialization of biorefineries. Improved sustainability can be attained through intensified process separation with a reduction in production cost, equipment sizes, energy consumptions and flexibility of the process.

Chapter THREE

Paper 2, REPro: RSMOptiTech

Reactive Extraction of Propionic Acid using Trioctylamine in 1–Decanol by Response Surface Methodology Optimization Technique

Inyang, Victoria M. and Lokhat, David (2020)

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Paper TWO

Reactive Extraction of Propionic Acid using Trioctylamine in 1–Decanol by Response Surface Methodology Optimization Technique

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Abstract

Reactive extraction, a novel technique was experimentally investigated for the removal of propionic acid which is usually present in low concentrations in aqueous solutions. The experiments were conducted according to statistical design to develop an appropriate regression model. This was aimed at analyzing and optimizing the process variables and extraction efficiency for propionic acid reactive extraction from dilute aqueous streams using trioctylamine as extractant and 1-decanol as organic diluent. Response Surface Methodology in combination with Box-Behnken design involving seventeen experimental runs was utilized for the propionic acid reactive extraction in this study. Three independent process variables were chosen as temperature (T), initial propionic acid concentration (C_{PAO}) in the aqueous phase and trioctylamine composition (C_{TOA}) in the organic phase. The statistical design analysis demonstrated that the propionic acid concentration and TOA composition had a significant effect while temperature had an insignificant effect on the response value as well as an interactive and quadratic effect on the response. The optimum conditions for propionic acid extraction were established as: T = 300.752 K C_{TOA} = 18.252 %v/v C_{PAO} = 0.408 kmol/m^3. Under these optimum conditions, the propionic acid experimental extraction yield was 89.788% which was in close conformity with the predicted yield value of 91.939%.

Keywords: propionic acid, reactive extraction, equilibrium studies, optimization, Box Behnken design.

1. Introduction

Organic acids such as propionic acid, malic acid, butyric acid, lactic acid, citric acid, succinic acid are produced via chemical synthesis from petroleum resources. However, there have been growing concern in recent times for a safer, cleaner and greener environmental technology for the manufacture of these acids through biological source or fermentation technology. The bio route has some bottlenecks that still needs to be overcome before commercialization can be feasible. The acid product by immobilization of cell hinders productivity increase in the system as a result of feedback process inhibition (Cho and Shuler, 1990). Furthermore, the high acid recovery cost in downstream processing is the major challenging step.

This high cost is as a result of the acids being present in very dilute form leading to complications in recovery. Propionic acid which is considered an important carboxylic acid is principally used for preservation of animal feedstuff, hay, fodder, grains, and in baked foods and cheese consumed by humans. Additionally, the by-products of propionic acid can be used for making antiarthritic drugs, flavors and fragrance, perfumes, plasticizers, and as solvents (Keshav et al., 2009e). The conventional method for removal of these acids consists of microbes' removal followed by acid precipitation as calcium salts which are insoluble in water. These calcium salts are then converted to free acid by treatment with sulphuric acid (Kertes and King, 1986). This traditional technique for recovery of carboxylic acids such as propionic acid generates a lot of calcium sulphate sludge and is a complicated process. Hence the search for an alternative form of recovery of these acids.

Bioconversion integration and separation to enhance bioreactor productivity has gained much attention in the chemical industry for acid recovery from dilute aqueous solution and fermentation broth. Extractive separation method in fermentation technology offers a distinct advantage of improved productivity in the reactor, one-step continuous recovery of the product and decrease in recovery cost in the downstream processing technology (Wasewar et al., 2003). A number of research works on reactive extraction have been reported in the literature (Djas and Henczka, 2018, Eda et al., 2018, Keshav et al., 2009a, Kumar et al., 2010, Uslu, 2009, Wasewar et al., 2002a, Wasewar et al., 2011). Majority of the studies are based on the effects of different extractants, diluents, salts, pH, temperature, and concentration of acids. Effectively solvating extractants like high molecular weight aliphatic amines have been utilized primarily for the reactive separation of carboxylic acids such as propionic acid (Kertes and King, 1986, Yang et al., 1991, King, 1992, Keshav et al., 2009a, Wasewar et al., 2009). The wide usage of amines is as a result of its low cost and high value of distribution coefficients. Commonly used extractants employed in the study of reactive extraction of carboxylic acids include: Tri-noctylphosphine oxide (TOPO) (Keshav et al., 2008b), tri-n-butyl phosphate (TBP) (Kumar et al., 2011, Keshav et al., 2008b, Wasewar et al., 2009, Wasewar et al., 2011, Harington and Hossain, 2008), tri-noctylamine (TOA) (Eda et al., 2018, Eda et al., 2015, Keshav et al., 2008c, Kumar et al., 2010, Rasrendra et al., 2011), Alamine 336 (Wasewar et al., 2002b, Senol, 2013b, Senol, 2005a), and Aliquat 336 (Keshav et al., 2009a, Keshav et al., 2009c, Kumar and Babu, 2008, Wasewar et al., 2010, Wasewar et al., 2011). Diluents are usually added to extractants to improve the physical properties through providing solvation, controlling the density and viscosity of the solvent phase and also devoid of the formation of a third phase which affects the extraction power with specific interaction (Wasewar, 2005). Diluents may consist of more than one component, active or inert diluents. Different active polar and electron or proton diluents (aromatic hydrocarbons/halogenated aliphatic, higher alcohols, nitrobenzenes, ketones) helps enhance the extraction process while inert diluents (benzene, long-chain paraffin) limits the capacity of the solvent.

Several factors affect the characteristics of the reactive extraction system in equilibrium studies. Three important process variables include nature and concentration of the acid to be extracted, the extractant concentration, the nature of diluent employed and temperature (Tamada and King, 1990b, Qin et al., 2003, Kumar et al., 2008). The choice of an appropriate technique for the evaluation of these process variables is of utmost importance with a minimum number of experimental runs. Response surface methodology (RSM) is an efficient optimization technique for statistical design of experiments, model development and for finding complex processes to optimize the target yield(s) during downstream processing of the extraction process. It is also a statistical tool used to create a link between a set of defined experimental variables and the observed results. It is widely employed in the modelling and optimization for separation and purification processes for different solute extraction from aqueous solutions (Marchitan et al., 2010). These fermentation process parameters are optimized and analyzed using response surface method (RSM) by employing a Box-Behnken design to maximize the efficiency of the extraction process (% E) and distribution coefficient, K_D. The statistical design of the experiment is used for process parameter optimization to prevent drawbacks obtained from classical methods.

This research study is centered on the application of Box Behnken in data analysis, optimizing process parameters and exploring appropriate conditions to be employed in the reactive extraction process for optimal extraction (yield) efficiency and distribution coefficient. The focus of this work is on the effective and efficient extraction of the acids from dilute aqueous streams by employing trioctylamine as extractant mixed with 1-decanol as diluent. The optimum parameters of the intensified reactive extraction process will be applied to determine the reaction rate kinetics of the overall extraction process.

Materials and Method

Experimental Chemicals Used

All the chemicals, propionic acid ($C_3H_6O_2$), density 0.993g/mL, Trioctylamine (TOA), $[CH_3(CH_2)_7]_3N$, density 0.809g/mL and 1-decanol, density 0.829g/mL deployed in this study at purity of 98% were purchased from Sigma-Aldrich and deionized water used throughout the experiment was obtained using an Elga PURELAB Option Q purification system from our laboratory (chemical engineering analytical laboratory). Phenolphthalein indicator (pH) and 0.1M Sodium hydroxide were also purchased from Sigma-Aldrich. All chemicals were used as supplied with no further purification.

Methods

Equilibrium Studies

Reactive extraction equilibrium studies were conducted by preparing 25 mL aqueous solution (0.4-1 kmol/m^3 concentration of propionic acid) and 25 mL organic phase solution was prepared by mixing (10-30) % of Trioctylamine extractant (v/v) i.e. 0.229-0.687 kmol/m^3) in 1- decanol at temperatures between (298.15-313.15K) in an orbital shaker which was placed in the oven for 5 hours at 120 rpm, the two phases were kept to settle for 2 hours. The aqueous phase analysis was carried out using the titration method (Alders, 1959) with 0.1N NaOH and phenolphthalein as an indicator to obtain propionic acid concentration. The organic phase concentration of propionic acid was determined through material balance technique. The experimental runs were carried out in triplicate to confirm the reproducibility of results using exact process conditions.

Experimental Design

Box-Behnken design (BBD) with three-level variables was used to carry out the different experimental runs for the optimization of the process variables used in the extraction process. The Design-Expert version 10.0 (Statease Inc., Minneapolis, USA) was employed in this study. The un-coded value of the different factor and their corresponding coded levels employed in the experiment is presented in Table 1.

The first step in response surface methodology is the search for a suitable interactive effects estimation relating the independent variables (factors) and the dependent variables (response) (Marchitan et al., 2010). The interactive effects of temperature, solvent composition and acid extraction on the efficiency of reactive extraction was appropriately carried out. Secondly, analysis of variance (ANOVA) was conducted on the results obtained by utilizing the statistical design package, Design expert 10.0 software and different three-dimensional graphs were generated for interpretation. Lastly, response optimization of the individual process parameters; propionic acid concentration, extractant ratio (%v/v) and temperature (K) were estimated to gain maximum value of the response, extraction efficiency (E%).

Table 1. Range of different factors for reactive extraction of Propionic acid

			Level	
Factors	Units	Coded Values	Low	High
Temperature	K	Factor X_1	298.15	313.15
Solvent Composition (v/v)	%	Factor X_2	10	30
Acid Concentration	Kmol/m^3	Factor X_3	0.400	1.000

Theory of reactive extraction

The propionic acid reactive extraction using the extractant, trioctylamine (TOA) in the diluent, 1-decanol can be obtained by the complex formation in the interfacial reaction (Ingale and Mahajani, 1996) which can be expressed as:

$$[HA]_{aq} + [pR]_{org} \quad \leftrightarrow \quad [HA.R_p]_{org} \tag{1}$$

As the complexation of the propionic acid-TOA is being formed, there is a corresponding organic phase extraction. The extraction mechanism is illustrated in Figure 1.

The law of mass action is applied in the computation of the extractant constant and reacting molecules that is, the ratio of the product molecules concentrations to that of reactant species.

$$K_R = [(HA).(R)_p]_{org} / [HA]_{aq}[R]_{p_{org}} \tag{2}$$

K_R is estimated to be dependent on the properties of the acid and diluent solvation efficiency.

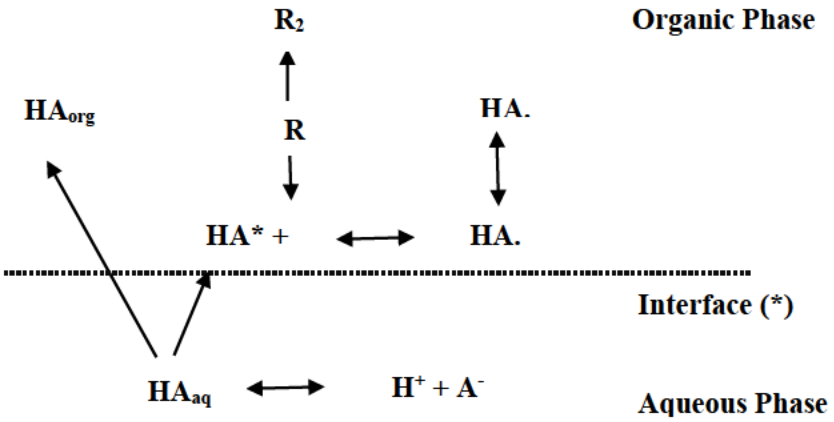

Fig 1. Reactive extraction mechanism of propionic acid (HA) using TOA in 1-decanol (R)

The aqueous phase acid dissociation can be represented as:

$$[HA]_{aq} \quad \leftrightarrow \quad A^- + H^+ \qquad\qquad K_{HA} = {[H^+][A^-]}/{[HA]_{aq}} \tag{3}$$

K_D is given as the ratio between the total organic phase acid concentration in all obtainable forms (complexes, dimmers, and partition) and the total concentration of the forms obtained (both dissociated and undissociated) in raffinate phase. For physical extraction, K_D is defined as:

$$K_D^{diluent} = [HA]_{org} / [HA]_{aq}$$

The acid distribution coefficient by chemical extraction can be defined as:

$$K_D^{chem} = \frac{[HA]_{org} - v[HA]_{org}^{diluent}}{[HA]_{aq}}$$

Where v is the volume of the diluent and $[HA]_{org}^{diluent}$ is the propionic acid extracted unto the immiscible organic phase by the diluent. The total distribution coefficient is expressed as a function of extraction constant and the amount of reacting species.

$$K_D^{overall} = \frac{[HA.R] - v[HA]_{org}^{diluent}}{[HA]_{aq}} = \frac{K_R[HA]_{aq}[R]_{org}^{p} - v[HA]_{org}^{diluent}}{[HA]_{aq}}$$

$$= K_R\,[R]_{org} + \frac{v[HA]_{org}^{diluent}}{[HA]_{aq}} = K_R\,[R]_{org} + vK_D^{diluent} \quad (4)$$

The propionic acid reactive extraction process performance was assessed by the extraction efficiency and distribution coefficient, K_D at equilibrium as the ratio of the concentration of acid in the organic phase $[HA]_{org}$ to the concentration in aqueous phase $[HA]_{aq}$ as shown in equations 5 and 6

Distribution coefficient ($K_D = \frac{[HA]_{org}}{[HA]_{aq}}$ (5)

Extraction efficiency (%E) = $\frac{K_D\ X\ 100}{1+\ K_D}$ (6)

Results and Discussion

The propionic acid extraction from a dilute aqueous stream can be accomplished by the presence of diluents (1-decanol) only but low solubility of the acid in 1-decanol leads to low organic phase distribution coefficient. Therefore, for higher distribution coefficient, propionic acid recovery with extractant (trioctylamine) and diluent (1-decanol) was conducted. The mechanism is shown in figure 1. The formation of propionic acid - trioctylamine complexes via strong amine interaction and propionic acid and its high affinity supports more acid distribution in the immiscible organic phase and thus high yield of extraction. The extraction of propionic acid comprises nitrogen atom interaction of trioctylamine and propionic acid through hydrogen bonding.

The process was analyzed and optimized using response surface methodology (RSM) to examine the combined or interactive effects of temperature, propionic acid concentration, and trioctylamine composition. Experiments were performed using Box-Behnken design (BBD) with each of the three-level variables in the optimization of the process parameters used in the extraction process. Table 2 illustrates the Box-Behnken experimental response design matrix with the corresponding extraction yields. The

experimental model responses in coded variable terms obtained from the regression analysis of the experimental design matrix is given by equation 7 and 8.

$$K_D = 5.10-2.57X_1-1.66X_2+2.50X_3+1.58X_1X_2-1.44X_1X_3+2.02X_2X_3-1.27X_1^2+1.31X_2^2+0.45X_3^2 \quad (7)$$

$$\%E = 83.57-10.12X_1-7.41X_2+9.43X_3-2.78X_1X_2+2.05X_1X_3+6.54X_2X_3-9.74X_1^2+1.41X_2^2-2.02X_3^2 \quad (8)$$

Where %E and K_D is the predicted extraction yield and distribution coefficient and X_1, X_2, X_3 are the coded terms of three parameters (independent variables) temperature, acid concentration, (C_{PAO}, Kmol/m^3) and extractant composition ($C_{TOA,}$ %v/v) respectively.

Table 2. Experimental design of variables (coded) for propionic acid extraction efficiency E% and distribution coefficient

Independent Variables (factors)				Responses	
Run	X_1	X_2	X_3	K_D	%E
1	0.000	0.000	0.000	4.915	83.095
2	-1.000	0.000	1.000	10.507	91.310
3	0.000	1.000	-1.000	1.784	64.083
4	0.000	0.000	0.000	4.793	82.738
5	0.000	0.000	0.000	5.316	84.167
6	1.000	0.000	1.000	3.118	75.714
7	-1.000	-1.000	0.000	12.333	92.500
8	0.000	-1.000	-1.000	7.000	87.500
9	0.000	-1.000	1.000	7.889	88.750
10	0.000	0.000	0.000	5.563	84.762
11	1.000	0.000	-1.000	0.931	48.214
12	0.000	1.000	1.000	10.765	91.500
13	-1.000	1.000	0.000	3.706	78.750
14	0.000	0.000	0.000	4.915	83.095
15	1.000	-1.000	0.000	3.404	77.292
16	1.000	1.000	0.000	1.102	52.417
17	-1.000	0.000	-1.000	2.574	72.024

Statistical Analysis

The analysis of variance (ANOVA) was employed to predict the correlation between independent process parameters and the corresponding responses (extraction yield and distribution coefficient) of propionic acid utilizing trioctylamine in 1-decanol. An equation with second-order polynomial was obtained for extraction efficiency and distribution coefficient of propionic acid as presented in equations 7 and 8 respectively. ANOVA is shown in Table 3. The F-value of 24.00 and low p-value of 0.0002 for the model indicates that the model is highly significant. The input variables T (X_1), C_{PAO} (X_2) and C_{TOA} (X_3), the interaction (X_2X_3) and the quadratic terms X_1^2 are all significant while the interaction (X_1X_2), (X_1X_3) and the quadratic term

X_2^2 and X_3^2 are not significant. The linear terms were found to be more significant than the interacting terms and quadratic terms. The linear terms have significant ($p<0.05$) and antagonistic effect on the yield of extraction which implies increase with a decrease in trioctylamine concentrations. Also, the synergistic effect of the input variables (linear term) significantly affected the extraction yield. The values of correlation coefficient (R^2 = 0.9686) and adjusted R^2 (R^2 = 0.9282) confirm the reliability of the model to the experimental results. The adequate precision which is the measure of signal to noise ratio gives a comparison between predicted values and average prediction error. A ratio greater than 4 indicates an adequate signal. A predicted residual sum of squares (PRESS) value obtained from the result is an indication of good predictability of the model developed. Low values of standard deviation, SD and variation coefficient, CV are desirable and this shows the experimental degree of precision. The values of adequate precision, PRESS, standard deviation and variation coefficient obtained in this work (Table 3) indicates high precision and the model reliability.

Table 3. Analysis of variance (ANOVA) and response surface regression model for propionic acid reactive extraction (extraction efficiency)

Source	Coded terms	Coefficient	Sum of Squares	Degree of freedom	Mean Square	F-Value	P-value Prob > F	Remarks
Model			2617.77	9	290.86	24.00	0.0002	significant
Constant		83.57						
Linear								
T	X_1	-10.12	819.04	1	819.04	67.58	< 0.0001	
C_{PAO}	X_2	-7.41	439.44	1	439.44	36.26	0.0005	
C_{TOA}	X_3	9.43	711.63	1	711.63	58.72	0.0001	
Interaction								
$C_{PAO}T$	X_1X_2	-2.78	30.94	1	30.94	2.55	0.1541	
$C_{TOA}T$	X_1X_3	2.05	16.87	1	16.87	1.39	0.2766	
$C_{PAO}C_{TOA}$	X_2X_3	6.54	171.17	1	171.17	14.12	0.0071	
Square								
T^2	X_1^2	-9.74	399.23	1	399.23	32.94	0.0007	
$C_{PAO}C_{PAO}$	X_2^2	1.41	8.32	1	8.32	0.69	0.4348	
$C_{TOA}C_{TOA}$	X_3^2	-2.02	17.16	1	17.16	1.42	0.2729	
Residual			84.84	7	12.12			
Statistics								
Lack of Fit			81.92	3	27.31	37.41	0.0022	Significant
Pure Error			2.92	4	0.73			
Corrected Total			2702.61	16				
Adequate precision		16.122						
PRESS		1315.30						
Standard deviation		3.48						

Mean	78.70
CV %	4.42
R^2	0.9686
R^2(adjusted)	0.9282

Residual Analysis

Residual analysis is used to confirm the adequacy of the model (Liu et al., 2004). Figures 2 and 3 were used to determine the residual analysis of the design model and to confirm the normality and assumption of constant variance in ANOVA for response surface methodology. The residual plots of the normal probability are shown in Figure 2. Each of these points lies very close to the diagonal which indicates that the error terms (residual plots) are dispersed normally. The residual plot versus the predicted response is represented in Figure 3 and describes a random residual pattern on the mutual sides of the zero line. Figure 4 shows the predicted response against the actual response plot which substantiates the reliability and suitability of the empirical model.

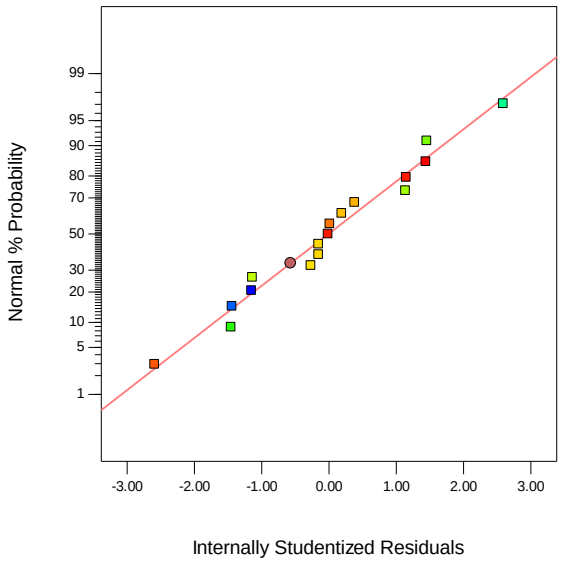

Fig 2. Normal probability plot of studentized residuals for propionic acid extraction yield.

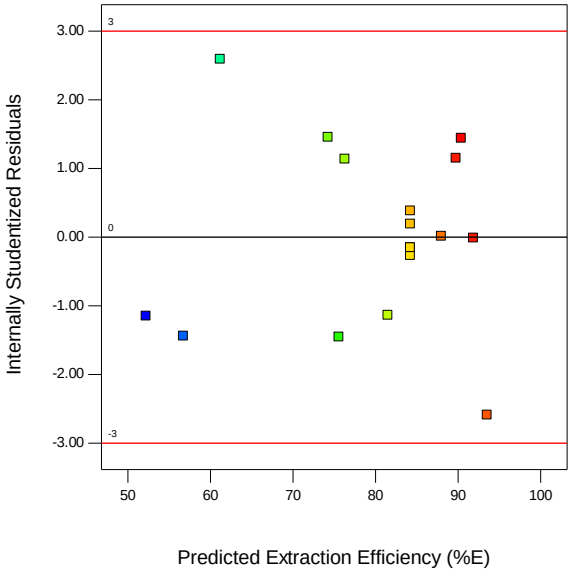

Fig 3. The predicted extraction yield of propionic acid and studentized residuals plot

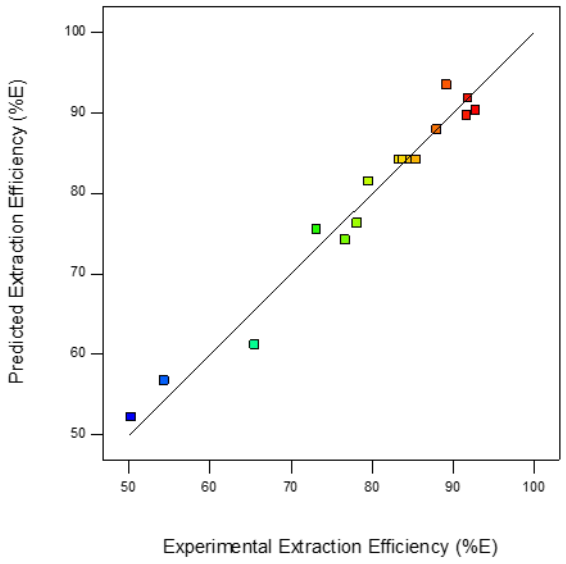

Fig 4. Comparison of plots of the predicted and actual value of propionic acid extraction yield

Response Surface Analysis

The model selected reasonably described the combined influence of the three process variables on propionic acid reactive extraction efficiency (%E). The three-dimensional (3D) graphs of the response surfaces were necessary to explain the combined influence of temperature, initial propionic acid concentration and TOA concentration on the yields of extraction as presented in Figures 5-7.

Figure 5a and 5b demonstrates the effects on the interaction between the concentration of propionic acid and temperature on the distribution coefficient and extraction efficiency, it was noticed that propionic acid extraction yield increases with a corresponding increase in propionic acid initial concentration regardless of the temperature. It can be interpreted from the figure that the responses increased with a corresponding increase in propionic acid concentration regardless of the temperature. This is because the tendency of extractant overloading increases with solute concentration (Qin et al., 2003). The extraction efficiency decreases with a rise in acid concentration and on further temperature enhancement. This could be due to the disturbance of trioctylamine extractant and the interaction of solute molecules in the immiscible organic phase with thermal energy increase leading to a reduction in the formation of the complex formed (Kumar et al., 2011).

From Figure 6a and 6b, which presents the effects on the interaction between TOA composition and temperature on the distribution coefficient and yield of extraction. It can be interpreted from the figure that the responses increased with an increase in extractant concentration irrespective of the temperature. This could be as a result of the increase in extractant concentration which increases the extractability of the

extractant and further helps attain extraction equilibrium and complex formation (Li et al., 2006). The equilibrium complexation reactions take place at the organic-aqueous interface and is an exothermic process. The propionic acid-TOA complex brings about orderliness in the reactive extraction process thus decreasing the randomness and the entropy of the system. Also, temperature increase also increases the kinetic energy of the molecules thereby interrupting certain interactions and acid-amine molecule combinations to form a stable complex at the interface (Tang et al., 2011). Another reason could be as a result of the exothermic reactions of the transfer of proton and formation of hydrogen bond which decreases the system entropy (Wasewar, 2012).

Figure 7a and 7b represents the individual and combined effect of TOA composition and propionic acid initial concentration on the responses. The responses increased with propionic acid initial concentration while decreasing with TOA composition in the organic phase. This might be because of the presence of 1-decanol, a polar organic solvent being reduced with an increase in extractant ratio owing to H-bonding between C=O of the acid-extractant complex and the proton of the polar diluent (Wang et al., 2009a). Therefore, the acid loading decreases with TOA composition in 1-Decanol as the medium of the solvent turns out to be less favorable. The extraction degree was somewhat affected by propionic acid concentration. That is, slightly higher extraction efficiency was attained at lower propionic acid concentration. This could be as a result of TOA being a controlling factor for the propionic acid-trioctylamine complex at higher initial propionic acid concentration.

The numerical optimization of the process variables was obtained by using the design expert software. The objective was to maximize the extraction efficiency of propionic acid by minimizing the process variables. After applying the Box-Behnken design, the optimal conditions for propionic acid extraction using trioctylamine in 1-decanol was predicted as T =300.752 K, C_{TA0} = 0.408 kmol/m^3, C_{TOA} = 18.252%v/v with extraction efficiency of 91.939%. At these optimum conditions, the experiments were carried out in triplicates to validate the model predicted. The extraction efficiency at the optimum conditions was found experimentally to be 89.788% which were in close agreement with its predicted value of 91.939%.

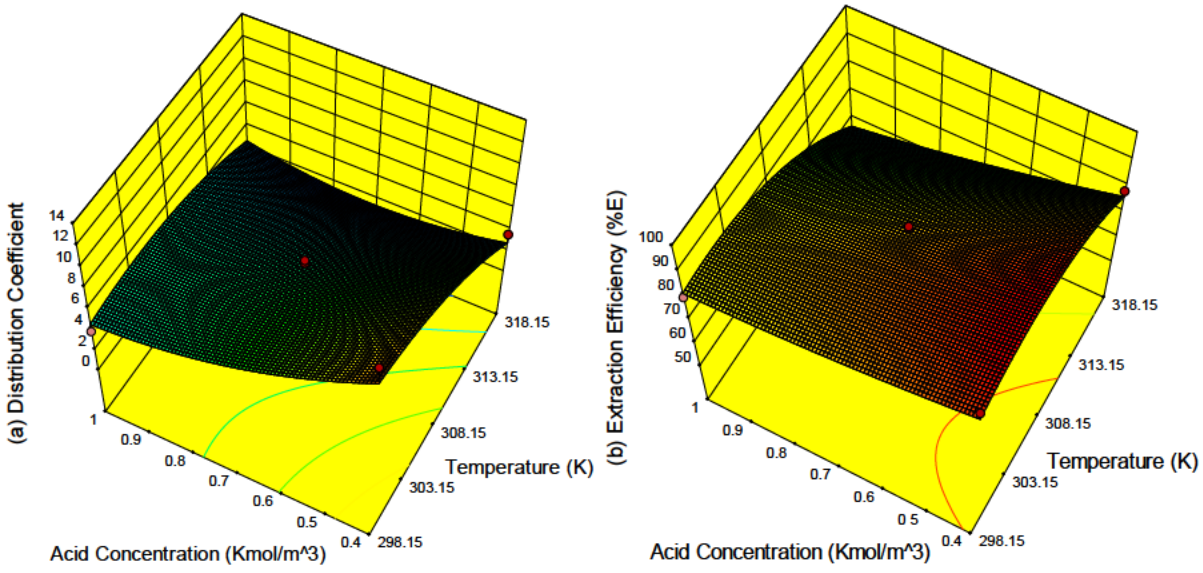

Fig 5 a&b: Three-dimensional (3D) surface plot showing the effect of interaction between propionic acid concentration and temperature variables on (a) distribution coefficient and (b) extraction efficiency

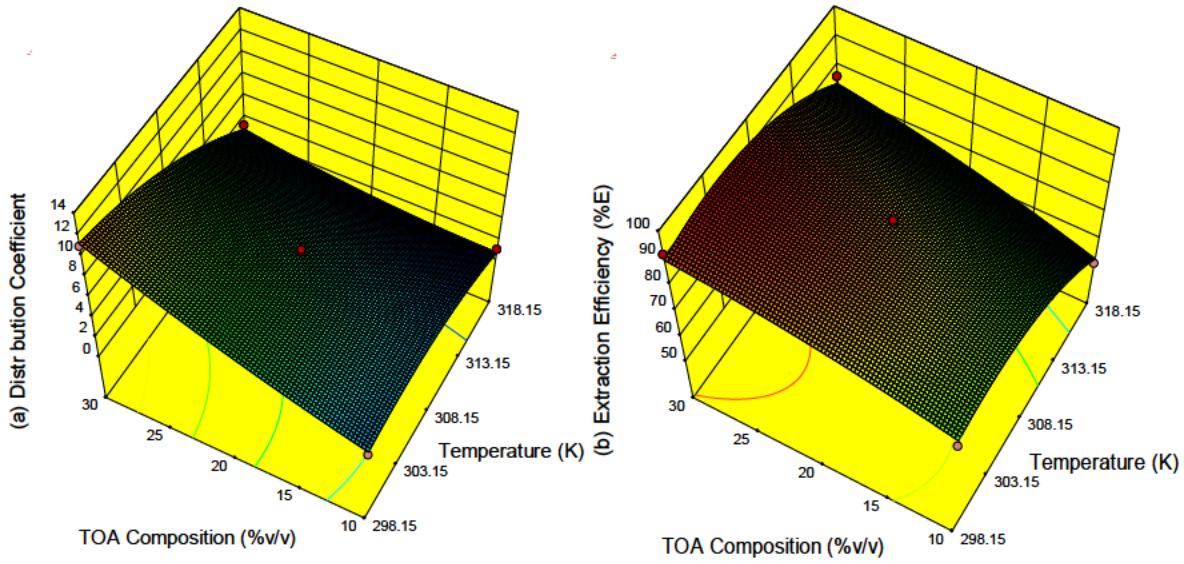

Fig 6a&b: Three-dimensional (3D) surface plot showing the effect of interaction between TOA composition and temperature variables on (a) distribution coefficient and (b) extraction efficiency

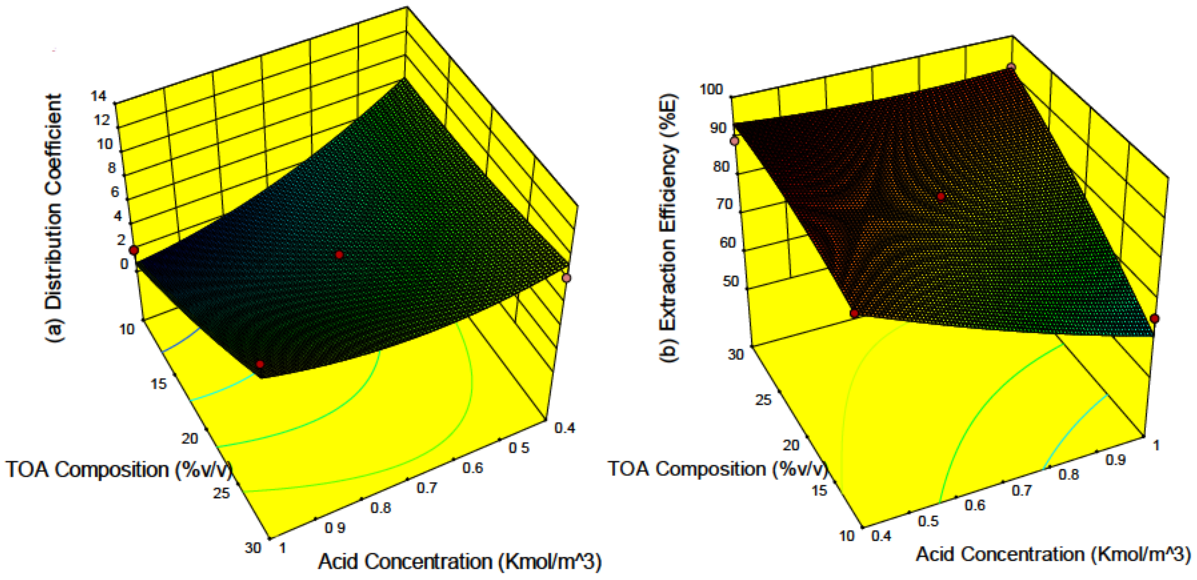

Fig 7a&b: Three-dimensional (3D) surface plot showing the effect of acid concentration in the aqueous phase and TOA composition in the organic phase (a) distribution coefficient and (b) extraction efficiency

Conclusion

Propionic acid reactive extraction from the aqueous stream was conducted using trioctylamine dissolved in 1-decanol. Three different process variables, temperature (T), initial propionic acid concentration (C_{PAO}) and trioctylamine composition (C_{TOA}) were optimized using RSM to maximize the percentage of extraction yield. Box Behnken design was employed in this work to study the interactive effect and also develop a predictive model for reactive extraction of propionic acid. The distinct and combined interactive effect of temperature, initial concentration of propionic acid and TOA concentration on propionic acid extraction yield were investigated. The C_{TOA} and C_{PAO} exhibited an antagonistic and a synergistic effect on propionic acid extraction yields respectively. The analysis of variance (ANOVA) was employed in the RSM model analysis. The quadratic model developed was significant with F-value of 24.00 and low p-value of 0.0002. Extraction efficiency was found to increase with a corresponding increase in propionic acid initial concentration and decrease in TOA concentration while temperature increase had no significant effect on the yield. The propionic acid extraction efficiency was found to be 91.939% (predicted) and 89.788% (experimental) showing a proximate validation at the optimum conditions of T = 300.752 K, C_{TOA} = 18.252 %v/v, and C_{PAO} = 0.408 kmol/m^3. These findings and results are necessary in the overall and optimum design of propionic acid recovery process and other carboxylic acids which are usually present in very dilute aqueous solution as well as fermentation broth.

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Chapter FOUR

Paper 3, REMal: EquiStu by RSM

Reactive Extraction of Malic Acid using Trioctylamine in 1–Decanol: Equilibrium Studies by Response Surface Methodology Using Box Behnken Optimization Technique

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Reactive Extraction of Malic Acid using Trioctylamine in 1–Decanol: Equilibrium Studies by Response Surface Methodology Using Box Behnken Optimization Technique

Victoria Inyang* & David Lokhat

Reactive extraction is a significant technique employed for the removal of organic acids such as carboxylic acid which are usually present in low concentrations in aqueous solutions. This technique was explored by applying Response Surface Methodology (RSM) in process parameter optimization for malic acid recovery from aqueous streams using Trioctylamine as extractant and 1-decanol as organic diluent. Malic acid, a C_4 dicarboxylic acid has a wide variety of applications in the polymer, food, chemical and pharmaceutical industries. The optimization of the response function: extraction efficiency was systematically carried out using three process parameters for reactive extraction: temperature, initial malic acid concentration and extractant (Trioctylamine) composition. Response Surface Methodology in combination with Box-Behnken design involving seventeen experimental runs was employed for malic acid reactive extraction in this study. A statistical second-order polynomial predicted an extraction efficiency of 97.53%. The optimum conditions of the process variables were found to be: temperature: 304.73 K, acid concentration: 0.25 kmol/m^3, Trioctylamine composition: 23.54% (v/v). Under these optimum conditions, the experimental response of extraction efficiency of 93.25% was obtained. The experimental results obtained was in close conformity with the predicted values by numerical optimization using Response Surface Methodology. These findings can pave the way for the reactive separation process design for recovery of carboxylic acids from dilute aqueous waste streams as well as a fermentation broth.

Introduction

Carboxylic acids are usually present in low concentrations in aqueous stream. Interest in the recovery of these acids from dilute aqueous solutions with acid concentrations lower than 10 % (w/w), has received considerable attention (López-Garzón and Straathof, 2014). Most recent research is targeted at carboxylic acid separation process selection with low material consumption and less energy requirement in the downstream processing. An intensified process that satisfies these requirements is reactive separation since significant improvements are achieved in both stages of reaction and separation. Carboxylic acids such as butyric acid, lactic acid, propionic acid, malic acid are useful bulk chemicals for several industries. Malic acid is a C_4-dicarboxylic acid and also an intermediate of the tricarboxylic acid cycle. It has a variety of applications in polymer, food, chemical and pharmaceutical industries (Zelle et al., 2008). The downstream recovery technique for carboxylic acids accounts for 30-50% of the overall production cost (Hulse, 2004, Straathof, 2011). Hence, the current interest in finding a more cost-effective recovery technique. Reactive extraction is a significant technique for the separation of important carboxylic acids which leads to a high solute distribution coefficient as a result of combining physical and chemical phenomena (Datta et al., 2015b). The factors that are favourable for carboxylic acids reactive extraction include an existing functional group which increases capacity and selectivity in solute molecules, a high driving force of complexing agents as a result of low concentration and low volatility of the solute (Hong et al., 2001). The application of reactive extraction to different carboxylic acid from dilute aqueous solution has been successfully carried out; such as; Latic acid (Wasewar et al., 2002b, Wasewar, 2005), Itaconic acid (Wasewar et al., 2010, Wasewar et al., 2011) Succinic acid (Kurzrock and Weuster-Botz, 2011, Eda et al., 2015), Levulinic acid (Brouwer et al., 2017, Kumar et al., 2010), pyruvic acid (Marti et al., 2011) tartaric acid (Sharma et al., 2017), propionic acid (Keshav et al., 2008b, Keshav et al., 2009e, Keshav et al., 2009d). The appropriate solvent selection as constituents of the organic phase is an underlining factor for high distribution coefficient and extraction efficiency. High viscous extractants for example phosphorus bonded, oxygen-bearing and hydrocarbon, high molecular weight aliphatic amines with diluents are often employed in the carboxylic acid reactive extraction process for improvement of physical properties such as interfacial surface tension and viscosity (Gorden et al., 2015, López-Garzón and Straathof, 2014).

In general; there are primary, secondary and tertiary amines in amine-type extractants. Among these amines, the tertiary amines offer better advantage in reactive extraction because the primary and secondary amines tend to react irreversibly with carboxylic acids and therefore, the stripping of solvent becomes difficult (Han et al., 2000). Reactive extraction using long-chain aliphatic tertiary amines (anion exchange extractants such as trioctylamine) with seven to nine carbon atoms in each alkyl group has been studied as the most effective, efficient and widely employed extractants for carboxylic acids. When dissolved in different modifiers (solvents), they are powerful extractant reagents for the carboxylic acids (Uslu and İsmail Kırbaşlar, 2009). They provide high extraction efficiency (> 90%) and are less expensive as compared with the oxygen donor or phosphorus-based extractants(Wasewar, 2005). These extractants used in the reactive extraction processes in organic acid separation can be recycled thus making them effective and efficient. Ratchford et al. (1951) studied the effects of amine structure and the solvent properties. The solvation of the whole amine-acid complex is based on dipole-dipole interaction and has been found to play a key role in the neutralization reaction between acid and amines. Amine-based extractants are highly favourable for carboxylic acid extraction, for example, the citric acid process was technically feasible using tertiary amine extractant (Wennersten, 1983). In addition to high efficiency and selectivity, they provide for product concentration through extraction at about ambient temperatures. These extractants are often used with an organic solvent as diluent which has a significant effect on the extraction performance, acid loading and stoichiometric association (Bízek et al., 1993, Marinova et al., 2005, Kertes and King, 1986, Tamada and King, 1990a). The diluent may consist of one or more components, inert or active. Various active polar and proton or electron-donating diluents (halogenated aliphatic/aromatic hydrocarbons, ketones, nitrobenzenes, higher alcohols), enhance the extraction. On the other hand, inert diluents (long-chain paraffin, benzene etc.), limit the extractant capacity (Kumar and Babu, 2008, Wasewar, 2012,

Wasewar et al., 2011). Significantly, diluents with a moderate polarity such as a long chain or higher alcohols (for example 1-octanol and 1-decanol) greatly improves the solvation power of the acid-amine complex. They also influence the basicity of the amine and improve phase separation and the stability of the ion-pair (acid-amine complex) formed. Thus preventing third phase formation which limits the extraction ability giving a high distribution coefficient (Wasewar, 2005). Significant research studies have been conducted on the influence of diluents on amine extractants in carboxylic acids recovery (Tamada and King, 1990b, Tamada and King, 1990a, Marinova et al., 2005, Senol, 2004). With this background, 1-decanol with moderate polarity, water-insoluble diluent and less toxic has been considered in the present study. And so, TOA in combination with 1-decanol has been chosen for this work as effective extractant and diluent respectively.

Several studies have been conducted on the reactive extraction process on organic acid separation from fermentation aqueous waste stream. However, studies which employ statistical technique on the experimental design of malic acid recovery from aqueous solution using an intensified process such as reactive liquid-liquid separation process is limited in the literature. The selection of a suitable technique for evaluating different process parameter is important as well as any interactions involved while minimizing the number of experimental runs. This research study is centered on the application of Box Behnken in data analysis, optimizing process parameters and exploring appropriate conditions to be employed in the reactive extraction process for optimal extraction efficiency and distribution coefficient.

The study intends to enhance the extraction yield for effective and efficient recovery of malic acid from dilute aqueous solution by employing trioctylamine as extractant mixed with high polarity solvent,1-decanol as diluent. Also, the major factor influencing the reactive extraction process include temperature, the concentration of the extractant and acid. This work is also aimed at analysing, optimizing and finding appropriate conditions of these process variables using response surface method (RSM) by employing a Box-Behnken design to maximize the efficiency of the malic acid reactive extraction process (% E). The statistical design of experiment is used for process parameter optimization for the malic acid extraction to prevent drawbacks obtained from classical methods. The optimum parameters of the intensified reactive extraction process will be used to determine the reaction rate kinetics of the extraction process. Response surface methodology (RSM) is an effective tool for statistical design of experiments, model development and for finding complex processes to optimize the target yield (s). It is also a statistical tool used to create a link between a set of defined experimental variables and the observed results. The adopted stepwise procedure in this study is as shown (Fig. 1).

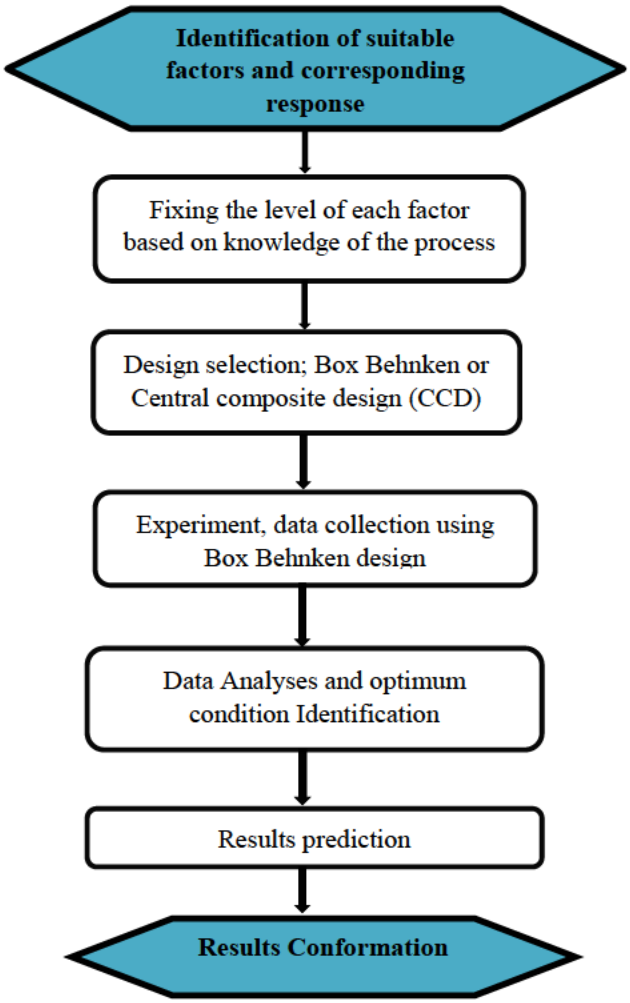

Figure 1. RSM step-wise procedures adopted in the study

Results and Discussion

The experimental data was analyzed using Response Surface Methodology (RSM) to examine the combined effects of temperature, malic acid concentration and TOA composition and the results are reported (Table 1). Analysis of Variance (ANOVA) was employed to predict the correlation between independent process variables and the corresponding responses and a second-order polynomial equation was obtained for extraction efficiency of malic acid and is presented in "equation (1)".

$$E\% = 79.28+6.63X_1+7.93X_2-24.4X_3+1.18X_1X_2+4.15X_1X_3+7.35X_2X_3-12.12X_1^2-11.16X_2^2+5.94X_3^2 \quad (1)$$

Where the variable X_1 = temperature, X_2 = Acid concentration and X_3 = TOA concentration.

The regression model and ANOVA of extraction efficiency for reactive extraction of malic acid using TOA in 1-decanol are presented (Table 2). From the Table, the model F-value of 67.66 indicates the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob>F" less than 0.0500 indicate model terms are significant. In this case, X_1, X_2, X_3, X_1^2, X_2^2, X_3^2 are significant model terms. Also, values of "Prob>F" greater than 0.1000 indicate the model terms are measured as insignificant. The coefficient of correlation with lower P values are considered to to be more

important. The correlation coefficient values (R^2) was adequate (0.9886) for the response ($P \leq 0.05$) (Baş and Boyacı, 2007). The plots of the correlation coefficient and the adjusted values for comparing the model fitness is presented (Fig. 2). The adequate precision value which measures single to noise ratio is expected to be greater than 4. The model ratio gotten in this work is 24.866 which indicates an acceptable signal and can be employed to pilot the design space. The variation coefficient obtained is relatively low (CV=4.84%), which indicates the accuracy and reliability of the model. The contour plots and three dimensional (3D) graphs were generated as a result of the effects of the interaction between two independent variables on the response by maintaining one constant process variables at zero levels (coded**)** (Marchitan et al., 2010).

Std	**Run**	**Factor 1 Temperature K**	**Factor 2 TOA Composition %v/v**	**Factor 3 Acid Concentration kmol/m^3**	**Response 1 Extraction Efficiency %E**
10	1	0.000	1.000	-1.000	98.571
1	2	-1.000	-1.000	0.000	39.307
3	3	-1.000	1.000	0.000	53.030
16	4	0.000	0.000	0.000	79.264
7	5	-1.000	0.000	1.000	40.750
9	6	0.000	-1.000	-1.000	97.619
5	7	-1.000	0.000	-1.000	98.571
11	8	0.000	-1.000	1.000	34.833
14	9	0.000	0.000	0.000	79.307
17	10	0.000	0.000	0.000	79.394
4	11	1.000	1.000	0.000	75.030
12	12	0.000	1.000	1.000	65.191
6	13	1.000	0.000	-1.000	97.143
13	14	0.000	0.000	0.000	79.091
2	15	1.000	-1.000	0.000	56.606
8	16	1.000	0.000	1.000	55.917
15	17	0.000	0.000	0.000	79.351

Table 1. Experimental design of variables (coded) for malic acid extraction efficiency E%.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	7207.38	9	800.82	67.66	< 0.0001	significant
X_1-Temperature	351.61	1	351.61	29.71	0.0010	
X_2-TOA Concentration	503.34	1	503.34	42.53	0.0003	
X_3-Acid Concentration	4763.57	1	4763.57	402.49	< 0.0001	
X_1X_2	5.53	1	5.53	0.47	0.5164	
X_1X_3	68.85	1	68.85	5.82	0.0466	
X_2X_3	216.16	1	216.16	18.26	0.0037	
X_1^2	618.82	1	618.82	52.29	0.0002	
X_2^2	524.85	1	524.85	44.35	0.0003	
X_3^2	148.41	1	148.41	12.54	0.0095	
Residual	82.85	7	11.84			
Lack of Fit	82.79	3	27.60	2017.72	< 0.0001	significant
Pure Error	0.055	4	0.014			
Cor Total	7290.23	16				
Std.Dev = 3.44 R-Squared = 0.9886						

Mean = 71.12	Adj R-Squared = 0.9740						
C.V.% = 4.84	Adeq Precision = 24.866						

Table 2. Analysis of variance and response surface regression model for malic acid reactive extraction

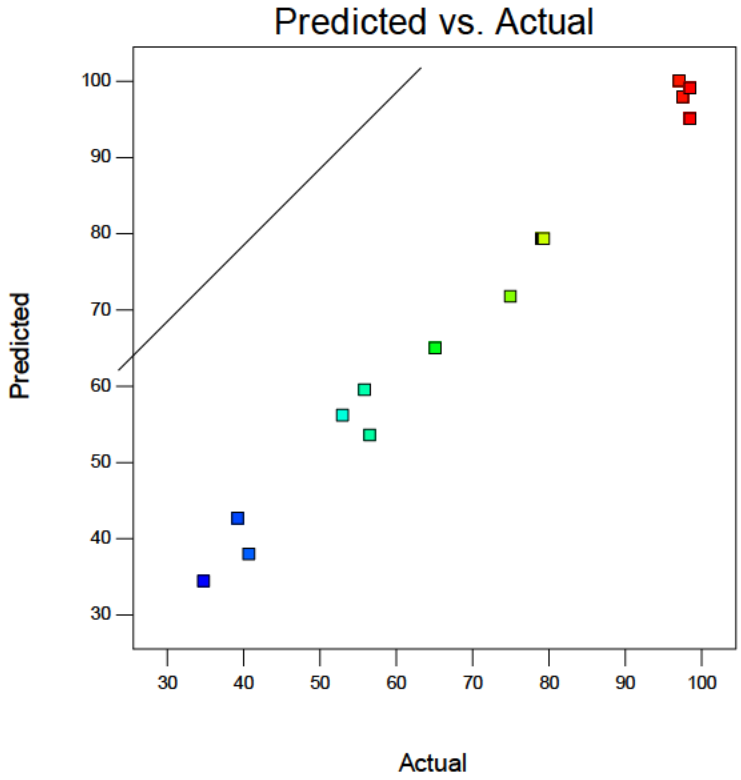

Figure 2. Predicted model plot against experimental extraction efficiency (%E) from RSM Model

Effect of the different variables on reactive extraction of malic acid. In order to access the effect of the different process variables on the extraction efficiency, experimental design of the single factor effect was adopted (one variable at a time). The three variables considered were temperature, initial acid concentration and trioctylamine composition. The experimental design was achieved by vaying one variable while holding the other two independent variable constant (see supplementary Table S1 and Fig. S1-S3 in the appendix B).

The models selected has explained the combined effect of three variables on the malic acid extraction efficiency (%E). The three dimensional (3D) graphs of the response surfaces and the corresponding contour lines map were necessary to explain the effects of the different process parameters as presented (Fig. 3-5). The experimental results illustrated (Fig. 3), presents the effects on the interaction between TOA composition and temperature on the extraction efficiency. It can be interpreted from the figure that extraction efficiency increases with an increase in extractant concentration (10-30%, v/v) irrespective of the temperature. This might be a product of the increase in extractant concentration which increases the extractability of the extractant and further helps to reach extraction equilibrium and the ability to form a complex (Li et al., 2006). The complexation reactions at equilibrium occur at the organic-aqueous interface and is an exothermic process. The malic acid-TOA complex brings about orderliness in the reactive extraction process thus decreasing the randomness and entropy of the system. The temperature increase also increases the kinetic energy of the molecules thereby interrupting certain interactions and acid-amine molecule combinations to form a stable complex at the interface (Tang et al., 2011). Another reason could

be as a result of the exothermic reactions of the transfer of proton and formation of hydrogen bond which decreases the system entropy (Wasewar, 2012).

The interactive effects of malic acid concentration and temperature on the extraction efficiency is elucidated (Fig. 4). It can be interpreted from the figure that the extraction efficiency decreased with an increase in malic acid concentration regardless of the temperature. This is because the tendency of extractant overloading increases with solute concentration (Qin et al., 2003). The extraction efficiency decreases with a rise in acid concentration and on further temperature enhancement. This might be due to the disturbance of extractant and solute molecules interaction in the organic phase with thermal energy increase leading to a reduction in the formation of the complex (Kumar et al., 2011).

The extraction efficiency at a higher solvent ratio (30%, v/v) initially increases up to a certain point and then starts decreasing with further increase in acid concentration (Fig. 5). This might be because of the presence of 1-decanol, a polar organic solvent being reduced with an increase in extractant ratio owing to H-bonding between C=O of the acid-extractant complex and the proton of the polar diluent (Wang et al., 2009a).

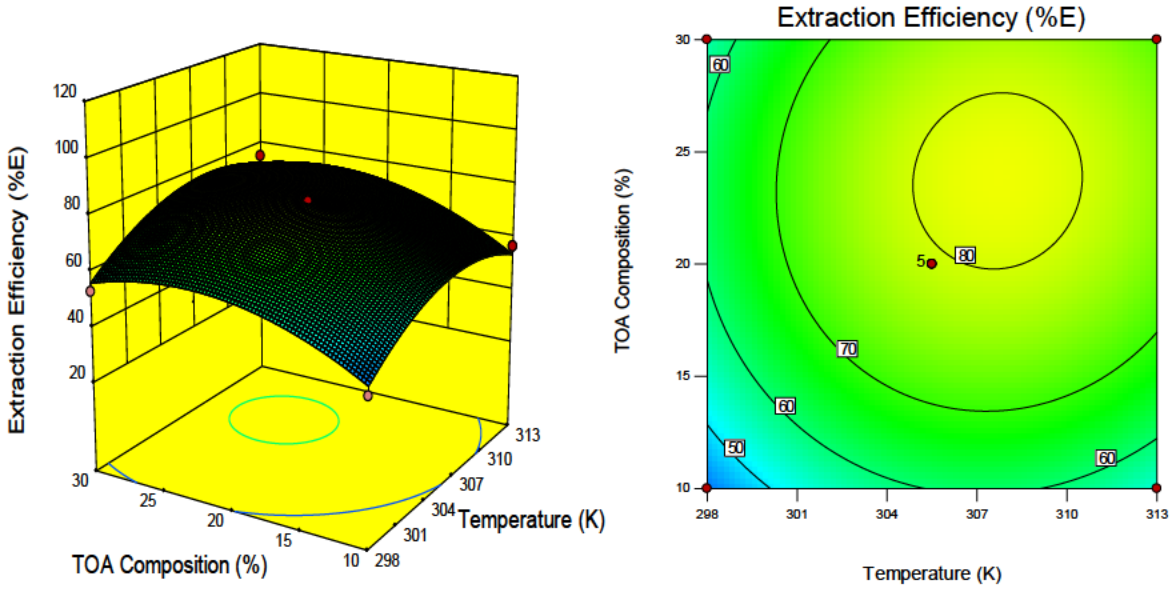

Figure 3. Response surface plot and a contour-lines map displaying the effects of interaction between TOA composition and temperature variables on extraction efficiency

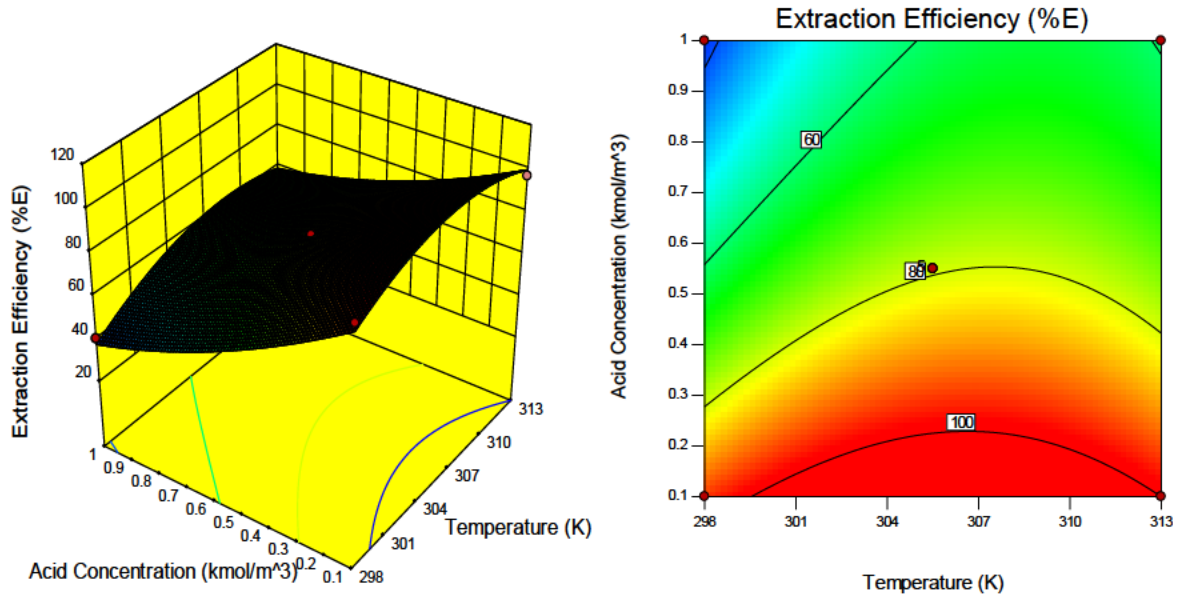

Figure 4. Response surface plot and a contour-lines map displaying the effects of interaction between acid concentration and temperature variables on extraction efficiency

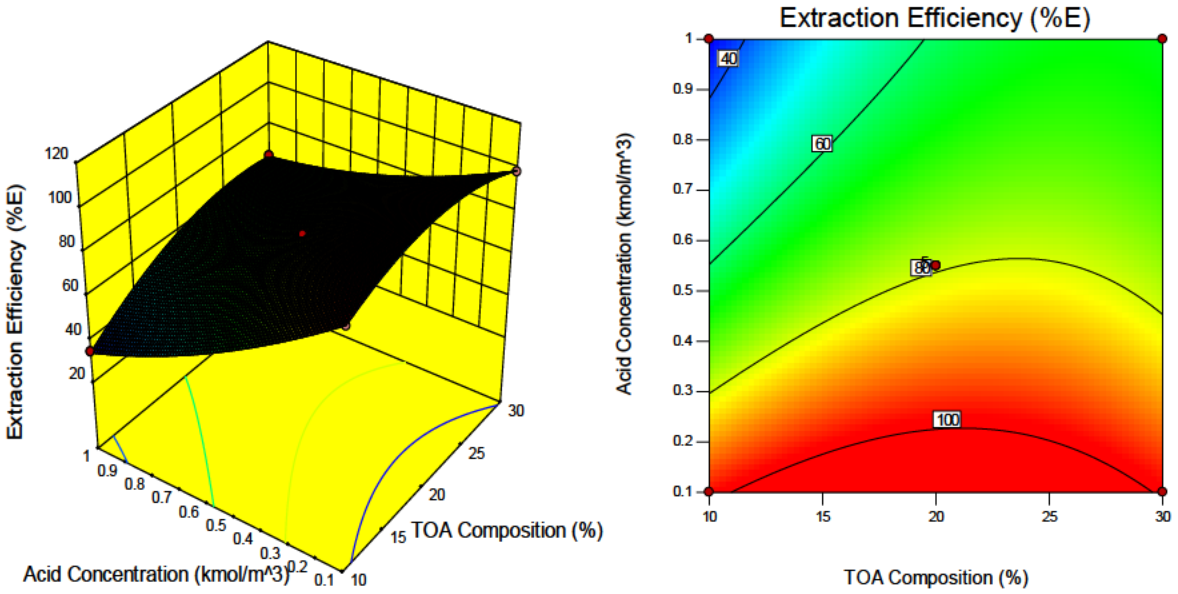

Figure 5. Response surface plot and a contour-lines map displaying the effects of interaction between acid concentration and TOA composition variables on extraction efficiency

Process variables optimization. The same software, design expert was employed in the numerical optimization of the process parameters to maximize the malic acid extraction efficiency. The predicted maximum values obtained from the model for the reactive extraction of malic acid for maximum extraction efficiency are temperature: 304.73 K, acid concentration: 0.247 kmol/m^3, Trioctylamine composition: 23.54 % (v/v) and the model prediction for the extraction efficiency under these optimum conditions as 97.53%.

Experimental verification and validation were conducted at the optimized process variables and the results obtained (93.25%) were in good agreement with the predicted model response values.

Materials and Methods

Experimental Chemicals Deployed. All the chemicals, Malic acid ($C_4H_6O_5$), density 1.61g/mL, Trioctylamine (TOA), $[CH_3(CH_2)_7]_3N$, density 0.809g/mL and 1-decanol, density 0.829g/mL deployed in this study at purity of 98% were purchased from Sigma-Aldrich and the experimental water was obtained using an Elga PURELAB Option Q purification system. Deionized water from our laboratory was used throughout the experiment. Phenolphthalein indicator and 0.1M Sodium hydroxide were also purchased from Sigma-Aldrich. All chemicals were used as supplied with no further purification.

Equilibrium Studies. Reactive extraction equilibrium studies were conducted by preparing 25 mL aqueous solution (0.1 kmol/m^3 concentration of malic acid) and 25 mL organic phase solution was prepared by mixing (10-30) % of Trioctylamine extractant (%v/v) equivalent to (0.229-0.687 kmol/m^3) in 1- decanol at temperatures between (298-313K) in an orbital shaker which was placed in the oven for 5 hours at 120 rpm, the two phases was kept to settle for 2 hours. The aqueous phase analysis was carried out using the titration method with 0.1N NaOH and phenolphthalein as an indicator to obtain malic acid concentration. The organic phase concentration of malic acid was determined through mass balance. The experimental runs were done in triplicate to confirm the reproducibility of results.

Experimental Design and Response Surface Methodology. The different experimental cycles were carried out using the design of experiment template obtained using Box-Behnken design (BBD) with three variables at three levels each in the optimization of the process variables used in the reactive extraction process. The Design-Expert version 10.0 (Statease Inc., Minneapolis, USA) was employed in this study. The un-coded (original) value of the different factors and their corresponding coded levels employed in the experimental design is as shown (Table 3).

Factors	Units	Coded Values	Level Low	High
Temperature	K	Factor X_1	298	313
Solvent Composition (v/v)	%	Factor X_2	10	30
Acid Concentration	kmol/m^3	Factor X_3	0.100	1.000

Table 3. Range of different variables for reactive extraction of Malic acid

There are three main stages in Response Surface Methodology which include:

Parameter selection and experimental design; finding a suitable estimation between independent process (factors) and the dependent (response) variables. (Marchitan et al., 2010).
Modeling of the response obtained from experimental results through regression and analysis of variance.
Response optimization; the optimum values of the independent process parameters; malic acid concentration, extractant ratio (%v/v) and temperature (K) were estimated to gain maximum value of the response, Extraction Efficiency (E%).

The relationship established between coded (x_i) and real (X_i) value is represented in "equation (2)" as

$$\text{Coded value } (x_i) = \frac{X_i - X_0}{\Delta X_i},\ i = 1,2,3.....,\ n \qquad (2)$$

Where ΔX is the phase change and X_0 is the real value at the center position

Taking into consideration all interactions of the input parameters (linear to linear and linear to quadratic), the behavior of the system can be described by "equation (3)".

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i<j}^{n} \sum_{j}^{n} \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

Where I and j are linear and quadratic coefficients respectively; n is the number of experimental parameters (n=3). β_0 is constant coefficient, β_i is the linear outcome or slope of input factor, $\beta_{ii} X_i$ is a quadratic outcome of input factor X_i and β_{ij} is linear effect interaction between input factors X_i and X_j, ε is the residual error.

Theory of reactive extraction of Malic acid. The reactive extraction process for malic acid accounts for the combined effect of physical and chemical extraction. Physical extraction (dimerization and ionization) involves solute separation which is free of complexities. In physical extraction, factors responsible and considered according to some researchers (Wasewar et al., 2010, Keshav et al., 2009e, Waghmare et al., 2013) are:

Aqueous phase ionization of Malic acid (as H^+A^-) and its corresponding non-facilitated transportation to the organic phase.

$$[HA]_{aq} \quad \leftrightarrow \quad A^- \quad + \quad H^+ \quad (4)$$

Un-dissociated Malic acid *Dissociated Malic acid*

Equilibrium distribution and partial malic acid dissociation between phases

$$[HA]_{aq} \quad \leftrightarrow \quad [HA]_{org} \quad (5)$$

Un-dissociated Malic acid *Dissociated Malic acid*

Organic phase acid dimerization

$$2[HA]_{aq} \leftrightarrow [HA]_{org}^2 \quad (6)$$

Distribution coefficient is presented with respect to dimerization coefficients according to (Keshav et al., 2008a):

$$K_D^{diluent} = P + 2P^2 D[HA]_{aq} \quad (7)$$

Where $P = {[HA]_{org}}/{[HA]_{aq}}$ $D = {[HA]_{2,org}}/{[HA\}_{org}^2}$

In chemical or reactive extraction (diffusion and solubility) of Malic acid, the process involved the contacting of a second phase extractant (trioctylamine and 1-decanol) that will reversibly react with the solute. The reaction with the liquid-liquid extraction which is attained in one-unit operation may be interpreted in three steps. Initially, transportation of reactants to the interface forming aqueous-organic phase interface from the bulk and interaction with the molecules of extractant, thus the formation of extractant-acid complex and finally, the complex that is formed is transported unto the organic phase for removal of the malic acid (Zhang et al., 2015). To explain and describe the mechanism of chemical extraction using "equation (9)", the equilibrium constant according to (Wasewar et al., 2010) is presented in Equation as:

$$Solute + n.Extractant \leftrightarrow Complex \quad (8)$$

$$K_c = \frac{[Complex]}{[Solute][Extractant]^n} \quad (9)$$

During the reactive extraction of malic acid, the three mechanisms of reaction involved (anion exchange, the formation of ion-pair and H-bond) were noted due to the acid-extractant complex formation in the solution dependent upon trioctylamine (extractant) basicity and the constant of dissociation of the extracted species (Gorden et al., 2015). The complex formed will remain at the interface otherwise it will orient

towards the interphase with any hydrophilic complexes formed in the organic phase (Poposka et al., 1998). When there exists any non-dissociated form of malic acid in the aqueous phase, the malic acid reaction with trioctylamine takes place through the formation of hydrogen bond leading to trioctylamine-malic acid complex formation of (1:1) and also (1:2), (1:3) at higher concentration of malic acid.

$$\underset{TOA}{R_3N} + \underset{MA}{HA} \leftrightarrow \underset{TOA-MA\ complex}{R_3N - HA} \quad (10)$$

This extracted acid by the amine extractant is generally known as an ammonium salt. The ion-pair formation complex occurs when Malic acid exists in the dilute aqueous phase in its dissociation form. The extent of association of the ion pair (acid radical and alkylammonium radical) leads to the quantification of extraction degree and stability (Hong et al., 2001).

$$\underset{TOA}{R_3N} + \underset{Malic\ acid\ (dissociated\ form)}{H^+ + A^-} \leftrightarrow \underset{TOA-MA\ complex}{R_3NH^+A^-} \quad (11)$$

The hydrogen bond formation could also be possible between the complex C = O of (1:1) trioctylamine-malic acid with 1-decanol which is present as a diluent in the oil phase (Wang et al., 2009a).

$$\underset{TOA-Acid\ complex}{R_3NH^+A^-} + \underset{1\text{-}Decanol}{C_{10}H_{21}OH} \leftrightarrow \underset{TOA\text{-}Acid\ \text{-}1\ Decanol\ Complex}{R_3NH^+A^-\ H^+OC_{10}H_{21}} \quad (12)$$

The malic acid reactive extraction process performance was assessed by the Extraction efficiency and Distribution coefficient (K_D) at equilibrium as the ratio of the concentration of acid in the organic phase $[HA]_{org}$ to the concentration in aqueous phase $[HA]_{aq}$ as shown in "equation (13)" and "equation (14)".

$$\text{Distribution coefficient } (K_D) = \frac{[HA]_{org}}{[HA]_{aq}} \quad (13)$$

$$\text{Extraction efficiency } (\%E) = \frac{K_D\ X\ 100}{1+ K_D} \quad (14)$$

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Author Contributions

VI and DL conceived the experiment(s) and the experimental set up. VI conducted the experiments and analysed the results under the supervision of DL. Both authors reviewed the manuscript.

Additional Information

Competing Interest: *The authors declare that they have no competing interests.*

Chapter FIVE

Paper 4, ButAcid RE using RSM

Butyric Acid Reactive Extraction using Trioctylamine in 1–Decanol: Response Surface Methodology Parametric Optimization Technique

Inyang, Victoria M. and Lokhat, David (2019)

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PAPER FOUR

Butyric Acid Reactive Extraction using Trioctylamine in 1–Decanol: Response Surface Methodology Parametric Optimization Technique

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Abstract

The optimization of the reactive extraction of butyric acid from an aqueous stream was effectively carried out using Response Surface Methodology (RSM). Three process parameters were studied, viz. initial butyric acid concentration, trioctylamine concentration, and temperature, to examine the interactive effects on extraction efficiency and distribution coefficient. A Box-Behnken design comprising of seventeen experimental runs was utilized in the reactive extraction study of butyric acid. Analysis of a second-order polynomial model yielded the following optimal conditions: Temperature 301.829 K, initial butyric acid concentration 0.493 kmol/m^3, trioctylamine composition 26.417 %v/v with the following responses: distribution coefficient = 28.795 and extraction efficiency of 96.666 %. Experimental validation of the model was carried out with the predicted process variables, and the responses obtained (distribution coefficient = 27.171, extraction efficiency = 96.450 %) were in close conformity to the predicted outcomes. Three-dimensional surface plots obtained from statistical analysis demonstrated that the butyric acid concentration and TOA composition had a more significant and interactive effect than the temperature on the response value in the reactive extraction process.

Keywords: Butyric acid, reactive extraction, equilibrium studies, optimization, Box-Behnken design.

1. Introduction

The new trend in the utilization of renewable feedstock, waste and by-products has made chemical production through a bio-based route using cheap and available biomass materials receive increasing attention by researchers. Butyric acid, a carboxylic acid with a short-chain, has great potential for chemical applications in cosmetics, pharmaceuticals, power generation, flavorings and food industries (Kumar et al., 2014, Entin-Meer et al., 2005). As a result of these wide-ranging applications, the butyric acid global market was valued at 227.5 million US dollars in 2015 with a projection to reach 542.8 million US dollars by 2024 (TransparencyMarketResearch, 2017). However, when produced via the biochemical route from the fermentation broth, there are challenges faced regarding the separation of the product, and it is necessary

to identify a cost and energy-effective approach. Fermentation is preferable over the competing chemical process because it is clean, green, has a high market value for products and also, uses cheaper feed sources. Therefore, obtaining high purity products and the prevention of by-products are important influencing factors. Also, an energy-efficient method of handling dilute aqueous streams and fermentation broths need to be developed to aid commercial production of carboxylic acids through bio routes (Huh et al., 2006, López-Garzón and Straathof, 2014). Currently, the conventional method for separation of these acids from dilute aqueous streams accounts for over 40% of the overall production rate due to a large amount of energy expended during product recovery (Cheng et al., 2012, Straathof, 2011). As a means to address these challenges, these acids can be recovered efficiently and effectively by reactive extraction.

Reactive extraction technique has gained attention in response to industrial pressure of replacing or modifying existing processes with modern ones to meet up with the requirements of high purity and bio-based products of substantially low cost (Keshav et al., 2009a, Wasewar, 2005, De et al., 2018, Kaur and Elst, 2014). The application of reactive extraction in separation techniques for carboxylic acids recovery from dilute aqueous streams is an effective and efficient process but optimizing the process still requires attention for different carboxylic acids with peculiarities (Chemarin et al., 2019, Eda et al., 2018, Wasewar et al., 2011, Wasewar and Yoo, 2012, Keshav et al., 2008c, Thakre et al., 2018). The three main factors affecting the equilibrium properties of carboxylic acid reactive extraction from dilute solutions are acid and extractant concentration, nature of the acid, and the extractant/diluent employed (Tamada and King, 1990b, Senol, 2013a, Senol, 2005b, Keshav et al., 2009b). Besides, the effect of factors which can be controlled or manipulated such as pH, temperature and formation of a third phase, is capable of limiting the complexing stage (Prochaska et al., 2014, Procházka et al., 2005, Senol, 2004, Keshav et al., 2009d). Research conducted by Senol et al. (2015) studied the impact of butyric acid distribution between water and extractants (tri-n-butylamine, TBA and tri-n-butyl phosphate, TBP) dissolved in different oxygenated aromatic or aliphatic diluents (1-octanol, ethyl pentanoate, acetophenone, ethyl nonanoate, ethyl butyrate, and diethyl malonate). The study also explored the extractability of pure diluent only at isothermal conditions (298 K). It was found that 1-octanol gave the highest extractant yield among the studied diluents. Also, the power of the complex formed was greater for tri-n-butyl amine than tri-n-butyl phosphate, which both favoured the acid-extractant formation. Keshav et al. (2008c) also conducted a preliminary study on the reactive extraction of propionic acid using trioctylamine in different diluents (methyl isobutyl ketone, hexane, toluene, heptane, petroleum ether, and kerosene) and higher extraction was obtained with higher alcohols only especially 1-decanol. Tuyun and co-workers carried out extensive studies on the extraction of different organic acids (glycolic, picolinic, D-(-)-Quinic, acrylic, and cyclic polyhydroxy carboxylic acid) using aliphatic amines (trioctylamine and tridodecylamine) in different diluents (acetates, alcohols, ketones). Reactive extraction with a single and mixed tertiary amine was found to be prominent, resulting

in a higher overall distribution ratio and extraction capability. Chemical extractions were studied, and better performances of the extractant-diluent combination over the diluent alone were observed. Also, active polar diluents such as higher alcohols were found to be the most suitable diluents for the amine extractant since the highest distributions were obtained (Datta et al., 2015a, Tuyun et al., 2011, Tuyun and Uslu, 2011, Tuyun and Uslu, 2015, Tuyun and Uslu, 2012b, Tuyun and Uslu, 2012a). Therefore, the choice and selection of the extractant and diluent used in this work were based on different studies that reported trioctylamine and higher alcohol (1-decanol) as being highly efficient. Tertiary amines are more advantageous over other extractants due to low affinity with water, low-cost effectiveness, ease of regeneration and high extractant yields

To date, most studies have been focusing on finding suitable extractants and diluents for carboxylic acid reactive extraction from dilute aqueous solutions, phase equilibrium studies and individual effects on different factors (acid and extractant concentration, nature of the acid, the different types of diluent employed and temperature) affecting the equilibrium studies. Commercial-scale establishment, overall design, and set up of reactive extraction requires knowledge on the interactive effect of these factors for optimal performance, which is currently uncommon in literature. Therefore, this study investigates the effects and interactions between the concentration of acid, the composition of extractant and temperature on distribution coefficients and extraction yields of butyric acid using trioctylamine in 1-decanol. The choice of an appropriate technique for the evaluation of these process variables is of utmost importance with the least possible number of experimental runs. Response surface methodology utilizing Box-Behnken design was employed in the analysis and optimization of the process variables to maximize extraction efficiency and the optimal recovery.

Materials and Method

Experimental Chemicals Deployed

Butyric acid ($C_3H_6O_2$), density 0.993 g/mL, trioctylamine (TOA), $[CH_3(CH_2)_7]_3N$, density 0.809 g/mL and 1-decanol, density 0.829 g/mL employed in this study at purity of 98 % were purchased from Sigma-Aldrich. Deionized water was obtained using an Elga PURELAB Option Q purification system, and this was used throughout the experiment in aqueous phase preparation. Phenolphthalein indicator (pH) and 0.1 M Sodium hydroxide were also purchased from Sigma-Aldrich. All the chemicals were used as supplied with no further purification.

Methods

Equilibrium Studies

Reactive extraction equilibrium studies were conducted by preparing a 25 mL aqueous solution (0.4-1 kmol/m^3 butyric acid concentration). The organic phase solution was prepared by mixing 25 mL (10-30) % of trioctylamine extractant (v/v) i.e. 0.229 – 0.687 kmol/m^3) in 1- decanol. The mixture was placed in an orbital shaker at oven temperatures between (298.15-318.15 K, i.e., 25-45 ^oC) for 5 hours at 120 rpm. The two phases were allowed to settle for 2 hours in a separating funnel at the same temperature. The aqueous phase analysis was carried out using the titration method with 0.1 M NaOH and phenolphthalein indicator to obtain the concentration of butyric acid. The butyric acid concentration in the organic phase was determined through material balance. The experimental analysis was done in triplicate under exact process conditions to confirm the reproducibility of results.

Experimental Design

The design of experiment (DOE) template obtained from a Box-Behnken design (BBD) with three-level variables was employed in carrying out the experimental runs to optimize the extraction process parameters. Design-Expert version 10.0 software (Statease Inc., Minneapolis, USA) was used for this purpose. The un-coded value of the different factors and their corresponding coded levels employed in the experiments are presented in Table 1.

Table 1. Range of different variables for reactive extraction of butyric acid

			Level	
Factors	Units	Coded Values	Low	High
Temperature	K	Factor X_1	298.15	318.15
Solvent Composition (v/v)	%	Factor X_2	10	30
Acid Concentration	kmol/m^3	Factor X_3	0.400	1.000

The first step in response surface methodology is the search for a suitable model relating the independent variables (factors) and the dependent variables (responses) (Marchitan et al., 2010). Secondly, analysis of variance (ANOVA) is typically conducted on the tentative results obtained by utilizing the statistical design package, Design expert 10.0 software, and different three-dimensional graphs were generated. Lastly, response optimization of the individual process parameters, viz. butyric acid concentration, extractant ratio (%v/v) and temperature (K) were carried out to gain the maximum value of the response, Extraction Efficiency (%E).

Theory of butyric acid reactive extraction

Reactive extraction of butyric acid using extractant (trioctylamine) and diluent (1-decanol) can be explained using three principles: (i) aqueous phase butyric acid ionization (K_{HA}), (ii) organic phase partitioning of undissociated butyric acid (P), and (iii) organic phase butyric acid dimerization (D) (Kertes and King, 1986). The following reaction expressions can be used to describe the phenomena:

Aqueous phase butyric acid ionization

$$[BA]_{aq} \leftrightarrow A^- + B^+ \quad (1)$$

$$K_{HA} = [B^+][A^-]/[BA]_{aq} \quad (2)$$

Organic phase partitioning of undissociated butyric acid

$$[BA]_{aq} \leftrightarrow [BA]_{org} \quad (3)$$

$$P = [BA]_{org}/[BA]_{aq} \quad (4)$$

Organic phase butyric acid dimerization

$$2[BA]_{aq} \leftrightarrow [BA]^2_{org} \quad (5)$$

$$D = [BA]_{2,org}/[BA]^2_{org} \quad (6)$$

The butyric acid reactive extraction process performance was assessed by the distribution coefficient, K_D at equilibrium as the ratio of organic phase butyric acid concentration $[BA]_{org}$ to the concentration of butyric acid in the aqueous phase $[BA]_{aq}$ as shown in equation 7 and the extraction efficiency was calculated using equation 8

$$\text{Distribution coefficient } (K_D) = \frac{[BA]_{org}}{[BA]_{aq}} \quad (7)$$

$$\text{Extraction efficiency } (\%E) = \frac{K_D\ X\ 100}{1+\ K_D} \quad (8)$$

Results and Discussion

Regression model analysis

Table 2. Experimental design of variables (coded) for butyric acid extraction efficiency E% and distribution coefficient

Independent variables (factors)	Response

Run	Temperature T(k)	Acid Concentration (kmol/m^3)	TOA Composition (%v/v)	Distribution Coefficient (K_D)	Extraction Efficiency (%E)
1	0.000	1.000	-1.000	8.023	88.917
2	0.000	-1.000	-1.000	12.333	92.500
3	1.000	1.000	0.000	16.647	94.333
4	0.000	1.000	1.000	20.053	95.250
5	1.000	-1.000	0.000	21.857	95.625
6	-1.000	0.000	-1.000	13.000	92.857
7	-1.000	0.000	1.000	31.308	96.905
8	0.000	0.000	0.000	16.500	94.286
9	0.000	0.000	0.000	17.667	94.643
10	-1.000	1.000	0.000	14.789	93.667
11	1.000	0.000	-1.000	10.667	91.429
12	0.000	0.000	0.000	16.872	94.405
13	0.000	-1.000	1.000	25.667	96.250
14	-1.000	-1.000	0.000	31.000	96.875
15	0.000	0.000	0.000	17.261	94.524
16	0.000	0.000	0.000	16.143	94.167
17	1.000	0.000	1.000	22.333	95.714

The Box-Behnken independent variables for experimental analysis with the corresponding distribution coefficient and extraction yield are presented in Table 2. The experimental model obtained in coded variable terms from the regression analysis of the experimental design matrix is given by a second-order polynomial equation 9 and 10:

$$K_D = 16.89-2.32X_1-3.92X_2+6.92X_3+2.75X_1X_2-1.66X_1X_3-0.33X_2X_3+3.50X_1^2+0.69X_2^2-1.06X_3^2 \quad (9)$$

$$\%E = 94.40-0.40X_1-1.14X_2+2.30X_3+0.48X_1X_2+0.06X_1X_3+0.65X_2X_3-0.86X_1^2-0.14X_2^2-1.04X_3^2 \quad (10)$$

Where %E and K_D is the calculated responses of extraction yield and distribution coefficient and X_1, X_2, X_3 are the coded terms of three parameters (factors) temperature (T, K), acid concentration, (kmol/m^3), and extractant composition (%v/v), respectively. The analysis of Variance (ANOVA) was used for correlation prediction between independent process parameters and the corresponding responses as presented in Tables 3 and 4 for distribution coefficient and extraction yield, respectively. From the table, it was deduced that; the f-value and corresponding low p-value obtained are a good indication of a highly significant model. The input variables (X_1), (X_2) and (X_3), the interaction (X_2X_3) and the quadratic term X_1^2 are all significant while the interaction (X_1X_2), (X_1X_3) and the quadratic term X_2^2 and X_3^2 are the non-

significant terms. The linear terms were established as more significant terms than the interacting and quadratic ones. This implies that the linear terms have significant, as well as an antagonistic effect on the responses. Also, the synergistic effect of the input variables (linear term) significantly affected the extraction yield. Also, the higher values of correlation coefficient and modified R^2 values confirm the model fitness to the experimental results while the adequate precision of the model, which measures signal to noise ratio, gives a comparison between predicted values and mean prediction error. An adequate signal is indicated with a ratio greater than 4. A smaller predicted residual sum of squares (PRESS) value is an indication of good predictability of the model developed. Low values of standard deviation and variation coefficient, CV are desirable, and this shows the experimental degree of precision. Summarily, the values of adequate precision, PRESS, standard deviation, and variation coefficient obtained in this work (Table 3 and 4) indicate high precision and model reliability.

Table 3. Analysis of variance (ANOVA) and response surface regression model for butyric acid reactive extraction (distribution coefficient)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	648.09	9	72.01	22.25	0.0002	significant
X_1-Temperature	43.21	1	43.21	13.35	0.0081	
X_2-Acid Concentration	122.82	1	122.82	37.96	0.0005	
X_3-TOA Composition	382.78	1	382.78	118.30	< 0.0001	
X_1X_2	30.25	1	30.25	9.35	0.0184	
X_1X_3	11.03	1	11.03	3.41	0.1074	
X_2X_3	0.42	1	0.42	0.13	0.7279	
X_1^2	51.48	1	51.48	15.91	0.0053	
X_2^2	2.00	1	2.00	0.62	0.4581	
X_3^2	4.71	1	4.71	1.46	0.2666	
Residual	22.20	7	3.24			
Lack of Fit	21.20	3	7.07	19.48	0.0075	significant
Pure Error	1.45	4	0.36			
Cor Total	670.74	16				
Adequate precision	17.555					
PRESS	341.46					
Standard deviation	1.80					
Mean	18.36					
CV %	9.80					
R^2	0.9662					
R^2(adjusted)	0.9228					

Table 4. Analysis of variance (ANOVA) and response surface regression model for butyric acid reactive extraction (extraction efficiency)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	63.95	9	7.11	47.67	< 0.0001	significant
X_1-Temperature	1.28	1	1.28	8.60	0.0219	
X_2-Acid Concentration	10.31	1	10.31	69.19	< 0.0001	
X_3-TOA Composition	42.40	1	42.40	284.43	< 0.0001	
X_1X_2	0.92	1	0.92	6.16	0.0421	
X_1X_3	0.014	1	0.14	0.095	0.7668	
X_2X_3	1.67	1	1.67	11.19	0.0123	
X_1^2	3.10	1	3.10	20.83	0.0026	
X_2^2	0.081	1	0.081	0.54	0.4859	
X_3^2	4.53	1	4.53	30.39	0.0009	
Residual	1.04	7	0.15			
Lack of Fit	0.90	3	0.30	8.48	0.0330	significant
Pure Error	0.14	4	0.035			
Cor Total	64.99	16				

Adequate precision	26.997
PRESS	14.65
Standard deviation	0.39
Mean	94.26
CV %	0.41
R^2	0.9839
R^2(adjusted)	0.9633

Residual Analysis

The suitability of the residual model is confirmed using the diagnostic tool, residual analysis (Liu et al., 2004). The residual plots of the normal probability are shown in Figure 1, while Figure 2 depicts the scheme of predicted response against the experimental response for distribution coefficient and extraction efficiency, respectively, which substantiates the consistency of the empirical model. The plots were employed in the determination of the model residual analysis and confirmation of the normality and assumption of constant variance in ANOVA for response surface methodology. The different points lie alongside the diagonal, indicating normal dispersions of the error terms (residual plots).

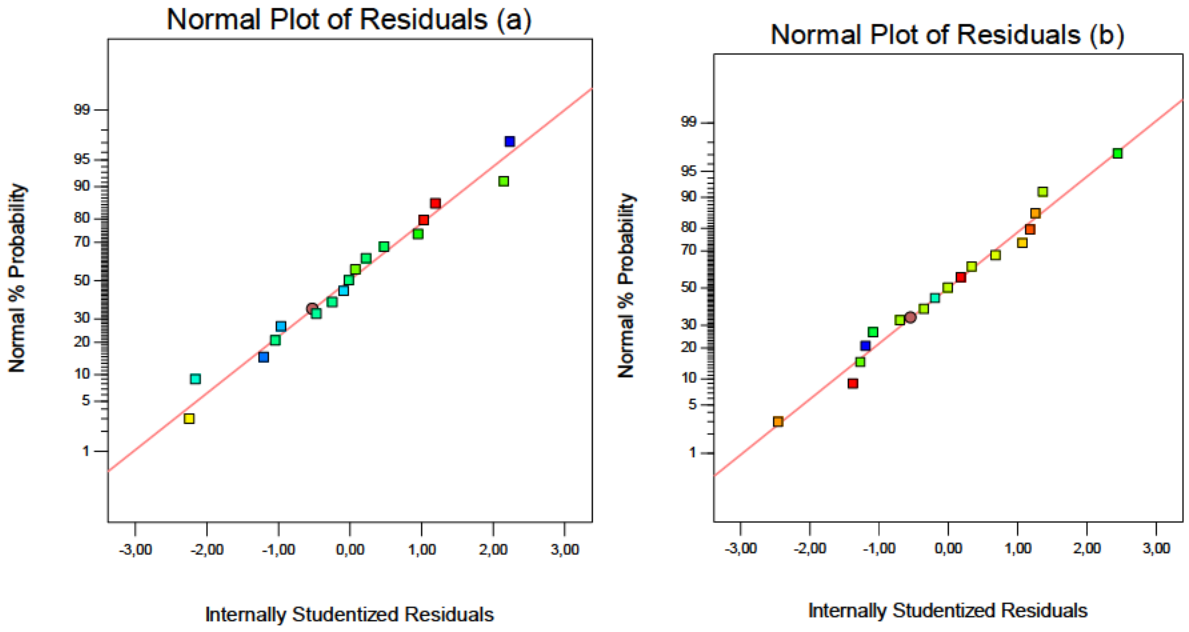

Fig 1. Normal probability plot of internally studentized residuals for butyric acid a) distribution coefficient and b) extraction yield

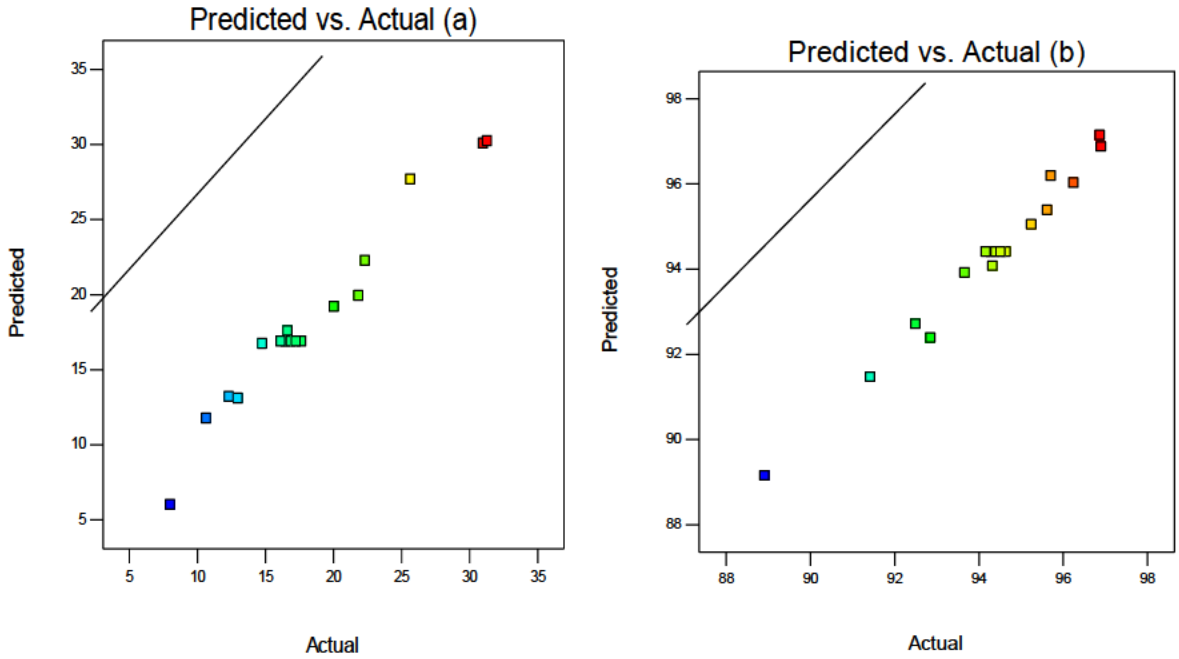

Fig 2. Comparison of plots of the predicted and actual value of butyric acid (a) distribution coefficient and (b) extraction yield

Response Surface Analysis

The model satisfactorily explained the outcome of the process parameters on the responses (extraction yield and distribution coefficient). The combined effect of butyric acid initial concentration, temperature, and trioctylamine composition on the responses were explained using the 3D graphs in Figures 3 to 5. The experimental results in Figure 3 demonstrate the effect of the interaction between the concentration of butyric acid and temperature on the responses. From the figure, it can be elucidated that the distribution coefficient and extraction efficiency decreased with an increase in acid concentration with insignificant effect of the temperature because with an increase in the concentration butyric acid, the tendency of overloading the extractant (trioctylamine) molecule increases.

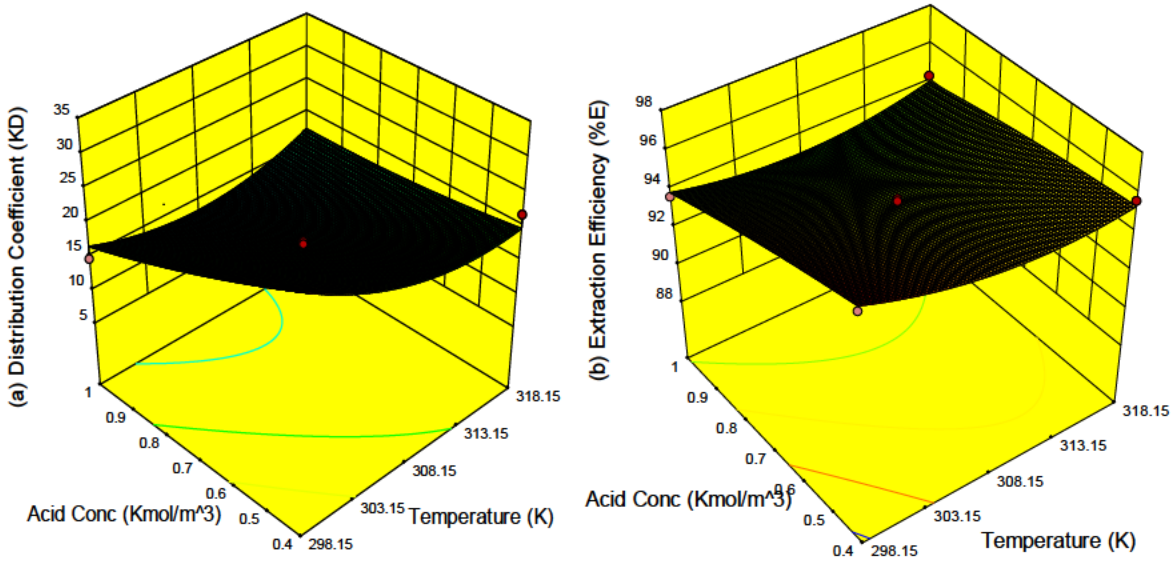

Fig 3: Three-dimensional (3D) surface plot showing the effect and interactions between butyric acid concentration and temperature variables on (a) distribution coefficient and (b) extraction efficiency

The effects of the interaction between the concentration of trioctylamine and temperature variables on the responses are depicted in Figure 4. It can be interpreted from the figure that the responses increased with a corresponding increase in trioctylamine concentration regardless of the temperature. This is because the extractant ability increases with an increase in the extractant concentration, thus aiding equilibrium attainment in the direction of forming a complex (Li et al., 2006). The equilibrium complex formation occurs at the interface, and the process is exothermic. This ultimately constitutes a decrease in entropy of the reactive extraction system studied.

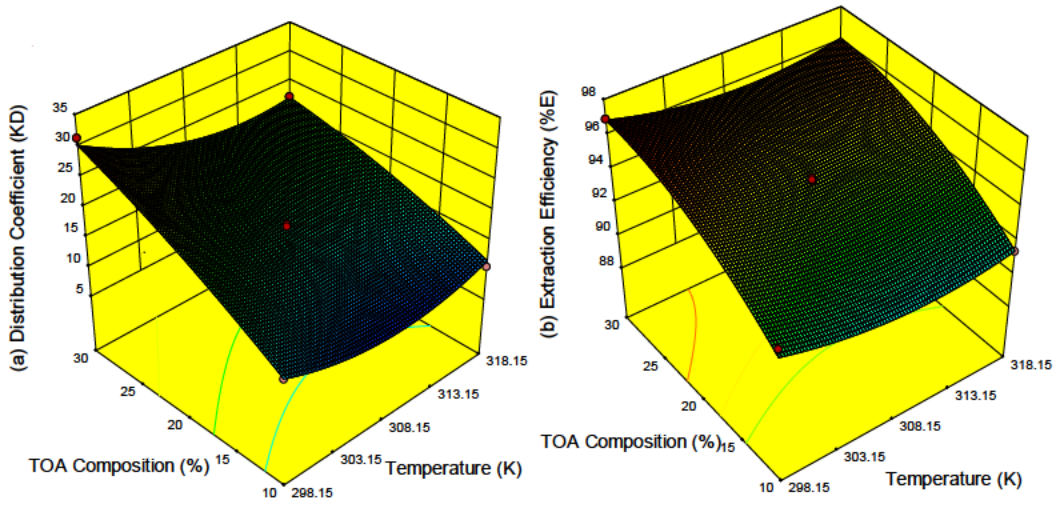

Fig 4: Three-dimensional (3D) surface plot showing the effect and interactions between TOA composition and temperature variables on (a) distribution coefficient and (b) extraction efficiency of butyric acid

The interactive effect of the butyric acid concentration and trioctylamine on the distribution coefficients and extraction efficiency is represented in Figure 5. An increase in the responses was observed with an increase in trioctylamine composition. Furthermore, a slight decrease in the responses was noted with an increase in the initial concentration of butyric acid. The degree of extraction was affected by the butyric acid concentration, that is, with a lower concentration of butyric acid, higher extraction efficiency was achieved. This might be as a result of the trioctylamine extractant being a determining factor for the complex formed. A similar trend was observed in previous work on propionic acid and malic acid extraction (Inyang and Lokhat, 2020a, Inyang and Lokhat, 2020b).

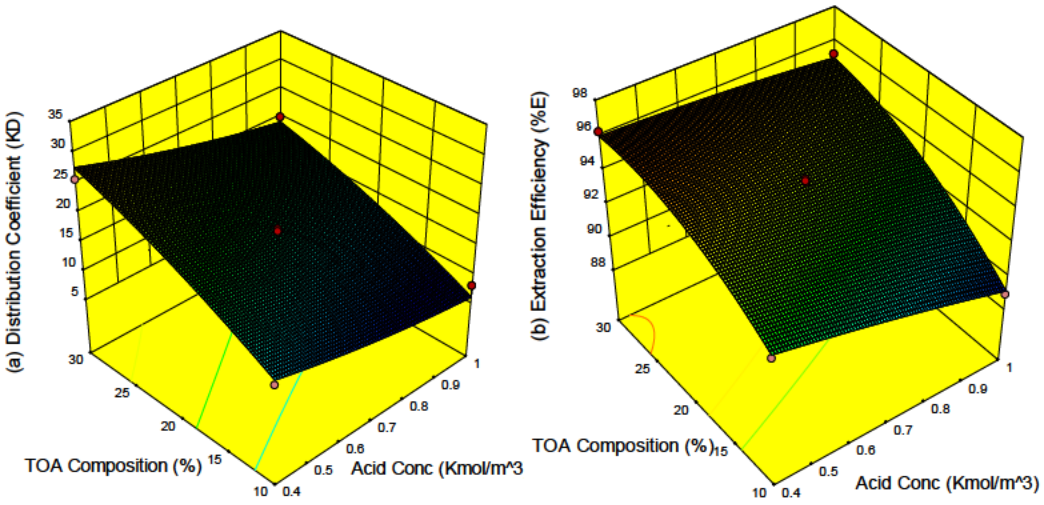

Fig 5: Three-dimensional (3D) surface plot showing the effect of butyric acid concentration in the aqueous phase and TOA composition in the organic phase on (a) distribution coefficient and (b) extraction efficiency

Finally, optimization of the reactive extraction process variables was conducted via the same software to minimize the factors and maximize the responses. The application of Box-Behnken design for the butyric acid reactive extraction yielded the following optimal conditions: Temperature 301.829 K, initial butyric acid concentration 0.493 kmol/m^3, trioctylamine composition 26.417 %v/v with the following responses: distribution coefficient = 28.795 and extraction efficiency of 96.666 %. Experimental model validation was carried out on the predicted process variables, and the responses obtained (distribution coefficient = 27.171, extraction efficiency = 96.450 %) was in close conformity to the predicted responses.

Conclusion

The reactive extraction of butyric acid from the aqueous stream was carried out using trioctylamine in 1–decanol. Box Behnken parametric optimization technique was utilized in the experimental design. Statistical regression analysis and ANOVA were also carried out with the experimental results obtained. The values of adequate precision, PRESS, standard deviation, and variation coefficient obtained indicate high precision and model reliability. The collective effect of temperature, preliminary concentration of butyric acid with TOA composition on the acid extraction yields was explored. The responses (extraction yield and distribution coefficient) decreased with initial concentration increment of butyric acid, which further increased with a rise in trioctylamine concentration irrespective of the temperature. The butyric acid reactive extraction RSM model optimization yielded the following optimal conditions: Temperature 301.829 K, initial butyric acid concentration 0.493 kmol/m^3, trioctylamine composition 26.417 %v/v with the following responses: distribution coefficient = 28.795 and extraction efficiency of 96.666 %. Experimental model validation was carried out with the predicted process variables, and the responses obtained (distribution coefficient = 27.171, extraction efficiency = 96.450 %) was in close conformity to the values obtained from experimental runs. The present study will be useful for the design of reactive separation processes and equipment for the extraction and recovery of low concentrations of carboxylic acids, especially from dilute aqueous solutions.

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Chapter SIX

Paper 5, KinStu on Prop & Mal Acids RE

Kinetic Studies on Propionic and Malic Acid Reactive Extraction Using Trioctylamine in 1-Decanol

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PAPER FIVE

Kinetic Studies on Propionic and Malic Acid Reactive Extraction Using Trioctylamine in 1-Decanol

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Abstract

The effectiveness and efficiency of the reactive extraction technique for recovery of propionic acid (PA) and malic acid (MA) from aqueous solution was investigated. Kinetic studies for the solute (acid) – solvent (trioctylamine dissolved in 1-decanol) system were carried out and mass transfer coefficients experimentally determined. These parameters are necessary for proper design of an extraction unit. The studies were carried out using dilute solutions of the acids with concentration range of 0.2 to 0.6 kmol/m^3 and trioctylamine (10 %v/v) in 1 decanol as extractant at 303.15 K. The effect of stirring speed, acid and extractant concentration at different time intervals were studied. The kinetic process parameters such as reaction order, mass transfer coefficient and rate constant were evaluated using the experimental data. From the results obtained, the reaction was found to be an instantaneous second-order chemical reaction occurring in the organic diffusion film. The values of the rate constants were found to be 0.430 m^3/mol s and 0.332 m^3/mol s respectively for propionic acid and malic acid while the mass transfer coefficient, k_m was also obtained for propionic acid (9 x 10^{-6} m/s) and malic acid (3x10^{-6} m/s). These are useful for the design of an extraction unit for carboxylic acids recovery from dilute aqueous solutions.

Keywords: Propionic acid, Malic acid, Reactive extraction, Kinetic studies

1.0 Introduction

Fermentation technology for production of industrial organic chemicals, and in particular organic acids is long known. Product purity and medium efficiency resulting in dilute aqueous solutions are two major obstacles. Due to the rise in petroleum prices, over the last decade, there has been renewed interest in the production of chemicals from fermentation processes. Biotechnology has the potential for new, efficient and low-cost fermentation processes for chemical production from biomass feedstock. With the availability of different and selective microorganisms, carbohydrate fermentation represents a promising route for new bio-product production (Corma et al., 2007). Currently, the commercial influence of fermentation-derived bio-products is however limited, due to challenges in the recovery of products. Therefore, developments of more effective techniques are essential to allow for chemicals obtained by fermentation to further penetrate the industry (Datta et al., 2015b).

Carboxylic acids with low molecular weight like propionic acid (PA), malic acid (MA) formic acid (FA) and butyric acid (BA) are important bulk chemicals with several industrial applications in the food industry, for the production of pharmaceuticals, in the textile industry as commodity chemicals and many more (Zelle et al., 2008, Keshav et al., 2009e). There has been an increasing interest in these chemicals as a result of growing demand in its potential areas of application as well as their recovery from dilute aqueous solutions. Due to its hydrophilic nature, it is difficult to extract these acids by conventional methods, therefore reactive extraction of carboxylic acids has been considered as a potential technological approach for the acid recovery from very dilute aqueous streams.

The choice of extractants can be oxygen-bearing (phosphorus or carbon bonded) or basic nitrogen-bearing extractants (amine-based). The efficiency of amine-based extractant is usually higher than those with the oxygen donor. However, these amine extractants have to be non-toxic to microbes for consideration in extractive fermentation for carboxylic acids produced through bio routes. The extractants are generally employed with diluents to overcome problems of corrosion and high viscosity. Diluents have significant effects on extraction performance, acid loading and stoichiometric association especially when it involved those with functional groups (Bízek et al., 1993, Keshav et al., 2008c, Keshav et al., 2009e). Usually, two types of diluents are obtainable: active and inactive diluents. Inactive diluents (aromatic and aliphatic hydrocarbons) offer minimum solvation of the polar complexes and very low acid distribution in the organic phase. In addition, the formation of third phase in the solvent phase at high concentrations of acid poses another challenge which further restricts their usage (Han et al., 2000). The functional groups in active diluent (alcohol, ketone, halogenated aromatics and chlorinated hydrocarbon) allows a better solvation of the carboxylic acid-amine extractant complex (ion-pair) to be achieved as a result of their polar properties (Tamada and King, 1990a, Tamada and King, 1990b). Moreover, diluents with moderate polarity for example alcohols with high carbon chain (like 1-decanol) greatly enhances the solvation power of the formed complex. Furthermore, increasing the chain length of the diluents increases water co-extracted unto the solvent phase (Hong et al., 2002). The interaction of the acid and tertiary amine may cause an undesirable third phase formation which could possibly be avoided by employing appropriate diluents (Li et al., 2002, Senol et al., 2015). With this background in mind and in place, 1-decanol with moderate polarity, water-insoluble diluent with less toxicity has been considered in this study.

Reactive extraction studies with particular extractant giving high distribution coefficient have been successfully carried out for carboxylic acids recovery from aqueous solutions. Nikhade et al. (2004) studied citric acid extraction using Alamine 336 in methyl isobutyl ketone (MIBK). From the studies, it was shown that the reaction fell within regime 1, which corresponds to a slow reaction which occurs in the solvent phase and kinetically-controlled. The reaction between the citric acid and Alamine 336 was established to

be of first order with respect to each reactant and second order overall. The value of the overall rate constant was calculated as 0.013 $m^3kmol^{-1}s^{-1}$. Wasewar et al. (2002b) also explored kinetics and equilibrium studies of reactive extraction of lactic acid utilizing Alamine 336 in two different diluents: MIBK and decanol. A Lewis-type stirred cell proposed by Doraiswamy and Sharma (1984) for data interpretation was employed in the study so as to obtain the required kinetic data and extraction theory along with a chemical reaction. From their report, reaction kinetics was unaffected by phase ratio and agitation speed which implied that the reaction fell in regime 3, that is, the extraction was accompanied by a fast-chemical reaction occurring in the diffusion film (Wasewar et al., 2002b, Wasewar et al., 2002a). The reaction was a first-order with respect to lactic acid for both diluents employed.

Also, the organic phase concentration had no effect on the reaction and the rate constant was 1.38 s^{-1} and 0.21 s^{-1} for MIBK and decanol respectively. Kyuchoukov et al. (2004) investigated lactic acid extraction from aqueous stream using the extractant, Aliquat 336 with 1-decanol and *n*-dodecane as organic diluent. In their study, the extraction efficiency was found to increase with the extractant concentration. Chen et al. (2013) carried out an investigative study on the reactive extraction of KCl and NH_4Cl using tributylamine extractant with 1-butanol. In their study, they proved that the extractant used was effective and can be regenerated with a recovery efficiency of about 91.0%. Marti et al. (2011) obtained equilibrium and kinetic data for pyruvic acid reactive extraction using trioctylamine (TOA) and Alamine 336 in 1-octanol or oleyl alcohol. According to the theory of Doraiswamy and Sharma (1984), the kinetic data revealed that, the reaction between pyruvic acid and trioctylamine in 1-octanol fell in regime 3, wherein extraction is accompanied by a fast-chemical reaction that occurs in the diffusion film.

The reaction was established to be of first order with regards to each reactant concentration, and second order overall with the value of rate constant obtained as 0.94 L mol^{-1} s^{-1}. From previous research studies, it has been shown that TOA is the most effective and efficient extractant among tertiary amines, for carboxylic acid recovery especially from very dilute solutions as a result of its strong basicity supported by its long chain length. Therefore, TOA in combination with 1-decaonol has been chosen for this work as effective extractant and diluent respectively. Modelling of a reactive extraction process requires both equilibrium and kinetic data together with mass-transfer considerations for the required system. Although considerable work on equilibrium studies of some carboxylic acid-amine extractant systems can be found in the literature, limited information relating to the kinetics of propionic and malic acids is obtainable.

The present work reports the experimentally determined kinetic data of propionic and malic acid and the corresponding parameters evaluation for reactive extraction process intensification from dilute aqueous streams/fermentation medium.

2.0 Experimental Materials and Methods

2.1 Materials

All the chemicals, propionic acid ($C_3H_6O_2$ density 0.993g/mL), Malic acid ($C_4H_6O_5$, density 1.61g/mL), Trioctylamine (TOA, $[CH_3(CH_2)_7]_3N$ density 0.809g/mL) and 1-decanol ($C_{10}H_{22}O$, density 0.829g/mL) employed in this study at purity of 98% were purchased from Sigma-Aldrich and deionized water was obtained using an Elga PURELAB Option Q purification system and used throughout the experiment. Phenolphthalein indicator (pH) and Sodium hydroxide (NaOH; molar mass 40g/mol) of reagent grade were also purchased from Sigma-Aldrich. All chemicals were used as supplied with no further purification.

2.2 Experimental Method

Kinetic Studies

Reactive extraction kinetic studies of propionic and malic acid were conducted using a jacketed glass reactor fitted with a stirrer (equipped with a water jacket to provide isothermal conditions) of inner diameter of 7 cm and interfacial area 38.49 cm^2 with a flat bottom (Figure 1). The vessel was charged with 100 mL aqueous solution (between 0.2-0.6 $kmol/m^3$ concentration of the acids). To it, 100 mL organic phase solution was prepared by mixing (10-30) % of Trioctylamine extractant (v/v) i.e. 0.229 $kmol/m^3$) in 1-decanol. Agitation was immediately started after feeding in the samples at a moderate speed. The constant temperature in the vessel was maintained by circulation of water from a water bath, with a digital temperature controller to maintain the temperature within ±0.1K. Samples were drawn out at different intervals for analysis. The aqueous phase analysis was carried out using the titration method with 0.1M NaOH and phenolphthalein as an indicator to obtain propionic acid concentration. The organic phase concentration of propionic acid was determined through material balance technique. The experimental runs were carried out in triplicate to confirm the reproducibility of results. Mixtures used in the experiments were gravimetrically prepared using an OHAUS PA 214 scale which has a precision of ± 10^{-4} g.

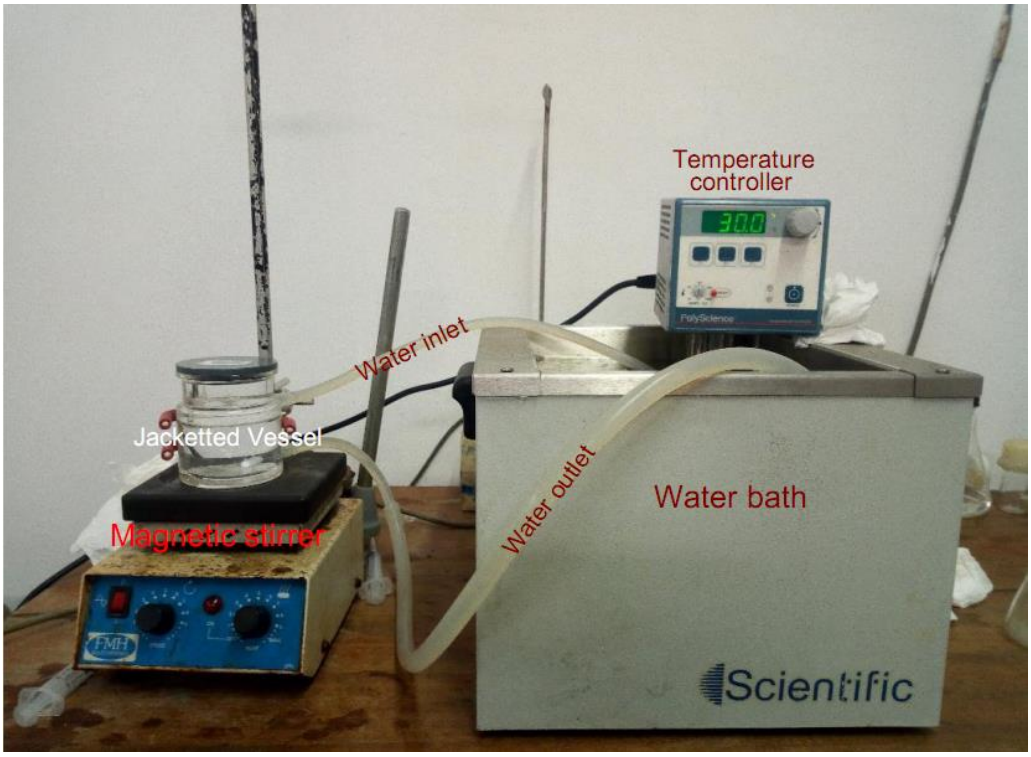

Figure 1. Experimental setup for kinetic studies on propionic and malic acid reactive extraction

2.3 Theory of extraction accompanied by a chemical reaction

Doraiswamy and Sharma (1984) recommended the comprehensive extraction mechanism followed by a chemical kinetic reaction in an agitated cell in order to determine chemical reaction effects on the extraction rate. Based on film and renewal theories, hydrodynamic and physicochemical factors, four different extraction regimes accompanied by reaction have been identified and classified into: very slow, slow, fast, and instantaneous reaction regimes. These regimes of reaction depend largely on the reaction rates and diffusion of species. Therefore, the effects of significant parameters, such as the stirring speed (N), volume phase ratio (V_{org}/V_{aq}), and acid and amine concentrations, on the extraction rate needs to be studied to determine the intrinsic kinetics of reactive extraction.

2.3.1 Determination of individual mass transfer coefficients in organic phase

Mass transfer coefficient is primarily influenced by the interfacial area of the reactor to confirm the reaction regime. Because the propionic and malic acid has appropriate distribution coefficients in the water/decanol system, the aqueous diffusion film resistance can be neglected, while considering the resistance of organic diffusion film. The mass-transfer rate (molar flux) for the transport of acid molecules from the aqueous to organic phase, is given by Equation 1.

$$\frac{V_{org}}{A}\frac{dC_{org}}{dt} = K_L\left[C^*_{org} - C_{org}\right] \quad (1)$$

Where A represents the interfacial area (m^2), V_{org} is the volume of the organic phase (m^3), and C^*_{org} is the interface acid concentration and K_L is the mass transfer coefficient in the bulk solution (m/s).

Equation 1 can be simplified by integration to give a relation between organic phase acid concentration and time as shown in equation 2.

$$\ln\left[\frac{C^*_{org}}{C^*_{org}-C_{org}}\right] = \frac{K_L A}{V_{org}}t \quad (2)$$

2.3.2 Reaction kinetics

The chemical reaction between the studied acids and trioctylamine extractant is a reversible type, specifically under high loading conditions in the organic phase. Hence, to prevent difficulties caused by reversibility, the initial reaction rates approach (controlled by the forward reaction) is taken into consideration to establish the reactive extraction kinetics (Hanna and Noble, 1985). The specific rate of extraction, R_A ($kmol \cdot m^{-2} \cdot s^{-1}$) in the present study, was evaluated from the experimental data using Equation 3

$$R_A = \frac{V_{org}}{A}\left[\frac{dC_{org}}{dt}\right]_{t=0} \quad (3)$$

Following the guidelines provided by Doraiswamy and Sharma (1984) to verify the mechanism of the extraction accompanied with a chemical reaction, the kinetic equation for this system (Regime 3) is given in Equation 4

$$R_A = \left(\left[C^*_{org}\right]\sqrt{\frac{2}{\alpha+1}k_{\alpha\beta}\left[C^*_{org}\right]^{\alpha-1}\left[(T_{org})in\right]^{\beta}D_A}\right) \quad (4)$$

where α and β are the orders of the reaction with respect to the studied acids and extractant, respectively; k is the reaction rate constant, T_{org} is the TOA concentration in the bulk of solution and D_A is the diffusion coefficient of acid into the extractant/diluent system ($m^2 \cdot s^{-1}$).

3.0 Results and Discussion

Experiments were carried out to describe the kinetics of reactive extraction of propionic acid and malic acid. The theory accompanied by the chemical reaction has been given in section 2.3, the initial rate of extraction was calculated for different acid concentration and trioctylamine using Figures 2 to 5. Figures 2 and 3 represent plots of concentration against time for propionic acid while Figures 4 and 5 shows plots for malic acid concentration versus time. Regression analysis of concentrations against time plots were carried

out to obtain $\left[\frac{dC_{org}}{dt}\right]$ at time = 0 and the specific extraction rate, R_A (kmol·m^{-2}·s^{-1}) was obtained from Equation 3.

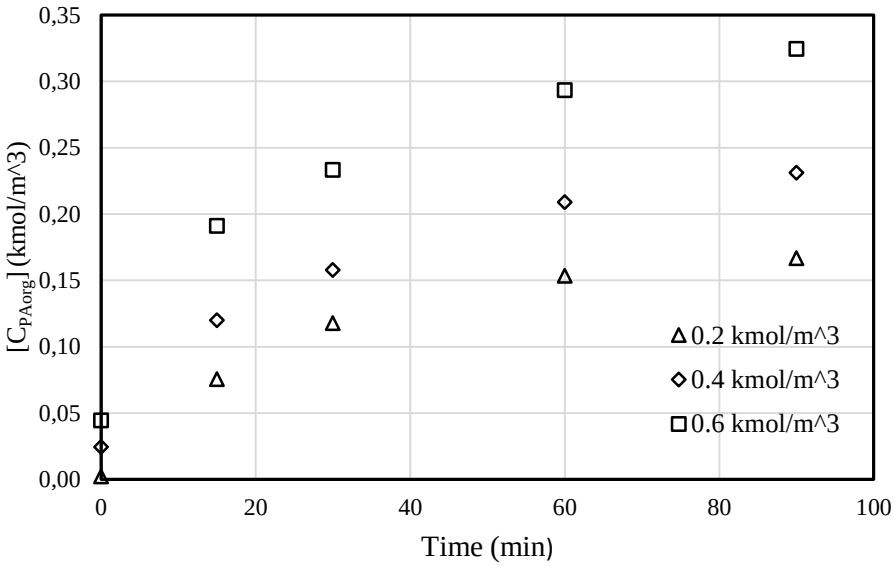

Figure 2. Propionic acid variation in organic phase against time for different initial acid concentration (0.2 - 0.6 kmol/m^3) using 30% trioctylamine in 1-decanol at 298K

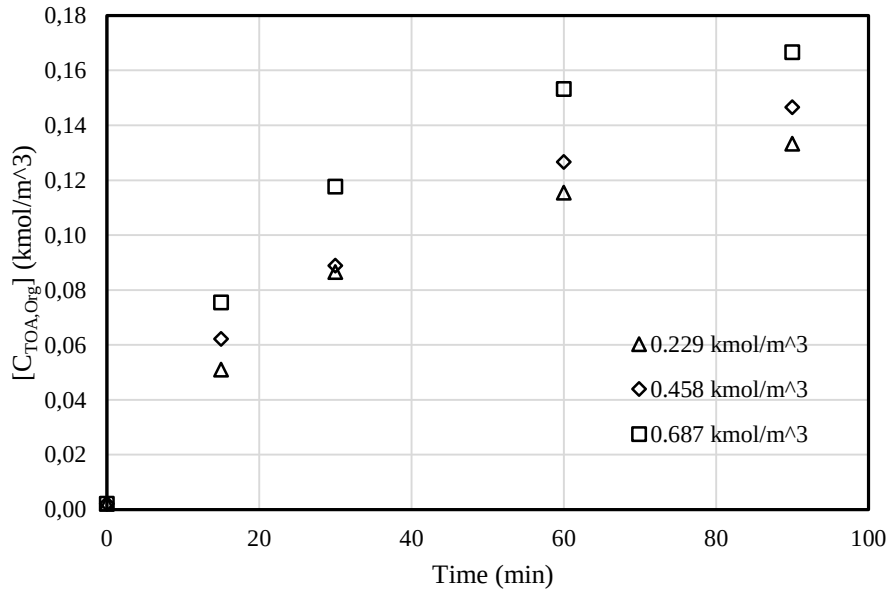

Figure 3. Propionic acid variation in organic phase against time for different trioctylamine concentration (0.229-0.687 kmol/m^3) using 0.2 kmol/m^3 of acid at 298K

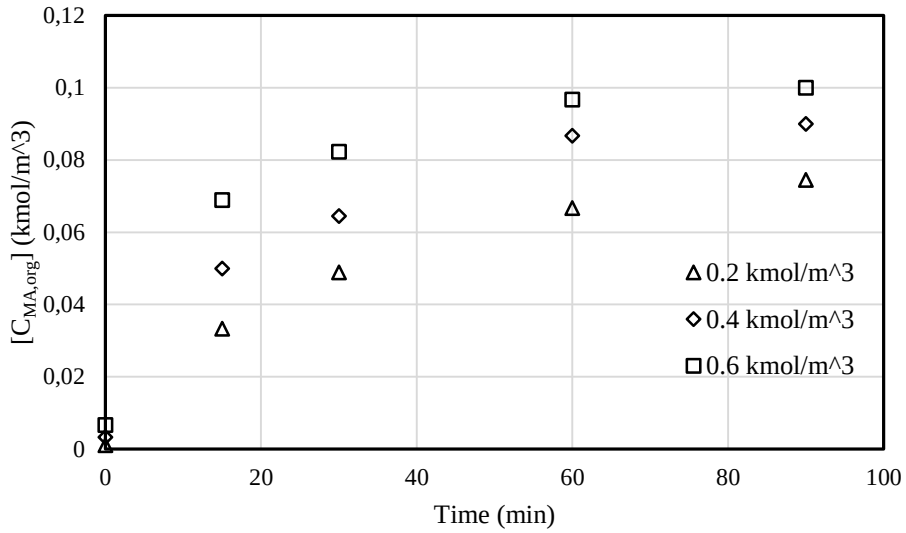

Figure 4. Malic acid variation in organic phase against time for initial acid concentration (0.2- 0.6 kmol/m^3) using 30% trioctylamine in 1-decanol at 298K

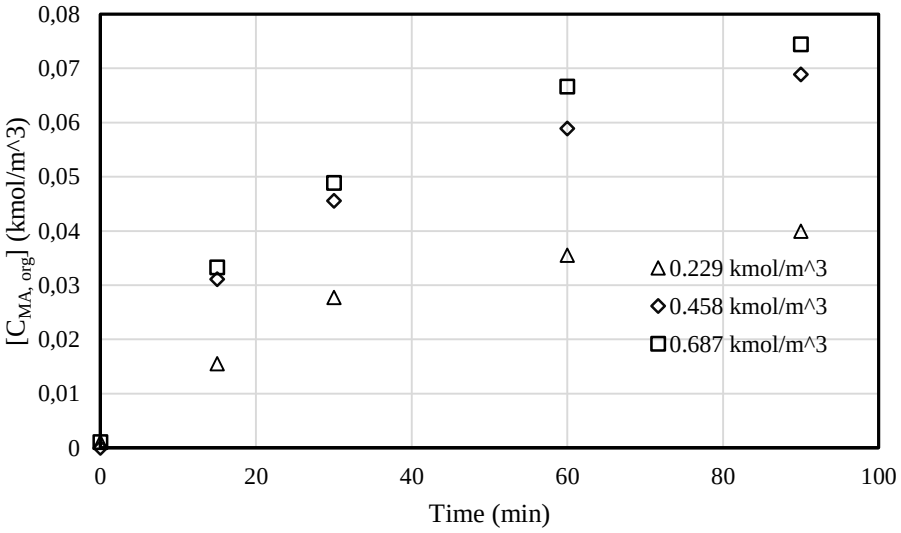

Figure 5. Malic acid variation in organic phase against time for different trioctylamine concentration (0.229-0.687 kmol/m^3) using 0.2 kmol/m^3 of acid at 298K

Regression analysis of acid concentration against time was carried out to determine the specific extraction rate. Figures 6 and 8 represent the effect of variation propionic acid and malic acid concentration respectively on the specific extraction rate. The acid concentration was varied from 0.2 to 0.6 kmol/m^3 at a constant trioctylamine concentration (30 %v/v, 0.687 kmol/m^3). The order of reaction was deduced to be first order with respect to acid concentration. Similarly, order of reaction with respect to trioctylamine concentration was determined by varying the concentration between 10 to 30%v/v equivalent to 0.229 to

0.687 kmol/m^3 at constant propionic and malic acid concentration (0.2 kmol/m^3). Figures 7 and 9 depict the effect of organic phase trioctylamine concentration on the specific extraction rate. From the results obtained, the extraction rates increased linearly with the concentration of trioctylamine extractant, therefore the reaction is first order.

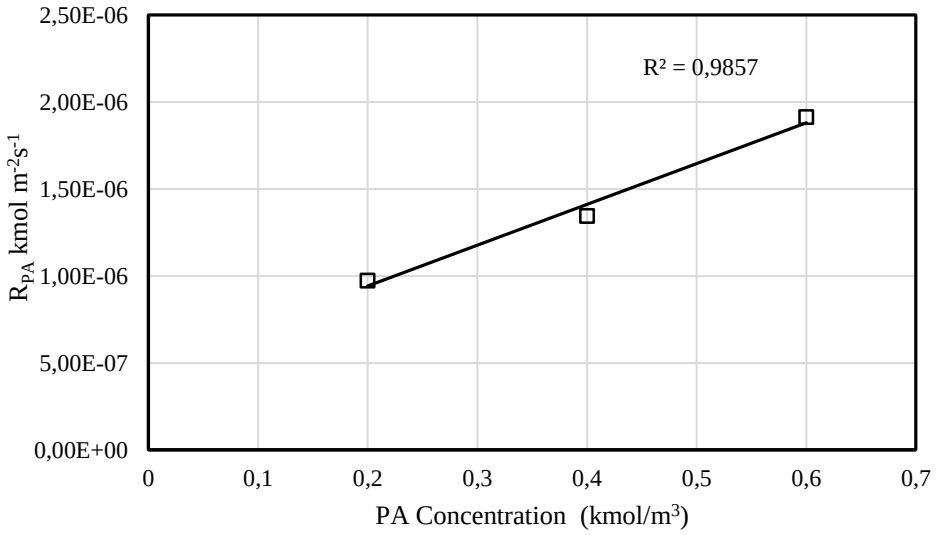

Figure 6. Effect of propionic acid organic phase concentration on the specific rate of extraction using 30%v/v (0.687 kmol/m^3) TOA in 1-decanol

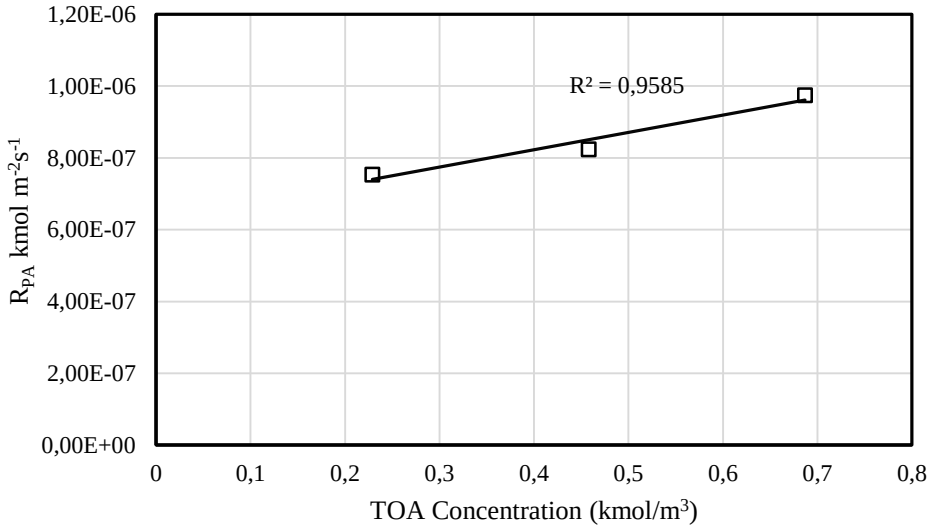

Figure 7. Effect of TOA concentration on the specific rate of extraction at 0.2 kmol/m^3 initial propionic acid.

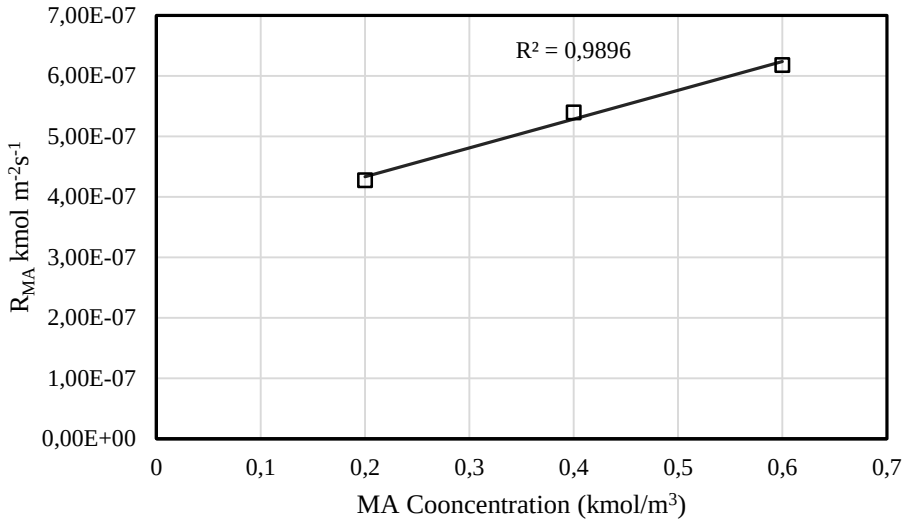

Figure 8. Effect of malic acid organic phase concentration on the specific rate of extraction using 30%v/v (0.687 kmol/m^3) TOA in 1-decanol

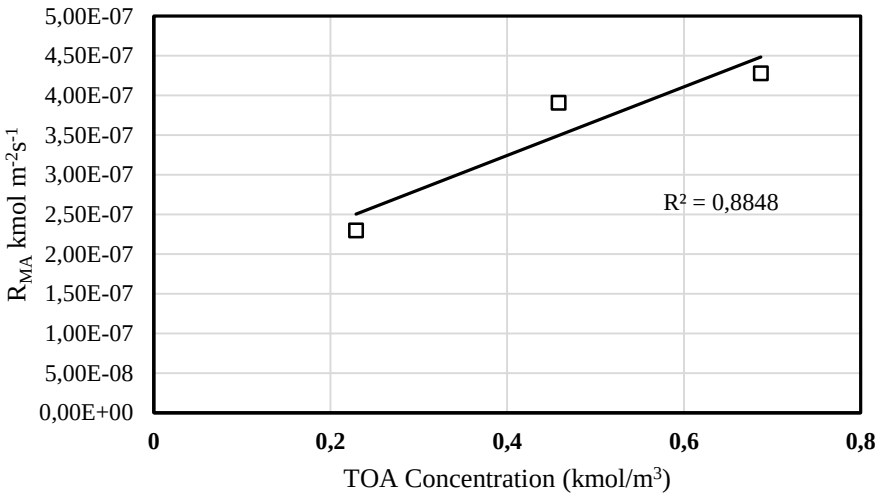

Figure 9. Effect of TOA concentration on the specific rate of extraction at 0.2 kmol/m^3 initial malic acid

Figures 6 and 7 for propionic acid and 8 and 9 for malic acid confirm that the reaction of the acids and extractant which is accompanied by relatively fast reaction and the overall order of reaction is 2 with an assumption that the acid reacts with TOA within a very small distance of the surface and none in the bulk liquid. Another assumption is that TOA concentration at the interface is same with the bulk of organic phase. The assumption is being validated with the following:

$$\frac{\sqrt{K_{\alpha\beta}D_A}}{K_m} > 3 \quad (5)$$

From equation 4 in section 2.3.2, the specific rate of extraction (R_A) for α = 1 and β =1 can be expressed as:

$$R_A = \left(\left[C^*_{org} \right] \sqrt{k_2 \left[(T_{org}) \right] D_A} \right) \quad (6)$$

Figures 10 and 11 show the effect of stirring speed varied between (80-100 rev/min) on specific rate of extraction for acid concentration of 0.2 kmol/m^3 and TOA concentration of 0.687 kmol/m^3 in 1-decanol (30 %v/v). In the speed range, a flat interface was observed with equal geometrical and interfacial area for extraction. R_A was established to be independent of the stirring speed, thus a fast-chemical reaction taking place in the diffusion film.

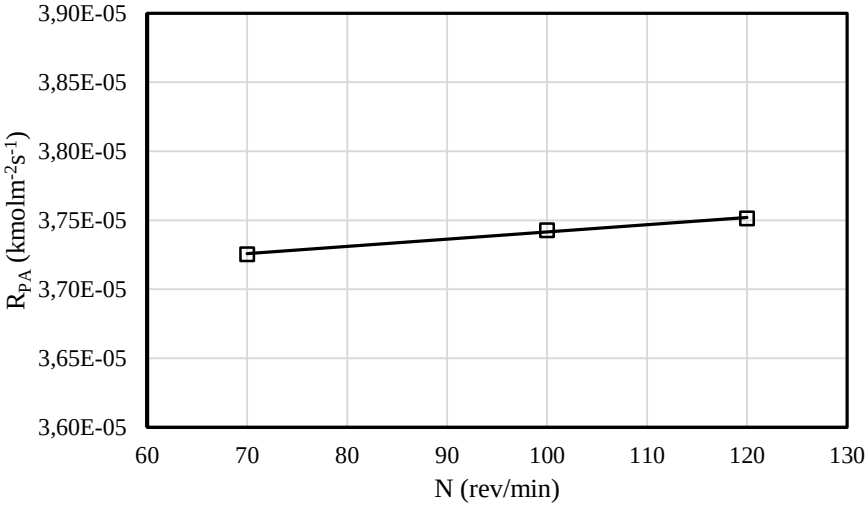

Figure 10. Effect of stirring speed on reaction rate for propionic acid extraction (0.2 kmol/m^3) using 0.687 kmol/m^3 TOA in 1-decanol at 298 K

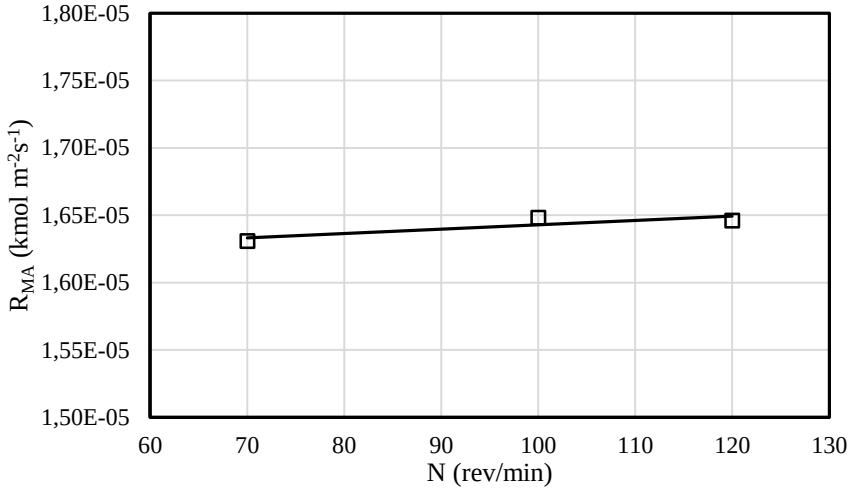

Figure 11. Effect of stirring speed on reaction rate for malic acid extraction (0.2 kmol/m^3) using 0.687 kmol/m^3 TOA in 1-decanol at 298 K

The diffusion coefficient of acid in the solution (D_A) was calculated using Wilke and Chang (1955) relations and the value obtained was 2.166 x 10^{-9} m^2/s for propionic acid and 1.774 x 10^{-9} m^2/s for malic acid. The molar volumes of propionic and malic acid were obtained as 67.93 cm^3/mol (at 298.15 K) and 94.72 cm^3/mol (at 303.15 K) respectively (Bald and Kinart, 2011, Cárdenas et al., 2017). By employing Equation 6, the second-order rate constant (k_2) was obtained from Figures 12 and 13 and estimated as 0.430 m^3/mol s and 0.332 m^3/mol s for propionic acid and malic acid respectively.

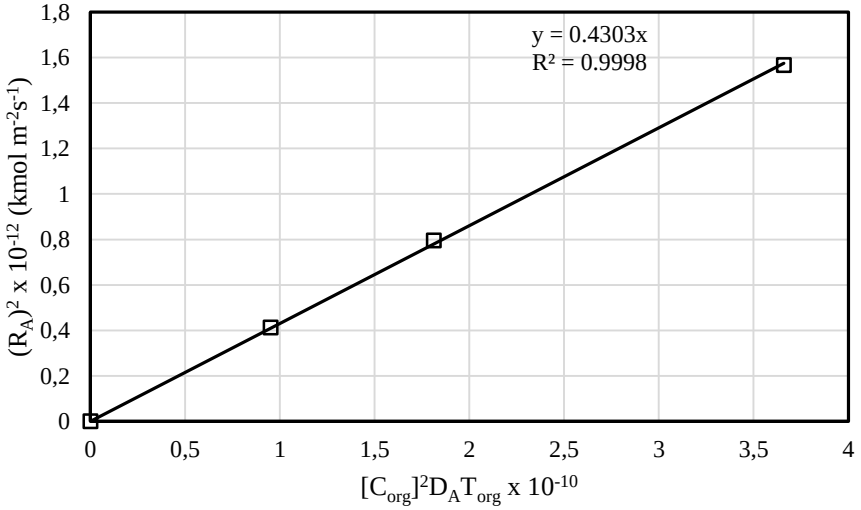

Figure 12. The second-order rate constant calculation for the reaction between propionic acid and TOA in 1-decanol

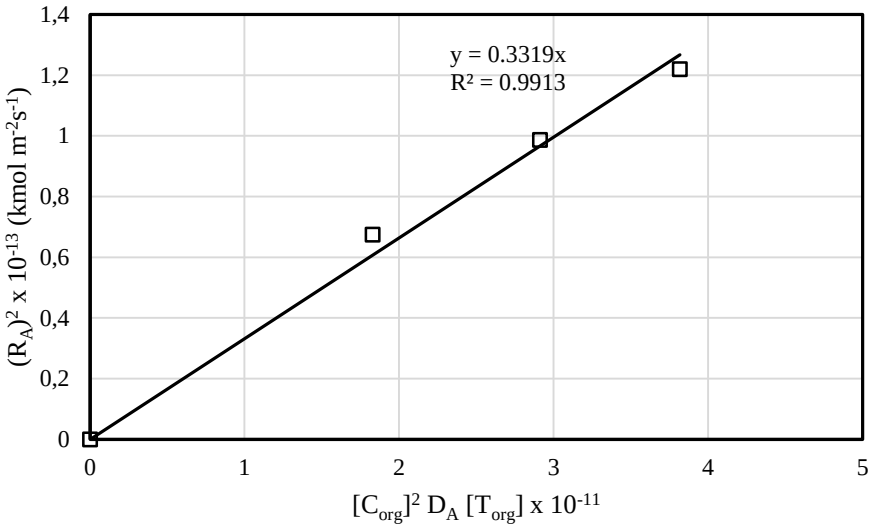

Figure 13. The second-order rate constant calculation for the reaction between malic acid and TOA in 1-decanol

The determination of the reaction regime requires approximate values of mass transfer coefficients k_m in the organic phase. This is necessary to confirm that the reaction condition is fast chemical reaction which occurs in the diffusion film. The values of k_m were obtained for the acid-extractant system at different speeds by measurement of organic phase concentration as a function of time. Thus, by integrating Equation 1, the expression (Equation 7) was derived and used to correlate the experimental data.

$$\ln\left[\frac{C^*_{org}}{C^*_{org}-C_{org}}\right] = -K_L\left[\frac{A}{V_{org}}\right] + \ln\left[\frac{C^*_{org}}{C^*_{org}-C_{org}}\right] \quad (7)$$

Therefore, the graph of $\ln\left[\frac{C^*_{org}}{C^*_{org}-C_{org}}\right]$ against time in Figures 14 and 15 was used to obtain the values of k_m for propionic acid (9×10^{-6} m/s) and malic acid (3×10^{-6} m/s) respectively by regression analysis.

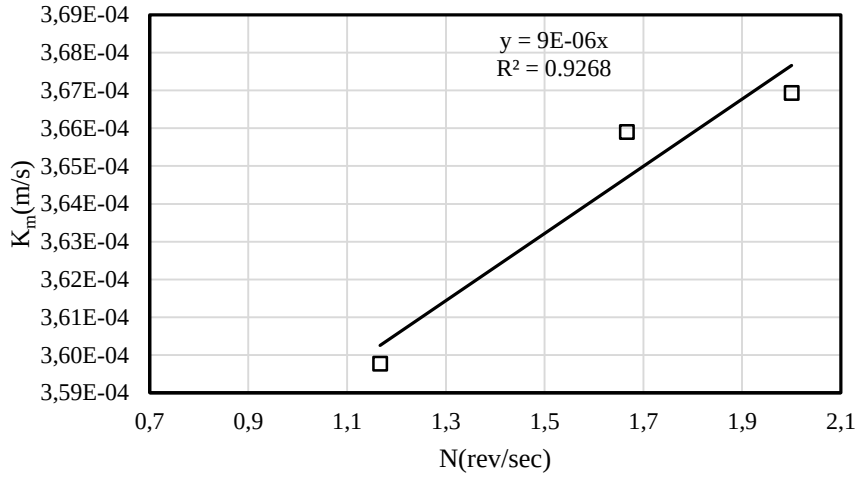

Figure 14. Variation of mass transfer coefficient with stirring speed for propionic acid concentration (0.2 kmol/m^3) at 298 K

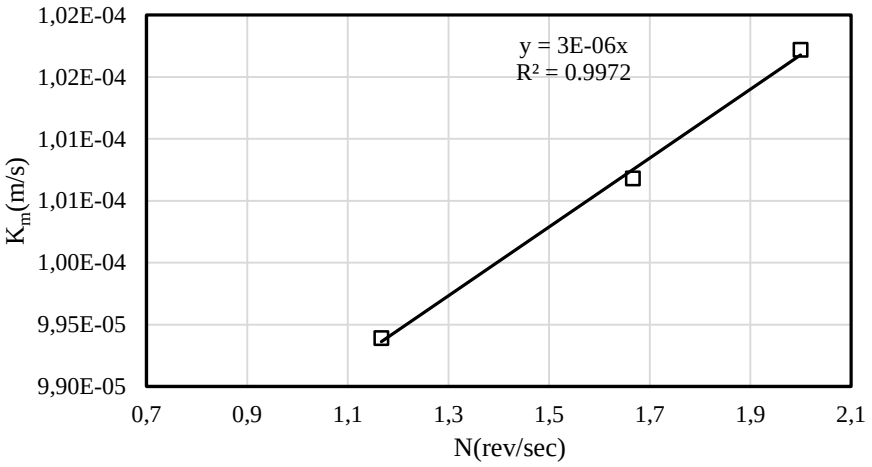

Figure 15. Variation of mass transfer coefficient with stirring speed for malic acid concentration (0.2 kmol/m^3) at 298 K

To validate the reaction regime as an instantaneous chemical reaction occurring in the organic diffusion film, Equation 5 was employed for the range of agitation speeds (70 - 120) rpm. $\frac{\sqrt{K_{\alpha\beta}D_A}}{K_m}$ gave values of 3.389 and 10.167 which is greater than 3. Therefore, the results obtained can be confirmed to be a second-order reaction which occurs in the organic diffusion film.

Comparison of the results obtained from different researchers for rate constants and order of reaction for different carboxylic acids reactive extraction using different solvents is shown in Table 1. Generally, the

basicity of tertiary amines extractant increases with the chain length of amine (Hong et al., 2002, Eyal and Canari, 1995, Matsumoto et al., 2003, Hong and Hong, 2000). Furthermore, increase in hydration with the alkyl chain length of the tertiary amine was also noted (Hong et al., 2002). Because of the high basicity of the trioctylamine, a more stable complex is formed in the organic phase between the acid and extractant. The extractability of the carboxylic acids is not only dependent on the tertiary amine but also on the diluent employed. Nevertheless, in active diluents such as higher alcohols for example, 1-decanol as used in this work, the extraction ability of the amines is proportional to their chain length. Therefore, in addition to the basicity of the amine, the water-enhanced solubility is also a factor for the values of the rate constant obtained in this work. These outcomes on the kinetic studies of reactive extraction system of propionic and malic acid will be useful in the design of an extraction process for recovery of carboxylic acids from dilute aqueous solutions.

Table 1. Kinetic studies results reported in literature for different carboxylic acids using amine extractant in diluents

Acid	Extractant	Diluent	Reaction Regime	Order of Reaction	Rate Constant	References
Propionic acid	Trioctylamine	1-Decanol	3	2	0.430 m^3/mol s	Present work
Malic acid	Trioctylamine	1-Decanol	3	2	0.332 m^3/mol s	Present work
Pyruvic acid	Tributylamine	n-Butyl acetate	3	2	0.419 m^3/mol s	Pal and Keshav (2015)
Pyruvic acid	Trioctylamine	1-Octanol	3	2	0.940 m^3/mol s	Marti et al. (2011)
Phenyl acetic acid	Alamine 336	Kerosene	3	1	0.900 s^{-1}	Gaidhani et al. (2002)
Lactic acid	Alamine 336	MIBK	3	1	1.380 s^{-1}	Wasewar et al. (2002b)
		Decanol	3	1	0.210 s^{-1}	Wasewar et al. (2002a)
Propionic acid	Tri-n-Octylphosphine oxide	Hexane		2	46.91 $(m^3/kmol)^2/s$	Keshav et al. (2008d)

Conclusion

The reactive extraction kinetics of propionic and malic acid using trioctylamine dissolved in 1-decanol were investigated using a stirred, jacketed vessel. Experiments were performed to study the effect of the acid concentrations, trioctylamine extractant concentration and speed of agitation on the overall extraction performance. The extraction theory has been employed to derive the extraction kinetics. From the analysis of the results obtained, the reaction was a fast reaction (second-order reaction) which occurs in the organic

diffusion film. The values of the rate constant were found to be 0.430 m^3/mol s and 0.332 m^3/mol s for propionic acid and malic acid respectively and mass transfer coefficient, k_m was also obtained for propionic acid (9 x 10^{-6} m/s) and malic acid (3x10^{-6} m/s) at 303.15 K. The present findings can aid in the design of reactive extraction units.

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Chapter SEVEN

Paper 6, ProAcid Recov by ELM using RSM &ANN

Propionic acid recovery from dilute aqueous solution by emulsion liquid membrane (ELM) technique: Optimisation using response surface methodology (RSM) and artificial neural network (ANN) experimental designs

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PAPER SIX

Propionic acid recovery from dilute aqueous solution by emulsion liquid membrane (ELM) technique: Optimization using response surface methodology (RSM) and artificial neural network (ANN) experimental design

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Abstract

Emulsion liquid membrane (ELM) technique was experimentally explored for the extraction and recovery of propionic acid existent in very dilute aqueous solutions. The formulation of the liquid membrane consists of trioctylamine as carrier, 1-deacanol as modifier, sorbitan monooleate (Span 80) as surfactants in heptane and sodium carbonate (Na_2CO_3) as a stripping agent. The interactive effects of different parameters such as propionic acid concentration, sodium carbonate concentration, trioctylamine concentration, treat ratio and extraction time on the propionic acid extraction efficiency were investigated. Response surface methodology (RSM) and artificial neural network (ANN) was employed for experimental design, optimization, construction and interpretation of response/output surface plots so as to analyze the effect of input variables on extraction efficiency in addition to the combined effects between variables. The modelling and prediction abilities of both methodologies have been compared using the coefficient of determination (R^2) values. According to the analysis, R^2 value of 0.9997 was obtained from RSM while 0.9998 was obtained by ANN model. Further, from the results obtained, both models gave close and accurate predictions of the response values. The optimum solution achieved by RSM led to an experimentally determined extraction efficiency of 92.28% in the propionic acid extraction by ELM process. Thus, the present study has shown that the ELM process is very efficient in the extraction of low concentration of carboxylic acids.

Keywords: Propionic acid, emulsion liquid membrane, extraction, optimization, response surface methodology, artificial neural network, process recovery.

1.0 Introduction

The current need for the manufacture of bio-based chemicals employing a environmentally friendly approach has been intensified due to the need to recover valuable products from seemingly insignificant dilute process solutions. Carboxylic acids process recovery from aqueous solution (present in < 10%) have been researched for several years due to persistent difficulties in separation and also in the bid to fashion ways to reduce separation costs in the chemical and fermentation industry (Keshav et al., 2008c). Propionic

acid and its derivatives are amongst the carboxylic acids that can be manufactured by fermentation. They have vast potentials and as an important product in the chemical market, are in high demands. Propionic acid is a highly versatile chemical with several industrial uses. It is majorly used in preserving and in the prevention of moulds in grains such as in animal feeds, hays and silages and also in human food for baking and in cheese. The derivatives of propionic acid are used in the manufacture of flavourings and fragrance, solvents, antiarthritic drugs and plasticizers (Keshav et al., 2008c, Yang et al., 2007, Playne, 1985). These wide applications of propionic acid and its derivatives have triggered a lot of interest in its recovery, which is the main challenge in any chemical industry and which this study seeks to address. Albeit, development or modification of a productive fermentation-based/biomass derived process is primarily determined by the downstream recovery method of propionic acid which is up-to 40-50% of the overall production costs (López-Garzón and Straathof, 2014, Straathof, 2011, Pal et al., 2009, Pal and Dey, 2013).

A number of traditional methods such as precipitation, ion exchange, solvent extraction, chromatography, microfiltration and ultrafiltration to recover propionic acid from very dilute aqueous solutions and fermentation broth have been studied but there are several limitations as a result. Limitations include: low distribution coefficients, high cost, large amount of waste generation posing environmental problems and material requirements (Srivastava et al., 2017). Therefore, the research gap is to continue the search for an alternative technology or process to overcome the inherent shortcomings of the traditional separation process which no doubt is a requirement for a successful implementation of the fermentation-based methods.

In this study, a more promising economic recovery technique, emulsion liquid membrane (ELM) is considered for propionic acid recovery from dilute aqueous streams. It was first proposed by N.N. Li in 1968 for hydrocarbon separation (Rania et al., 2007). ELM technique has been effectively applied in the separation of antibiotics and proteins, sugars, amino acids (Berrios et al., 2010, Kohli et al., 2018), separation of precious metals, lignin and dye contaminants from wastewater (Rania et al., 2007, Kumar et al., 2019a, Sulaiman et al., 2014b, Ma et al., 2017) and few organic acids recovery (Lee, 2011, Jusoh et al., 2016, Kumar et al., 2018, Jusoh et al., 2019). The ELM technique offers a simplified and unique separation process for the targeted species with several advantages. This include: combination of both extraction and stripping stages as a single step for product purification and concentration, high extraction efficiency, large surface area hence high mass transfer rate, operational simplicity, efficient for low concentration of solutes, low cost, minimal energy consumption and material requirement (Othman et al., 2019, Jiao et al., 2013, Mokhtari and Pourabdollah, 2012, Noah et al., 2016, Chaouchi and Hamdaoui, 2015, Kumar et al., 2018).

The extraction chemistry of ELM technique is comparable to the traditional solvent extraction except that the transport process is controlled by kinetics instead of equilibrium parameters (Kumbasar, 2010b). The

extraction yield depends on the operating parameters and conditions in addition to the type of surfactant, solvent and carrier as well as the concentration (Berrios et al., 2010). Hence, the efficiency of the emulsion process can be said to be influenced by the operating membrane parameters and their properties (Ng et al., 2010). Therefore, the purpose of this study is to effectively understand the dynamics of the ELM extraction process using trioctylamine as a carrier for propionic acid recovery from aqueous solution. In order to achieve this purpose, this work is aimed at experimentally investigating the major process parameters that can affect the degree of extraction and also establish the optimal conditions required for the recovery process by varying the experimental conditions. It is therefore necessary to choose an appropriate experimental technique to evaluate the important parameters together with the possible interactions while minimizing the experimental runs other than the conventional practice of single factor optimization (Yetilmezsoy et al., 2009). The quantification and identification of different interactions among the studied parameters can be achieved by response surface methodology (RSM) and artificial neural network (ANN) analysis (Ravikumar et al., 2005, Marchitan et al., 2010). Response surface methodology and artificial neural response are statistical tools and employed in the optimization of various processes. The methodology uses mathematical and statistical techniques to develop, improve and optimize different process parameters. They also offer important design application which can be used to develop and formulate new products and also enhance existing products designs. RSM and ANN can be used in modeling the relationships between a number of measurable variables (factors) and one or two responses and in finding the combination of the factor levels that may yield the optimum response.

To the best of knowledge, there are no studies dealing with this type of comparative study using the RSM and ANN modeling approach for the optimization of emulsion liquid membrane for propionic acid extraction which is one aspect of novelty emerging from the present study. With this elucidated information in view, propionic acid recovery from aqueous phase in a batch reactor by ELM was studied to investigate the parametric interactive effect and develop an optimal ELM technique utilizing a three level Box-Behnken design. This was further analyzed and compared with the results of the artificial neural network analysis.

2.0 Theory of Propionic acid ELM Extraction Mechanism

Propionic acid ELM extraction functions firstly, through formation of a primary water in oil (W/O/W type) emulsion where the internal phase comprises the stripping agent, and the oil phase contains the trioctylamine extractant and surfactant. The W/O/W emulsion is treated with propionic acid solution, and ELM globules are formed in the process. The ELM globules in this work consists of water (Na_2CO_3 solution for stripping) in an oil phase (carrier, TOA extractant in decanol & surfactant, span 80 in heptane) in water (propionic acid solution) emulsions. The interfaces between both phases (water and oil) are called liquid

membranes. The propionate ions are removed by the TOA extractant present in the oil phase and further stripping into the internal Na_2CO_3 droplets. This process is depicted in Figure 1.

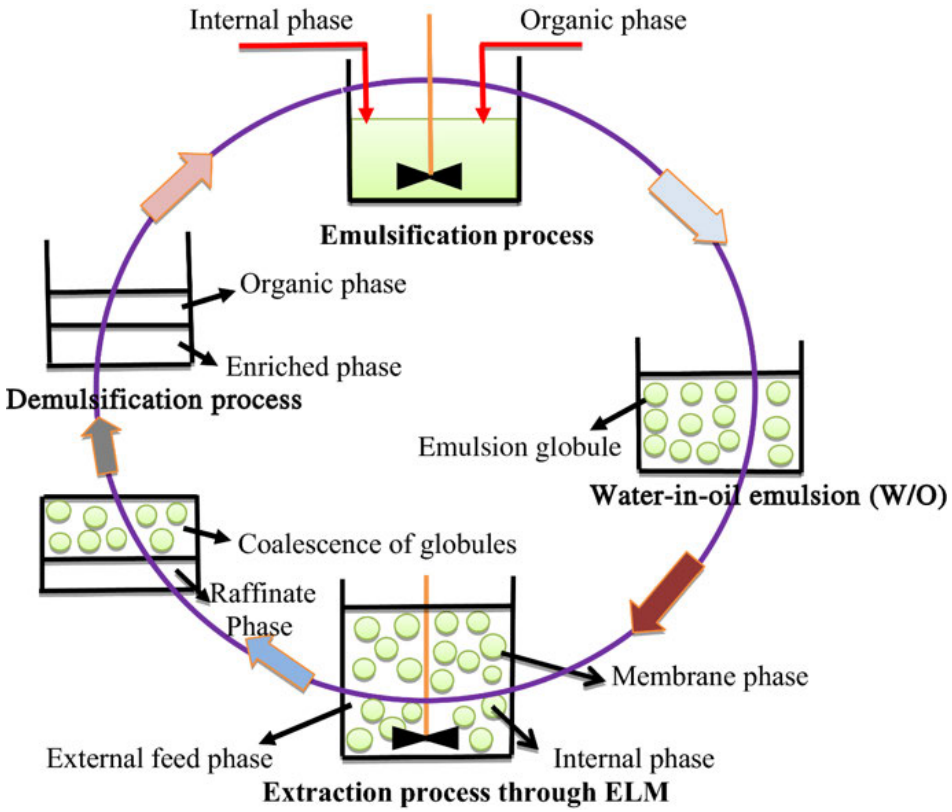

Figure 1. A schematic presentation of emulsion liquid membrane (ELM) process [Kumar et al. (2019a)]

The solute transportation process in the ELM takes place between the external and internal phase by means of the propionic acid concentration gradient from a high to low region. Propionate ions are extracted, stripped and concentrated in one single step since the ELM reaction is very fast because of the large interfacial area, thus neglecting the equilibrium limitations. A diagram interpreting the propionate ions extraction using ELM method is presented in Figure 2. The propionic acid transport through the liquid membrane can be explained in two steps: the external and internal interface reactions. The complexation reaction between undissociated propionic acid (HA) and TOA (pR) occurs at the external interface forming the acid-extractant complex ($HA.R_p$) as shown in Equation 1.

$$[HA]_{aq} + [pR]_{org} \longrightarrow [HA.R_p]_{org} \quad (1)$$

The formed complex disperses to the internal interface through the liquid membrane and propionic acid is released by the stripping reaction as represented in Equation 2.

$$2[HA.R_p]_{org} + [Na_2CO_3]_{aq} \longrightarrow [(pR_2^+)_2CO_3^{2-}]_{org} + 2[NaHA]_{aq} \quad (2)$$

The TOA extractant diffuses back to the external interface and further dissociates into water and carbon-dioxide therefore regenerating free amines as illustrated in Equation 3.

$$[(pR_2^+)_2CO_3^{2-}]_{org} \longrightarrow 2[pR]_{org} + [CO_2]_{aq} + [H_2O]_{aq} \quad (3)$$

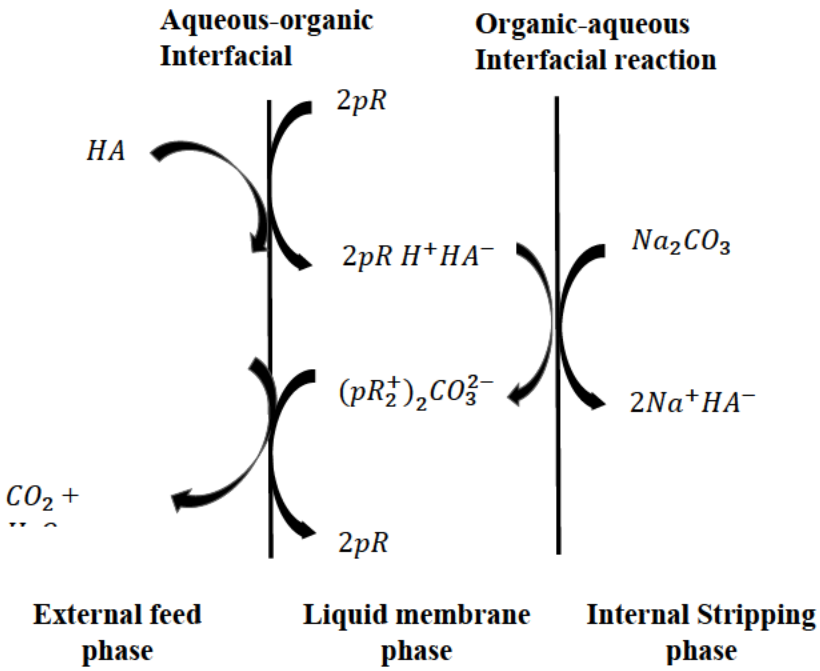

Figure 2. A schematic representation of propionic acid extraction using emulsion liquid membrane technique [modified and adopted from Jusoh et al. (2019)]

3.0 Materials and Method

3.1 Chemicals

Propionic acid ($C_3H_6O_2$, 98% purity, density 0.993g/mL), Trioctylamine (TOA, $[CH_3(CH_2)_7]_3N$, 98% purity, density 0.809g/mL), decanol ($C_{10}H_{22}O$, 98% purity, density 0.829g/mL), Sodium carbonate (Na_2CO_3, 99% purity, density 2.54 g/mL), Span 80 (Sorbitan monooleate, $C_{24}H_{44}O_6$, density 0.99 g/mL), Heptane ($CH_3(CH_2)_5CH_3$, 99% purity, density, 0.6837 g/mL) were all procured from Sigma-Aldrich and deionized water was obtained using an Elga PURELAB Option Q purification system from the laboratory (Chemical Engineering Analytical Laboratory) and used throughout the experiment. All chemicals were used as supplied without further purification.

3.2 Preparation of aqueous solutions of propionic acid and sodium carbonate

Propionic acid aqueous solutions were prepared by dissolving the desired concentration (0.05-0.1 kmol/m^3) which was weighed out using OHAUS PA 214 model scale in deionized water. Similarly, the internal

stripping phase (sodium carbonate Na_2CO_3) aqueous solutions with the required concentration (0.1-0.2 kmol/m^3) were prepared by dissolving the weighed amount of Na_2CO_3 pellets into deionized water. The aqueous solutions were uniformly mixed and homogenized with magnetic stirrer.

3.3 Preparation of membrane phase

The emulsion liquid membrane phase which was a water-oil (w/o) type was prepared by following the method described by Ahmad et al. (2015). The organic membrane phase was prepared in 250 mL glass beaker by mixing the different diluents in their proper proportions. This membrane phase contained (2-8% v/v trioctylamine as carrier in decanol, span 80 (4% v/v, as surfactant or stabilizer) in heptane. The organic membrane phase was homogenized under an agitation speed of 200 rpm for 3 mins before the drop wise addition of the internal stripping phase reagent (sodium carbonate Na_2CO_3, 0.1-0.2 kmol/m^3) in the ratio of 1:1 (v/v). This homogenized organic membrane phase was then agitated using a high-speed homogenizer (IKA RW 14 basic digital mixer) at 2000 rpm for 20 mins at room temperature to form a w/o type of stable emulsion. À stability check was conducted through an experimental observation of the prepared emulsion. A stable liquid emulsion was obtained after the emulsion was kept for 30 minutes after different trials with 4% (v/v) span 80 in n-heptane (which was utilized for the extraction). All the emulsion was freshly prepared before proceeding with the extraction experiments.

3.4 ELM Extraction of propionic acid

Propionic acid ELM extraction process were conducted in a batch mode utilizing a 200 mL volumetric flask. Exactly 25 mL of the prepared ELM was charged into the glass beaker and to this, aqueous propionic acid (predetermined external phase) was added as per the experimental design treat ratio (ratio of the emulsion organic phase to aqueous phase). The mixtures were stirred in an orbital shaker for varying time interval at 120 rpm at temperature of 23 ±2 ^oC. Upon completing the extraction process, the external aqueous phase was separated from emulsion phase by means of a separating funnel and further subjected to filtration using filter paper for separation of any small droplets size and particles. The clear aqueous phase was then analyzed for propionic acid concentration.

3.5 RSM Experimental design of the extraction process

The experiments were conducted in line with the Box-Behnken design (BBD) experimental design for the optimization of propionic acid recovery. The statistical analysis was achieved using Design-Expert version 10.0 (Statease Inc., Minneapolis, USA) and with five important process parameters at three levels each selected as independent variables. The effect of initial propionic acid concentration in aqueous phase (X_1), concentration of sodium carbonate in the stripping phase (X_2), fraction of carrier (TOA) in heptane (X_3),

treat ratio (X_4), and batch extraction time (X_5) on the extraction yield were studied. The un-coded and coded values of the different factors employed in the experiment are reported in Table 1. Consequently, a sum of 46 experiments were investigated at three levels including six replicates at the central points. The experimental plan in coded form of the process parameters (factors) and their corresponding extraction yield (response) were tabulated, as shown in Table 2.

Table 1. Range of different factors for Propionic acid recovery using emulsion liquid membrane

	Factors	Units	Low	High
Coded values			-1.000	1.000
Un-coded values	X_1	kmol/m^3	0.05	0.1
	X_2	kmol/m^3	0.1	0.2
	X_3	%v/v	3	8
	X_4	v/v	1	3
	X_5	min	5	25

3.6 Artificial neural network design of the extraction process

Neural Power, version 2.5 (CPC-X software, Carnegie, PA, USA), was employed in the analysis of the experimental data set in this study. The computation and robustness of the network parameters were ensured with the training and testing of data respectively (Moghaddam et al., 2010). The networks inputs were trained with incremental back-propagation which is the commonly used algorithm (Betiku and Taiwo, 2015). The total hidden layers and network neurons were determined by training various feed-forward networks of different architectures and optimizing selection by minimizing the mean-squared-error (Sanders et al.) performance function and improvement of simplification competence. Therefore, the optimal topology (architecture) of ANN model selected for this study involves a multilayer full feed-forward neural network with incremental back-propagation (IBP) and hyperbolic tangent (Tanh) as the transfer function consisting of five (5) inputs, one hidden layer with 4 neurons and one (1) output layer including single neuron (5:4:1). The optimal architecture of ANN model in this case is shown in Figure 3.

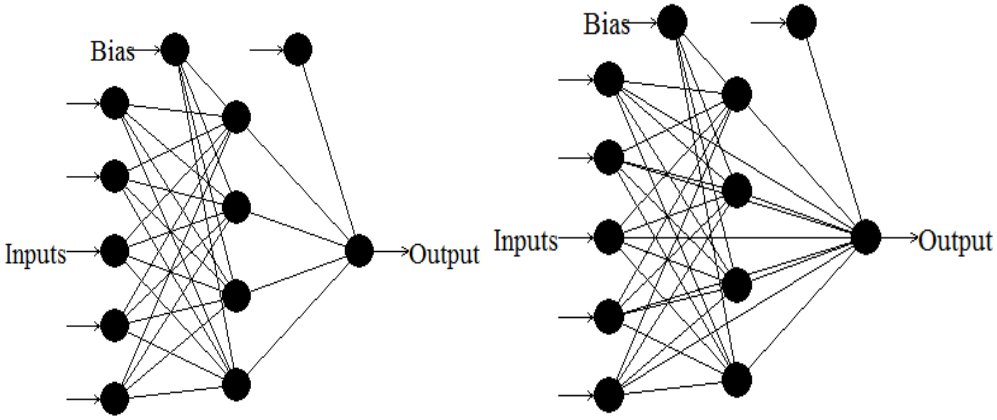

Figure 3. Architecture of ANN-model used for prediction of Propionic acid ELM extraction efficiency
(a) Multilayer normal feed forward and (b) Multilayer full feed forward

The data sets used for the ANN model were trained using average Determination Coefficients (Bozell et al.), average Correlation Coefficient (R) and Root Mean Square Error (Sanders et al.) as the stopping criteria at 1,1 and 0.0001 respectively.

3.7 Analytical method

The aqueous phase propionic acid concentration was analyzed by a colorimetric method (Taylor, 1996) using a Uv/Vis spectrometer (model WPA Light wave II LABOTEC). The method is established on color intensity measurement with absorbance reading at a 248 nm wave length. The concentration of propionic acid in the organic phase was calculated by mass balance. The extraction (yield) efficiency was obtained from Equation 4 as shown.

$$\text{Extraction efficiency (\%E)} = \frac{X_{1(initial)} - X_{1(final)}}{X_{1(initial)}} \text{ x } 100 \qquad (4)$$

Where $X_{1(initial)}$ is the aqueous phase initial propionic acid concentration before extraction with ELM and $X_{1(final)}$ is the propionic acid concentration after extraction at different time intervals as given in the experimental design.

4 Results and Discussion

An overall of 46 experimental runs were conducted and a quadratic regression model was obtained. Probable predictions from Response Surface Methodology (RSM) and Artificial Neural Network (ANN) were obtained on the response function (extraction efficiency) as shown in Table 2. By comparison of the RSM and ANN predictions, similarities and deviations of the predicted results can be observed. The similarities may be as a result of both methods estimating the true responses of the actual process while the

deviations occur because of the distinctive interpolation capabilities for solving the RSM and ANN regression problems.

4.1 Performance of ANN and RSM model

The data from the experimental design (Table 2) obtained from Box Behnken design were used for construction of the neural network model. A total sum of 46 experiments has been employed in the construction of the ANN model. About 80% of the overall experimental data set was utilized for training while 20% was used for testing of the ANN model.

The network inputs and targets were normalized before training in this study to prevent bias in the prediction that could appear as a result of very small or large weights (Sarkar et al., 2009). A multilayer full feedforward with incremental back propagation and a hyperbolic tangent (Tanh) as the transfer function is the preferred ANN model used consisting of 5-4-1 topologies. The root mean square error (Sanders et al.), the coefficient of determination (R^2) and the average deviation coefficient (ADC) were 0.1654, 0.9998 and 0.9996 respectively were obtained from the data set. It is evident from the result comparison between the actual and predicted responses, that ANN supported the selected (known) data for training while generalizing the testing (unknown) data sets. Thus indicating that ANN model can be employed to adequately give a good description of the input variables for propionic acid extraction.

The regression analysis was developed through the application of various regression models on the experimental data and the quadratic model (coded terms) and their interactions explained the role of each variable on the response (extraction efficiency). Table 3 shows the parameters which comprise: coefficient of regression (Coef), f-value (f) and p-value (p) for the regression model. The coefficients representing the linear, quadratic and cross products of the terms (X_1, X_2, X_3, X_4 and X_5). Where X_1 is the propionic acid concentration, X_2 represents the sodium carbonate concentration, X_3, fraction of TOA, X_4 is the treat ratio and X_5 is the extraction time.

Table 2. Experimental design of variables (uncoded) and responses of predicted values of response surface method (RSM) and artificial neural network (ANN) for propionic acid recovery using emulsion liquid membrane (ELM)

	Variables					Response		
Run order	**Propionic Acid Concentration X_1, kmol/m^3**	**Sodium Carbonate Concentration X_2, kmol/m^3**	**Fraction of TOA X_3, %v/v**	**Treat ratio X_4, v/v**	**Batch Extraction Time X_5, mins**	**Experimental Extraction Efficiency (%E)**	**RSM Predicted Values (%E)**	**ANN Predicted Values (%E)**
1	0.075	0.15	5	2	15	86.22	86.15	74.78 *
2	0.1	0.15	8	2	15	77.33	77.33	77.33
3	0.075	0.1	8	2	15	77.78	77.78	77.78
4	0.05	0.15	8	2	15	88.00	88.00	88.00
5	0.1	0.1	5	2	15	91.00	91.00	91.00
6	0.05	0.1	5	2	15	78.00	78.00	74.78*
7	0.05	0.15	2	2	15	95.33	95.33	95.33
8	0.075	0.1	5	3	15	81.78	81.78	81.78
9	0.075	0.15	8	2	5	91.56	91.56	91.56
10	0.075	0.15	5	2	15	85.33	86.15	86.13
11	0.1	0.15	2	2	15	87.67	87.67	74.78*
12	0.05	0.15	5	1	15	84.67	84.67	84.67
13	0.075	0.15	2	2	5	84.00	84.00	84.00
14	0.075	0.15	2	3	15	76.00	76.00	76.00
15	0.075	0.15	2	1	15	82.22	82.22	82.22
16	0.05	0.15	5	2	25	52.67	52.67	74.78*
17	0.1	0.15	5	2	25	89.67	89.67	89.67
18	0.075	0.1	5	2	25	72.00	72.00	72.00
19	0.075	0.15	2	2	25	94.22	94.22	94.23
20	0.075	0.1	5	2	5	87.11	87.11	87.11
21	0.1	0.15	5	1	15	85.00	85.00	74.78*
22	0.075	0.15	5	2	15	86.22	86.15	86.13
23	0.075	0.15	5	1	25	72.44	72.44	72.45
24	0.075	0.15	5	3	5	96.89	96.89	96.80

25	0.075	0.2	8	2	15	80.89	80.89	80.89
26	0.075	0.2	5	1	15	76.00	76.00	74.78*
27	0.075	0.15	8	3	15	68.89	68.89	68.89
28	0.075	0.15	8	1	15	96.44	96.44	96.42
29	0.075	0.1	2	2	15	76.89	76.89	76.89
30	0.075	0.1	5	1	15	91.56	91.56	91.58
31	0.05	0.2	5	2	15	85.33	85.33	74.78*
32	0.075	0.15	5	3	25	79.11	79.11	79.11
33	0.075	0.2	5	2	5	87.11	87.11	87.11
34	0.05	0.15	5	3	15	69.33	69.33	69.33
35	0.075	0.15	5	2	15	86.22	86.15	86.13
36	0.05	0.15	5	2	5	64.67	64.67	74.78*
37	0.1	0.2	5	2	15	85.33	85.33	85.33
38	0.075	0.15	5	2	15	86.22	86.15	86.13
39	0.1	0.15	5	3	15	72.67	72.67	72.67
40	0.075	0.15	5	1	5	88.44	88.44	88.44
41	0.075	0.15	8	2	25	76.89	76.89	74.78*
42	0.075	0.2	5	2	25	83.11	83.11	83.11
43	0.075	0.2	2	2	15	68.44	68.44	68.44
44	0.075	0.2	5	3	15	91.56	91.56	91.56
45	0.075	0.15	5	2	15	86.67	86.15	86.13
46	0.1	0.15	5	2	5	78.33	78.33	74.78*

* Testing data set

The adequacy of the regression mathematical model for the propionic acid recovery was examined for statistical significance using the analysis of variance (ANOVA) (data detailed in Table 4). From the results obtained, it can be noted that the model is adequate with the R^2 value and standard deviations of 0.9997 and 0.44 respectively. Also, the primary purpose of ANOVA is for comparison of the residual and data variation about the average mean. From the variation comparison, the significance of the regression used to predict the response can be evaluated taking into consideration the sources of experimental variance (Bezerra et al., 2008). The significance of the regression model can thus be assessed using Fischer distribution (F-test) and probability (P-value).

Table 3. Regression model for propionic acid recovery using emulsion liquid membrane (ELM)

Term	**Coeff.**	**f**	**P**
Const.	86.15	475.61	< 0.0001
X_1	12.67	*3358.28*	*< 0.0001*
X_2	2.78	*161.51*	*< 0.0001*
X_3	-2.44	*125.05*	*< 0.0001*
X_4	3.78	*298.76*	*< 0.0001*
X_5	-8.44	*1492.63*	*< 0.0001*
X_1x X_2	-3.25	*221.09*	*< 0.0001*
X_1x X_3	-0.75	*11.78*	*0.0186*
X_1x X_4	0.75	*11.78*	*0.0186*
X_1x X_5	5.83	*712.30*	*< 0.0001*
X_2x X_3	2.89	*174.70*	*< 0.0001*
X_2x X_4	6.33	*839.64*	*< 0.0001*
X_2x X_5	2.78	*161.51*	*< 0.0001*
X_3x X_4	-5.33	*595.37*	*< 0.0001*
X_3x X_5	-6.22	*810.40*	*< 0.0001*
X_4x X_5	-0.44	*4.14*	*0.0977*
X_1^2	-16.74	*3060.51*	*< 0.0001*
X_2^2	-5.74	*359.91*	*< 0.0001*
X_3^2	-1.41	*45.22*	*0.0011*
X_4^2	-3.85	*338.82*	*< 0.0001*
X_5^2	1.93	*84.70*	*0.0003*
X_1^2xX_2	-2.36	*58.35*	*0.0006*
X_1^2xX_3	-1.97	*40.72*	*0.0014*
X_1^2xX_4	-10.69	*1197.06*	*< 0.0001*
X_1^2xX_5	8.28	*717.17*	*< 0.0001*
X_1xX_2^2	-9.42	*928.01*	*< 0.0001*
X_1xX_3^2	-17.25	*3114.15*	*< 0.0001*
X_1xX_4^2	-11.75	*1444.88*	*< 0.0001*
X_2^2xX_3	5.78	*349.37*	*< 0.0001*
X_2^2xX_4	-2.33	*56.99*	*0.0006*
X_2^2xX_5	3.67	*140.71*	*< 0.0001*
X_2xX_3^2	-4.11	*176.90*	*< 0.0001*
X_2xX_4^2	-4.22	*186.58*	*< 0.0001*
X_3^2xX_4	-12.22	*1563.42*	*< 0.0001*
X_3^2xX_5	7.33	*562.82*	*< 0.0001*
X_3xX_4^2	4.22	*186.56*	*< 0.0001*
X_1^2xX_2^2	21.25	*1575.29*	*< 0.0001*

$X_1^2 x X_3^2$	19.08	*1905.62*	*< 0.0001*
$X_1^2 x X_4^2$	12.36	*799.59*	*< 0.0001*
$X_2^2 x X_3^2$	-3.00	*47.10*	*0.0010*
$X_2^2 x X_4^2$	8.67	*393.10*	*< 0.0001*

Table 4. Analysis of Variation for propionic acid recovery using emulsion liquid membrane (ELM)

Source	DF	C.V.%	p-value	R^2	SD
Model	40	0.53	<0.0001	0.997	0.44

Figure 4 shows the parity plot of the response between the experimental data and the predicted response plots of Response Surface Methodology (RSM) and Artificial Neural Network (ANN). The closeness of the predicted points to the actual points demonstrates the dependability and consistency of both models.

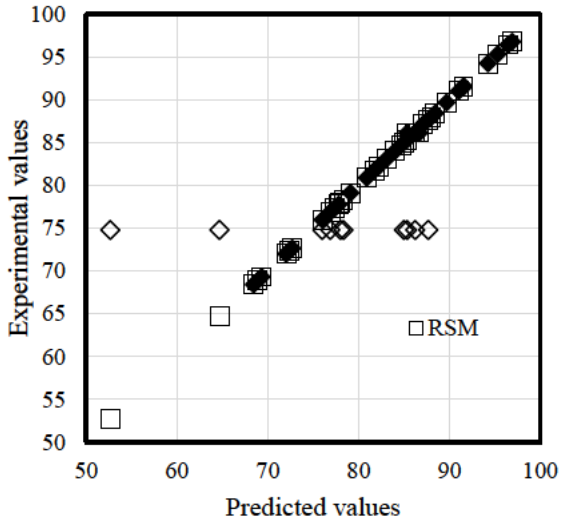

Figure 4. Parity plot of extraction efficiency using RSM and ANN

4.2 Effect of process variables on extraction efficiency

The combined effect of the concentration of propionic acid and Na_2Co_3 on extraction efficiency as illustrated in Figure 5a was found to increase with an increase in sodium carbonate concentration irrespective of propionic acid concentration. This might be as a result of larger Na_2Co_3 reaction potential at high concentrations with propionic acid causing a complex hydrogen ion disparity between the external feed phase and the internal stripping phase. This disparity in hydrogen ion will be higher with minimum propionic acid concentration and maximum concentration of sodium carbonate (Lee, 2011). From Figure 5a, it can be noticed that as sodium carbonate concentration exceeds 0.15, the extraction efficiency begins to decrease. This may be because above this value, the difference in concentration between the external and internal phase reduces the emulsion stability leading to emulsion coalescence, thus a reduction in the overall surface area available for mass transfer. The process turns out to be a mass transfer controlled process (Yu et al., 2008). According to Fick's law, increase in lactic acid

concentration increases the driving force in both the organic and aqueous phase which in turn increases the overall propionic acid stability rate through the emulsion liquid membrane (García et al., 2013). Extraction efficiency decreased with further increase in propionic acid concentration regardless of increase in sodium carbonate concentration as depicted by the 3D and contour plots. This might be because as the propionic acid concentration increases, the internal droplets comprising of the stripping agent in the superficial region became more saturated causing diffusional path increase in length through the emulsion globule and an additional stripping reagent is needed to enhance the emulsion capacity for extraction (Reis et al., 2011).

The influence of propionic acid concentration and fraction of trioctylamine on the percentage of extraction is depicted in Figure 5b. The percentage of extraction was found to increase with increase in trioctylamine concentration to a high-level regardless of the concentration of propionic acid. The formation of propionic acid – trioctylamine complex occurs at increased carrier concentration, thus increasing the extraction efficiency (Inyang and Lokhat, 2020b). At a lower level of trioctylamine concentration, the propionic acid extraction as a result of passive transport together with the facilitated transport is related as it dissolved in the organic phase due to the concentration gradient between the organic and external phase as earlier encapsulated and schematically depicted in the propionic acid ELM mechanism in Figure 2. This passive transport allows the propionic acid diffusion to the stripping phase which will be stripped by a reagent in the emulsion (Ng et al., 2010). The extraction efficiency decreases at increasing trioctylamine value, which may be because high concentration of carrier precedes higher amount of amine-propionic acid complex. This occurs at the interface of the aqueous-organic membrane and also leads to the increase in the viscosity of the organic phase which then causes a decrease in diffusivities of the carrier and the complex formed. This leads to an increase in emulsion drop size thus decreasing the extraction efficiency as also reported by Lee and Kim (2011) and Garcia et al. (2013).

The extraction efficiency of propionic acid was observed to increase with the increase in sodium carbonate concentration irrespective of the trioctylamine fraction as shown in Figure 6a. However, at higher concentration of sodium carbonate, there was a decline in the extraction yield. At increasing concentration of Na_2CO_3, propionic acid extraction efficiency increased up to a particular level, then a decline in the yield was noticed with an increase in trioctylamine concentration. This might be as a result of the carrier concentration increase leading to the availability of a larger capacity of the carrier to react with propionic acid in forming a complex. Nevertheless., further increasing the carrier concentration leads to a reduction in the viscosity of the emulsion to withstand shear stress due to the agitation thereby causing emulsion breakage. Furthermore, the extraction yield of propionic acid increased as a result of higher capacity in the reaction between Na_2CO_3 and propionic acid-trioctylamine complex at the internal stripping phase. But, further Na_2CO_3 increase leads to a decrease in propionic acid recovery as a result of the osmotic emulsion swelling due to higher ionic strength in the internal

stripping phase. Similar results were obtained by a recent research study conducted by Jusoh et al. (2019) and Goyal et al. (2011b).

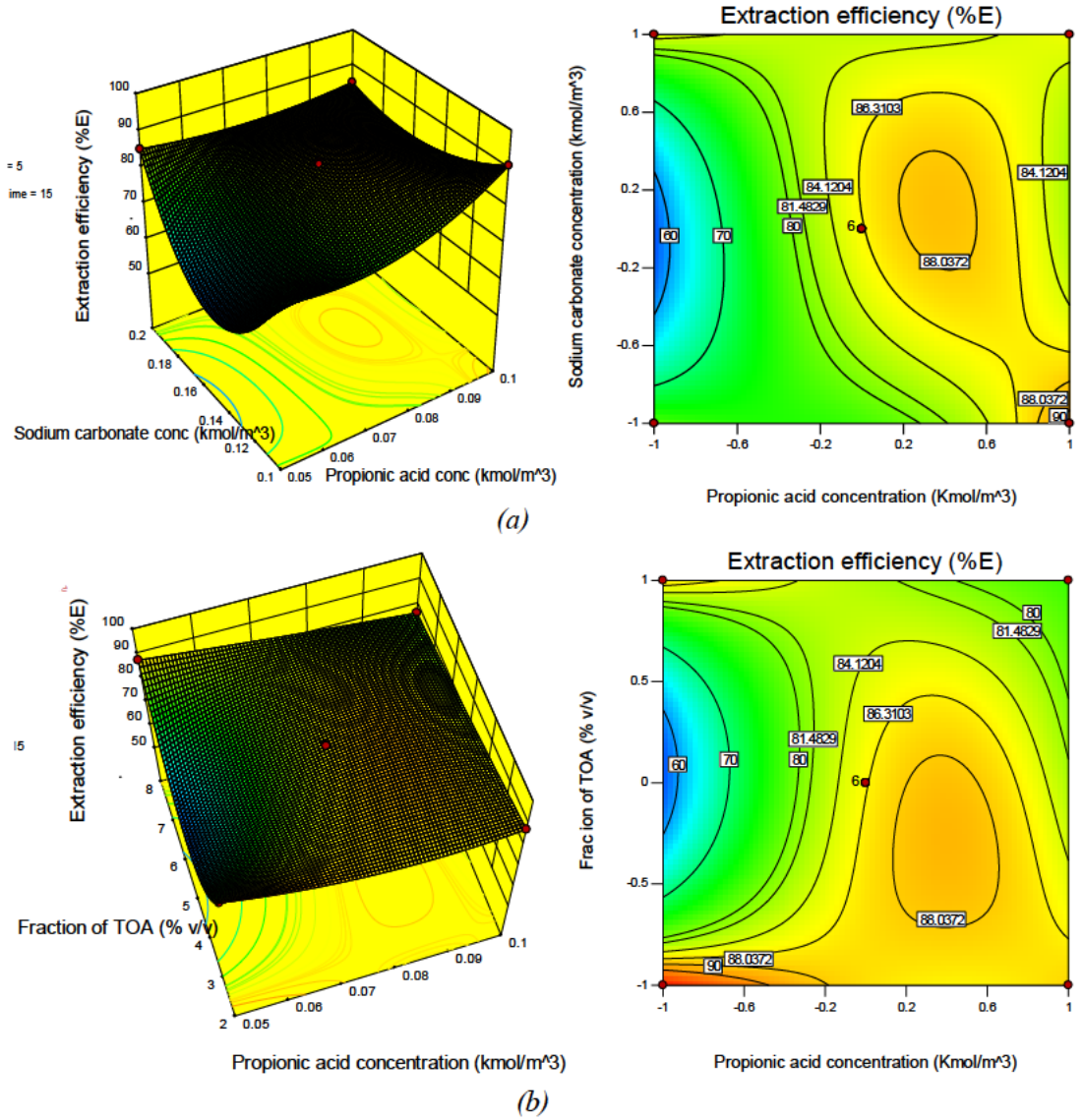

Figure 5. 3D Surface and contour plots of propionic acid recovery using emulsion liquid membrane (ELM) showing the effects of variables on extraction efficiency: (a) Na_2CO_3 and propionic acid concentration and (b) TOA extractant and propionic acid concentration

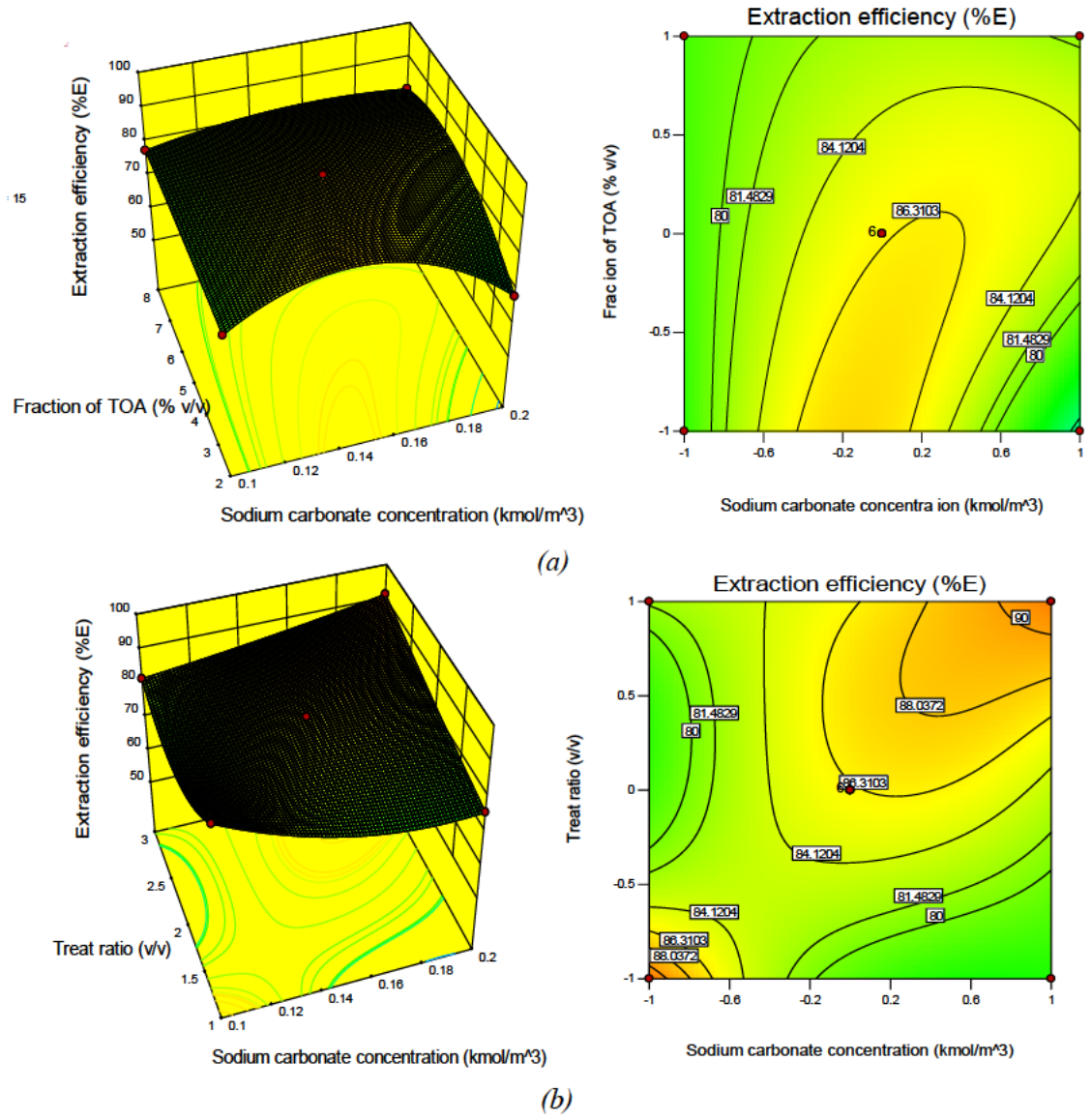

Figure 6. 3D Surface and contour plots of propionic acid recovery using emulsion liquid membrane (ELM) showing the effects of variables on extraction efficiency: (a) TOA extractant and Na_2CO_3 concentration and (b) treat ratio and Na_2CO_3 concentration

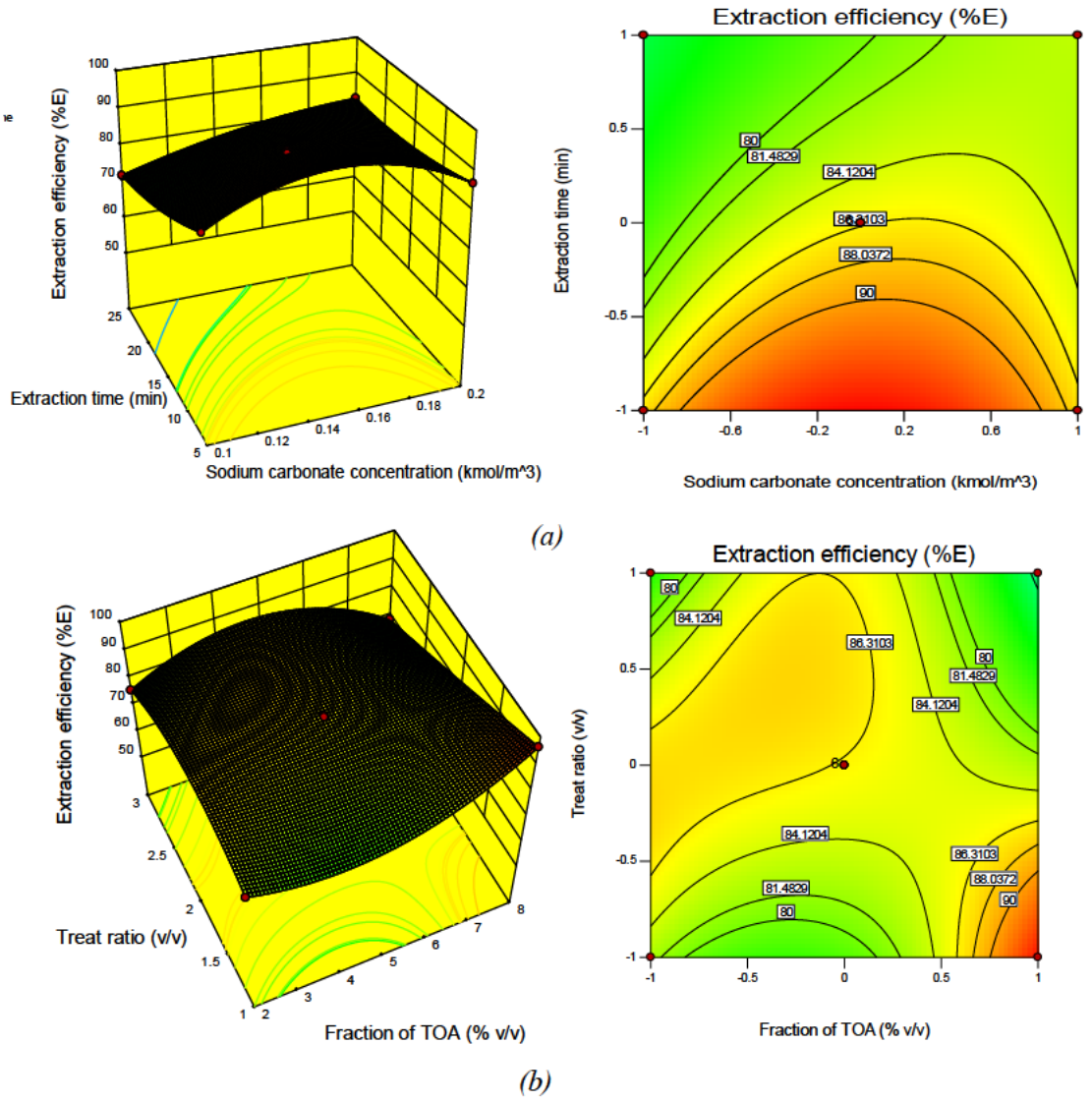

Figure 7. 3D Surface and contour plots of propionic acid recovery using emulsion liquid membrane (ELM) showing the effects of variables on extraction efficiency: (a) extraction time and Na_2CO_3 concentration and (b) treat ratio and TOA concentration;

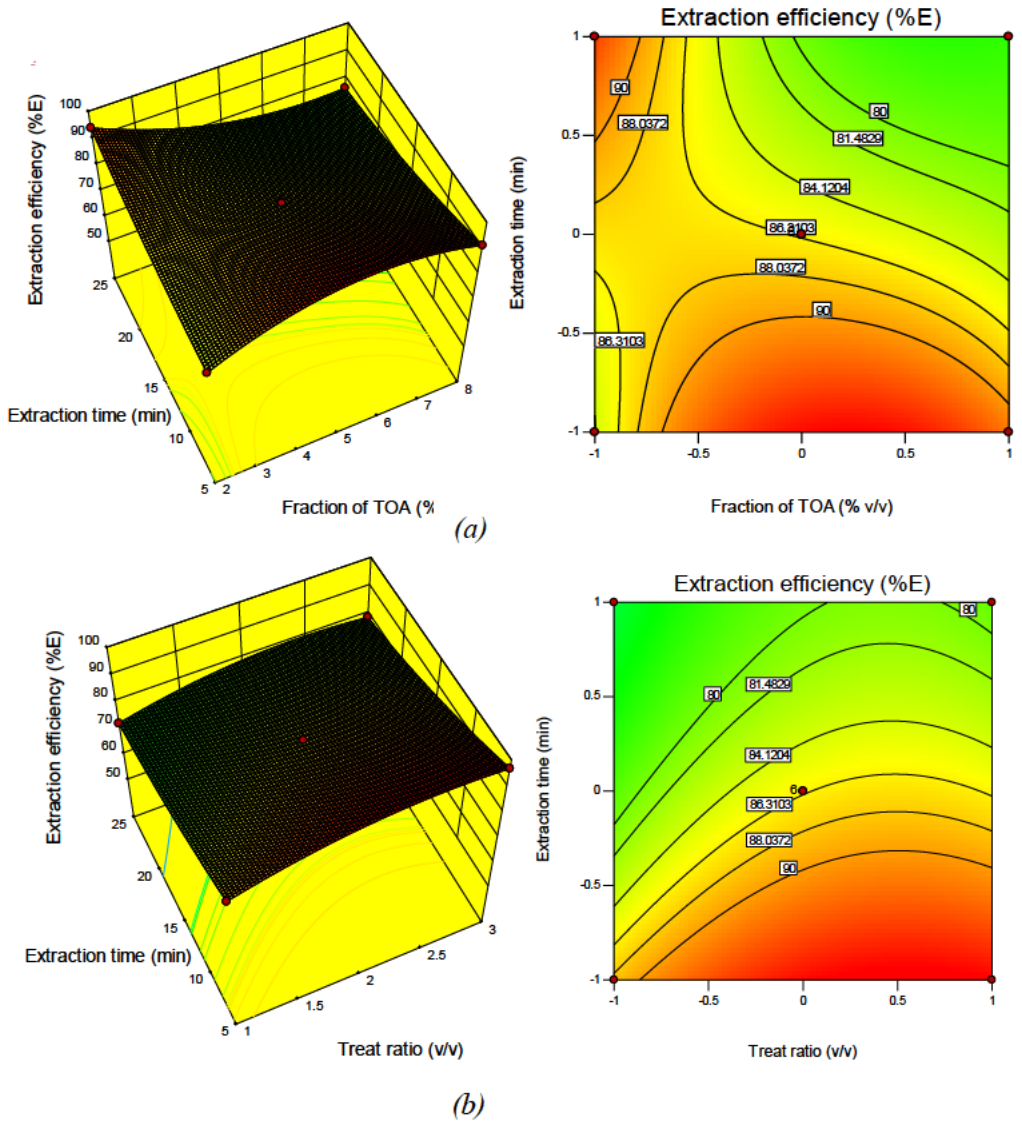

Figure 8. 3D Surface and contour plots of propionic acid recovery using emulsion liquid membrane (ELM) showing the effects of variables on extraction efficiency: (a) extraction time and TOA concentration and (b) extraction time and treat ratio.

Figure 6b displayed the interaction between the concentration of Na_2CO_3 and treat ratio on the extraction efficiency. For the concentration of Na_2CO_3 at all levels, the propionic acid extraction efficiency increases with the treat ratio. This is because increase in the treat ratio leads to a reduction in osmotic pressure between the external feed phase and the emulsion and a corresponding dispersion of the emulsion thus increasing the extraction efficiency. The extraction efficiency decreases on further increase in the treat ratio because of the small globules formed which causes breakage in the emulsion. Conversely, a lesser effect was observed for the concentration of Na_2CO_3 at different levels of the treat ratio. This is as a result of the system osmotic swelling being controlled by the treat ratio thus causing breakage. This breakage occurs at lower level of treat ratio causing Na_2CO_3 leakage to the external feed phase leading to low recovery.

The combined effect of the stripping reagent, Na_2CO_3 concentration and extraction time on the extraction efficiency is shown in Figure 7a. The extraction efficiency was found to increase with the extraction time and Na_2CO_3 concentration. Higher concentration of Na_2CO_3 causes a high hydrogen ion difference between the external feed phase and internal stripping phase compared to lower concentration of Na_2CO_3. Extraction efficiency was levelled off at increased extraction time which might be as a result of sufficient time to exhaust all the stripping (Na_2CO_3) reagent present in the internal phase. Therefore, at lower concentration of Na_2CO_3, the rate of stripping of propionic acid in the process was the limiting step.

The interaction between treat ratio and trioctylamine concentration on the percentage of extraction is presented in Figure 7b. The percentage of extraction increased with analogous increase in treat ratio and concentration of trioctylamine up to a certain level where it was found to decrease. Initially, with the increase in treat ratio, the membrane volume decreased and reduced the possibility of membrane swelling. The increase in propionic acid concentration per globule enhances the extraction rate at the aqueous and organic phase interface, therefore, increase in treat ratio increases the percentage of extraction (Goyal et al., 2011a). Nonetheless, increase in treat ratio negatively affects the extraction yield as a result of a decrease in emulsion globules and mass transfer area. Additionally, increasing the treat ratio increases the globule size to some extent which in reverse leads to a reduction in the surface area (Kumbasar, 2010a). Also, increasing the carrier concentration, promotes the solute transport between the emulsion and dilute aqueous phase while the rate of stripping almost remains constant. Thus, propionic acid-trioctylamine complex is not stripped in the liquid membrane phase which decreases the extraction efficiency at higher concentration of trioctylamine (Kumbasar, 2010b).

The percentage of extraction was noticed to increase with an equivalent increase in fraction of trioctylamine and extraction time (Figure 8a). Further increasing the concentration of TOA and extraction time, a slight decrease in extraction time was observed. This might be as a result of the stripping reagent being exhausted in the internal phase to further react with the propionic acid-trioctylamine complex that is being transported. This reduces the fraction of troctylamine at the interface, thus decreasing the extraction efficiency.

Figure 8b illustrates the interactive effect of batch extraction time and treat ratio and treat ratio on the percentage of extraction. At lower treat ratio, the dispersed emulsion in the feed phase tends to form larger droplets thereby decreasing the surface area between both phases, thus decreasing the extraction efficiency. Lower treat ratio also increases the treatment cost as more emulsion liquid membrane will be required. Increasing the extraction time, increases the overall mass transfer between the external feed and emulsion phases. There is a levelling off of the extraction efficiency at higher extraction time which may be as result of exhausting the emulsion in the process.

4.3 Importance of process variables

The relative importance of the different variables (propionic acid concentration, sodium carbonate concentration, TOA fraction, treat ratio and extraction time) on propionic acid recovery obtained from the hybridized genetic algorithm of ANN model is presented in Figure 9. The highest significant contribution was recorded by TOA fraction of 30% which indicates that the type of extractant is the major influencing factor and plays a primary role in carboxylic acid recovery while the least was the treat ratio with significance contribution of 12.5%.

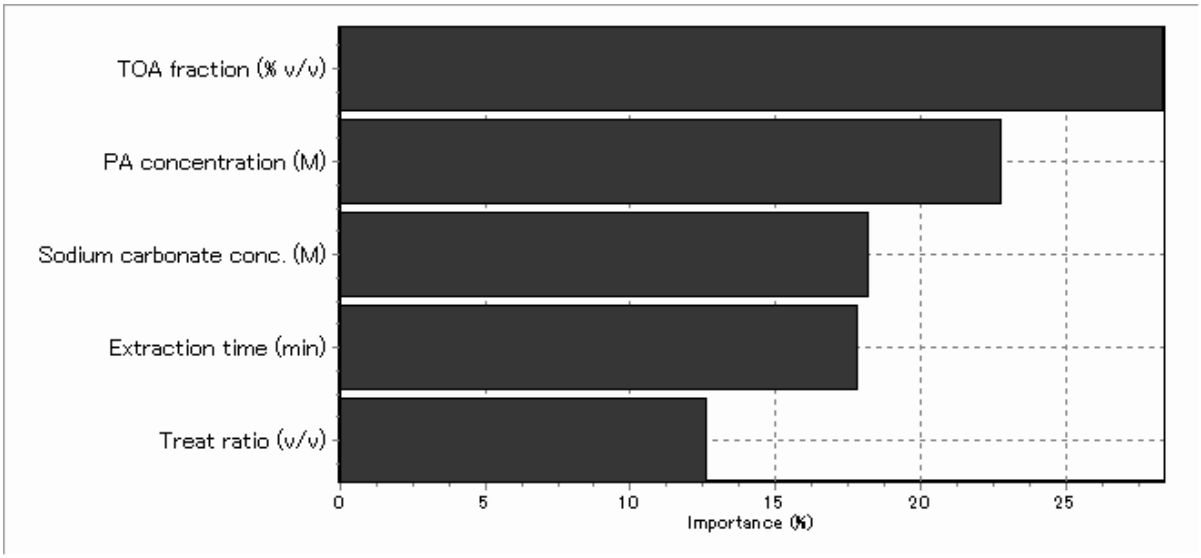

Figure 9. Analysis of relative importance of effective parameters by generic algorithm in the recovery of propionic acid using ELM

4.4 Optimization by RSM model

In this study, numerical optimization was carried out using the RSM optimization to obtain the optimum value of the studied variables in order to maximize the response function (extraction efficiency). The optimal solution of the ELM process determined by RSM are as presented in Table 5. In such conditions, the extraction efficiency obtained experimentally was 92.28%.

Table 5. Optimal conditions of propionic acid extraction using ELM by means of RSM

Variables (Inputs)					**Response**	
Propionic Acid Concentration X_1, kmol/m^3	**Na_2CO_3 Concentration** X_2, kmol/m^3	**Fraction of TOA** X_3, %v/v	**Treat ratio** X_4, v/v	**Extraction Time** X_5, mins	**RSM Predicted Values (%E)**	**Experimental Extraction Efficiency (%E)**
0.082	0.13	7.45	1.17	12	93.68	92.28

Conclusion

The extraction of propionic acid employing the technology of emulsion liquid membrane (ELM) has been explored and carried out successfully. RSM and ANN numerical approaches with comparisons were usefully applied in the modelling and optimization of the ELM process alongside experimentations and validations. The design of experiments was conducted; regression analysis and quadratic models were developed for the propionic acid extraction efficiency using these models which were found to be satisfactorily effective and accurate in predicting responses and values. Artificial neural network (ANN), an artificial intelligence-based technique was trained so as to develop an alternative model to RSM from ANN's mimics. Analysis of variation (ANOVA) and regression revealed a higher coefficient of determination, R^2 value of 0.9998 for ANN model. Investigation of the effects of operating parameters on the extraction of propionic acid by ELM has also been explored. The major factor influencing the extraction efficiency was found to be the extractant composition. Optimal operating conditions were thereafter obtained using Box-Behnken design of RSM. Results confirmation tests were completed to validate the predicted optimal operating conditions which include: propionic acid concentration = 0.082 kmol/m^3, Na_2CO_3 concentration = 0.13 kmol/m^3, fraction of TOA = 7.45 %v/v, extraction time = 12 mins, treat ratio = 1.17 %v/v with the experimental response. The percentage of propionic acid extraction was experimentally obtained as 92.28% under these conditions which was in close proximity with the numerical predicted value of 93.68%.

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Chapter EIGHT

Paper 7, MaAcid Recov by ELM using RSM

Parametric study of emulsion liquid membrane (ELM) of malic acid

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PAPER SEVEN

Parametric study of the extraction of malic acid using emulsion liquid membrane (ELM)

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Abstract

Extraction and recovery of malic acid by emulsion liquid membrane (ELM) using trioctylamine as a carrier in 1-decanol, sorbitan monooleate (Span 80) as a surfactant in heptane, and sodium carbonate as a stripping agent, was conducted. The interactive effects of four different process variables, which include malic acid concentration, sodium carbonate concentration, trioctylamine concentration and treat ratio, on the malic acid extraction efficiency were investigated using response surface methodology (RSM). At the optimal conditions of malic acid concentration = 0.097 kmol/m^3, Na_2CO_3 concentration = 0.16 kmol/m^3, fraction of TOA = 7.49 %v/v and treat ratio = 1.5 %v/v, the experimental recovery of malic acid was up to 85.91% as against the predicted response of 86.97%. Hence, the ELM process showed capability in the extraction of low concentrations of carboxylic acids and can be easily scaled up and combined with other processes in separation and other relevant industries.

Keywords: Malic acid, emulsion liquid membrane, extraction, optimization, response surface methodology, process recovery.

1.0 Introduction

The emergence of several novel separation processes is essential in biotechnology as part of the evolution of the downstream processing of products. Liquid membrane extraction is an example of such a novel process which can be applied in organic acid recovery from dilute aqueous streams, which have proven difficult over the years. An emulsion liquid membrane (ELM) has great potential for downstream processing of organic acids. The recovery of different organic acids from dilute aqueous industrial waste streams and fermentation broth has been the prevalent challenge in the biochemical industry due to high separation costs (John et al., 2008) and other attendant issues. The aqueous waste streams of several industries contain low molecular weight carboxylic acids (such as malic acid, butyric acid, propionic acid, acetic acid etc.). The recovery of these organic acids is beneficial and important due to several applications in a number of industries like food, pharmaceuticals, cosmetics, polymers, fine chemicals and others (Roque et al., 2015).

The traditional techniques for organic acid separation are not cost-effective and naturally unfavourable (Manzak and Tutkun, 2011). Therefore, industries are constantly finding better alternative separation techniques to recover low solute concentrations. To overcome the challenges associated with techniques existing previously, liquid membrane recovery processes offer a suitable option. They offer several

benefits such as: energy-saving, low consumption of chemicals, low maintenance cost, offers large surface area and provides high rate of mass transfer and easy scale-up as it is simple to combine with other separation processes (Mozia, 2010, Kumbasar, 2010b). Therefore, emulsion liquid membrane (ELM) has been considered a promising and favourable technique for the recovery of organic acids since it is significantly cheaper than the solvent extraction separation technique (40% less costly).

2.0 Emulsion liquid membrane processes

Emulsion liquid membrane processes have been applied in industrial separations such as phenol recovery from wastewater (Mortaheb et al., 2008, Balasubramanian and Venkatesan, 2014), palladium recovery from electroplating wastewater (Noah et al., 2016, Kakoi et al., 1996), silver extraction from wastewater (Sulaiman et al., 2014a, Othman et al., 2006a, Othman et al., 2006b), recovery of lignin from pulping wastewater (Zing-Yi et al., 2014) and cadmium removal (Zeng et al., 2016). The recent improvement in the emulsion liquid membrane process is in the downstream processing of bio-succinic acid in the quest to search for an alternative separation technique (Lee and Hyun, 2010, Lee, 2011). In this study, and complementary to our ongoing work on bio-succinic acid and propionic acid, the extraction of malic acid by ELMs was first attempted in the current study. To achieve high extraction efficiency, the effects of different operating extraction parameters were explored in a batch ELM system. The primary water-in-oil emulsion was carried out using trioctylamine as a carrier, 1-decanol as a diluent, sodium carbonate as aqueous stripping agent, and Span 80 as a surfactant. Several operating parameters were investigated including malic acid concentration, sodium carbonate concentration, treat ratio (organic to internal ratio) and TOA fraction in organic phase on the malic acid extraction efficiency. Also, response surface methodology (RSM) was applied to perform the interactive studies and optimization of the studied process variables on malic acid recovery.

3.0 Experimental Section

3.1 Chemicals

All chemicals, as shown in Table 1, were procured from Sigma-Aldrich, while deionized water used during the experiment was obtained using an Elga PURELAB Option Q purification system. All chemicals were used without further purification.

Table 1. Experimental chemical properties

Component	Formula	Purity (%)	Density (g/mL)
Malic acid	$C_4H_6O_5$	98	1.61
Trioctylamine	$[CH_3(CH_2)_7]_3N$	98	0.81
1-decanol	$C_{10}H_{22}O$	98	0.83
Sodium carbonate	Na_2CO_3	99	2.54

Span 80 (Sorbitan monooleate)	$C_{24}H_{44}O_6$		0.99
Heptane	$CH_3(CH_2)_5CH_3$	99	0.68

3.2 Experimental ELM preparation and recovery process

The aqueous solutions of malic acid were prepared by weighing out the required amount of pure acid to produce a solution of the desired concentration (0.05 - 0.1 kmol/m^3) using OHAUS PA 214 model scale and dissolving in deionized water. Similarly, the sodium carbonate Na_2CO_3 internal stripping aqueous phase solution with the required concentration (0.1 - 0.2 kmol/m^3) was prepared by dissolving the required amount into deionized water. These aqueous solutions were homogenously mixed with a magnetic stirrer.

The emulsion liquid membrane phase, water-oil (w/o) type, was prepared by adopting the method described by Ahmad et al. (2015). The organic membrane phase was prepared in a 250 mL glass beaker by mixing the different diluents in their proper proportions. This membrane phase contained; 2-8% v/v trioctylamine as a carrier in decanol, and span 80 (4% v/v, as surfactant or stabilizer in heptane). The organic membrane phase was homogenized under an agitation speed of 200 rpm for 3 minutes before the drop-wise addition of the internal stripping phase reagent (sodium carbonate Na_2CO_3, 0.1-0.2 kmol/m^3) in the ratio of 1:1 (v/v). This homogenized organic membrane phase was then agitated using a high-speed homogenizer (IKA RW 14 basic digital mixer) at 2000 rpm for 20 minutes at room temperature to form a w/o type of stable emulsion. À stability check was conducted through an experimental observation of the prepared emulsion. A stable liquid emulsion was obtained after the emulsion was kept for 30 minutes after different trials with 4% (v/v) span 80 in n-heptane (which was utilized for the extraction). All the emulsion was freshly prepared before proceeding with the extraction experiments.

Malic acid ELM extraction process was conducted in a batch mode utilizing a 200 mL volumetric flask. Exactly 25 mL of the prepared ELM was charged into the glass flask and to this, a predetermined external aqueous phase of malic acid was added as per the experimental design treat ratio. The mixtures were stirred in an orbital shaker for a fixed time of 15 minutes at 120 rpm at a temperature of 23 ±2 ^oC. The external aqueous phase was separated from the emulsion phase after the extraction process using a separating funnel and further subjected to filtration using filter paper for the separation of any small droplets size and particles. The clear aqueous phase was then analyzed for malic acid concentration.

3.3 Analytical method

The aqueous phase concentration of malic acid was analyzed by means of a colorimetric method (Taylor, 1996) using a UV/VIS spectrometer (model WPA Lightwave II LABOTEC). The method is established on color intensity measurement with absorbance reading at a 252 nm wavelength. The

concentration of malic acid in the extract phase was determined by mass balance. The extraction (yield) efficiency was obtained from Equation 1 as shown.

$$\text{Extraction efficiency (\%E)} = \frac{X_{1(initial)} - X_{1(final)}}{X_{1(initial)}} \text{ x } 100 \quad (1)$$

Where $X_{1(initial)}$ and $X_{1(final)}$ are the aqueous phase initial malic acid concentration before extraction with ELM, and is final malic acid concentration after extraction, respectively.

3.4 RSM Experimental design of the ELM extraction process

The Box-Behnken design (BBD) of response surface methodology (RSM) experimental design was employed to conduct the experiments on malic acid recovery. The statistical analysis was done using Design-Expert version 10.0 (Statease Inc., Minneapolis, USA) and with four independent process parameters at three levels each. The effect of the initial concentration of malic acid in the aqueous phase (X_1), the concentration of sodium carbonate in the stripping phase (X_2), the fraction of carrier (TOA) in heptane (X_3) and treat ratio (X_4) on the extraction yield was explored. The un-coded and coded values of the different factors employed in the experiment are reported in Table 2. A sum of 29 experiments was investigated at the three levels including five replicates at the central points as depicted in Table 3.

Table 2. Range of different factors for Propionic acid recovery using emulsion liquid membrane

	Factors	Units	Low	High
Coded values			-1.000	1.000
Un-coded values	X_1	kmol/m^3	0.05	0.1
	X_2	kmol/m^3	0.1	0.2
	X_3	%v/v	3	8
	X_4	v/v	1	3

3.5 ELM Extraction mechanism

The ELM Extraction mechanism consists of the transport of malic acid between respective phases, with trioctylamine as a carrier and sodium carbonate, Na_2CO_3, as an internal stripping phase. The solute transport process takes place between the external and internal phases through the decrease in the concentration of malic acid from a high to low region. The extraction and stripping occurs in one single step due to the fast ELM reaction as a result of the large interfacial area, therefore the equilibrium limitations are avoided. Malic acid transport via the liquid membrane can be described in two steps: the external and internal interface reactions. The complexation reaction between undissociated malic acid $[H_2A]$ and trioctylamine (bR) occurs at the external interface forming the acid-extractant complex ($[H_2A].R_b$) as shown in Equation 2.

$$[H_2A]_{aq} + [bR]_{org} \longrightarrow ([H_2A].R_b)_{org} \quad (2)$$

The formed complex disperses to the internal interface through the liquid membrane and malic acid is released by the stripping reaction as represented in Equation 3.

$$2([H_2A].R_b)_{org} + [Na_2CO_3]_{aq} \longrightarrow [(bR_2^+)_2CO_3^{2-}]_{org} + 2[NaH_2A]_{aq} \quad (3)$$

The TOA extractant diffuses back to the external phase and further dissociates into water and carbon-dioxide, therefore, regenerating free amines as illustrated in Equation 4.

$$[(bR_2^+)_2CO_3^{2-}]_{org} \longrightarrow 2[bR]_{org} + [CO_2]_{aq} + 2[H_2O]_{aq} \quad (4)$$

4 Results and Discussion

An overall of 29 experimental runs were conducted and a quadratic regression model was obtained. The experimental response function (extraction efficiency) obtained is shown in Table 2.

Table 3. Box-Behnken design of process variables (uncoded) and experimental response values of malic acid extraction using ELM

Process variables		**Response**			
Run order	**Malic Acid Concentration X_1, kmol/m^3 (M)**	**Sodium Carbonate Concentration X_2, kmol/m^3 (M)**	**Fraction of TOA X_3, %v/v**	**Treat ratio X_4, v/v**	**Experimental Extraction Efficiency (%E)**
1	0.075	0.15	5	2	68.22
2	0.1	0.15	5	3	92.50
3	0.075	0.2	5	3	55.56
4	0.075	0.15	8	3	59.78
5	0.075	0.15	8	1	74.22
6	0.05	0.1	5	2	62.00
7	0.05	0.2	5	2	82.33
8	0.05	0.15	2	2	53.33
9	0.1	0.2	5	2	96.67
10	0.1	0.15	5	1	80.67
11	0.075	0.15	5	2	64.89
12	0.075	0.1	5	3	61.33
13	0.075	0.1	5	1	62.00
14	0.1	0.15	8	2	94.50
15	0.075	0.15	2	3	59.33
16	0.05	0.15	5	1	67.33
17	0.1	0.15	2	2	86.00
18	0.05	0.15	5	3	56.00
19	0.075	0.1	8	2	64.00
20	0.1	0.1	5	2	94.00
21	0.075	0.15	5	2	66.67
22	0.075	0.15	2	1	57.56
23	0.075	0.2	8	2	65.56
24	0.075	0.2	2	2	59.11
25	0.075	0.15	5	2	65.78
26	0.05	0.15	8	2	71.67
27	0.075	0.15	5	2	65.56
28	0.075	0.1	2	2	54.89

29	0.075	0.2	5	1	65.11

4.1 Regression model analysis

The regression model equation developed in coded terms through the application of multiple regressions on the experimental data is represented in Equation 5. The quadratic model described the function of the individual variable and their interaction on the extraction yield.

Extraction efficiency, %E = $66.22+12.64X_1+2.18X_2+4.96X_3-1.87X_4-4.42X_1 x\ X_2-2.46X_1 x\ X_3+5.79X_1 x\ X_4-0.67X_2 x\ X_3-2.22X_2 x\ X_4-4.06X_3 x\ X_4+14.20X_1^2-0.10X_2^2-2.93X_3^2-4.00X_4^2$ (5)

Where X_1 is the propionic acid concentration, X_2 represents the sodium carbonate concentration, X_3, fraction of TOA and X_4 is the treat ratio. The f-value and p-value as itemized in Table 4 were used to determine the significance of each model coefficient. The significant terms have p > f values less than 0.05 and insignificant terms have values of p>0.1. The probability p (p > f) values were employed as a tool to assess the significance of the model coefficients. Smaller p values indicate a high significance of the correlation with the corresponding coefficients (Jiao et al., 2013).

The suitability of the regression model for the malic acid recovery was examined for statistical significance utilizing the analysis of variance (ANOVA) test (Table 4). From the results, it can be noted that the model is adequate with an R^2 value and standard deviations of 0.9376 and 4.57, respectively. Also, the primary purpose of ANOVA is for comparison of the residual and data variation about the average mean. From the variation comparison, the significance of the regression used to predict the response can be evaluated taking into consideration the sources of experimental variances (Bezerra et al., 2008). The adequate precision greater than 4 is desirable and measures the signal to noise ratio, a ratio of 13.097 indicates an adequate signal for this model.

Table 4. Regression model for malic acid recovery using emulsion liquid membrane (ELM)

Source	**Sum of squares**	**Degree of freedom**	**Mean square**	**f-Value**	**Prob > F**
Model	4394.98	14	313.93	15.03	< 0.0001
X_1-Malic acid Conc.	1916.90	1	1916.90	91.75	< 0.0001
X_2-Sodium carbonate conc.	56.82	1	56.82	2.72	0.1214
X_3-Fraction of TOA	295.02	1	295.02	14.12	0.0021
X_4-Treat ratio	41.77	1	41.77	2.00	0.1792
$X_1 x\ X_2$	78.03	1	78.03	3.73	0.0738
$X_1 x\ X_3$	24.17	1	24.17	1.16	0.3003
$X_1 x\ X_4$	134.17	1	134.17	6.42	0.0238
$X_2 x\ X_3$	1.78	1	1.78	0.085	0.7748
$X_2 x\ X_4$	19.75	1	19.75	0.95	0.3474
$X_3 x\ X_4$	65.79	1	65.79	3.15	0.0977
X_1^2	1308.62	1	1308.62	62.64	< 0.0001
X_2^2	0.067	1	0.067	3.221E-003	0.9555

X_3^2	55.62	1	55.62	2.66	0.1250
X_4^2	103.66	1	103.66	4.96	0.0428
Residual	292.50	14	20.89		
Lack of Fit	285.88	10	28.59	17.28	0.0072
Pure Error	6.62	4	1.65		
Cor Total	4687.47	28			

Table 5. Analysis of variation for malic acid recovery using emulsion liquid membrane (ELM)

Source	C.V.%	Mean	R^2	SD	Adeq precision
Model	6.61	69.19	0.9376	4.57	13.10

4.2 Residual Analysis

The diagnostic tool which is the residual analysis was used to check the suitability of the residual model (Liu et al., 2004). The residual plots of the normal probability and studentized residual plots are shown in Figures 1 and 2, while Figure 3 shows the parity plot for extraction efficiency, which authenticates the consistency of the empirical model. The plots were employed in the determination of the model residual analysis and confirmation of the assumption and normality of constant variance in ANOVA for response surface methodology. The different points lie alongside the diagonal, indicating normal dispersions of the error terms (residual plots).

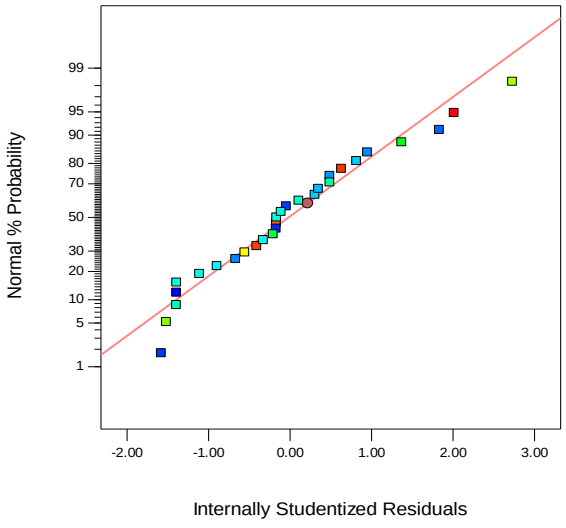

Figure 1. Normal probability plot of studentized residuals for malic acid extraction yield using ELM.

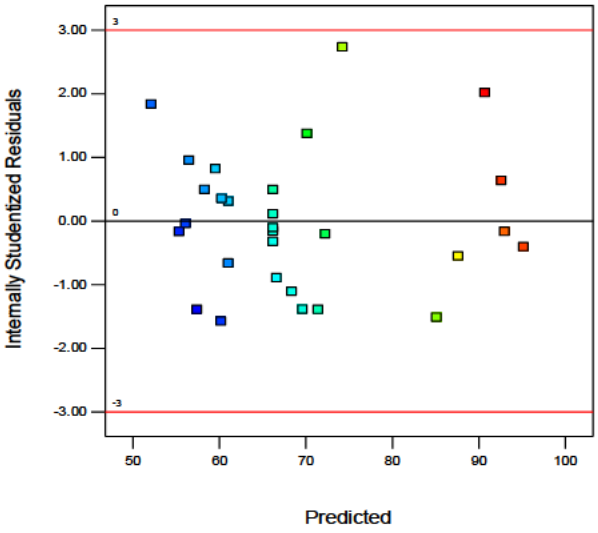

Figure 2. The predicted ELM extraction yield of malic acid and studentized residuals plot

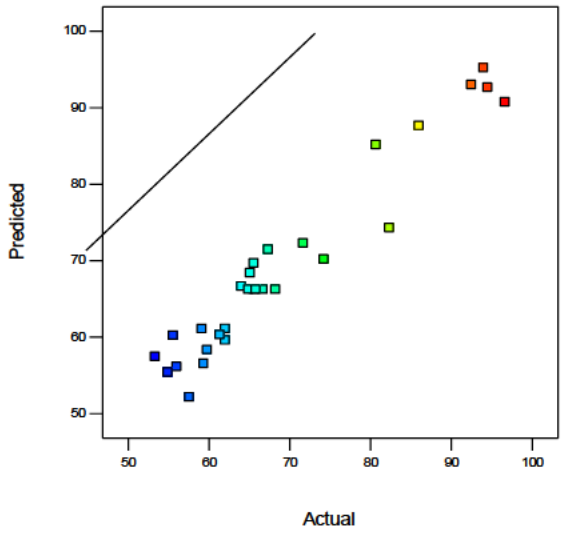

Figure 3. Predicted vs actual plot of malic acid ELM extraction efficiency

4.3 Effect of process variables on the extraction efficiency of malic acid

The interactive effect of the concentration of sodium carbonate and malic acid on the extraction yield illustrated in Figure 4 increased with an increase in sodium carbonate concentration irrespective of the concentration of malic acid. This might be because sodium carbonate has a greater potential to react at higher sodium carbonate concentration with malic acid. At low concentration, sodium carbonate is insufficient to completely strip malic acid from the liquid membrane phase, thus causing the saturation of malic acid complex in the membrane. At a higher concentration of sodium carbonate, there is an

increase in the solute internal stripping phase which may cause a delay in the accumulation of the complex in the membrane phase, thus leading to an increase in extraction performance.

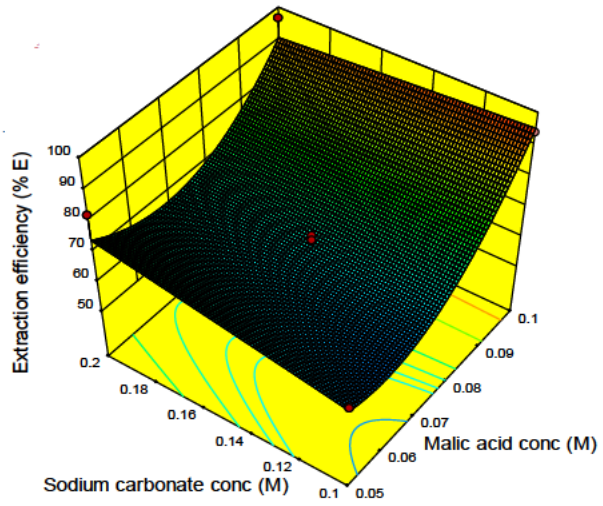

Figure 4. Effect of malic acid and sodium carbonate concentration on extraction efficiency

The effect of trioctylamine malic acid concentration is illustrated in Figure 5. The extraction performance was found to increase with an increase in trioctylamine and malic acid concentrations. The malic acid-trioctylamine complex formation occurs on increasing carrier concentration, therefore increasing the extraction efficiency. The extraction of malic acid increased from 70% to 90% when the concentration of trioctylamine was increased from 3 %v/v to 8 %v/v respectively. A higher concentration of trioctylamine can cause the malic acid movement towards the external interface. Thus, trioctylamine and malic acid reversibly react forming a complex at the external phase which then diffuses through the membrane phase. The concentration gradient of the complexes throughout the liquid membrane increases the flux of malic acid across the membrane.

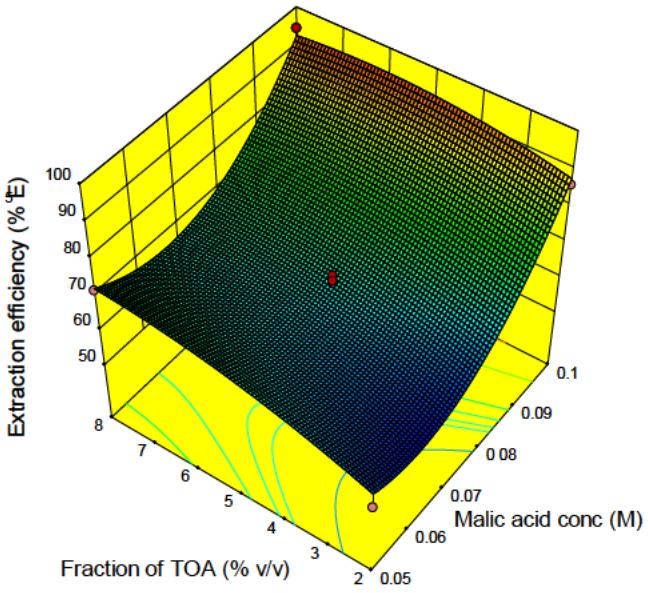

Figure 5. Effect of malic acid concentration and TOA fraction on extraction efficiency

Figure 6 illustrates the effect of the interaction between TOA fraction and concentration of sodium carbonate on malic acid extraction yield. The extraction performance of malic acid was noted to increase with the increase in the concentration of sodium carbonate irrespective of the trioctylamine concentration. The extraction performance of malic acid increased due to higher capacity in the reaction between sodium carbonate and malic acid-trioctylamine complex at the internal interface. Nevertheless, further increasing the sodium carbonate concentration reduces the malic acid recovery, because of the osmotic swelling which occurs in the emulsion as a result of the increased tendency of stripping in the internal phase. Thus, leading to transport of water from the external feed phase to the internal phase resulting in emulsion breakage.

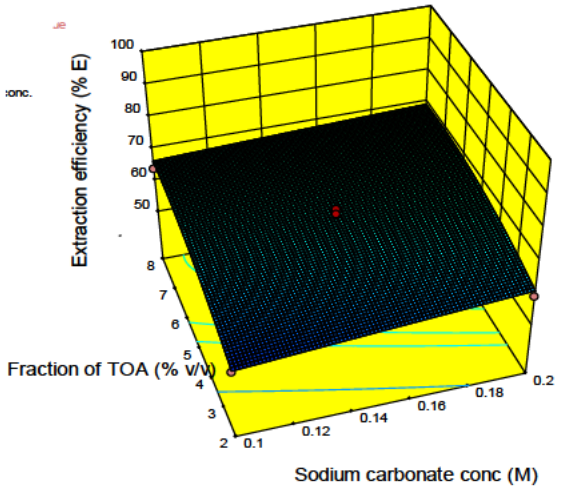

Figure 6. Effect of TOA fraction and sodium carbonate concentration on extraction efficiency

The effect of treat ratio and TOA fraction on the malic acid extraction efficiency is illustrated in Figure 7. The extraction yield was found to increase slightly with an increase in TOA fraction and treat ratio towards a higher level. At a higher level of TOA fraction and treat ratio, the extraction performance was found to decrease. The extraction rate at the interface is enhanced with an increase in malic acid concentration per globule, therefore the extraction efficiency increases with an increase in treat ratio (Goyal et al., 2011a). But further increasing the treat ratio, negatively affects the extraction efficiency due to the decrease in the number of emulsion globules per unit volume of the external phase and mass transfer area. Furthermore, an increase in the treat ratio slightly increases the globule size which inversely reduces the interfacial area (Kumbasar, 2010a). An increase in TOA fraction promotes solute transportation since there is a high carrier concentration at the interface, but the rate of stripping remains constant. Thus, the malic acid-trioctylamine complexes cannot be stripped in the membrane phase thereby leading to a decrease in the extraction performance of the process at a higher level of TOA fraction.

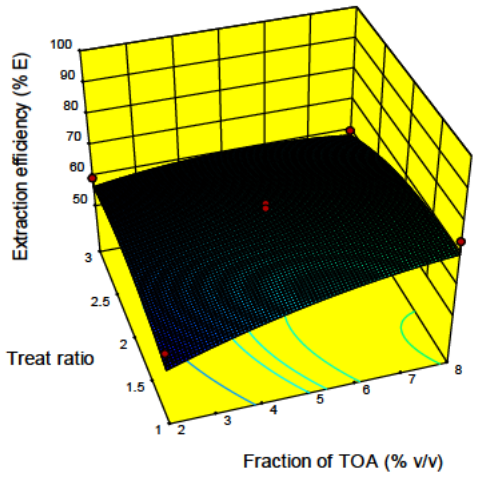

Figure 7. Effect of treat ratio and TOA fraction on extraction efficiency

4.4 Optimization of malic acid ELM extraction

The optimum value of the variables was obtained by fitting models of input combinations into Equation 5 to maximize the extraction efficiency using RSM numerical optimization technique. The optimal conditions for the malic acid ELM process were obtained as follows: malic acid concentration = 0.097 kmol/m^3, Na_2CO_3 concentration = 0.16 kmol/m^3, fraction of TOA = 7.49 %v/v and treat ratio = 1.5 %v/v. To validate the results and confirm the adequacy of the predicted model for maximum extraction efficiency, a set of experiments was carried out using the predicted values of the parameters. The percentage of malic acid extraction was experimentally obtained as 85.91% under these optimized values which was in close conformity with the numerical predicted response of 86.97% and therefore viable.

5 Conclusion

Recovery of malic acid by emulsion liquid membrane (ELM) has been carried out successfully and optimized using response surface methodology (RSM). A stable emulsion was obtained from the formulation in this study with the liquid membrane consisting of trioctylamine as a carrier, 1-decanol as a modifier, sorbitan monooleate (Span 80) as a surfactant in heptane, and sodium carbonate (Na_2CO_3) as a stripping agent. The results of this study yielded optimal conditions as follows: malic acid concentration = 0.097 kmol/m^3, Na_2CO_3 concentration = 0.16 kmol/m^3, fraction of TOA = 7.49 %v/v and treat ratio = 1.5 %v/v. Under these conditions an experimental investigation yielded an extraction efficiency of 85.91% compared to the predicted response of 86.97%. From the results obtained, the efficacy of the ELM process for malic acid recovery, in terms of the percentage yield, has been satisfactorily demonstrated.

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Chapter NINE

CONCLUDING REMARKS AND FUTURE RESEARCH SCOPE

CONCLUDING REMARKS AND FUTURE RESEARCH SCOPE

Conclusion

The present study addressed the downstream recovery of low molecular weight carboxylic acids from very dilute aqueous streams which poses a great challenge in the biochemical industry. Two intensified separation processes: reactive extraction and emulsion liquid membrane technique were considered. These were applied to recovery of biomass derived carboxylic acids with the aqueous phase feed concentration ranges of 0.1-1 kmol/m^3 for the different carboxylic acids which represents the actual aqueous waste streams and fermentation composition. These have been achieved in different ways as laid out in the journal papers presented in this thesis.

Three independent process variables; temperature, initial organic acid concentration in the aqueous phase and trioctylamine composition in the organic phase were taken into consideration as variables impacting the distribution coefficient and extraction yields for the reactive extraction technique. Chemical extraction studies were interpreted with the formation of 1:1 and 2:1 complexes. The Box-Behnken design of experiments was found to adequately represent the interactive effect and extraction of the studied carboxylic acid from dilute aqueous solution using trioctylamine in 1-decanol as extracting solvent. The design of experiments conducted; statistical regression analysis and quadratic models were developed for the organic acid extraction efficiency using these models which were found to be satisfactorily effective and accurate in predicting responses and values for the reactive extraction. The values of adequate precision, PRESS, standard deviation and variation coefficient obtained indicates high precision and the RSM model reliability. The process variables were also optimized using RSM to maximize the percentage of extraction yield. At optimum conditions, the predicted and experimental values of degree of extraction are found to be 91.94% and 89.79% for propionic acid, 97.53% and 93.25% for malic acid, 96.67% and 96.45% for butyric acid. A low concentration of acid had a significant effect on the distribution of the acid. However, at higher concentration values of the extractant (such as 0.4-0.1 M), a small synergistic effect was observed.

In the reactive extraction kinetics of propionic and malic acid with trioctylamine, carried out in stirred, jacketed vessel. the speed of agitation has no effect on the initial specific rate of extraction but the latter varies linearly with the acid and amine concentrations. The order of the reaction of the studied acids and TOA was found to be second order. The reaction regime was found to instantaneously occur in organic diffusion film. In this region, the diffusion contribution is minimized and the extraction rate becomes mainly controlled by chemical reactions. The values of the rate constant were found to be 0.430 m^3/mol s and 0.332 m^3/mol s for propionic acid and malic acid respectively and mass transfer

coefficient, k_m was also obtained for propionic acid (9 x 10^{-6} m/s) and malic acid (3x10^{-6} m/s) at 303.15 K. The kinetic and equilibrium optimization studies are useful in the design of a reactive extraction unit.

The Emulsion liquid membrane (ELM) based extraction technique was experimentally explored for the extraction and recovery of propionic and malic acid existent in very dilute aqueous solutions (0.05 - 0.1). RSM and ANN techniques are used to obtain predictive models for the estimation of the degrees of extraction of the propionic ELM process. The ANOVA results for RSM model (F-value = 475.61, P-value = <0.0001 and R^2 =0.997) and ANN model (RMSE = 0.1654, ADC = 0.9996 and R^2 = 0.9998) dictate better fit of model predicted and experimental values of degree of extraction. Investigation of the effects of operating parameters on the extraction of propionic as well as malic acid by ELM has also been explored which include: initial acid concentration, sodium carbonate concentration, trioctylamine concentration, treat ratio and extraction time on the propionic acid degree of extraction. Optimal operating conditions were thereafter obtained using Box-Behnken design of RSM. The percentage of propionic and malic acid extraction was experimentally obtained as 92.28% and 85.91% which was in close proximity with the numerical predicted values of 93.68% and 86.97% respectively.

Significance and Impact of the Research

In assessing the extraction performance of both intensified separation process studied, reactive extraction is equilibrium driven and requires longer time of extraction while emulsion liquid membrane is non-equilibrium driven and therefore shorter extraction time, therefore less energy intensive. Significant characteristics or properties such as small quantity of organic phase and extractant, very fast extraction time, increased solute transfer rate and selectivity through the membrane, high selectivity and applicability in specie removal from very low to high concentrations and governed by a non-equilibrium mass transfer were noted for the ELM process. The data generated from this study can be used for design of a large scale separation unit for this specific system, based on the ELM technique.

Future Research Scope

Interesting follow-up on this investigative studies for further research work would comprise of the recommendations as follows:

The design and model development of a continuous system (fermentor + seperator) for the intensification of biochemical production of organic acids and economic analysis using SuperPro Designer, a comprehensive simulation tool for the design and evaluation of biochemical products. A broad array of research and scientific incursion that combines theory, modelling and simulation using these intensified techniques are not just necessities but imperative and apt in themselves.

The novel application of eco-friendly solvents (such as green solvents and ionic liquids) in the various reactive extraction and ELM processes will undoubtedly remain topics of great significance while

solving the major related environmental problems. The ELM process technology will certainly develop a new horizon for further research studies and improvement to individual scientists' chemists and engineers, and the membrane community in general. A hybrid of both separation techniques may be another interesting research focus.

Appendices

The content of these appendices can be summarized as follows:

Appendix A shows instrument calibration plots used during the experiments, A.1 and A.2 are the plots of actual temperature against the display temperature sensor. A.3 and A.4 are the calibration curve for aqueous phase analysis of ELM extraction of propionic acid and malic acid respectively.

Appendix B (B1-B3) shows different Tables of the experimental design for single factor effects (one variable at a time, OVAT) for the reactive extraction of propionic, malic and butyric acid respectively which supports and serves as a supplementary data for paper 2, 3 and 4 respectively. The title of each paper is also presented in the appendix followed by each of the Table.

In appendix C (C1-C12), different contour, 3D and residual plots of the different predictive extraction models are presented which were not captured in the main text to avoid overcrowding of information are presented.

Appendix D (D1-D5) represents the different raw experimental data for reactive extraction and emulsion liquid membrane process of the different acids studied.

Appendix E is a list of chemicals used in this study

Finally, appendix F (F1-F8) shows some of the experimental figures captured in the study.

Appendix A: Instruments calibrations

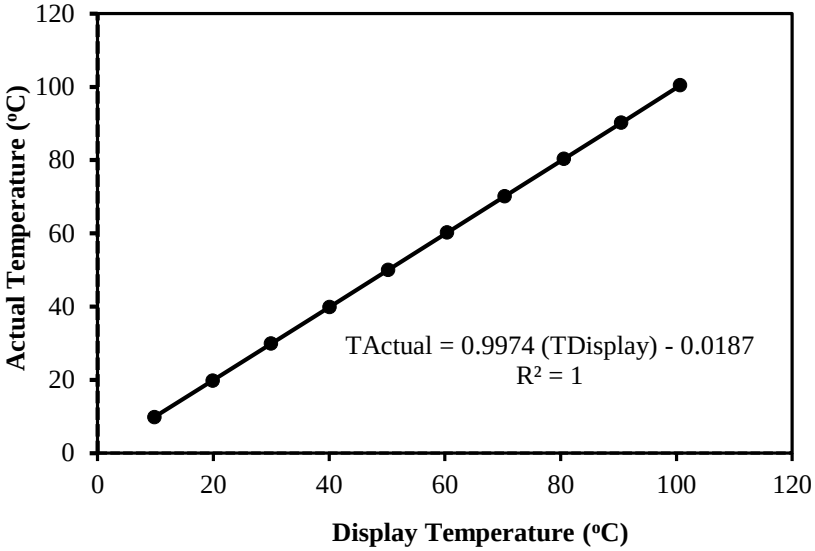


Figure A.1. Temperature sensor calibration plot

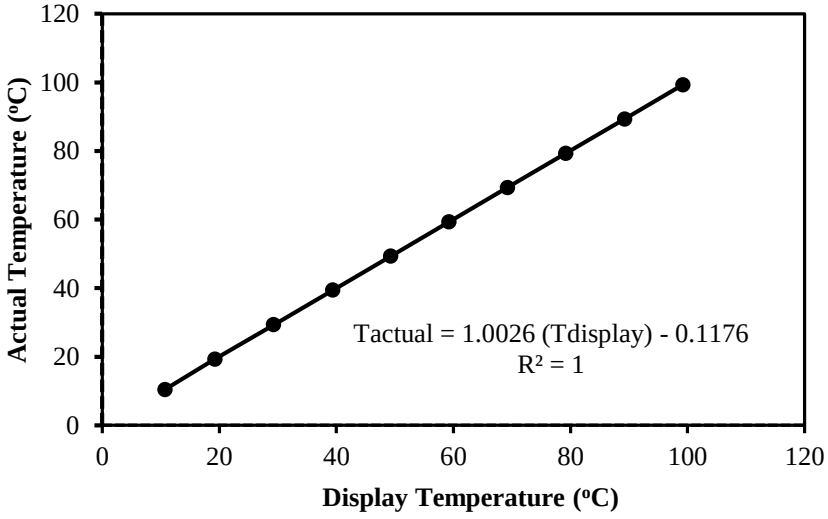


Figure A.2. Temperature sensor calibration plot

The concentrations of propionic acid and malic acids in the aqueous phase for the emulsion liquid membrane experiments were determined using UV-VIS spectrophotometer at 248 nm and 252 nm respectively. The acid concentrations are then calculated by mass balance. The calibration curves for measuring unknown concentrations of propionic and malic acids are Figures A.3 and A.4 respectively. For the calibration curve, the stock solutions of 0.1kmol/m3 of the acid are prepared. From these stock solutions, samples of aqueous solution are prepared in the concentration range of (0.02 to 0.1 kmol/m3) for the acids to find out the corresponding absorbance and generate calibration curves.

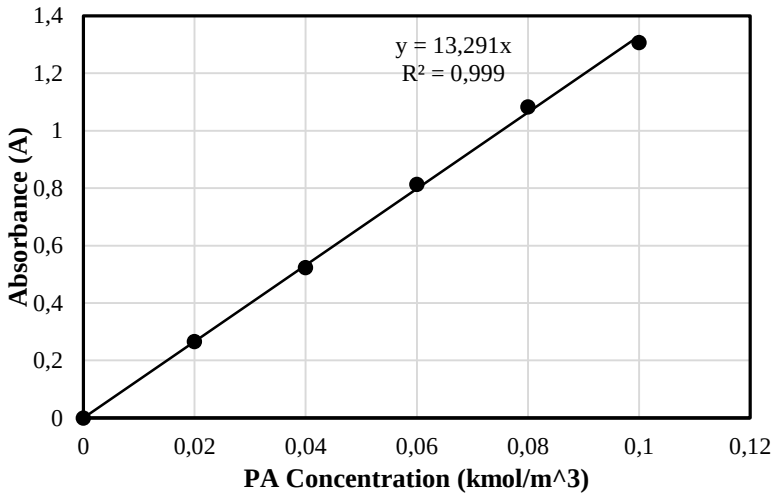


Figure A.3. Calibration curve for aqueous phase analysis of ELM extraction of propionic acid concentration at 248 nm using UV-VIS Spectrophotometer

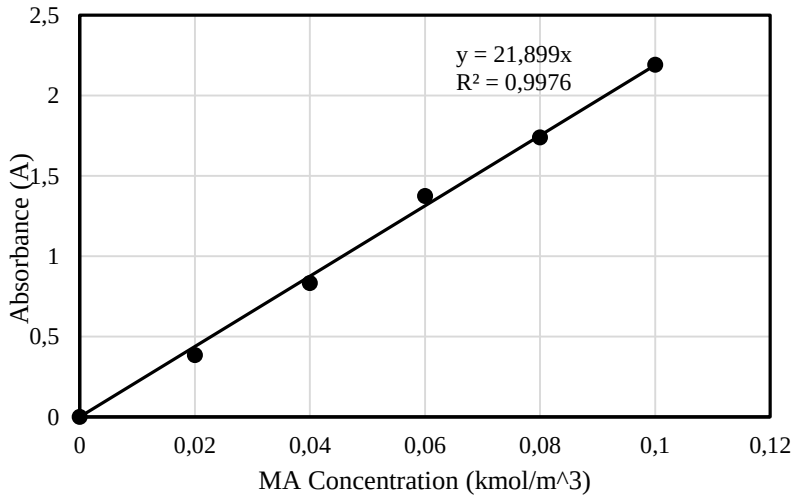


Figure A.4. Calibration curve for aqueous phase analysis of ELM extraction of malic acid concentration at 252 nm using UV-VIS Spectrophotometer

Appendix B. Single Factor Effects

Reactive Extraction of Propionic Acid using Trioctylamine in 1–Decanol by Response Surface Methodology Using Box Behnken Optimization Technique

Table B.1. Experimental design for single factor effects for propionic acid reactive extraction.

	Factor 1	Factor 2	Factor 3	Response	
Run	Temperature	TOA Concentration	Acid Concentration	Distribution Coefficient	Extraction Efficiency
	K	%	kmol/m^3	K_D	%E
1	298.15	20	0.4	12.3333	92.5000
2	308.15	20	0.4	5.8571	85.4167
3	318.15	20	0.4	3.4037	77.2917
4	318.15	10	0.7	0.9310	48.2143
5	318.15	20	0.7	1.6006	61.5476
6	318.15	30	0.7	3.1176	75.7143
7	308.15	30	0.4	7.8889	88.7500
8	308.15	30	0.7	9.2439	90.2381
9	308.15	30	1	10.7647	91.5000

Reactive Extraction of malic Acid using Trioctylamine in 1–Decanol: Equilibrium Studies by Response Surface Methodology Using Box Behnken Optimization Technique

Table B.2. Experimental design for single factor effects for malic acid reactive extraction.

	Factor 1	Factor 3	Factor 2	Response	
Run	Temperature	Acid Concentration	TOA Concentration	Distribution Coefficient	Extraction Efficiency
	K	$kmol/m^3$	%	K_D	%E
1	298.15	1	20	0.6878	40.7500
2	305.20	1	20	0.9293	48.1667
3	313.15	1	20	1.2684	55.9167
4	313.15	0.55	10	1.3045	56.6061
5	313.15	0.55	20	1.9577	66.1905
6	313.15	0.55	30	3.0049	75.0303
7	305.20	30	0.1	69.0000	98.5714
8	305.20	30	0.55	8.6653	89.6537
9	305.20	30	1	1.8728	65.1905

Reactive Extraction of butyric Acid using Trioctylamine in 1–Decanol: Equilibrium Studies by Response Surface Methodology Using Box Behnken Optimization Technique

Table B.3. Experimental design for single factor effects for butyric acid reactive extraction.

	Factor 1	Factor 2	Factor 3	Response	
Run	Temperature	TOA Concentration	Acid Concentration	Distribution Coefficient	Extraction Efficiency
	K	%	kmol/m3	K_D	%E
1	298.15	20	0.4	31.0000	96.8750
2	308.15	20	0.4	24.2632	96.0417
3	318.15	20	0.4	21.8571	95.6250
4	318.15	10	0.7	10.6667	91.4286
5	318.15	20	0.7	14.2727	93.4524
6	318.15	30	0.7	22.3333	95.7143
7	308.15	30	0.4	25.6667	96.2500
8	308.15	30	0.7	23.0000	95.8333
9	308.15	30	1	20.0526	95.2500

Appendix C. Plots of the different predictive extraction models

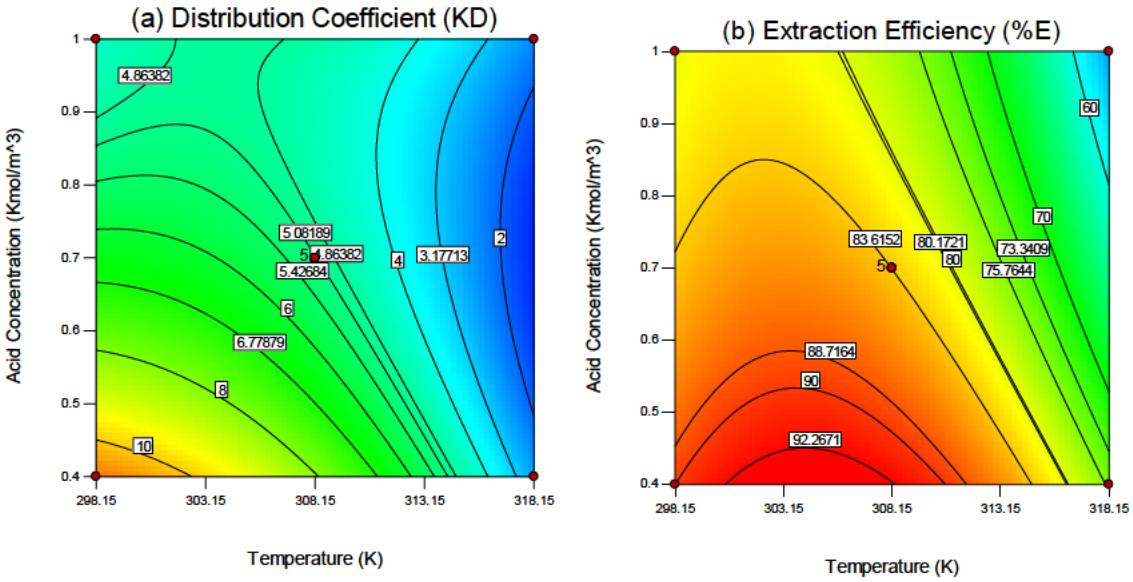


Figure C.1: Contour plots showing the effect of interaction between propionic acid concentration and temperature variables on (a) distribution coefficient and (b) extraction efficiency

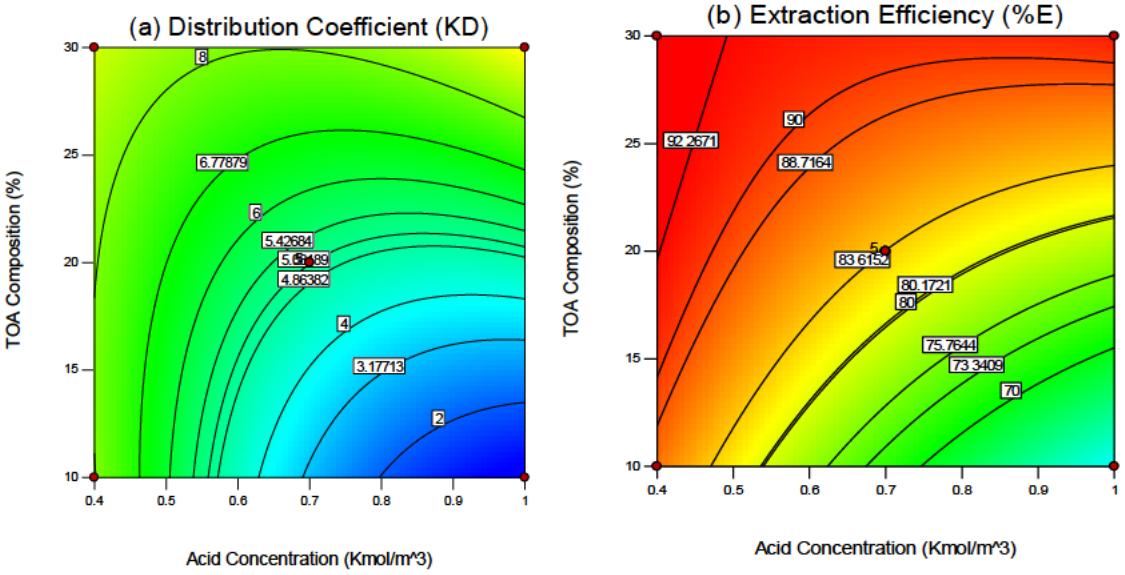


Figure C.2: Contour plots showing the effect of acid concentration in the aqueous phase and TOA composition in the organic phase (a) distribution coefficient and (b) extraction efficiency.

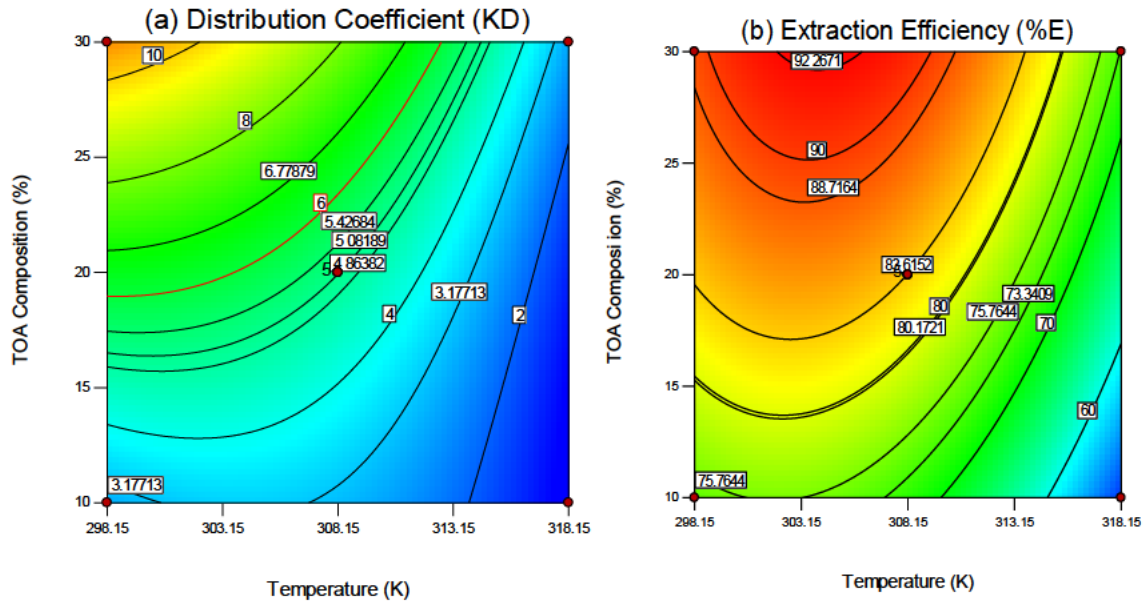


Figure C.3: Contour plots showing the effect of interaction between TOA composition and temperature variables on (a) distribution coefficient and (b) extraction efficiency

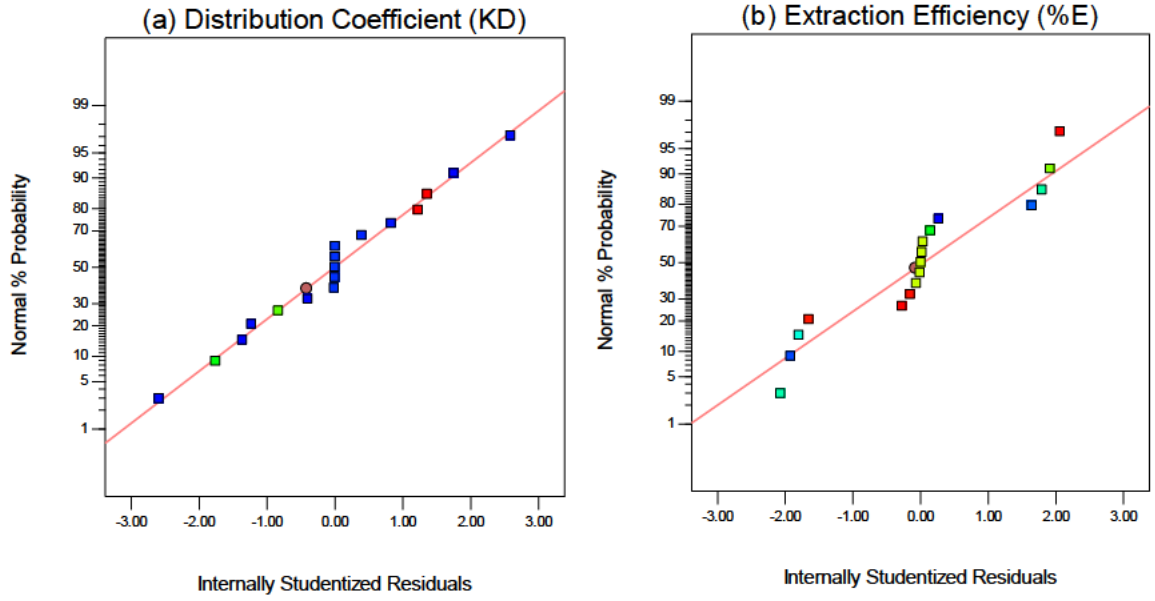


Figure C.4. Normal probability plot of studentized residuals for malic acid (a) distribution coefficient (b) extraction yield.

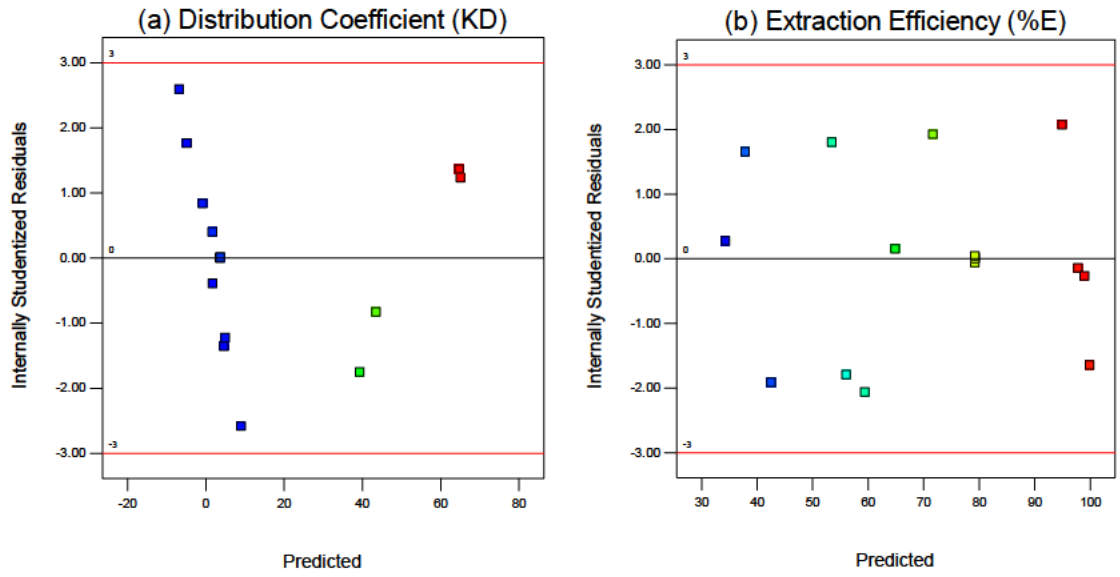


Figure C.5. The predicted (a) distribution coefficient (b) extraction yield of malic acid and studentized residuals plot

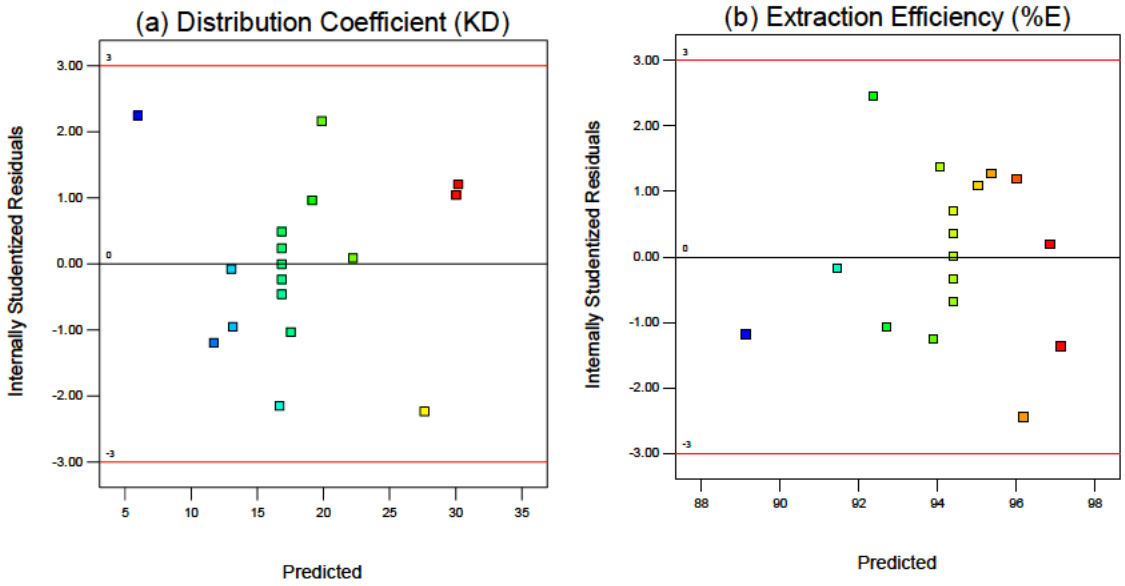


Figure C.6. The predicted (a) distribution coefficient (b) extraction yield of butyric acid and studentized residuals plot

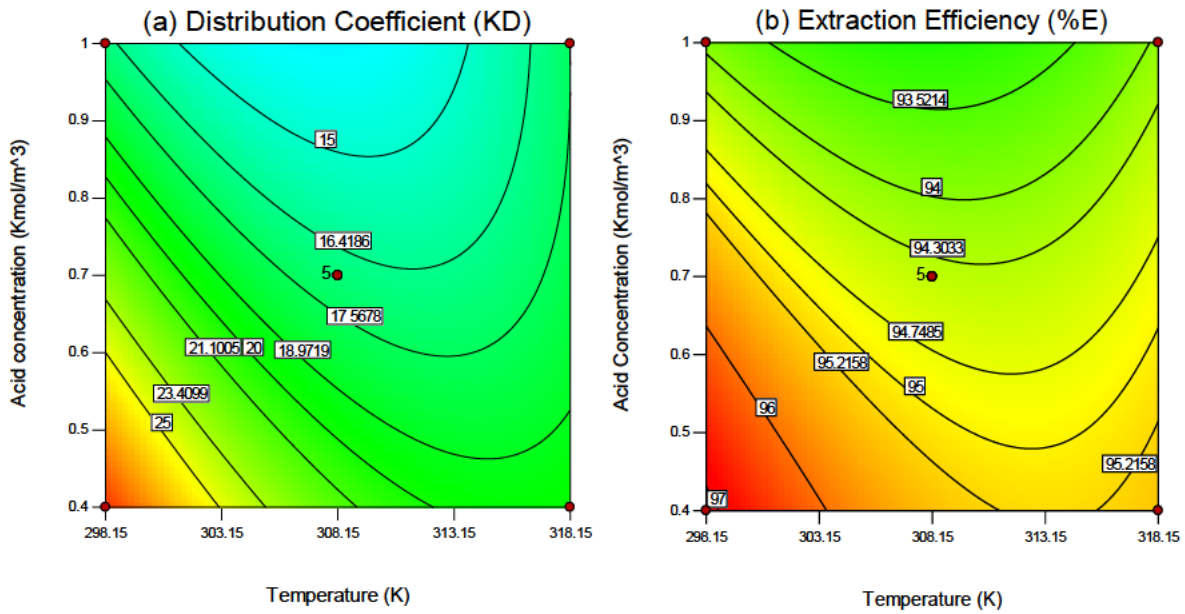


Figure C.7: Contour surface plots showing the effect of interaction between butyric acid concentration and temperature variables on (a) distribution coefficient and (b) extraction efficiency

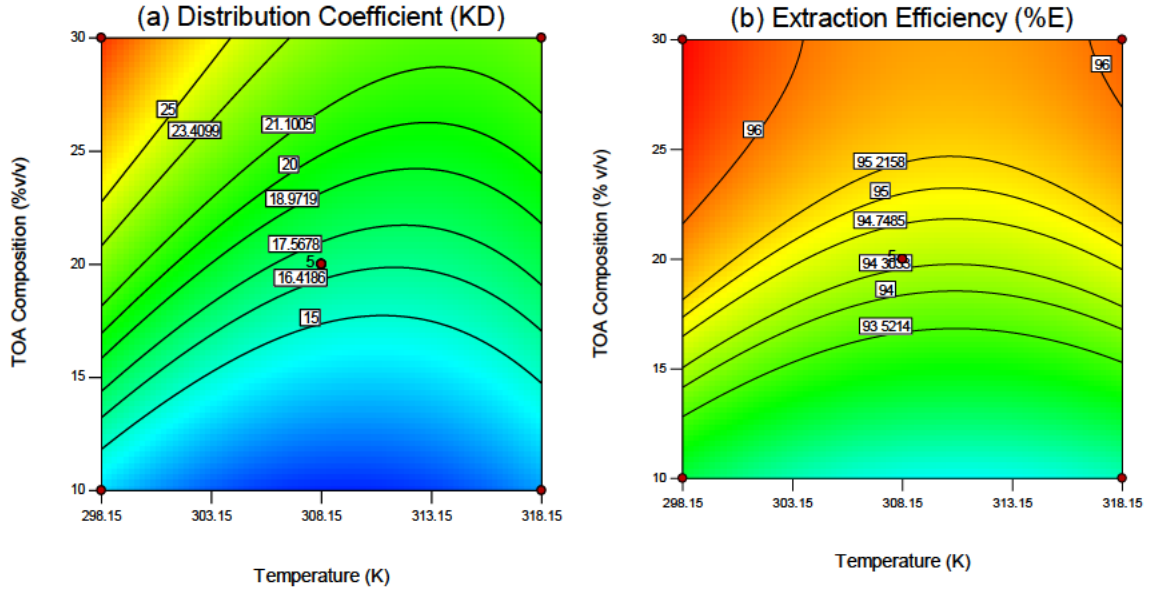


Figure C.8: Contour surface plot showing the effect of interaction between TOA composition and temperature variables on (a) distribution coefficient and (b) extraction efficiency of butyric acid

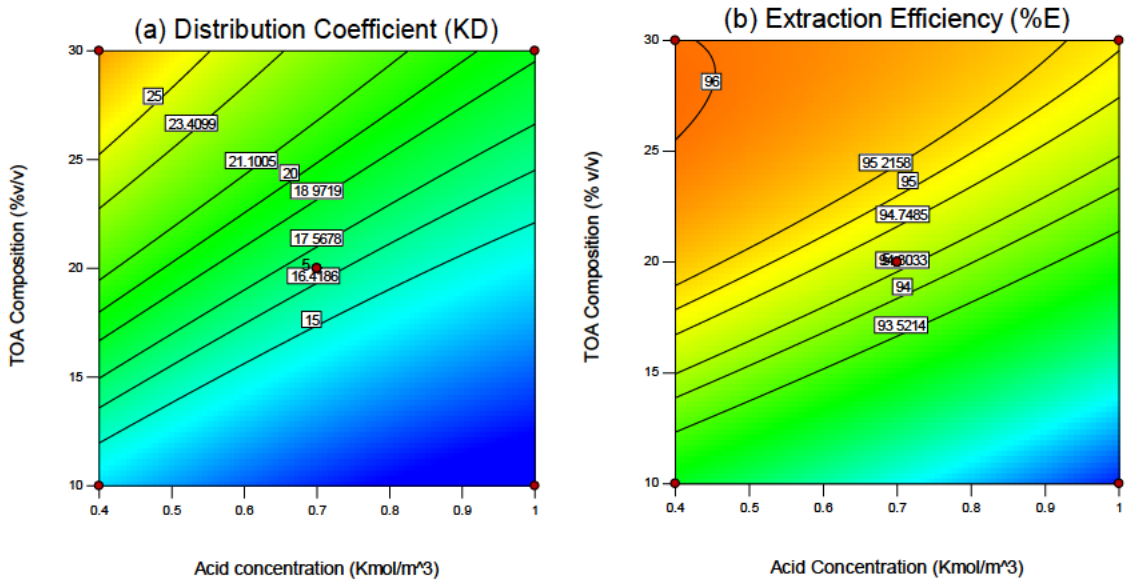


Figure C.9: Contour surface plot showing the effect of TOA composition and butyric acid concentration in the aqueous phase in the organic phase on (a) distribution coefficient and (b) extraction efficiency

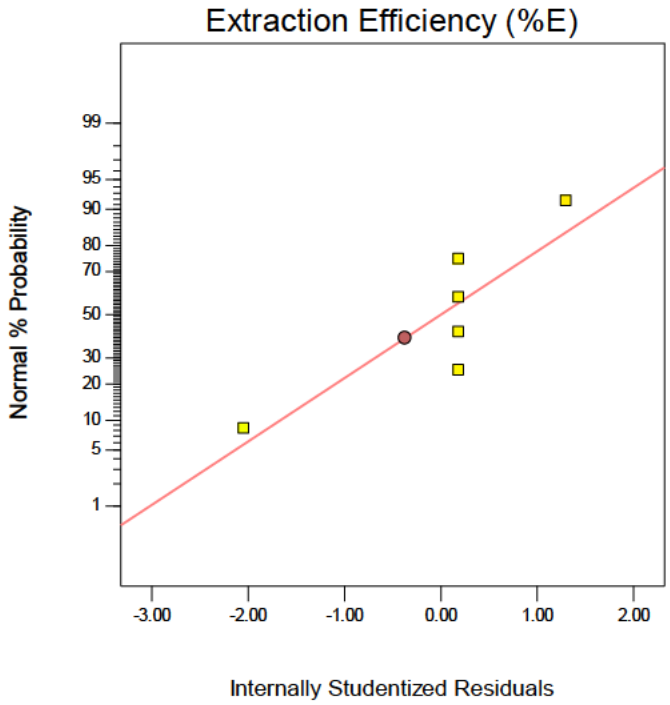


Figure C.10. Normal probability plot of studentized residuals for propionic acid ELM extraction yield.

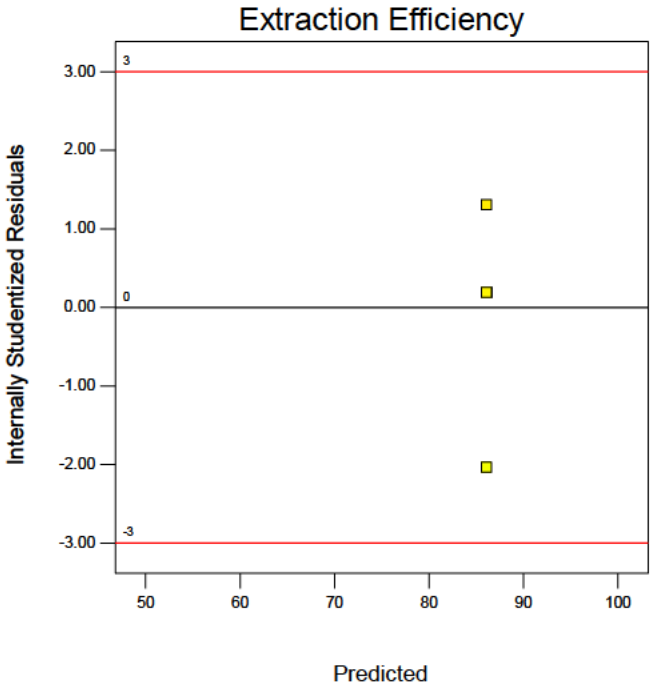
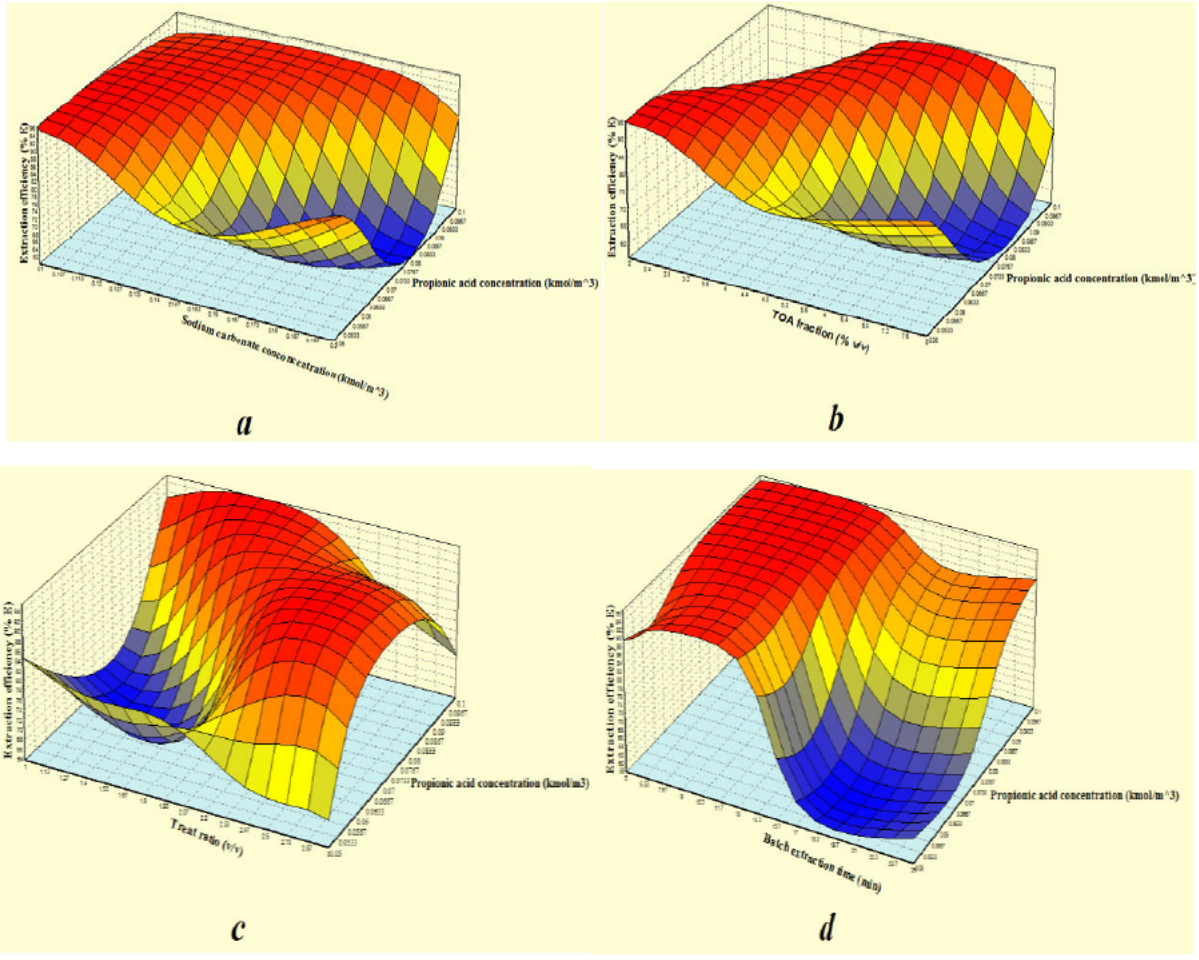


Figure C.11. The predicted extraction yield of propionic acid ELM process and studentized residuals plot



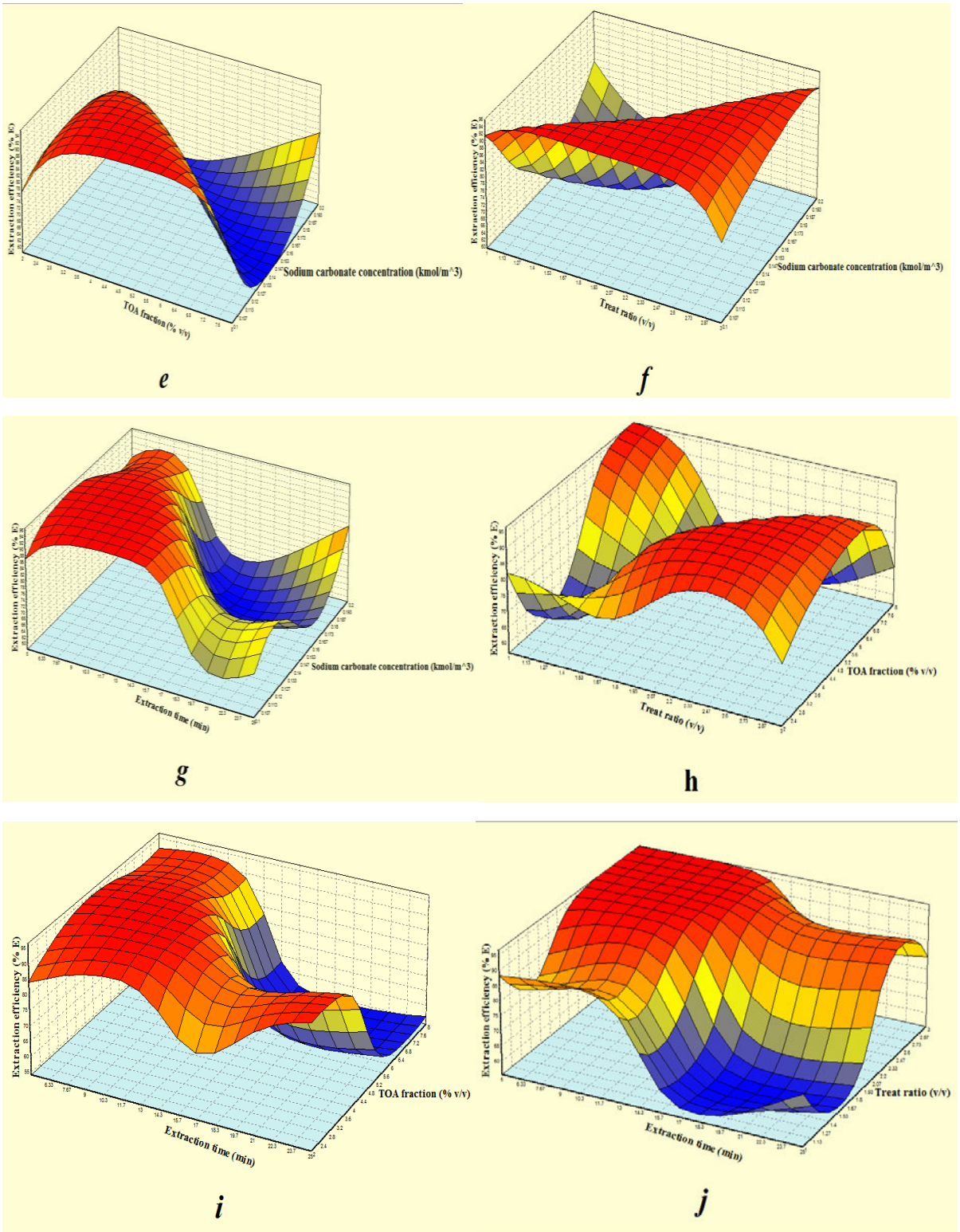


Figure C.12. 3D ANN Surface plots of propionic acid recovery using emulsion liquid membrane (ELM) showing the effects of variables on extraction efficiency: (a) Na_2CO_3 and propionic acid concentration; (b) TOA fraction and propionic acid concentration; (c) treat ratio and propionic acid concentration (d) extraction time and propionic acid concentration (e) TOA fraction and Na_2CO_3 concentration; (f) treat ratio and Na_2CO_3 concentration; (g) extraction time and Na_2CO_3 concentration; (h) treat ratio and TOA fraction; (i) extraction time and TOA fraction; (j) extraction time and treat ratio.

Appendix D. Raw experimental data

Table D.1. Raw experimental data for propionic acid reactive extraction process

Run	Temp [K]	PA conc [kmol/m^3]	TOA Comp [%]	Amount of NaOH 1 [ml]	Amount of NaOH 2 [ml]	Amount of NaOH 3 [ml]	Avg NaOH [ml]	NaOH conc [kmol/m^3]	Amount of aq phase [ml]	Aq Phase acid conc [kmol/m^3]	Org Phase acid conc [kmol/m^3]	Dist coeff [K_D]	Extraction efficiency [%E]
1	308.15	0.7	20	4.7	4.8	4.7	4.733	0.1	4	0.118	0.582	4.915	83.095
2	298.15	0.7	30	2.5	2.4	2.4	2.433	0.1	4	0.061	0.639	10.507	91.310
3	308.15	1	10	14.3	14.5	14.3	14.367	0.1	4	0.359	0.641	1.784	64.083
4	308.15	0.7	20	4.9	4.8	4.8	4.833	0.1	4	0.121	0.579	4.793	82.738
5	308.15	0.7	20	4.5	4.4	4.4	4.433	0.1	4	0.111	0.589	5.316	84.167
6	318.15	0.7	30	6.8	6.8	6.8	6.800	0.1	4	0.170	0.530	3.118	75.714
7	298.15	0.4	20	1.2	1.2	1.2	1.200	0.1	4	0.030	0.370	12.333	92.500
8	308.15	0.4	10	2	2	2	2.000	0.1	4	0.050	0.350	7.000	87.500
9	308.15	0.4	30	1.8	1.8	1.8	1.800	0.1	4	0.045	0.355	7.889	88.750
10	308.15	0.7	20	4.3	4.2	4.3	4.267	0.1	4	0.107	0.593	5.563	84.762
11	318.15	0.7	10	14.5	14.5	14.5	14.500	0.1	4	0.363	0.338	0.931	48.214
12	308.15	1	30	3.3	3.5	3.4	3.400	0.1	4	0.085	0.915	10.765	91.500
13	298.15	1	20	8.5	8.5	8.5	8.500	0.1	4	0.213	0.788	3.706	78.750
14	308.15	0.7	20	4.7	4.8	4.7	4.733	0.1	4	0.118	0.582	4.915	83.095
15	318.15	0.4	20	3.6	3.6	3.7	3.633	0.1	4	0.091	0.309	3.404	77.292
16	318.15	1	20	19.1	19	19	19.033	0.1	4	0.476	0.524	1.102	52.417
17	298.15	0.7	10	7.8	7.9	7.8	7.833	0.1	4	0.196	0.504	2.574	72.024
Optimum	300.752	0.408	18.252	1.7	1.6	1.7	1.667	0.1	4	0.042	0.366	8.792	89.788

Table D.2. Raw experimental data for malic acid reactive extraction process

Run	Temp [K]	MA conc [kmol/m^3]	TOA Comp [%]	Amount of NaOH 1 [ml]	Amount of NaOH 2 [ml]	Amount of NaOH 3 [ml]	Avg NaOH [ml]	NaOH conc [kmol/m^3]	Amount of aq phase [ml]	Aq Phase acid conc [kmol/m^3]	Org Phase acid conc [kmol/m^3]	Dist coeff [K_D]	Extraction efficiency [%E]
1	305.5	30	0.1	0.2	0.2	0.2	0.200	0.05	7	0.001	0.099	69.000	98.571
2	298	10	0.55	46.3	47	46.9	46.733	0.05	7	0.334	0.216	0.648	39.307
3	298	30	0.55	36.1	36.3	36.1	36.167	0.05	7	0.258	0.292	1.129	53.030
4	305.5	20	0.55	16	15.9	16	15.967	0.05	7	0.114	0.436	3.823	79.264
5	298	20	1	47.4	47.4	47.4	47.400	0.05	4	0.593	0.408	0.688	40.750
6	305.5	10	0.1	0.3	0.4	0.3	0.333	0.05	7	0.002	0.098	41.000	97.619
7	298	20	0.1	0.2	0.2	0.2	0.200	0.05	7	0.001	0.099	69.000	98.571
8	305.5	10	1	91.5	91	91.2	91.233	0.05	7	0.652	0.348	0.535	34.833
9	305.5	20	0.55	16	15.8	15.8	15.867	0.05	7	0.113	0.437	3.853	79.394
10	305.5	20	0.55	16	15.9	15.9	15.933	0.05	7	0.114	0.436	3.833	79.307
11	313	30	0.55	13.8	13.7	13.7	13.733	0.05	5	0.137	0.413	3.005	75.030
12	305.5	30	1	48.8	48.7	48.7	48.733	0.05	7	0.348	0.652	1.873	65.190
13	313	20	0.1	0.4	0.4	0.4	0.400	0.05	7	0.003	0.097	34.000	97.143
14	305.5	20	0.55	16	16.2	16.1	16.100	0.05	7	0.115	0.435	3.783	79.091
15	313	10	0.55	23.9	23.9	23.8	23.867	0.05	5	0.239	0.311	1.304	56.606
16	313	20	1	35.3	35.2	35.3	35.267	0.05	4	0.441	0.559	1.268	55.917
17	305.5	20	0.55	16	15.9	15.8	15.900	0.05	7	0.114	0.436	3.843	79.351
Optimum	304.731	23.538	0.247	2.4	2.3	2.3	2.333	0.05	7	0.017	0.230	13.820	93.252

Table D.3. Raw experimental data for butyric acid reactive extraction process

Run	Temp [K]	BA conc [kmol/m^3]	TOA Comp [%]	Amount of NaOH 1 [ml]	Amount of NaOH 2 [ml]	Amount of NaOH 3 [ml]	Avg NaOH [ml]	NaOH conc [kmol/m^3]	Amount of aq phase [ml]	Aq Phase acid conc [kmol/m^3]	Org Phase acid conc [kmol/m^3]	Dist coeff [K_D]	Extraction efficiency [%E]
1	308.15	1	10	4.4	4.4	4.5	4.433	0.1	4	0.111	0.889	8.023	88.917
2	308.15	0.4	10	1.2	1.2	1.2	1.200	0.1	4	0.030	0.370	12.333	92.500
3	318.15	1	20	2.3	2.3	2.2	2.267	0.1	4	0.057	0.943	16.647	94.333
4	308.15	1	30	1.9	1.9	1.9	1.900	0.1	4	0.048	0.953	20.053	95.250
5	318.15	0.4	20	0.7	0.7	0.7	0.700	0.1	4	0.018	0.383	21.857	95.625
6	298.15	0.7	10	2.1	2	1.9	2.000	0.1	4	0.050	0.650	13.000	92.857
7	298.15	0.7	30	0.9	0.8	0.9	0.867	0.1	4	0.022	0.678	31.308	96.905
8	308.15	0.7	20	1.6	1.6	1.6	1.600	0.1	4	0.040	0.660	16.500	94.286
9	308.15	0.7	20	1.5	1.5	1.5	1.500	0.1	4	0.038	0.663	17.667	94.643
10	298.15	1	20	2.6	2.5	2.5	2.533	0.1	4	0.063	0.937	14.789	93.667
11	318.15	0.7	10	2.4	2.4	2.4	2.400	0.1	4	0.060	0.640	10.667	91.429
12	308.15	0.7	20	1.6	1.6	1.5	1.567	0.1	4	0.039	0.661	16.872	94.405
13	308.15	0.4	30	0.6	0.6	0.6	0.600	0.1	4	0.015	0.385	25.667	96.250
14	298.15	0.4	20	0.5	0.5	0.5	0.500	0.1	4	0.013	0.388	31.000	96.875
15	308.15	0.7	20	1.5	1.5	1.6	1.533	0.1	4	0.038	0.662	17.261	94.524
16	308.15	0.7	20	1.7	1.6	1.6	1.633	0.1	4	0.041	0.659	16.143	94.167
17	318.15	0.7	30	1.2	1.2	1.2	1.200	0.1	4	0.030	0.670	22.333	95.714
Optimum	302.83	0.493	26.417	0.7	0.7	0.7	0.7	0.1	4	0.018	0.476	27.171	96.450

Table D.4. Raw experimental data for propionic acid emulsion liquid membrane (ELM) extraction process

Run	PA Conc [kmol/m^3]	Na_2CO_3 Conc [kmol/m^3]	Fraction of carrier %v/v	Treat ratio %v/v	Extraction Time mins	Aq Phase acid conc 1 [kmol/m^3]	Aq Phase acid conc 2 [kmol/m^3]	Aq Phase acid conc 3 [kmol/m^3]	Aq Phase acid conc Average [kmol/m^3]	Org Phase acid conc [kmol/m^3]	Extraction efficiency [%E]
1	0.075	0.15	5	2	15	0.011	0.011	0.009	0.010	0.065	86.222
2	0.1	0.15	8	2	15	0.022	0.022	0.024	0.023	0.077	77.333
3	0.075	0.1	8	2	15	0.015	0.016	0.019	0.017	0.058	77.778
4	0.05	0.15	8	2	15	0.005	0.006	0.007	0.006	0.044	88.000
5	0.1	0.1	5	2	15	0.009	0.009	0.009	0.009	0.091	91.000
6	0.05	0.1	5	2	15	0.011	0.011	0.011	0.011	0.039	78.000
7	0.05	0.15	2	2	15	0.002	0.003	0.002	0.002	0.048	95.333
8	0.075	0.1	5	3	15	0.013	0.014	0.014	0.014	0.061	81.778
9	0.075	0.15	8	2	5	0.005	0.004	0.01	0.006	0.069	91.556
10	0.075	0.15	5	2	15	0.011	0.011	0.011	0.011	0.064	85.333
11	0.1	0.15	2	2	15	0.011	0.012	0.014	0.012	0.088	87.667
12	0.05	0.15	5	1	15	0.009	0.008	0.006	0.008	0.042	84.667
13	0.075	0.15	2	2	5	0.012	0.012	0.012	0.012	0.063	84.000
14	0.075	0.15	2	3	15	0.018	0.019	0.017	0.018	0.057	76.000
15	0.075	0.15	2	1	15	0.013	0.013	0.014	0.013	0.062	82.222
16	0.05	0.15	5	2	25	0.019	0.025	0.027	0.024	0.026	52.667
17	0.1	0.15	5	2	25	0.011	0.01	0.01	0.010	0.090	89.667
18	0.075	0.1	5	2	25	0.022	0.015	0.026	0.021	0.054	72.000
19	0.075	0.15	2	2	25	0.005	0.004	0.004	0.004	0.071	94.222
20	0.075	0.1	5	2	5	0.01	0.009	0.01	0.010	0.065	87.111
21	0.1	0.15	5	1	15	0.017	0.015	0.013	0.015	0.085	85.000
22	0.075	0.15	5	2	15	0.011	0.011	0.009	0.010	0.065	86.222
23	0.075	0.15	5	1	25	0.02	0.022	0.02	0.021	0.054	72.444
24	0.075	0.15	5	3	5	0.002	0.002	0.003	0.002	0.073	96.889

25	0.075	0.2	8	2	15	0.015	0.01	0.018	0.014	0.061	80.889
26	0.075	0.2	5	1	15	0.017	0.018	0.019	0.018	0.057	76.000
27	0.075	0.15	8	3	15	0.024	0.023	0.023	0.023	0.052	68.889
28	0.075	0.15	8	1	15	0.002	0.002	0.004	0.003	0.072	96.444
29	0.075	0.1	2	2	15	0.013	0.016	0.023	0.017	0.058	76.889
30	0.075	0.1	5	1	15	0.006	0.006	0.007	0.006	0.069	91.556
31	0.05	0.2	5	2	15	0.007	0.007	0.008	0.007	0.043	85.333
32	0.075	0.15	5	3	25	0.018	0.019	0.01	0.016	0.059	79.111
33	0.075	0.2	5	2	5	0.009	0.01	0.01	0.010	0.065	87.111
34	0.05	0.15	5	3	15	0.015	0.015	0.016	0.015	0.035	69.333
35	0.075	0.15	5	2	15	0.011	0.011	0.009	0.010	0.065	86.222
36	0.05	0.15	5	2	5	0.017	0.017	0.019	0.018	0.032	64.667
37	0.1	0.2	5	2	15	0.015	0.014	0.015	0.015	0.085	85.333
38	0.075	0.15	5	2	15	0.011	0.011	0.009	0.010	0.065	86.222
39	0.1	0.15	5	3	15	0.027	0.027	0.028	0.027	0.073	72.667
40	0.075	0.15	5	1	5	0.009	0.009	0.008	0.009	0.066	88.444
41	0.075	0.15	8	2	25	0.017	0.017	0.018	0.017	0.058	76.889
42	0.075	0.2	5	2	25	0.013	0.013	0.012	0.013	0.062	83.111
43	0.075	0.2	2	2	15	0.022	0.022	0.027	0.024	0.051	68.444
44	0.075	0.2	5	3	15	0.006	0.006	0.007	0.006	0.069	91.556
45	0.075	0.15	5	2	15	0.01	0.011	0.009	0.010	0.065	86.667
46	0.1	0.15	5	2	5	0.021	0.022	0.022	0.022	0.078	78.333
Optimum	0.082	0.133	7.446	1.168	11.93	0.006	0.006	0.007	0.0063	0.076	92.276

Table D.4. (continued)

Table D.5. Raw experimental data for malic acid emulsion liquid membrane (ELM) extraction process

Run	MA Conc [kmol/m^3]	Na_2CO_3 Conc [kmol/m^3]	Fraction of carrier %v/v	Treat ratio %v/v	Aq Phase acid conc 1 [kmol/m^3]	Aq Phase acid conc 2 [kmol/m^3]	Aq Phase acid conc 3 [kmol/m^3]	Aq Phase acid conc Average [kmol/m^3]	MA acid conc 1:2 [kmol/m^3]	Org Phase acid conc [kmol/m^3]	Extraction efficiency [%E]
1	0.075	0.15	5	2	0.048	0.048	0.047	0.048	0.024	0.051	68.222
2	0.1	0.15	5	3	0.015	0.015	0.015	0.015	0.008	0.093	92.500
3	0.075	0.2	5	3	0.065	0.067	0.068	0.067	0.033	0.042	55.556
4	0.075	0.15	8	3	0.06	0.06	0.061	0.060	0.030	0.045	59.778
5	0.075	0.15	8	1	0.038	0.039	0.039	0.039	0.019	0.056	74.222
6	0.05	0.1	5	2	0.037	0.038	0.039	0.038	0.019	0.031	62.000
7	0.05	0.2	5	2	0.018	0.017	0.018	0.018	0.009	0.041	82.333
8	0.05	0.15	2	2	0.045	0.047	0.048	0.047	0.023	0.027	53.333
9	0.1	0.2	5	2	0.007	0.007	0.006	0.007	0.003	0.097	96.667
10	0.1	0.15	5	1	0.039	0.038	0.039	0.039	0.019	0.081	80.667
11	0.075	0.15	5	2	0.062	0.063	0.063	0.063	0.031	0.044	58.222
12	0.075	0.1	5	3	0.057	0.058	0.059	0.058	0.029	0.046	61.333
13	0.075	0.1	5	1	0.058	0.056	0.057	0.057	0.029	0.047	62.000
14	0.1	0.15	8	2	0.011	0.011	0.011	0.011	0.006	0.095	94.500
15	0.075	0.15	2	3	0.061	0.061	0.061	0.061	0.031	0.045	59.333
16	0.05	0.15	5	1	0.032	0.033	0.033	0.033	0.016	0.034	67.333
17	0.1	0.15	2	2	0.028	0.028	0.028	0.028	0.014	0.086	86.000
18	0.05	0.15	5	3	0.043	0.044	0.045	0.044	0.022	0.028	56.000
19	0.075	0.1	8	2	0.056	0.053	0.053	0.054	0.027	0.048	64.000
20	0.1	0.1	5	2	0.012	0.012	0.012	0.012	0.006	0.094	94.000
21	0.075	0.15	5	2	0.05	0.05	0.05	0.050	0.025	0.050	66.667
22	0.075	0.15	2	1	0.061	0.065	0.065	0.064	0.032	0.043	57.556
23	0.075	0.2	8	2	0.05	0.053	0.052	0.052	0.026	0.049	65.556
24	0.075	0.2	2	2	0.06	0.062	0.062	0.061	0.031	0.044	59.111

25	0.075	0.15	5	2	0.051	0.051	0.052	0.051	0.026	0.049	65.778
26	0.05	0.15	8	2	0.028	0.028	0.029	0.028	0.014	0.036	71.667
27	0.075	0.15	5	2	0.052	0.052	0.051	0.052	0.026	0.049	65.556
28	0.075	0.1	2	2	0.067	0.068	0.068	0.068	0.034	0.041	54.889
29	0.075	0.2	5	1	0.051	0.053	0.053	0.052	0.026	0.049	65.111
Optimum	0.097	0.16	7.49	1.5	0.028	0.027	0.027	0.027	0.014	0.083	85.911

Table D.5. (continued)

Appendix E Chemical data table

Table E.1. Data table of chemicals used in this work.

All chemicals were supplied by Sigma-Aldrich which is now owned by Merck.

IUPAC name	Product number	Supplier specified purity [%]
Propionic acid	P1386	99
Butyric acid	B103500	99+
DL-malic acid	M0875	99
Trioctylamine	T81000	98
1-Decanol	150584	98
Sodium hydroxide solution	43617	Eluent concen (0.1M)
Phenolphthalein	105945	A.C.S. reagent
Heptane	34873	99
Cyclohexane	227048	99.5
SPAN (TM) 80	85548	1000-2000MPA.S
Sodium carbonate	S7795	Bioxtra

Appendix F. Experimental Figures



Figure F.1 Samples in separating funnel for the reactive extraction process



Figure F.2 Sample bottles where samples are taken for analysis



Figure F.3 Samples of the reactive extraction processes in an orbital shaker placed in an oven at the required temperature.



Figure F.4 Sample analysis indicating end point titration

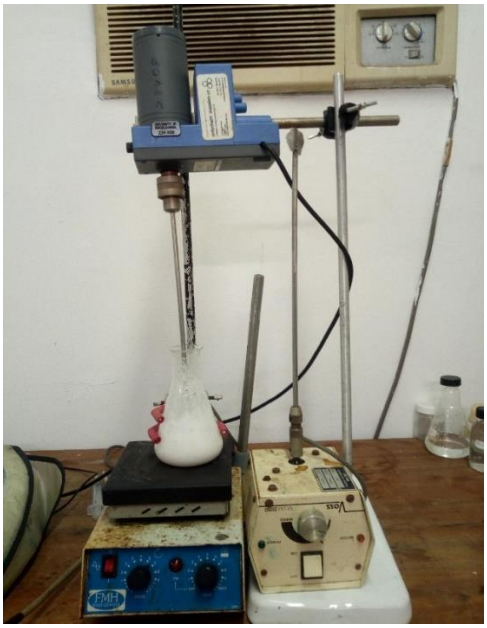


Figure F.5 Preparation of membrane phase using a high-speed homogenizer (IKA RW 14 basic digital mixer at 2000 rpm)



F.6 Samples of the emulsion liquid membrane (ELM) process



Figure F.7 Samples of the emulsion liquid membrane (ELM) process in an orbital shaker



Figure F.8 A Uv/Vis spectrometer (model WPA Light wave II LABOTEC)